NUREG/CP-0005

Proceedings of the Conference on

HIGH-LEVEL RADIOACTIVE SOLID WASTE FORMS

December 19 - 21, 1978 at Denver, Colorado

Leslie A. Casey, Ed.

United States
Nuclear Regulatory Commission

Office of Nuclear Material
Safety and Safeguards

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Sponsored by
Office of Nuclear Material Safety and Safeguards
U. S. Nuclear Regulatory Commission
Washington, D.C. 20555

Conference on High-Level Radioactive Solid Waste Forms

Sponsored by the Nuclear Regulatory Commission

TUESDAY MORNING, 19 DECEMBER 1978

8:30 Plenary Session I, Vitreous Forms; Dr. Robert B. Leachman, Chairperson, U.S. Nuclear Regulatory Commission

1. Welcome—*Conference Information*
2. Relation of Solids to Waste Management—*Dr. Fred A. Donath, University of Illinois*
3. Physical Properties of Waste Glass—*Mr. John Mendel, Battelle Pacific Northwest Laboratory*

10:30 Break

4. Microscopic Properties of Glasses—*Dr. Pedro B. Macedo, Catholic University of America*
5. Large-Scale Waste Glass Production—*Dr. Claude Sombret, Centre de Marcoule, France*
6. Surface Leaching—*Dr. Lawrence L. Hench, University of Florida*

12:00-
1:00 Lunch Break

TUESDAY AFTERNOON, 19 DECEMBER 1978

1:00 Plenary Session II, Encapsulations Techniques and Failure Modes; Dr. Annie Sugier, Chairperson, Commissariat a L'Energie Atomique, France

1. Corrosion in Canisters and Claddings of Various Metals—*Dr. Jeffrey W. Braithwaite, Sandia Laboratories*
2. Ceramic & Pure-Metal Canisters in Buffer Material—*Mr. Per-Erick A. Ahlström, Kärnbranslesäkerhet, Sweden*
3. Interface Interactions Between Solids—*Dr. Robert N. Anderson, San Jose State University*

3:00 Break

4. Matricies of Wastes and Inert Media—*Dr. J. Van Geel, Gelsenberg AG, Federal Republic of Germany*
5. Thermal Stresses and Cracking—*Mr. Steven C. Slate, Battelle Pacific Northwest Laboratory*
6. Surface Loss by Exfoliation—*Dr. Thomas Tombrello, California Institute of Technology*

5:00-
6:00 Cash Bar

6:00-
7:30 Banquet

Nuclear Waste: Politics and Potential; The Honorable Harrison H. Schmitt, Senator, New Mexico (Ph.D. in Geology from Harvard, Apollo 17 geologist on the moon)

WEDNESDAY MORNING, 20 DECEMBER 1978

8:30 Plenary Session III, Spent Fuel, Crystalline, and Other Forms; Mr. William Holcomb, Chairperson, U.S. Environmental Protection Agency

1. Containment in Cement Forms—*Dr. Della Roy, Pennsylvania State University*
2. Calcine Production, Storage and Conversion—*Dr. Bill R. Dickey, Allied Chemical Corporation, Idaho Falls*
3. Properties of Spent Fuel Pellets—*Mr. M. Dean Houston, U.S. Nuclear Regulatory Commission*

10:30 Break

4. Uranium Oxides in Ores & Fuels—*Dr. Heinrich D. Holland, Harvard University*
5. Crystalline and Coated Forms—*Dr. Gregory McCarthy, Pennsylvania State University*
6. Metamict Degradation of Crystals—*Dr. Rodney C. Ewing, University of New Mexico*

12:00-
1:30 Luncheon

The Saga of Nature's Reactor at Oklo: Dr. Etienne Roth, Head of the Department of Research and Analysis, Centre d'études nucléaires de Saclay (among original researchers who confirmed the Oklo effect)

WEDNESDAY AFTERNOON, 20 DECEMBER 1978 AND THE BEGINNING OF THURSDAY MORNING, 21 DECEMBER 1978

Three concurrent workshops for open discussions: To initiate each, two short talks will present suggested issues from distinctly different points of view. The chairperson and a rapporteur will write the results for presentation to their workshop at the beginning of Thursday morning, 21 December.

1:30 **Workshop #1, Criteria for Solid Waste Forms**

3:30 Break *Chairperson:* Mr. Robert Bernero, U. S. Nuclear Regulatory Commission

Issue Presenter—Optimistic: Ms. Karen Adelson, Westinghouse Electric Corp.
Issue Presenter—Cautious: Dr. Thomas B. Cochran, Natural Resources Defense Council

A discussion of the ability of regulators to establish and to adhere to sufficiently meaningful criteria of solids to achieve safe regulation in high-level waste disposal.

Workshop #2, Stabilities of Alternate Waste Forms
Chairperson: Ms. Leslie A. Casey, U.S. Nuclear Regulatory Commission
Issue Presenter—Optimistic: Dr. Rustum Roy, Pennsylvania State University
Issue Presenter—Cautious: Dr. Robert O. Pohl, Cornell University

A discussion of the ability and likelihood of learning the characteristics of alternative waste forms and utilizing these in the choice of the optimum form for actual disposal. Included are: results of the National Academy of Sciences Panel on Waste Solidification; scientific and engineering properties; present knowledge and abilities; schedules; and costs.

Workshop #3, Limitations in Predicting Long-Term Performance
Chairperson: Mr. James C. Malaro, U. S. Nuclear Regulatory Commission
Issue Presenter—Optimistic: Dr. Bernard Cohen, University of Pittsburgh
Issue Presenter—Cautious: Dr. Terry Lash, Natural Resources Defense Council

Systems analyses which are used to predict long-term performance in waste disposal have led to a dominant reliance upon geologic retention, but an insignificant reliance upon the post-emplacement durability of the waste solids. These predictions are pertinent to the extent that all effects have been anticipated and that the data are measured and accurate. The discussion is whether basic reliance is wisely placed upon such predictions or whether, alternatively, the durability of solids has importance beyond transportation and retrievability.

5:00-
7:00 **Cash Bar**

7:30 **Presently Unscheduled Discussion Groups**

THURSDAY MORNING, 21 DECEMBER 1978

8:30 **Workshops** (3 concurrent sessions) continued for amending reports

9:30 **Plenary Session IV, Assessments;**
Dr. Harry Landon, Chairperson, U.S. Nuclear Regulatory Commission
1. Workshop Summaries by Workshop Chairpersons
2. Details of Forthcoming Disposals—*Dr. Goetz K. H. Oertel, Division of Waste Products, U.S. Department of Energy*
3. Conference Summary—*Dr. Hans Frauenfelder, University of Illinois (Chairman of the Review Committee, American Physical Society study of Nuclear Fuel Cycles and Waste Management)*

1:00 p.m. **Adjournment**

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DISTRIBUTION

PREFACE

One of the key factors in the future of nuclear energy is the development of safe waste disposal technologies. The Nuclear Regulatory Commission (NRC), in December 1978, held a Conference in Denver entitled "High-Level Radioactive Solid Waste Forms" to address aspects of this important topic. The proceedings for this Conference are contained herein.

The Conference included presentations by speakers prominent in their field, three workshops, and luncheon and banquet presentations as well as informal evening discussion groups. The leading individuals were invited to summarize ongoing research at appropriate institutions. Speakers presented the full range of new information, as well as their own work. In addition to including complete coverage of relevant topics, an objective of the Conference was to provide a comprehensive record that encompassed a broad range of views extending from cautious to optimistic.

Presentations and discussions concentrated on developments and applications of materials sciences for high-level radioactive waste disposal and included solidification of wastes, waste canisters, and potential buffering overpacks. The speakers were from both national and international programs and included representatives from government, academia, private industry, and public interest groups. Presentations covered U.S. developments in vitrification, calcination, cementation, and crystallization; a joint German-Belgian effort designed to develop matrices of high-level waste "pebbles" in an inert metal; a review of France's large scale vitrification program; and Swedish developments in the area of advanced canisters and surrounding overpacks.

The three workshops provided an opportunity for open discussions consistent with issues presented by the two Issue Presenters at each workshop. A goal of the workshops was to apply technical facts to policy development.

The more than 200 participants were provided background information prior to attending the 3 day conference. Included was a summary of the recent 1978 report, "Solidification of High-Level Radioactive Wastes" by the National Academy of Sciences.

The Nuclear Regulatory Agency would like to express its gratitude to the many individuals who contributed to this Conference. We are especially indebted to the Conference organizers, Ms. Leslie A. Casey, Dr. R. B. Leachman and Mr. R. Dale Smith as well as to the Program Committee, Dr. Robert B. Leachman, Dr. Thomas B. Cochran, Mr. William F. Holcomb, and Dr. Goetz H. Oertel. We would also like to thank the speakers for their excellent contribution. SCS Engineers, Reston, Virginia 22091, provided Conference support and assistance in preparing the proceedings.

ACRONYMS AND INITIALISMS

ALARA - As Low as Reasonably Achievable
AMRAW - Assessment Method for Radioactive Waste
ANL - Argonne National Laboratory
ANU - Australian National University
APS - American Physical Society
AVM - Marcoule Vitrification Plant
BNL - Brookhaven National Laboratories
BWR - Boiling Water Reactor
CM - Continuous Melting
COGEMA - Compagnie Générale des Matières Nucléaires
CVD - Chemical Vapor Deposition
DOE - U.S. Department of Energy
DSC - Differential Scanning Calorimeter
EMA - Electron Microprobe Analysis
EPA - U.S. Environmental Protection Agency
EPRI - Electric Power Research Institute
HAC - High Alumina Cement
HEPA - High Efficiency Particulate Air
HIP - Hot Isostatic Pressing
HLLW - High Level Liquid Waste
HMI - Hahn-Meitner Institute
HPL - High Pressure Laboratory
ICM - In-Can Melting
ICPP - Idaho Chemical Processing Plant
INEL - Idaho National Engineering Laboratory
IRG - Inter-Agency Review Group
IRRS - Infrared Reflection Spectroscopy
ISO International Standards Organization
I-P - Portland Pozzolanic Cement
KBS - Nuclear Fuel Safety Project
LASL - Los Alamos Scientific Laboratory
LLL - Lawrence Livermore Laboratories

LWR - Light Water Reactor
MTR - Materials Testing Reactor
NEPA - National Environmental Protection Act
NMSS - Office of Nuclear Material Safety and Safeguards of NRC
NRC - U.S. Nuclear Regulatory Commission
NRDC - Natural Resources Defense Council
OFHCC - Oxygen Free High Conductivity Copper
ORNL - Oak Ridge National Laboratories
PCI - Pellet/Clad Interaction
PIVER - Pilot Vitrification Plant at Marcoule
PNL(BPNL) - Battelle Pacific Northwest Laboratories
PSV - Project Salt Vault
PWR - Pressurized Water Reactor
PyC - Pyrolitic Carbon
RIT - Royal Institute of Technology
SKBF - Swedish Nuclear Fuel Supply Project
SNWDG - Simulated Nuclear Waste Disposal Glass
SRL - Savannah River Laboratories
STEM - Scanning Transmission Electron Microscopy
TRU - Transuranic
WCF - Waste Calcining Facility
WFP - Waste Fixation Program
WIPP - Waste Isolation Pilot Plant
WISAP - Waste Isolation Safety Analysis Program
WSEP - Waste Solidification Engineering Prototype

Introductory Remarks

Robert Leachman - U.S. NRC

Comments:

This is a conference sponsored by the Nuclear Regulatory Commission, more specifically by the licensing part of the Nuclear Regulatory Commission. We should like to start this morning with some words of welcome by a representative of Governor Lamm of Colorado. This is Mr. Malcolm Murry, who is the Governor's assistant for Natural Resources Matters.

Mr. Malcolm Murry

Comments:

On behalf of Governor Lamm, I would like to welcome you to our lovely city of Denver, one that is also a very innovative city. Those of you who arrived yesterday or read the paper this morning may have noticed that we have a very novel way of disposing of some of our nonradioactive hazardous waste. We disperse them widely into the atmosphere so that everybody gets a chance to breathe them. Air pollution is certainly a problem in Denver, and I think that it is one that we wrestle with quite often. This brings to mind a comparison to the issues that you are dealing with today. Air polution is a relatively short-term problem. We, in Denver -- with some technological solutions, some changes in the way we use the automobile -- hope to solve our air pollution within the next ten to twelve years if all of the engineering projections come out right. We are very optimistic. Ten or twelve years seems a long time, but it is nothing in terms of the period of time that the problems that you are dealing with are going to be with the public and with mankind. You are dealing with periods of thousands of years rather than periods of ten to twelve years. The other thing that struck me when I looked at the brochure for this presentation was that I have virtually no knowledge of most of the subjects to be discussed, and that as a layman I am relatively ignorant and very dependent on scientific and engineering wisdom and knowledge of you people. I think I am certainly not any different from the public at large. And I would urge on you that one of the issues to keep at hand, while you discuss many of the issues that will be before you, is that success dealing with nuclear waste will deal as much with the technical solutions that you will come up with, as with the public's ability to understand and perceive a sense of security from the solutions that you come up with. As a member of the public, I look on the debate that surrounds nuclear waste management with a good deal of interest, although not much understanding. I think that is a feeling which you will find in a large part of the public. So I urge you to consider how you will translate your solutions to these issues to the public at large.

Thank you and welcome to Denver.

Robert Leachman

Comments:

Denver has some relevance to other matters of waste management, although not planned in our location of Denver as a conference site. As some of you who read the news might have followed, the Rocky Mountain Arsenal just a little bit to the Northeast of the city was the site where there has been experience with deep geological injection of hazardous waste, namely nerve gas waste, with an unplanned consequence of some regional earthquakes or disturbances. Secondly, Denver has experience with regard to nuclear waste from the Rocky Flats location, a subject that has aroused very understandable public interest because some wastes on the storage pad leaked and were transmitted outside the confines of the Rocky Flats site. So Denver is a city that has had some little experience with waste management that are relevant to our conference.

I should like to start by saying a few words about the people who are involved and about the procedures that we will be following and then I should like to say a few words about the purpose of the conference and what we hope to achieve from it. The conference planning was done by me, and by Leslie Casey. We both have been in the licensing part of the Nuclear Regulatory Commission, but have recently moved to other waste management activities. Dale Smith has continued these tasks with regard to the planning of this conference.

As you probably noticed in the Conference brochure, a new journal of Nuclear Waste Management and Technology is appearing. Lawrence Cranberg is the editor of it. Their inaugural issue will be using the prepared talks given at this conference.

We feel it is very important in this conference to have accurate recordings of what is taking place in the conference. The verbatim discussions of the Conference will be recorded and will be written in the Proceedings of this Conference, the Proceedings going to all of you who are registered and reaching you in the course of 2 or 3 months. Now let me go to something of more substance, the purpose of the Conference. We all know that nuclear waste management is a very important subject in the nation's energy picture, it being a key point in the future of nuclear energy. We are all aware that there are many studies that are underway and many considerations -- and, indeed, reconsiderations -- by the Federal Government. Reports with very high level of authorship are appearing, for example, from the Interagency Review Group. The National Academy of Sciences has released one report on solid wastes and has also issued one on geological siting criteria, both sponsored by the Nuclear Regulatory Commission. A supplement to the later report is actually underway which will go beyond just the geological site criteria and questions how they relate to what goes into the repositories. So we are finding that there is a trend of greater attention to the waste management in general, but specifically to the solid form of the waste and how the solid form of the wastes tie into the overall picture of nuclear waste management. Licensing is, of course, a very important subject in the conduct of the energy business of our country. It is very important that the licensing procedure go fairly, properly, legally, and (hopefully) smoothly and expeditiously. One of our purposes in being here is to try to assure that we, in a thorough and fair way and also expeditious way, take care of the licensing problems. Our purpose is to establish a public record -- a report, something for reference. So I have asked the people who are giving presentations to provide broad surveys, as much as they can, of the different work that is being done and make comparisons as much as possible. I urge you to speak up, raise your questions, have your questions thereby in the public record in the form of the Proceedings of this Conference. Those of you who think that some things have not yet properly been considered should raise these and so thereby have the fact in the public record that you have stated that certain things are inadequate, need attention, should be reconsidered, or whatever is the thrust of your point.

There are different categories of responses, so we hope that you will adhere to them. In these plenary sessions, we will be considering rather highly technical aspects of the waste management. In the workshops, there will be more of applications and policy, and so there will be broader ranging discussions. We have alotted rooms for Wednesday evening for discussion groups. Those subjects that people feel have not been in the schedule should properly be considered then. Let me mention one other thing. When you are recognized for a question, I ask you to state your name and your affiliation. It is quite adequate to have your affiliation be private citizen if you wish.

Bob Watt - Physicist interested in nuclear wastes, retired from Los Alamos

Question:

I am curious as to the relation between this group and Bill Bishop's.

Robert Leachman

Response:

The Nuclear Regulatory Commission staff has had many changes recently. Bill Bishop is now at the National Aeronautics and Space Administration. It was indeed Bill Bishop's group in the licensing part of the Nuclear Regulatory Commission that was the location where Leslie Casey and I started this conference activity and where much of the work is continuing. The answer is that we are one and the same.

Bob Watt

Question:

In relation to radioactive gases, and particularly krypton-85, does the NRC plan to regulate that or does the EPA?

Robert Leachman

Response:

It is my understanding that the regulations of that will be from the Nuclear Regulatory Commission. To go into more detail about the way we are presently structured in the Nuclear Regulatory Commission, one group handles the high level radioactive wastes, another handles other things. The other things happen to include gases, but that is only an internal detail of the organization within the Nuclear Regulatory Commission.

The answer to your question is the Nuclear Regulatory Commission will regulate it, but in the same way that the regulations apply for other subjects. Specifically, the Environmental Protection Agency will write the regulations that apply to the effects upon the public and the Nuclear Regulatory Commission in general will write regulations as apply to the repository themselves, with these regulations consistent with the overall requirements of the EPA regulations.

Bob Watt

Question:

Part of the reason I asked about the relative storage of volatile versus solid wastes has to do with iodine. Iodine is normally of course in HEPA filters. Is it expected then that this Conference should cover iodine as a solid waste, or will that be regulated elsewhere?

Robert Leachman

Response:

In the specific case that you mentioned, of iodine as a solid or prepared in what is intended to be a solid, yes we will be covering that.

Dr. Lawrence Cranberg - Editor of Nuclear Waste Management and Technology

Comment:

The journal is in the process of appearing. It will initially be a quarterly . It will be international, and it will be devoted to the topics in this field.

Robert Leachman

I should like now to go into the invited presentations. The committee that put together our program provided guidance on our program. This Program Committee was Tom Cochran from the Natural Resources Defense Council, William Holcomb from the Environmental Protection Agency, Goetz Oertel from the Department of Energy and myself. We thought it would be a good orientation in starting this series of technical talks on solids themselves to have a presentation by a person who is very familiar with the overall situation, to show us how solids fit into the overall repository concern. We are very fortunate to have a person who has an unusual ability to make this relationship. This is Dr. Fred Donath from the University of Illinois.

PLENARY SESSION I, VITREOUS FORMS

ROBERT B. LEACHMAM - U.S. NUCLEAR REGULATORY COMMISSION
CHAIRPERSON

RELATION OF SOLIDS TO NUCLEAR WASTE ISOLATION

Fred A. Donath
University of Illinois

ABSTRACT

In a geologic repository the solid waste form will be subjected to demanding physical and chemical conditions that reflect both geologic and engineered factors. These conditions are an effective confining pressure of about 10 MPa, possible differential pressure up to 35 MPa, possible temperatures up to 400°C, and the likely presence of water in a reducing environment. Behavior of the waste form in the selected geologic environment must be predicted over unprecedented periods of time. From the standpoint of both the waste isolation system and of the waste form in that system, the thermal period of a geologic repository is the most critical. It is during the first several hundred years after closure of the repository when heat production is dominated by the decay of fission products that the repository contents and surroundings are likely to be subjected to the greatest thermal, mechanical, and chemical stress. Thus, most physical and chemical changes within the waste form or host rock that would affect the relationships among the waste, the host rock, and contained fluids would be expected to proceed at the highest rate during this period. Although thermal loading can be controlled, a maximum thermal loading that will not compromise the isolation system is desirable because this would minimize waste form and repository volumes. The higher temperatures that will result can be expected to contribute to increased rates of waste/rock/fluid interactions within the repository, higher stress levels, and other effects. The waste form must therefore be thoughtfully tailored to the host medium, contained fluids, and other characteristics of the specific geologic system selected for waste isolation.

INTRODUCTORY REMARKS

I have been asked to comment on the importance of solid waste forms to nuclear waste isolation, the conditions to which these might be subjected during burial, and changes that might occur in the waste form or in its immediate environment which could significantly affect the security of waste isolation. This is a tall order, and in the time allotted one can only touch on a few of the more important general points. My comments will be directed to the isolation of high level reprocessing wastes emplaced in a deep geologic repository, and are based in part on several recent studies in which I have participated. More entensive discussions can be found in the reports that resulted from these studies.[1,2,3]

The potential hazard from deeply buried radionuclides depends upon three important aspects: first, the amount and rate of supply of radionuclides to a transport medium (i.e., groundwater); second, the pathways and rate of groundwater movement; and third, the degree of retardation of radionuclide movement caused by chemical interactions with the geologic media through which the groundwater moves. All three aspects influence, and any one of the three conceivably could independently control, the potential hazard imposed by radionuclide migration from a geologic repository. For example, if the waste form were completely stable and inert, no radionuclides would be available to the groundwater for transport. Or, if the pathways were sufficiently long and the rate of groundwater movement were sufficiently slow, any radionuclides dissolved in the groundwater would decay to innocuous levels before reaching the biosphere. Finally, if strong coupling occurs between dissolved radionuclides and the geologic media through which the groundwater moves, by sorption or other processes, the radionuclides would be immobilized and would not reach the biosphere. The waste form has its greatest influence on the first important aspect of the waste isolation system--viz., the availability of radionuclides for transport--but the waste form can be an influential factor with respect to groundwater transport and radionuclide retardation, as well. A waste form could be designed to reduce hydraulic conductivity locally and to enhance geochemical retardation.

As implied by my preceding remarks, the supply of radionuclides, the groundwater flow regime, and geochemical retardation constitute the important aspects of a waste isolation system. The solid waste form is but one factor, albeit an important and even in some instances conceivably a controlling one, in a complex system of many factors that can affect the security of waste isolation. It cannot be emphasized strongly enough that the geologic disposal medium, the waste form, or any other waste isolation factor cannot be evaluated without due consideration to the total system of which these are a part. Because of the variability among geologic environments potentially suitable for nuclear waste isolation, no single waste form is likely to be most satisfactory for all possible waste isolation systems. The waste form must be thoughtfully tailored to the host medium, to its contained fluids, and to other characteristics of the specific geologic system selected for waste isolation. I shall return to this concept later, but it might be helpful first to consider the general conditions of pressure, temperature, and water that could exist in a sealed geologic repository and to which the solid waste form might be subjected.

PRESSURE ENVIRONMENT OF A GEOLOGIC REPOSITORY

The state of stress in the host rock at the depth of burial will largely reflect the weight of the overburden, the tectonic history of the region, and rheologic properties of the rock. Figure 1 shows the observed variation of vertical stress with depth based on the available

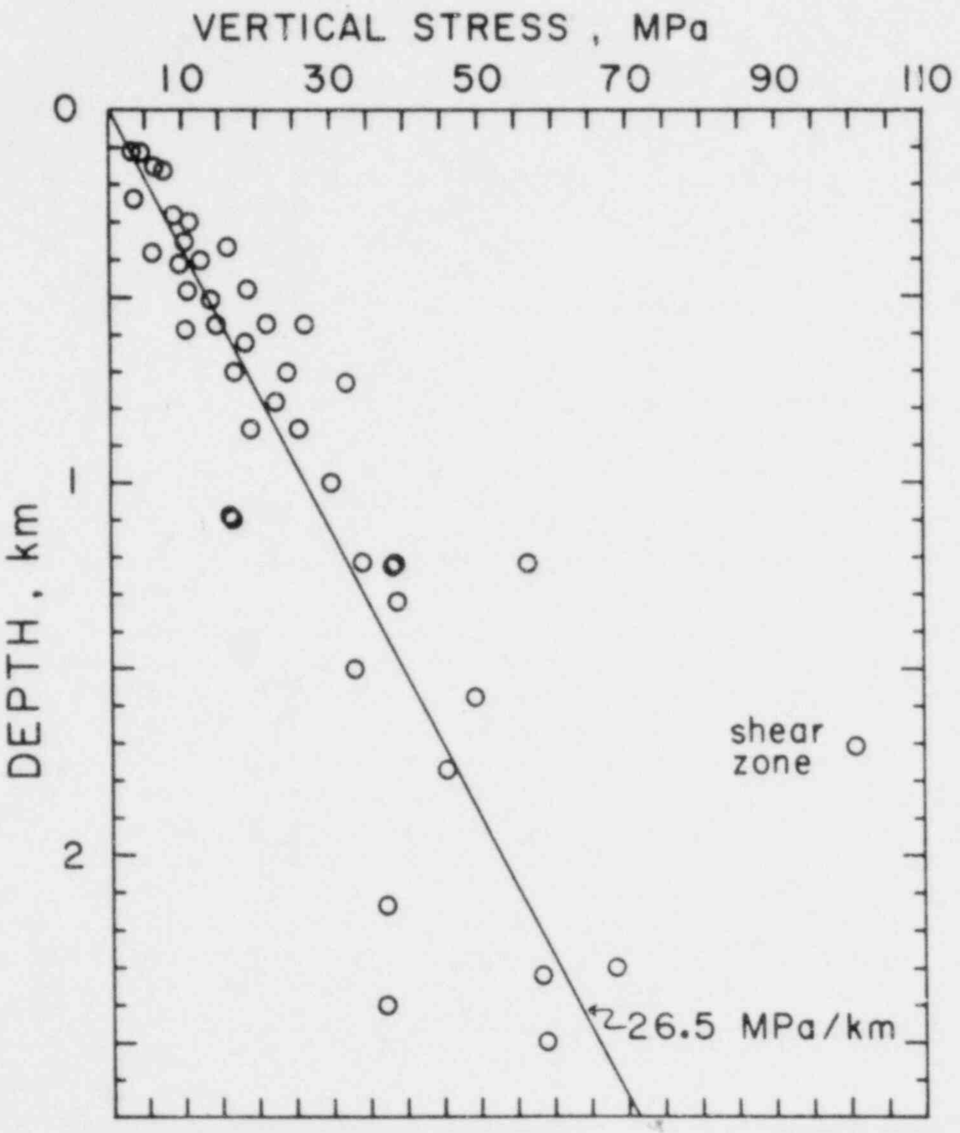

Figure 1. Vertical component of stress for depths greater than 100 m.

data from strain-relief measurements.[4] The line corresponding to an average density of overburden of 2.7 gm/cm is shown for comparison. The data are generally consistent with the assumption that the vertical stress corresponds to the weight of the overburden. Thus, the vertical stress at a depth of 600m, roughly 2000 ft, would be about 16 MPa (160 bars or 2,300 psi). The horizontal stress will equal the vertical stress only if the rock is incapable of sustaining shear stress, a situation that at a depth of 600 meters would likely be true only for rock salt. The sustained differential stress, or strength of rock, can be a function of time, as well as of rock type and environmental conditions such as pressure and temperature. The systematic decrease in strength of a marble as the strain rate is decreased by several orders of magnitude is shown in Figure 2. The lowered resistance to deforming stresses at slow strain rates--or, to stresses sustained over long periods of time--would be characteristic behavior for any rock that deforms primarily by intracrystalline processes. For most common rocks intracrystalline flow requires confining pressures well in excess of 16 MPa, or very high temperatures. The results shown in Figure 2 are for tests at 25°C and 200 MPa, a pressure depth equivalent of about 7.5 km (about 25,000 ft). At the likely depth for a geologic repository most common rocks subjected to high differential stress will deform by processes dominated by fracture and intergranular movements--i.e., cataclastic processes. Figure 3 shows the results of some experiments on a sandstone under conditions identical to those for the marble just discussed. The sustained differential stress is independent of the strain rate. One can conclude from these results that rocks which deform by cataclastic (as contrasted with "plastic") processes, will sustain existing stress differences for indefinite periods.[5] For this sandstone at these conditions the sustained differential stress could exceed 400 MPa. I have confirmed the time-independence of cataclastic processes in several ways, including the deformation of marble under lower confining pressures at which cataclastic processes predominate. It appears that time-independence may be characteristic of frictional processes in general. Figure 4 presents some results of laboratory experiments on faulting in several common rock types.[6] These results show the lack of effect of displacement rate both on the differential stress required to cause displacement on preexisting shear fractures and on the coefficient of friction.

Except possibly for rock salt, cataclastic processes will dominate in rocks at repository depths. If this is so and the existing stress differences can be expected to exist for indefinite periods, what are these stress differences likely to be? The extent of departure of the horizontal stresses from the vertical stress is limited only by the strength of the rock. For gravitational loading alone, the horizontal stresses would be predicted to be much lower than the vertical, and would be expected to fall along the line at the left side of Figure 5. The data given in Figure 5 are for in-situ stress measurements in South Africa.[4] The values at depths below 500 m fall between that predicted and the overburden pressure; at more shallow depths the

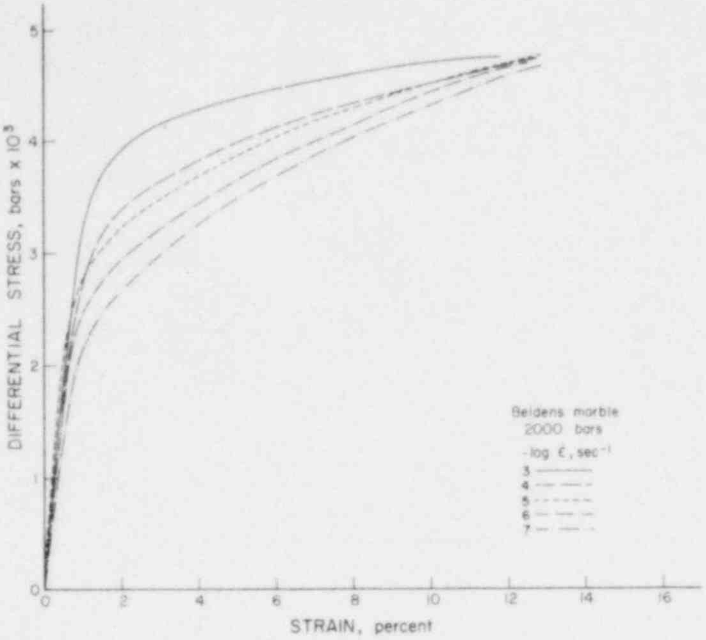

Figure 2. Stress-strain curves for marble deformed at different strain rates under 200 MPa confining pressure.

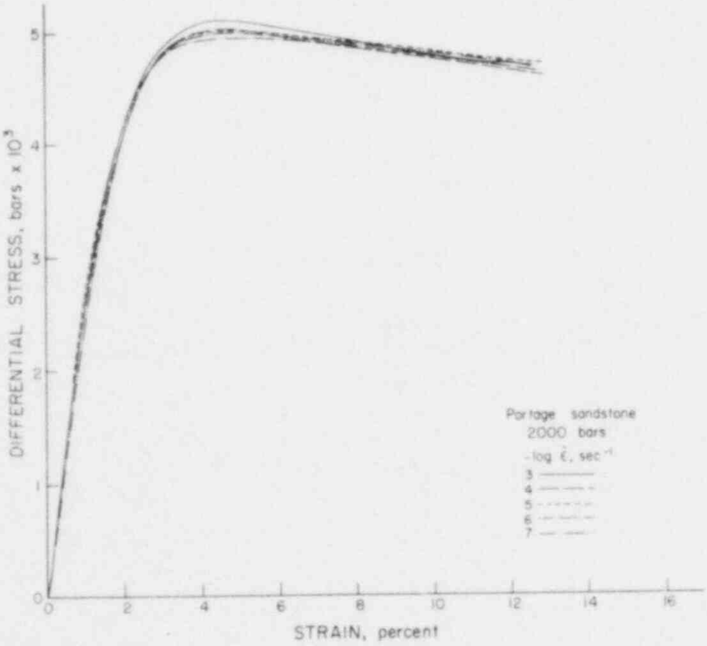

Figure 3. Stress-strain curves for sandstone deformed at different strain rates under 200 MPa confining pressure.

Figure 4a. Faulting stress vs. displacement rate, 80 MPa, 25°C.

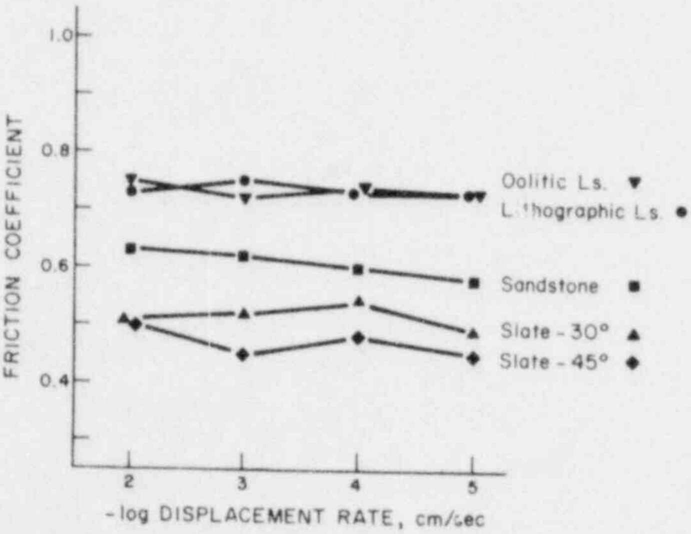

Figure 4b. Friction coefficient vs. displacement rate.

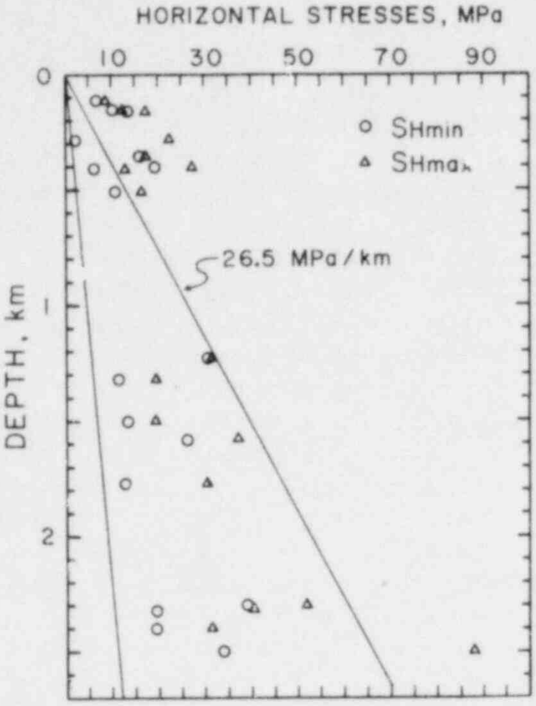

Figure 5. Horizontal stresses measured in southern Africa.

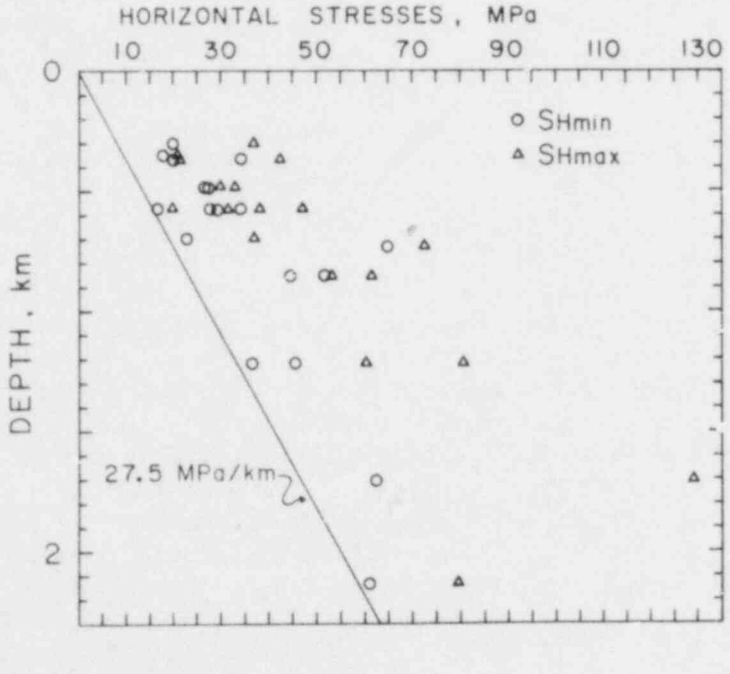

Figure 6. Horizontal stresses measured in Canada.

horizontal stresses exceed the vertical. Stress determinations in Canada are given in Figure 6 and indicate that horizontal stresses always exceed the overburden stress in those areas where measurements have been made.[4] Indeed, the horizontal stresses could show very high values at shallow depths. In one area in which I've worked recently, along the southern shore of Lake Ontario, the horizontal stresses were typically 11 MPa and occasionally as high as 20 MPa (nearly 3000 psi) within 200 feet of the surface. A summary of the then-existing data on in-situ stress measurements was made by Hoek and Brown[7] and is shown in Figure 7. From such relationships it is clear that at depths of 600 m or less, one could expect the horizontal stresses to exceed the overburden stress by several times. At a depth of 600 m this could mean horizontal stresses of possibly up to about 40 MPa, compared with a vertical stress of 16 MPa, which could result in a differential stress of 24 MPa. Recall, however, that except for salt, most rocks at this depth could sustain significant differential stress indefinitely--for the sandstone mentioned above this might be of the order of 35 MPa at that depth. The observed variation of the maximum component of shear stress, as determined from in-situ measurements,[4] is shown in Figure 8. The maximum shear stress is equal to one-half the differential stress. The data for rocks such as shale and sandstone are shown in Figure 8 as circles; those for granites and similar rocks are shown as triangles. As seen in this figure, at depths up to 600 m the shear stress has been measured to be as high as 15 MPa (i.e., a differential stress of 30 MPa), but this is still below the strength of most common rocks at those depths.

Two other factors that affect the local state of stress perhaps deserve mention. One is the change in stress distribution caused by excavation of the mined cavity, which could magnify the stress locally. This phenomenon is, in part, a function of the cavern geometry and will be analyzed as part of the depository design. The second is the effect of fluid pressure in pore spaces within the rocks. This might be more difficult to evaluate.

It has been well demonstrated that the effective stresses to which the rocks will respond are equal to the stresses in the solid framework minus the pore pressure in the voids.[8] Thus, if the pressure of fluids at a depth of 600 m were the normal hydrostatic head (about 6 MPa), the effective vertical pressure at that depth would be the weight of the overburden (16 MPa) minus the pore pressure (6 MPa), or 10 MPa. The strength of the saturated rock at 600 m depth would be lower than that of the unsaturated rock. This is because the rock strength is directly proportional to the effective pressure which is lowered by increased pore pressure, whereas the existing differential stress is not affected by pore pressure because the increased pore pressure reduces both the maximum and minimum principal stresses by equal amounts. As the pore pressure approaches the overburden pressure, the effective vertical stress approaches zero. In sedimentary basins the compaction of sediments can lead to pore pressure in excess of the normal hydrostatic

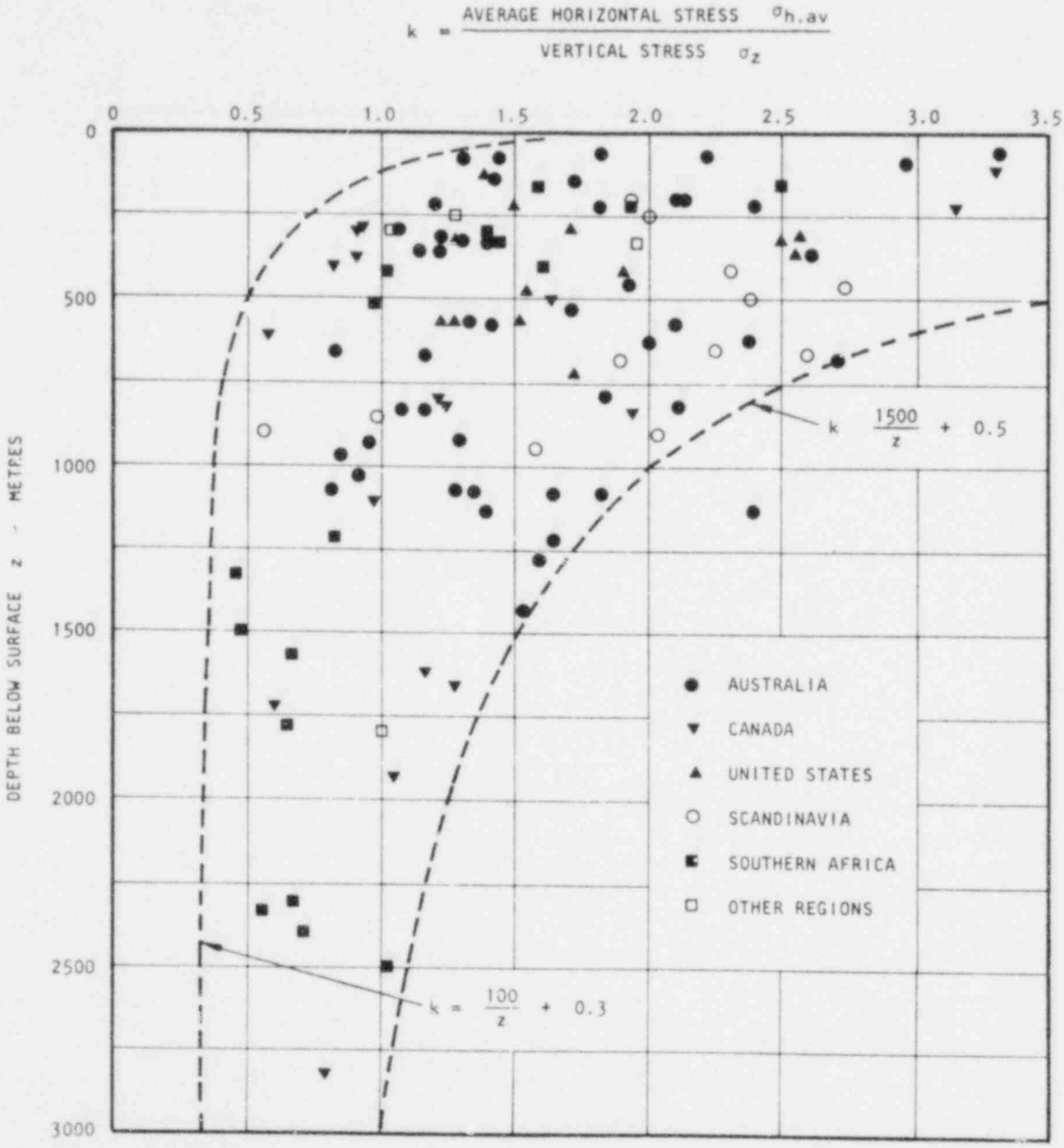

Figure 7. Variation of ratio of average horizontal stress to vertical stress with depth below surface.

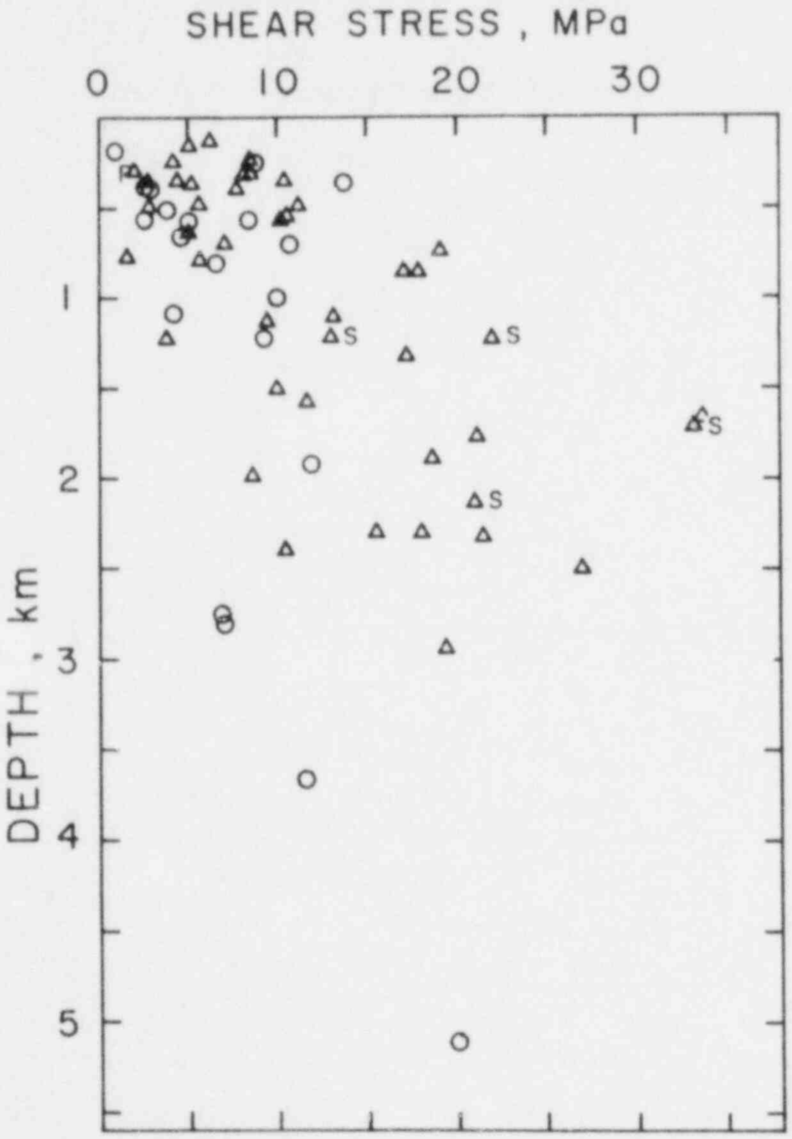

Figure 8. Maximum shear stress. Measurements in rock such as shale and sandstone are indicated as circles, and those in granite, quartzites, etc. are shown as triangles.

head, as in the Gulf of Mexico sediments. There, the ratio of pore pressure to overburden pressure can exceed 0.9 at depths below about 3000 m; even at depths less than 1500 m the pore pressure exceeds the normal geostatic ratio. High geostatic ratios reduce the strength of rocks and could contribute to faulting which, in turn, might be of consequence to the hydraulic transport characteristics of an area. However, in older sedimentary sequences it is likely that, except for rock salt and possibly shale, rock and fluid pressures that might exist at repository depths would not be sufficient to cause rock flow. With regard to rock behavior, the state of stress will be of concern primarily as an engineering consideration during the operational stage of the repository, but of less concern subsequent to its closure and decommissioning.

THERMAL ENVIRONMENT OF A GEOLOGIC REPOSITORY

The temperature of the repository will most certainly be dictated by the thermal loading produced by the high-level waste emplaced in the repository. Individual areas might have higher or lower gradients than the normal geothermal gradient of 25°/km, depending upon the geologic characteristics and history of the region, but it seems unlikely that the temperature at depths less than 1 km would exceed 50°C. More likely, they would be of the order of 35°C. Because higher ambient temperatures will result in higher predicted temperature distributions for a given planar heat density, the ambient temperature of a potential repository site is an important parameter for design considerations.

From the standpoint of both the waste isolation system and of the waste form in that system, the thermal period of a geologic repository is the most critical. The thermal period extends from the time of closure of the repository for several hundred years, during which time the heat production of the high-level waste is dominated by decay of the fission products. It is during this period that the repository contents and surroundings are likely to be subjected to the greatest thermal, mechanical, and chemical stress. Thus, most physical and chemical changes within the waste form or host rock that would affect the security of isolation would be expected to proceed at the highest rate during this period. A maximum thermal loading of the repository that will not compromise the isolation system is desirable because this would minimize waste form and repository volumes. However, excessive thermal loading could adversely affect the integrity of the waste form, as well as the hydraulic characteristics of the surrounding media and their retardation capability.[2]

It is not possible to say in terms of thermal power just what would constitute excessive thermal loading. That will depend on the particular waste form selected, on the configuration and thermal characteristics of the canister and its overpack, and on the thermal and mechanical properties of the host medium, among other factors. Depending largely on the planar heat density and on the geologic configuation and thermal properties of the geologic media, excessive thermal loading could lead to the opening of fractures and significant changes in the hydraulic properties of the media with resultant increased groundwater movement.[2,3] The planar heat density can be controlled in several ways: for example, aging of the wastes before emplacement, lower waste loadings of individual canisters, and wider spacing of canisters in the repository. Because the principal concern of this conference is the solid waste form, I will not elaborate further on thermal loading of the repository. However, it might be worth noting that thermal analyses have shown that the temperature distributions outside the repository do not differ greatly even between such disparate rock types as salt and granite. Indeed, although the thermal conductivity of salt is approximately twice that of granite, the maximum temperature developed in granite could be lower than that in salt because the larger volumetric heat capacity in granite more than offsets its lower thermal conductivity.

Of more concern with regard to the waste form is the temperature that may develop within it or, perhaps even more important, at the canister wall where reactions with the host media are most likely. Here again, this temperature can be controlled--principally by adjusting the power level of the canister and by improvement of the heat transfer capacity near the canister. For example, analysis has shown that a canister containing 3.5 KW at 10 years (2.5 MTHM) would have a maximum surface temperature of about 375°C, but if emplaced when it is 30 years old the maximum temperature would be about 200°C (S. C. Slate, pers. comm.). Because almost the entire temperature rise above ambient occurs across the backfill between the canister and the host medium, the thickness and thermal conductivity of the backfill is very important. From the standpoint of possible reactions, the chemical makeup of this material is equally important. Without specifying the power level of the canister and the thermal characteristics of its environs, it is not possible to specify the temperatures that will develop in the immediate vicinity of the canister. Moreover, such factors as the power level of the repository and geometric configuration of canisters and media would be needed to predict the rise of media temperatures above ambient. Suffice to say that both canister and repository temperatures could be kept quite low if higher temperatures were to present a problem for either the endurance of the waste form or with regard to possible chemical reactions among the emplaced materials, the host medium, and any contained fluids.

GENERAL CONDITIONS IN THE REPOSITORY ENVIRONMENT

In addition to pressure and temperature there is a third general factor that must be considered in evaluating possible repository conditions to which the solid waste form might be subjected following burial--viz., the presence of water.

Over geologic periods of time it is reasonable to assume that no geologic medium is completely impermeable. It can further be assumed that, in general, rocks at depth are saturated--that is, any existing pore space is filled with water or other fluid. With some finite permeability and some finite hydraulic gradient, water will move through these rocks. The normal hydrostatic pressure at a depth of 600 m would be about 6 MPa (870 psi). Immediately upon closure of the repository, 6 MPa is the pressure differential that will exist at the margins of the repository. It seems highly unlikely that any water present in the surrounding media would not move into the repository in such a pressure gradient in an attempt to equalize this pressure differential. Thus, it would seem reasonable to assume that possible reactions between the waste form and the host medium will take place in the presence of water. Except for a brief period immediately after closure, it is likely that this water will be anoxic--i.e., the waste form will be in a reducing environment.

In summary then, the general environmental conditions that could exist for any waste form emplaced in a geologic repository at a depth of 600 m are an effective confining pressure of about 10 MPa (about 1500 psi), possible differential pressure up to 35 MPa (about 5000 psi), temperatures up to 300°-400° in the near field and up to 200°C in the far field (but likely to be engineered to significantly lower values), and the presence of water in a reducing environment.

WASTE FORM ENDURANCE

What is likely to happen to the waste form under conditions such as those described? What changes are likely to occur? Clearly, answers to these questions cannot be advanced without specifying, as a minimum, the waste form and any engineered overpacking, the geologic medium into which it is to be placed, and the nature of contained fluids. Nevertheless, some general comments might be of value in developing perspective in this matter. By way of introduction and to provide some insight into the behavior of glass in a geologic environment, I will describe briefly some experiments I have run on a mixture of quartz grains and natural volcanic glass in connection with studies of diagenesis of sediments. In these experiments we subjected samples consisting of equal mixtures of silt-sized grains of quartz and basaltic glass to hydrostatic confining pressure and temperature in the presence of distilled water. The effects at a given confining (solid) pressure and pore pressure were studied as a function of time and temperature. The physical changes that took place in the solid fraction were determined by means of scanning electron microscopy, and mineralogic and chemical changes in the solid and liquid phases were determined by x-ray and atomic absorption spectroscopy, respectively. Figure 9 shows several silt-sized grains of basalt glass which had been subjected to 20 MPa effective pressure (40 MPa confining pressure, 20 MPa pore pressure) at 200°C in the presence of distilled water for a period of

Figure 9. Silt-sized grains of basaltic glass with overgrowth of clay minerals.

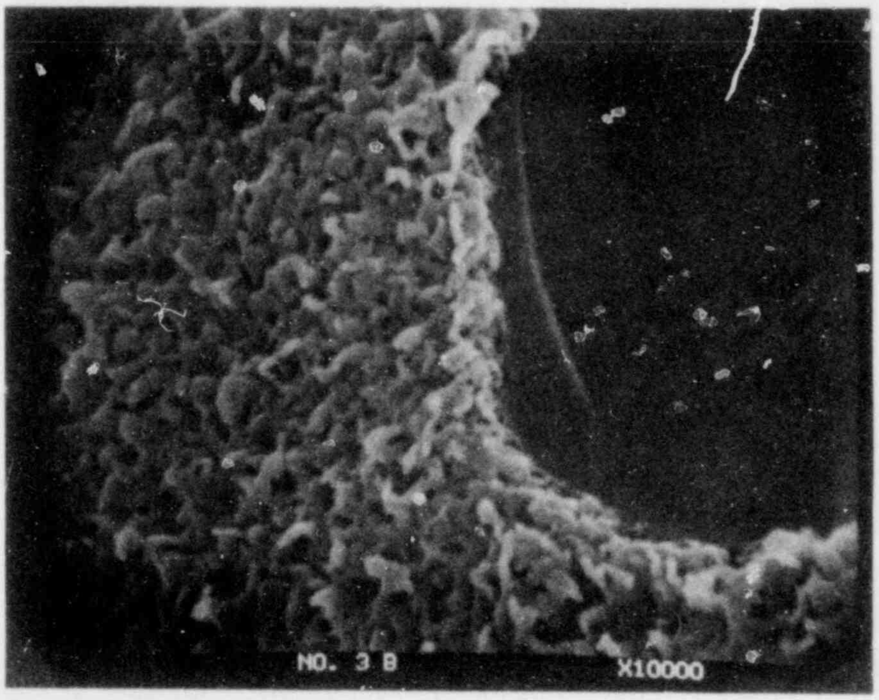

Figure 10. Enlargement of Figure 9 showing portion of grain of basaltic glass with clay mineral overgrowth.

30 days. An extensive overgrowth of clay minerals has developed on these grains, which is more clearly seen in Figure 10. The clay minerals have formed from the breakdown of the basaltic glass and tend to be preferentially deposited on the glass rather than on the quartz surfaces. This phenomenon has been observed for temperatures as low as 100°C and for periods as short as 14 days, but, as would be expected, the clay mineral development is more extensive with longer periods of time and at 200° rather than 100°C.

Waste-form philosophy to date has been almost exclusively directed at the development of stable and inert waste forms, with the greatest effort having been made on the development of a suitable glass waste form. It has been demonstrated that glass is unlikely to remain unaltered in a typical repository environment, but would likely devitrify, crack, and, ultimately, break down to form new mineral phases.[9] These changes could occur within a relatively short time after closure of the repository. Thus, glass does not appear to fulfill the desired criterion of long-term endurance. However, experiments such as those I described above suggest a totally different waste-form philosophy--viz., to develop a waste form that is deliberately intended to break down and whose decomposition products provide advantageous characteristics for waste isolation. Glass would certainly be a leading candidate for such a waste form. Any cracks developed in the glass during processing or subsequent to burial would soon become coated with minerals that could serve the dual function of reducing permeability and of providing numerous available sites for exchange and sorption of any radionuclides that might be released from the original matrix. Thus, the altered waste form could in this way contribute significantly both to reduced movement of fluids through the radionuclide source material and to enhanced retardation.

As mentioned earlier, the waste form has its greatest influence on the availability of radionuclides for transport. Presumably, it is recognition of this fact that has led to emphasis on long-term stability and inertness of waste forms. Considerable attention has been devoted to the development of waste forms that are characterized by low leachability because, clearly, the most important concern regarding the waste form is the rate at which radionuclides will be leached and transported away by groundwater. The leaching mechanism will depend upon the chemical reactions that proceed between the groundwater and components of the waste and waste form. Because of the large number of variables involved--such as waste type, waste form, overpacking material, host rock composition, groundwater composition, environmental conditions, rate of groundwater flow, and the like--it is not possible to specify the rate-controlling mechanisms. Some analyses indicate that nuclide solubility might be a far more important rate-limiting factor than leachability of the waste form. Although the waste form might break down completely, such that the contained radionuclides would be available for transport, the limited solubility of these nuclides in the repository environment would greatly restrict the rate at which these are transported away from the repository. If near-saturation of a radionuclide can be assumed to occur in the groundwater adjacent to the waste, the rate of transport of that radionuclide away from its source will be a function of its saturation concentration and the groundwater flow. Thus, those factors having the greatest influence on the saturation concentration would seem to deserve considerable attention. Not the least important among these factors is the groundwater chemistry which, of course, will be site specific. Once a potential site is identified, it would seem imperative that the important mineral phases in the geologic media and principal reactions taking place among them be identified. By determining stability fields of the dominant natural phases in the existing Eh-pH environment, it should then be possible to tailor a waste form with or without overpacking that will interact with the host rock and its contained fluids in such a way as to produce new thermodynamically stable and low solubility phases.

The ultimate objective of the solid waste form in nuclear waste isolation is to prevent radionuclides in the waste from becoming available to the transport medium--i.e., to the groundwater. As I've attempted to indicate in this brief overview, this objective can be achieved in several different ways. Which way might be most appropriate can only be determined after the total waste isolation system has been adequately characterized.

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Discussion Following

RELATION OF SOLIDS TO NUCLEAR WASTE ISOLATION

Presented by Fred A. Donath

Bob Watt - Los Alamos, private citizen
Question:
Can you say, in general, that below some depth, perhaps 500 meters, you will expect vertical fractures as opposed to horizontal?

Donath
Response:
No, I think as a generalization one would have to make a different statement: namely, that they are likely to be horizontal, because the horizontal stresses tend to exceed the vertical stresses in the vast majority of measurements.

Bob Watt
Question:
At depth? I thought your graph showed that the horizontal stress was less than the vertical for fairly deep systems.

Donath
Response:
Well, when you say fairly deep I assume that you are still referring to reasonable repository depth levels.

Watt
Comment:
At the moment I am considering 500m. I thought your break point was in the neighborhood of 500m.

Donath
Response:
If you wish to consider much greater depths, such as deep hole emplacement, then there may be situations in which the horizontal stress, or one of the horizontal stresses, will be the minimum principal stress and there will be vertical fractures.

Barry Naft - NUS Corporation
Question:
In your discussion you mentioned that one performance factor which would influence waste form criteria is groundwater flow rates. Isn't the physical separation of the repository (i.e., the distance from radwaste insertion in an aquifer to the nearest discharge point of the aquifer into a waterbody just as important a factor? What about engineered barriers; have you given up that as an influence on the waste form criteria?

Donath
Question:
Would you state again the specific aspect of your question with regard to the aquifer?

Naft
Question:
If I place one aquifer five miles, and another one 10 miles from the discharge to a water body, this might have more of an effect especially if they all have similar flow rates than the actual flow rate through the aquifer. In other words, in siting of the repository, the physical separation for any water bodies may be a significant factor too. You didn't discuss that at all. I was wondering if there was a reason for that.

Donath
Response:
I did not discuss aspects of groundwater transport for obvious reasons: insufficient time and the fact that emphasis here is on the solid waste form, but I would point out that there are only two ways which one can get radionuclides back to the biosphere. One is by physical transfer of the mass that contains those radionuclides or by solution in the groundwater and movement of that groundwater back to the biosphere. And the subject of analysis of groundwater flow is, of course, receiving a great deal of attention now. Simple generalizations cannot really be made about that. You have to understand boundary conditions and the hydraulic characteristics of the region in order to analyze this. Obviously distance to potential sources of aquifers or deep wells for irrigation or municipal purposes will be taken into consideration in risk analysis and assessment.

Naft
Question:
How about engineered barriers, would that be a consideration for the waste form?

Donath
Response:
Of course. I thought I had alluded to that at least, if not made direct reference, by speaking of the overpacking materials that would be taken into consideration with the waste form itself.

Larry Penberthy - Penberthy Electromelt Co.
Comment:
You referred to glass, but I think it is important throughout this whole meeting, that we keep in mind that not all glass is the same as all other glass. The glasses which have been in the forefront are those which are suited to in-can melting and hence are very high in fluxes, hence tend to be soluble, as opposed to the glasses which can be made in ceramic melters which are somewhat higher in temperature, but make much better use of the properties of silica and alumina. Alumina, in particular, is amphoteric, and it has possibilities of latching onto some of these ions we would like to hold.

Donath
Response:
That appears to be a comment rather than a question, and I would say that my reference to glass is not to either endorse or comment that it may not be appropriate. The message that I was trying to get across is that the waste form needs to be tailored to the environment and glass may be very appropriate and can be considered for different purposes in that.

Gregory McCarthy - Pennsylvania State University
Comment:
I can give some direct experimental evidence of just what Fred Donath said. We have studied a reference PNL glass after a 300°C hydrothermal treatment and found that it indeed is totally altered and devitrified in a matter of weeks. Materials are transported within the reaction capsule. But, if the alteration happens in the presence of basalt--and by analogy, shale, and granite--the crystalline waste-rock phases formed look as though they might be indefinitely stable at those temperatures and pressures. It is most important to consider that we could use even a reactive waste form if we know the total waste-rock interactions picture. Some of these concepts are in a reprint (G. J. McCarthy, et al., "Interactions Between Nuclear Waste and Surrounding Rock," Nature, 273, p. 216, 1978) that I will leave out at the desk during the break.

Leslie J. Jardine - ANL
Question:
Excessive thermal loadings of repositories may be avoidable by an alternative waste management strategy than is currently advocated. That is, separate only the Cs and Sr decay chains from the primary HLW stream. Removal of only these two isotopes reduces the heat content of the bulk of the waste by a factor of ≈100. The long-lived waste of fission products and actinides would be buried in the conventional geological repository. Problems and uncertainties pertaining to solid waste forms and/or geological formations caused by excessive thermal loadings provide serious obstacles to the licensing and NEPA requirements for future repositories. Removal of only the Cs and Sr should reduce the obstacles, since the thermal loading is reduced by ≈100 times. The separated Cs and Sr fraction could be either stored or used as beneficial isotopes until burial ultimately in a repository. A second separate repository with a high thermal loading specifically designed for accommodating the ≈30-year half-life of Cs and Sr might also be proposed since long-term geological stability for Cs and Sr isolation is not as critical as for long-lived actinides and select fission products. The technical feasibility and benefits of such a waste management strategy has not been given adequate evaluation but should since it offers an option that may help provide solutions to future licensing requirements for waste repositories. Do you have an opinion or comment?

Robert Leachman - NRC
Response:
The Nuclear Regulatory Commission did have a Convention on the question of partitioning in Seattle two years ago. Indeed, it is a worthwhile subject, but it is not our intention that it be a central part of our presentations here.

Jardine
Comment:
At that conference in Seattle no one really addressed the subject of only cesium and strontium.

Donath
Comment:
I would add to Leachman's comment that you still do have the problem of isolating the heat producing fission products for a given period of time. You may remove the problem of dealing with the effects of those in relation to the isolation of long-lived radionuclides, but you do have to isolate for a few hundred years, certainly, those fission products.

Jeff Stokes - IRT Corporation
Question:
What is your method of in-situ stress determination?
Comment:
I believe you also have to consider, in your definition of expected repository conditions, the possibility that in some kinds of formations the rock will flow and close around the waste, thus bringing the rock into intimate contact with it and the full overburden pressure to bear on it.

Donath
Response:
In response to your question, rather than going into detail, I would refer you to the article "State of Stress in the Earth's Crust," by A. M. McGarr and N. C. Gay, in the Annual Review of Earth and Planetary Sciences, Vol. 6, pp. 405-436, 1978, from which these figures were taken, which describes the techniques for stress measurement. In regard to your comment, one of the points I was trying to make is that it may not, in fact, happen that there will be pressure of the rock around the waste forms. That depends on the strength of the rock and the rheologic characteristics. If the processes of deformation are cataclastic processes, then they can sustain rather significant differential stress for significant periods of time, such that in granites and other silicate crystalline rocks--very likely in shale as well (certain types of shale)--that is not going to occur. In rock salt, it will certainly occur.

Judith Danielson - American Friends Service Committee
Question:
You mentioned tests on glass taking place over a period of 15 days. I wondered if this is the longest period of testing that has been done and if not, what is the length of time that the glass has actually been tested? Are there plans for more extensive testing?

Donath
Response:
There are extensive tests of a variety, some of which Gregory McCarthy mentioned. There is nothing significant about the period of time that I referred to, other than that is a very short period of time for glass to show the effects that it did. That is only one specific natural type of glass.

Jack McElroy - Battelle Pacific Northwest Laboratory
Question:
Most of the recent high-temperature, high-pressure tests on waste forms have been carried out at temperatures that exist in a dry repository. You said that the temperature of the waste canister is very dependent upon the heat transfer near the canister. Is it not true that the presence of water, in quantities sufficient to be of concern, will improve the heat transfer near the canister so that the canister temperature will decrease to be more nearly equal to that of the repository rock, which is much lower in temperature?

Donath
Response:
Those are very important points you are making. I hope everyone caught them. I would add further that the tests that I illustrate here were done at 200°C. We did some at 100°C and there is clay formation on that particular glass.

PHYSICAL PROPERTIES OF WASTE GLASS

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ABSTRACT

Physical Properties of Waste Glass

The physical properties of borosilicate glass make it a suitable waste form for the storage and disposal of high-level radioactive wastes. Waste glass has excellent radiation stability. As the result of over 10 years of testing it is known that the physical properties are relatively unaffected by high doses of contained radioactivity. Similar detailed studies have shown that the effects of self-heating in canisters of properly-formulated waste glass are also relatively minor. Glass is only one of a number of potentially satisfactory waste forms. It differs from the other waste forms mainly in that its processing has been developed to the point that a waste glass production plant is now operating in France. Using the known properties of waste glass as a baseline for comparison, important factors in the evaluation of alternate waste forms can be delineated. Among the factors that enter into the evaluation are: ability to deal with changing waste compositions, process complexity, waste loading, canister interactions, thermal stability, radiation stability, transmutation effects, and leachability.

1.0 INTRODUCTION

Various review groups have concluded that glass is a satisfactory first generation waste form.(1,2) Thus, the physical properties of waste glass, which have been studied enough to be well understood, can be used to illustrate the desirable generic properties of solid waste forms for all types of wastes destined for geologic isolation. A benchmark for comparison is needed because of the large number of waste forms that have been put forth as candidates.

We include in the generic properties not only the properties of the final product, but also considerations of the feasibility of making the solid form in a practical manner. These considerations consist first of obtaining an understanding of what has to be immobilized, that is, the source of the wastes. The process for treatment of the wastes must have the flexibility to accommodate a changeable, ill-defined, heterogeneous feed stream and convert it to a product with relatively homogeneous properties.

The relatively homogeneous product must have certain properties. Those properties should not degrade with time due to thermal or radiation effects. Glass appears to meet the requirements adequately; other waste forms undoubtedly do too, although as yet none are well enough characterized to warrant selection as a viable near-term waste form. Characterization is proceeding on several of these candidate waste forms. The goal is to demonstrate that the waste forms have acceptable properties when the total waste management system, which emphasizes multiple barriers, is considered.

2.0 RADIOACTIVE WASTES

National policy provides that all transuranic (TRU) wastes will be transferred to government custody for final dispostion in deep geologic isolation. The major classifications of TRU wastes and their treatments are shown in Figure 1. Transuranic wastes are generated in two basic forms: (1) liquids, sludges and slurries which are pumpable and are temporarily stored in tanks, and (2) solids such as filters, miscellaneous scrap and trash, a large proportion of which is combustible paper, plastic and rubber, and failed equipment. Spent fuel belongs in this category, if it is declared a waste. This paper will not discuss spent fuel, however it is the subject of some other papers in the conference.

Both liquid and solid wastes may require treatment before final packaging for shipment to the federal repository. Treatment of high-level liquid waste (HLLW), and the properties of the waste form to which it is converted by the treatment, has received the most attention, since this one stream contains over 99 percent of the nonvolatile fission products.

High-level liquid waste is generated as a nitric acid solution. At the Hanford and Savannah River plants, HLLW is neutralized and stored in mild steel tanks. Neutralizing the wastes causes formation of a precipitate which contains most of the radioactivity, except ^{137}Cs. One proposal for treatment of these wastes is to remove and purify the supernate and to immobilize and package only the precipitate, called sludge, for transfer to a federal repository. The radioactivity removed during purification of the supernate, mainly ^{137}Cs, would be combined with the sludge. In contrast, the HLLW at the Idaho National Engineering Laboratory (INEL) is not neutralized and is stored as an acid solution in stainless steel tanks. Part of the INEL waste inventory has been converted to a granular calcine, which is also stored in stainless steel tanks at the site. The HLLW from reprocessing spent power reactor fuel will also be stored for an interim period as an acid solution. This latter HLLW, which is 1-3 orders of magnitude more radioactive, is usually called commercial or power HLLW to distinquish it from the "defense" HLLW's of the Hanford, Savannah River and Idaho plants.

In a few hundred years most of the fission products will decay, leaving the long-lived TRU activity dominant. The non-high-level TRU wastes, which contain over 50% of the total TRU waste activity, are then equally as significant as high-level waste (HLW). Thus, it is important to recognize that although HLW has received most attention to date, there are other waste streams with equal long-term stability requirements for their waste forms. An example of such a waste stream is combustible solid TRU waste, a very heterogeneous and voluminous stream. Techniques are being developed to incinerate these wastes in the future. The TRU incinerator ashes are very fine powders which require further consolidation to be stable forms comparable with those being developed for HLW. There are current programs to develop techniques for converting incinerator ash to glass.

From the foregoing discussion, the diversity of the waste streams that are candidates for conversion to stable solid forms is apparent. Examples of the major constituents of the waste streams and representative concentration ranges are given in Table 1. The full importance of the diversity of compositions shown in Table 1 comes when it is recognized that: (1) the liquid wastes are really slurries with variable solids content, (2) variation from feed batch to feed batch may be large (depending on the process design a feed batch may represent a few days to several months operation) and (3) because of analytical difficulties with highly radioactive multicomponent slurries or powders, the chemical analyses of any given feed batch will have only limited accuracy. In essence what we are dealing with are nuclear refuse plants. Like other types of refuse plants, it is difficult to predict ahead of time what will be received at any given moment. The treatment plants simply have to be flexible enough to handle it.

The basic difference between commercial and defense HLW, that the commercial waste has much higher concentrations of fission products and actinides, is shown in Table 1. The remainder of this paper will emphasize commercial HLW because it represents the extreme case as far as self-heating and radiation effects are concerned.

3.0 RADIOACTIVE WASTE TREATMENT

Radioacitve wastes will be converted to solids possessing certain properties before they are placed in geologic repositories.

TABLE 1. Composition Ranges in Representative TRU Wastes

Constituent	HLW Commercial	HLW Defense	Incinerator Ash
Na_2O/Na_2CO_3	0-10	0-10	0-30
Fe_2O_3	3-29	6-61	0-11
Cr_2O_3	1-2	0-27	0-10
NiO	<1	1-11	0-3
Al_2O_3	---	0-86	17-33
MgO	---	---	0-8
MnO_2	---	4-40	---
CaO	---	---	0-24
TiO_2	---	0-18	---
SiO_2	---	---	10-55
Gd_2O_3	0-31	---	---
C	---	---	0-28
CaF_2	0-5	0-54	---
Na_2SO_4	---	0-5	0-5
NaCl	---	---	0-5
U_3O_8	0-12	2-14	---
FP Oxides	39-88	<1	---
Actinides	5-15	<1	---

Waste Form Criteria

The desirability of converting liquid HLW to a solid is widely recognized and is a specific regulation which currently applies to commercial high level wastes. The regulations,as given in 10 CFR 50 Appendix F, specify:

> ". . . High level liquid radioactive wastes shall be converted to a dry solid . . . and placed in a sealed container prior to transfer to a Federal repository in a shipping cask meeting the requirements of 10 CFR Part 71. The dry solid shall be chemically, thermally, and radiolytically stable to the extent that the equilibrium pressure in the sealed container shall not exceed the safe operating pressure for that container during the period from canning through a minimum of 90 days after receipt (transfer of physical custody) at the Federal repository. All of these high-level radioactive wastes shall be transferred to a Federal repository no later than 10 years following separation of fission products from the irradiated fuel."

The sealed containers for solidified HLW have come to be called canisters. The canister and its contained solidified waste form make up the waste package that will be held in interim storage for a short time and then transported to a geologic repository for disposal. Figure 2 shows a generic HLW waste package giving typical dimensions, and probable maximum heat generation rates and radiation doses. The dimensions of the canister can vary but those shown have come to be considered prototypical, and much of the waste management system is being designed around packages of these approximate dimensions.

Process Criteria

Manufacture of the HLW packages must be adaptable to routine, reliable operation in a radiation environment where materials may suffer damage, and where maintenance is expensive and time consuming.

4.0 WASTE FORM SELECTION

There are a large number of potential solidified radioactive waste forms.(3,4) Investigators have been addressing the problem since the early 1950's, and new suggestions continue to be made.(5,6)

Historically the first waste forms considered were crystalline clay shapes upon which radioisotopes were adsorbed, and then fired. Later, to get higher capacity, tailor-made ceramic sponges were substituted for natural clays. But glass was also an early candidate. Studies started in the mid-1950's at MIT in the U.S. and at Chalk River in Canada. Development of glass has continued until now there is an operating production plant for the preparation of waste glass monoliths at Marcoule, France, and a process is scope designed for the vitrification of Savannah River defense waste. The term monolith for the glass castings is used loosely since thermal and mechanical stresses will produce some cracking in waste glass.

Although many different solidified waste forms have been proposed for radioactive waste, they all fit in a few categories, shown in Table 2. It is convenient to consider internal structure and physical form separately since solidified wastes with different internal structure can have the same outward physical form. Currently, most of the attention concerning internal structure is focussed on differences between glass and crystalline forms; the attention in physical form is mainly on "monolithic" glass compared with many small spheres of solidified waste imbedded in a metal matrix.

TABLE 2 Waste Form Categories

Internal Structure

Disordered - Borosilicate glass
Phosphate glass

Ordered - Supercalcine
Titanate ceramic
Synthetic minerals

Mixed - Glass ceramics

Physical Form

Calcine powder
Monolithic glass or ceramic
Glass or ceramics in metal matrix
Coated particles in metal matrix

It is apparent that there are many waste forms which are probably satisfactory forms for the wastes sent to Federal repositories. The properties of some waste forms may make them more applicable to certain wastes than to others, but there are common factors involved in the selection of waste forms for all repository wastes. The most important selection factors are shown in Table 3.

TABLE 3 Factors in Selection of Radioactive Waste Forms.

Waste acceptance flexibility
Process adaptability to radioactive service
Canister interactions
Thermal stability
Radiation stability
Leach rate

The factors are interrelated. Probably not one of the factors can be optimized without adversely affecting one or more of the other equally important factors, therefore, compromises are required. Such compromises form the basis of the ALARA procedure.

The remainder of this paper will consider the waste form selection factors from Table 3 in more detail, and using HLW glass as a baseline, show how the factors can apply in the selection of alternate, backup, or second generation waste forms.

4.1 WASTE ACCEPTANCE FLEXIBILITY

Waste acceptance flexibility refers: (1) to the ability of a waste form to incorporate the large number of diverse components characteristic of radioactive waste streams, and (2) to the ability of the waste solidification process to operate with an ill-defined feed stream that will frequently fluctuate in composition.

Glass has the required processing flexibility because it is a nonstoichiometric material which accepts most cations in a random atomic network. Relatively large compositional variations in the waste streams are readily accomodated. The major exceptions to this omnivorous compatibility are anions, and many of these such as fluoride, are significantly soluble in waste glass.

Crystalline materials would appear to have less process flexibility because of their requirements of certain stoichiometries to achieve the desired properties. Solid solutions yield some processing flexibility within given crystals. Another route to processing flexibility would be to provide an excess of the reactants for each desired crystal form, such as is done in the proposed Synrock process.(5)

An important corollary to processing flexibility is that any waste form selected will not be a single defined composition. It may be a certain class of material, but it will have a range of compositions to accomodate the variations in waste composition shown in Table 1, and hence a range of physical properties. This is really what the development of a waste form is all about, to demonstrate that the waste form can have relatively homogeneous properties over the entire range of waste compositions it can be expected to incorporate. The practicality of making waste glass with relatively homogeneous properties over a wide range of waste compositions has been demonstrated, and the range is continuing to be expanded. The development of crystalline waste forms is as yet limited to a few selected waste compositions.

4.2 PROCESS ADAPTABILITY TO RADIOACTIVE SERVICE

Process complexity is of utmost importance, because the process has to be operated with cranes and remote mechanical arms on the other side of five foot thick concrete walls. With this sort of design requirement it is essential that the equipment be reliable, have a long life expectancy, and be maintainable by remote means. Obviously, the more complex the equipment the more difficult it is to satisfactorly meet these design requirements. It must also achieve reasonable processing rates, otherwise several parallel units would be required with a proportionate increase in complexity. Waste loading, usually expressed as wt% waste in the final solidified product, is also an important processing parameter. Low waste loading increases processing costs and decreases processing safety, since more canisters must be handled. Waste loadings of 45-50 wt% are sometimes possible in waste glass; 30 wt% waste loading is more typical. Discussions of waste loading, and heat dissipation from the loaded canisters, are presented in reports by McElroy(7) and Jardine(8).

Most glass-making processes are quite simple, being two- or three-step operations. An example is the in-can melting process developed at PNL. This is a two-step process in which the liquid waste is first calcined to a dry powder in a spray calciner. The spray calciner is simple, being essentially a heated chamber into which the waste is sprayed as fine droplets. The dried powder is combined with glass-making additives and dropped into one of two melters through a diversion valve. The valve permits the process to run continously since, while glass is being made in one melter, the previously filled melter on the other side can be disconnected, removed, and replaced with a new melter. Note that in this process the melter also becomes the container, or canister, for the waste glass, hence the name in-can melting. The non-radioactive pilot plant unit at PNL, shown in Figure 3, can handle over 220ℓ of waste/hour and convert it 50 kg glass/hour.

Many different waste glass processes have been developed. Some, such as the French AVM process described in another paper at this conference, are three-step processes, in that the glass is melted in a separate vessel and then discharged into the storage canister. The separate melting vessel can be a metallic melter, as in the AVM process, or it can be a ceramic melter, such as used by the glass industry. Ceramic melters have been under development for radioactive waste vitrification for about five years at PNL and in Europe.

The well-developed vitrification processes can be looked upon as examples for alternative processes to follow. In addition to producing a durable waste form in three steps or less, the alternative processes should have many of the features described at the beginning of this section.

Nearly all processes will have similar off-gas treatment requirements, because they all involve drying, denitrating, and consolidating of liquid wastes. These steps will almost always require temperatures up to, or in excess of, 1000°C. In general, crystalline waste forms will introduce requirements of sintering or pressing at elevated temperatures and pressures. Glass-ceramic waste forms may be achievable by annealing specially prepared vitrified waste forms. Cermets will require extrusion.

In summary, in designing and operating a remotely operated facility the objective is to keep it simple and make it reliable. In case of failure the equipment must be easily replaced or repaired. A major failure can shut down even a relatively simple remotely operated facility for many months.

4.3 CANISTER INTERACTIONS

The canister must be rugged for handling and it must be sealed by welding to contain the waste and prevent water from entering during interim storage. The canister must maintain its integrity during interim storage and be suitable for transporting the waste within a shipping cask to the final repository.

In many instances the waste canister may also be the processing vessel. In this case the canister must be able to withstand the processing conditions and then be suitable for storage. For in-can melting the canister is made of 304L stainless steel, if the vitrification temperature is limited to about 1050°C. Above this temperature a higher strength more corrosion resistant material, such as Inconel 601 is required; the upper limit is then about 1200°C. When the canister is not the process vessel, such as for casting monliths from a continous melter, the upper temperature requirement is about 700°C. This temperature will assure uniform filling of the canister. For this type canister it may be possible to use carbon steel if it is found acceptable for interim storage and final isolation.

No metal has been found that is optimum as a canister material in all parts of the waste management system. All proposed materials appear susceptable to some form of corrosive attack at some point in the system. Generally, 304LSS is the preferred canister material because of its extensive use in the nuclear industry. While 304LSS performs well during processing and can be protected during interim water storage by water quality control, it is generally accepted that stainless steel will stress corrison crack soon after being placed in salt.

Overpacks are one way of obtaining a canister that is compatible with the final isolation media. These can be installed around the canisters after the geologic media in which the canisters are to be emplaced has been determined, or the emplacement holes can be lined with sleeves of the preferred material. Overpacks can also be used for repairing a defective canister if a leak occurs during interim storage.

It is anticipated that waste canisters for other alternative waste forms will have the same considerations and requirements as those just described in another paper at this conference by Slate. A report by Slate and Maness(9) is also recommended for the interested reader.

4.4 THERMAL STABILITY

The thermal stability of HLW waste forms is important because the waste is self-heating. However, it is important to recognize two factors. First, as shown in Figure 2, the heat generation rate decreases rapidly. Second, handling heat transfer is a standard engineering problem. The system can be engineered to avoid undesirable temperatures.

All of the information is available to engineer the system for waste glass. The thermal conductivities of many waste glasses have been measured. At 100°C, the conductivities fall between 0.8 and 1.0 W/m°C, and at 400°C the range is between 1.0 and 1.2 W/m°C. Above the softening point of the glasses, about 600°C, the conductivity rises rapidly. The thermal conductvity of unconsolidated calcine is about a factor or four lower than that of glass; metal matrix waste forms usually have a thermal conductivity about 10 times higher than glass.

Thermal conductivity determines the temperature profile within the canister. Figure 4 shows a canister of borosilicate glass made in the WSEP program at PNL over 8 years ago by the in-can melting process. The radioactivity in this glass was designed to simulate commercial HLW. The glass, as initially made, was generating 90 watts/liter of self heat. The Δt between the canister surface and centerline was in agreement with engineering predictions. If desired the heat transfer in waste glass canisters can be increased approximately by a factor of 2 by the use of internal metal fins.

The plugged boreholes from which samples of radioactive glass have been taken are visible on the surface of the canister in Figure 4. In the 8 years since this glass was made examination of core drilled samples has shown that there has been no degradation in properties of the waste glass, even though during most of the time the glass was stored at 400-500°C. Degradation would not have been expected at these temperatures.

Thermal stability is a prime consideration in the comparison of glass and crystalline waste forms, because glasses are metastable and under some conditions can partially convert to crystalline materials. This crystallization, known as devtrification, has been studied thoroughly in several waste glasses. The maximum rate of devitrification of waste glasses usually occurs at about 700-750°C.

The two curves in Figure 5 serve to illustrate glass devitrification. We use leach rate to measure the effects of waste glass devitrification because this is the only physical property that changes significantly. In properly forumulated waste glasses the physical strength does not change appreciably. Most important, the glass does not fall apart, as is sometimes implied.

When waste glass is held at temperatures between 550 and 850°C., devitrification which causes an increase in leach rate, can occur. The effect is controlled by kinetics. If the canister is cooled through this temperature range at a cooling rate of greater than about 20°C.hour almost all devitrification can be avoided. The samples in Figure 5 were held two months at the temperature shown, then the leach rates were measured at 25°C. It is noteworthy that the two waste glasses in Figure 5, designed for quite different waste compositions, have differences in their baseline leach rate which are as great, or greater, than the maximum effect of devitrification.

In summary, the process can be designed to cool the canister fast enough to avoid almost all devitrification. At storage temperatures the thermal devitrification rate is so low that it can be discounted. Devitrification, if is does occur, has never been observed to cause more than an increase of a factor of 10 in leach rate, well within the leach rate variations observed between waste glasses of different compositions.

5.0 RADIATION STABILITY

It has been recognized from the earliest studies that the intense radiation fields within solidified nuclear wastes could cause measurable property changes. Consequently, all waste forms under serious consideration have been, or are being, evaluated with respect to radiation effects. Waste glasses have been most thoroughly studied, with specific reports of stored energy(10) and helium diffusion(11) as well as more general discussions(4,11,12) being recently presented.

Table 4 shows some displacement rate calculations from the various radiation damage sources present in radioactive wastes. These estimates show that damage from alpha-decay of the actinides is several orders of magnitude more important than any of the other contributors. For this reason, the work undertaken at PNL and elsewhere relies heavily on doping methods, using short half-life alpha emitters such as ^{244}Cm or ^{238}Pu. Using ^{244}Cm, and doping levels in the 1-8 wt% range, it is possible to simulate in a few years the damage which would occur in $>10^5$ years in commercial HLW. Because of its lower alpha activity, even longer times, beyond 10^6 years, have been simulated in defense wastes. Although there are still some unresolved questions concerning radiation effects (for example, a study of transmutation effects is only just beginning), it is clear for waste glasses, at least, that property changes are small.

Alpha-Recoil Damage

Although understanding of radiation damage in ceramic materials is not well developed, estimates concerning an expected damage rate are possible, both from simple theoretical estimates and empirically from previous

TABLE 4. Energy Dissipated in Elastic Collisions by Various Nuclear Radiations, and Accumulations of Elastic-Collision-Energies in Radioactive Wastes(10)

Nuclear Particle	Energy Dissipated in Elastic Collisions, KeV	Cumulative Number of Particles in Wastes, Aged 12 and 80 Years ($10^{17}/cm^3$)		Cumulative Amount of Collision Energy Dissipation in Wastes, Aged 12 and 80 Years (10^{19} KeV/cm^3)	
		12 yr	80 yr	12 yr	80 yr
α-RN(a) 100 KeV	100	8.1	17.1	8.1	17.1
α(6 MeV)	4 to 8	8.1	17.1	0.3 to 0.6	0.7 to 1.4
β(>0.5 MeV; average = 1.5 MeV)	< 0.1	3	5	< 0.3	< 0.5
γ(2 MeV)	≪ 0.1	< 3	< 5	≪ 0.3	≪ 0.5
Fission recoil	5000	2×10^{-5}	4×10^{-5}	0.001	0.002

(a) Recoiling product-nuclei formed in alpha disintegrations.

experimental work. The simplest models(14) and more sophisticated concepts(15) both suggest that a single ∿5 MeV alpha event will cause about 3000 displacements, with the alpha particle contributing only 10-20% of the total damage.(16) In a homogeneous glass there are ∿2 x 10^{22} "SiO_x" units per cm^3 glass. Consequently, one expects that the entire glass network will have been affected at ∿10^{19} α/cm^3 and that saturation of effects should be observed by this dose, providing secondary effects (e.g., defect clustering) do not become important. Saturation of effects is observed experimentally. For instance, in work on alpha decay damage in solids, a number of crystalline compounds have been studied for volumetric changes. All showed exponential tailing to a saturation, or equilibrium volume change, beyond which additional radiation had no effect. A review of work on pure actinide compounds was presented by Fuger.(17)

Some wastes won't contain enough alpha-active isotopes to cause radiation-induced effects to reach saturation even in 10^6 years. Others will contain sufficient concentrations of alpha active isotopes so that saturation of effects will be reached in less than a thousand years. Emphasis in the radiation effects studies using actinide doping of waste forms is on defining saturation effects.

Effects of Damage

With respect to radiation stability, parameters relating to physical and chemical durability must be evaluated. In work on waste glasses to date, radiation effects on density, microstructure, stored energy, physical strength and leachability have been measured. Figure 6 summarizes the density changes measured in several waste glasses and a supercalcine as a function of alpha dose. Both positive and negative density changes have been observed in waste glasses; the behavior is clearly composition dependent. The important point, however, is that in all waste glasses studied to date, the saturation density change is no more than about one per cent. This is as expected since the effect of alpha radiation is to promote amorphization and glass is already amorphous. More limited studies of glass-ceramics and crystalline supercalcine have been completed. In each of the latter studies, crystalline phases concentrate the ^{244}Cm dopant and rather quickly become x-ray amorphous, i.e., they become glass-like, with larger volume changes than occur in glasses. The importance of these changes has not been fully assessed; the samples did not crack or otherwise visually change. However, the effects of nonuniform density changes in adjacent crystals of a crystalline waste form are of concern, since they could degrade physical strength and integrity. Many examples exist in the literature of radiation-induced amorphization of crystalline components. The volume changes reported range from very small to as much as 30% at saturation.

A summary of the effects of radiation on waste glass is shown in Table 5. Stored energy is latent energy deposited in the glass when atoms are displaced from their original locations by radiation. The latent energy is released when the glass is heated. Calculations show that even if the stored energy were all released at once, which cannot occur, the increase in temperature of the glass would be less than 200°C, not a serious occurrence. The leach rate of highly irradiated waste glass changes by less than a factor of two. Limited measurements show no change in physical strength; more measurements are planned.

Transmutation refers to effects that could occur at the sites of radioactive decay, where a new chemical species, with a different ionic radius and valence than that originally present is produced. Examples are the decay of Cs^{+1} to Ba^{+2} and Sr^{+2} to Zr^{+4}. Because of its random structure, transmutation is not expected to affect glass stability, except perhaps in some devitrification crystals, if they tended to concentrate a particular isotope. Transmutation could have more serious consequences in crystalline waste forms if the lattice could not readily accept atoms with characteristics of the newly formed ones.

6.0 LEACH BEHAVIOR

Leaching of activity from the waste form, with subsequent migration of the water containing the dissolved radioisotopes into locations used by man, is the most important pathway that must be analyzed in assessing the risks of radioactive waste management. Before leaching can commence the waste canister must be breached, and water must be present. The waste

TABLE 5 Summary of Radiation Effects on Waste Glass

- Stored Energy
  < 60 Cal/gram
- Density Change
  $\leq$ one percent
- Leach Rate
  $\leq$ factor of two increase
- Physical Strength
  No change (limited data)
- Transmutation
  No effects expected
  Investigation continuing

management system will be designed: (1) to prolong the life of the canister, and (2) to minimize the presence of water. In addition the repository will be designed so that water leaving the repository will have to travel long distances, perhaps 10 or more km, before entering the biosphere. Tests have shown that all radioisotopes in waste, except ^{99}Tc and ^{131}I, have significant retardation factors, that is, they will migrate slower than the water "carrying" them by factors, ranging from 5 to more than 10,000. When all of these factors are considered, the preliminary analyses that have been made indicate that the geology provides sufficient retardation so that the leach rate of the waste form may be a relatively insignificant element in assuring waste isolation in a geologic repository. Nevertheless it is important to understand the leaching behavior of the waste form——it is an important element in our multi-barrier, defense in depth, waste management system.

The rate of release of activity is dependent on the surface area of the waste form which is exposed to water and on the rate of leaching per unit area in the prevailing environmental conditions. As is described by Slate, et. al., in another paper in this conference, waste glass in canisters is not monolithic. Thermal and mechanical stresses will typically produce cracking which increases the surface area about a factor of approximately 10 over that of a monolith. However, if the glass is held tightly by its surroundings the surface of the cracks will not be easily accessible to leaching.

In an evaluation of the effects of prevailing environmental conditions upon the rate of leaching of waste glass, temperature and pH are found to predominate over all others.

The effect of temperature on the rate of leaching is similar to the temperature effect in many chemical reactions. The reaction rate increases a factor of 10-100 for every 100°C increase in temperature. The type of reactions which control the release of radioisotopes also are affected by temperature. Below about 80°C a siliceous layer forms on glass surfaces, which acts to retard further leaching. Metasomatic reactions, in which new crystalline compounds form from some of the glass constituents, can also occur at the glass surface, particularly at elevated temperatures. The new compounds, which can be either clay-like, and absorptive, or be thermodynamically-stable hosts for certain radioisotopes, may actually be beneficial.

A large amount of work to define the hydrothermal reactions of waste forms has begun in the last two years. The major preliminary conclusion from this work is that both glass and crystalline waste forms are altered rapidly if the temperature is sufficiently high, as indeed are most inorganic oxide or silicate substances, including many candidate repository host rocks. Table 6 shows that neither waste glass nor supercalcine provide a barrier to the release of ^{137}Cs and ^{90}Sr at extreme hydrothermal conditions in salt brine. Figure 7 shows that the hydrothermal attack on several other materials, including granite, is of the same order of magnitude as that on waste glass. The tests shown in Table 6 and Figure 7 were accelerated by using very high temperatures to obtain results quickly. Maximum possible temperatures at which water can contact a solidified waste form in a repository are more likely in the range of 150°C, or less. As mentioned earlier, temperature control is a standard engineering procedure. The question of the maximum allowable temperature in the repository requires, and is getting, more engineering study. A maximum reference reporitory temperature of only 80°C has been selected for granite repositories in England and Sweden.

The effect of temperature on the leach rate of waste glass is shown in Figure 8. Representative leach rates at 25°C are 1×10^{-5} of glass/cm^2-day. Representative leach rates at 40-50°C, the ambient temperature at repository depths, are 5×10^{-6} to 5×10^{-5}g of glass/cm^2-day. If the latter leach rates are assumed to remain constant with time it can be calculated that leaching of the total activity from glass chunks of typical dimensions of 4-10 cm diameters would require several thousands of years. Actually the leach rate will continue to decrease, and lifetime of hundreds of thousands of years are possible. The leach rate of waste glass buried at Chalk River decreased to 5×10^{-11}g of glass/cm^2-day in just five years.(18)

TABLE 6. Hydrothermal Leaching Rates in Salt Brine at 350°C

	Percent in Original Sample Released to Brine in 7 Days	
	Supercalcine	Waste Glass
Cesium	46	80
Rubidium	80	82
Strontium	3.3	3.4
Silicon	0.5	0.2

The pH of the groundwater at Chalk River is 6.4. Waste glass is formulated to have a relatively constant leach rate over the pH range 4-9, considered the probable extremes to be normally found in nature. In non-salt repositories, the rock and surrounding soil will act as buffers and probably maintain the pH in an even narrower range. Salt repositories represent a separate case. The possibility of pH's as low as 2 in salt repositories has been reported. Glass generally has excellent resistance to acid attack. Waste glass, however, with a silica content usually in the range of 30-50%, has poorer acid resistance than high silica glasses. Below pH 4 the leach rate of waste glass can increase significantly. Even though the potential for a higher leach rate may exist in salt repositories, overall leaching will be limited because the amount of water present will be very low.

7.0 STATUS OF WASTE GLASS DEVELOPMENT

After twenty years of development waste glass technology has reached the stage of widespread implementation.(19) In France, England, Germany and the U.S., major vitrification programs are well advanced. Research and development is devoted to expanding the physical property data base to include more waste glass formulations, extending knowledge of expected behavior in geologic isolation, and refining the design of process equipment.

In the United States the vitrification technology previously developed for commercial HLW is being transferred for potential initial use with existing defense wastes at Savannah River, Idaho Falls and Hanford. If a decision is made to remove the liquid HLW from the storage tanks at Savannah River, the program currently underway will permit having a full scale vitrification plant in operation by 1988.(20) The plant will employ spray calcination coupled to either a continuous joule heated melter or to an in-can melter. The borosilicate glass will be contained in 2 ft. diameter by 10 ft. long stainless steel canisters. The canisters will probably be sent to a federal geologic repository.

In France, the AVM vitrification plant started operation this past summer. It employs a rotary calciner and continuous metallic melter to convert Marcoule HLW to a borosilicate glass. The 30 cm diameter by 1 cm long stainless steel waste canisters are stored in air cooled pits on site. Plans are underway to construct a vitrification plant (AVH) at the La Hague, France, reprocessing plant by 1983. The process would be similar to that used at Marcoule and higher activity HLW from reprocessed LWR type spent fuels would be vitrified.

In England, a full-scale radioactive demonstration plant is planned for operation at Windscale in the mid-eighties.(21) Construction of a fully radioactive pilot plant is now nearing completion and of a full-scale inactive development facility is underway. The process is a type of in-can melting where liquid waste is converted directly to glass in a stainless steel canister.

Germany also plans to vitrify its HLW. Two processes(19) VERA and PAMELA have been developed for converting the wastes to borosilicate glass. It is likely that a radioactive version of one of these processes will be constructed and operated at the WAK reprocessing plant at Karlsruhe. A larger version of the WAK process, or another well developed process, would be used to vitrify the HLW that will be produced at the planned Gorleben nuclear park in lower Saxony.

Several other countries (e.g., Belgium, India, Japan, and Italy) have active programs directed toward the incorporation of HLW in borosilicate glass.

While much of the research and development to date has been directed toward incorporating highly radioactive commercial type wastes into glass, it should be noted that initial use is occurring with lower activity HLW. Thus, while the results clearly show that high activity, high heat generating wastes can be safely immobilized in glass, the technology is being implemented in a conservative manner. This conservatism will also follow through to the repositories; high temperature storage conditions will not likely exist during early repository operation because of the backlog of aged fuel and low-heat waste. In the meantime, the R&D programs developing waste immobilization techniques need to be closely integrated with the repository programs to define repository design conditions that are acceptable for both the waste package and the host rock.

8.0 SUMMARY

There is a general consensus that the physical properties of glass make it a satisfactory choice as the waste form for the first generation of high-level waste solidification facilities. Glass can accomodate a very wide range of chemical elements. It is stable to very large radiation doses. It is formed at high temperatures, so it is free of volatiles. It possesses sufficient thermal stability at storage temperatures. Waste glass has a low leach rate at the perpetual repository temperature (approximately 40°C); it has a somewhat higher leach rate at the higher temperatures that will exist in the repository during the first few decades or centuries, but contact of water with the solidified waste form during this period will be minimal.

The development of alternative solidified waste forms is directed mainly toward further reductions in the release of activity which will occur if water contacts the waste form, particularly at elevated temperatures. The development of these alternative waste forms will benefit from the existing understanding of the physical properties of waste glass. The waste glass properties will serve as a bench mark for comparison during their development. One, or more, of the alternative waste forms may be available for use in second generation waste solidification plants.

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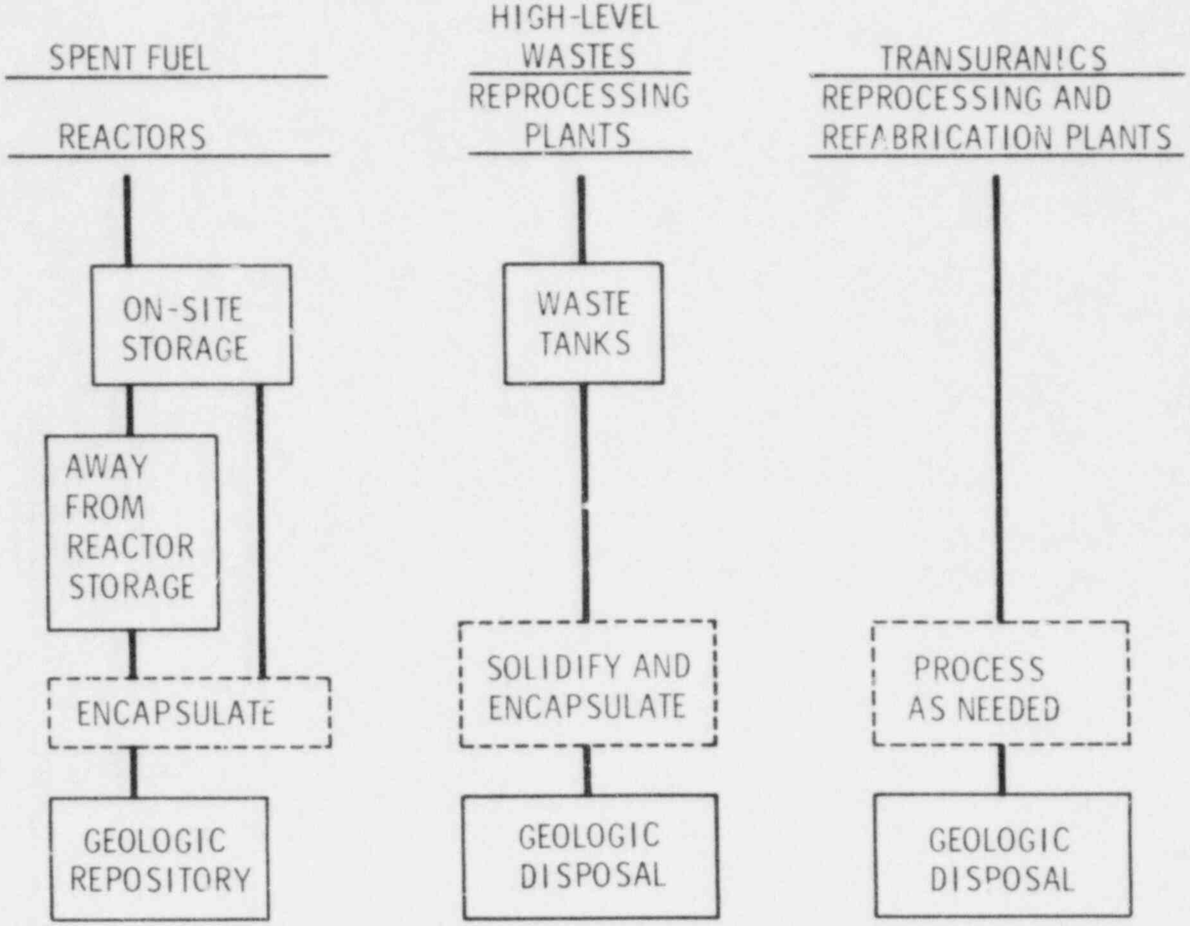
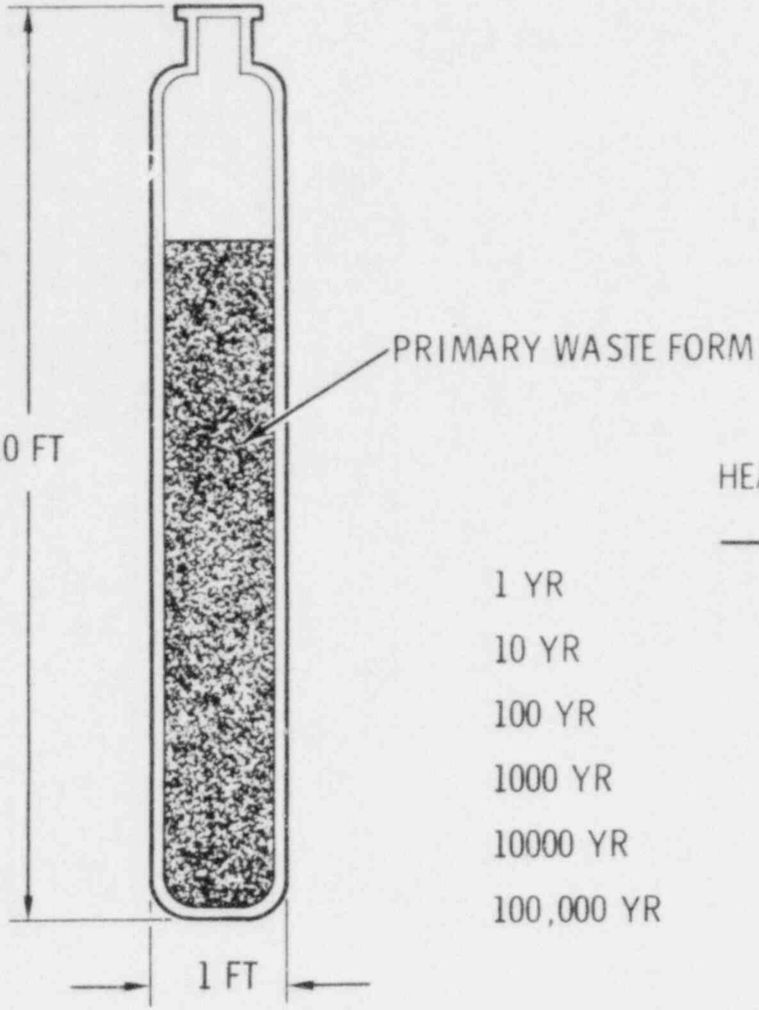


Figure 1. Radioactive Wastes Scheduled for Geologic Isolation



	HEAT GENERATION RATE, kW	CUMULATIVE α DOSE/GRAM	DOSE-RATE 1 FT FROM SURFACE
1 YR	22	1.0×10^{17}	1.1×10^{6} R/hr
10 YR	3.1	2.5×10^{17}	6.2×10^{4}
100 YR	0.36	7.1×10^{17}	5.8×10^{3}
1000 YR	0.02	1.5×10^{18}	1.6
10000 YR	0.006	3.0×10^{18}	1.3
100,000 YR	0.003	6.1×10^{18}	0.6

Figure 2. Typical HLW Package

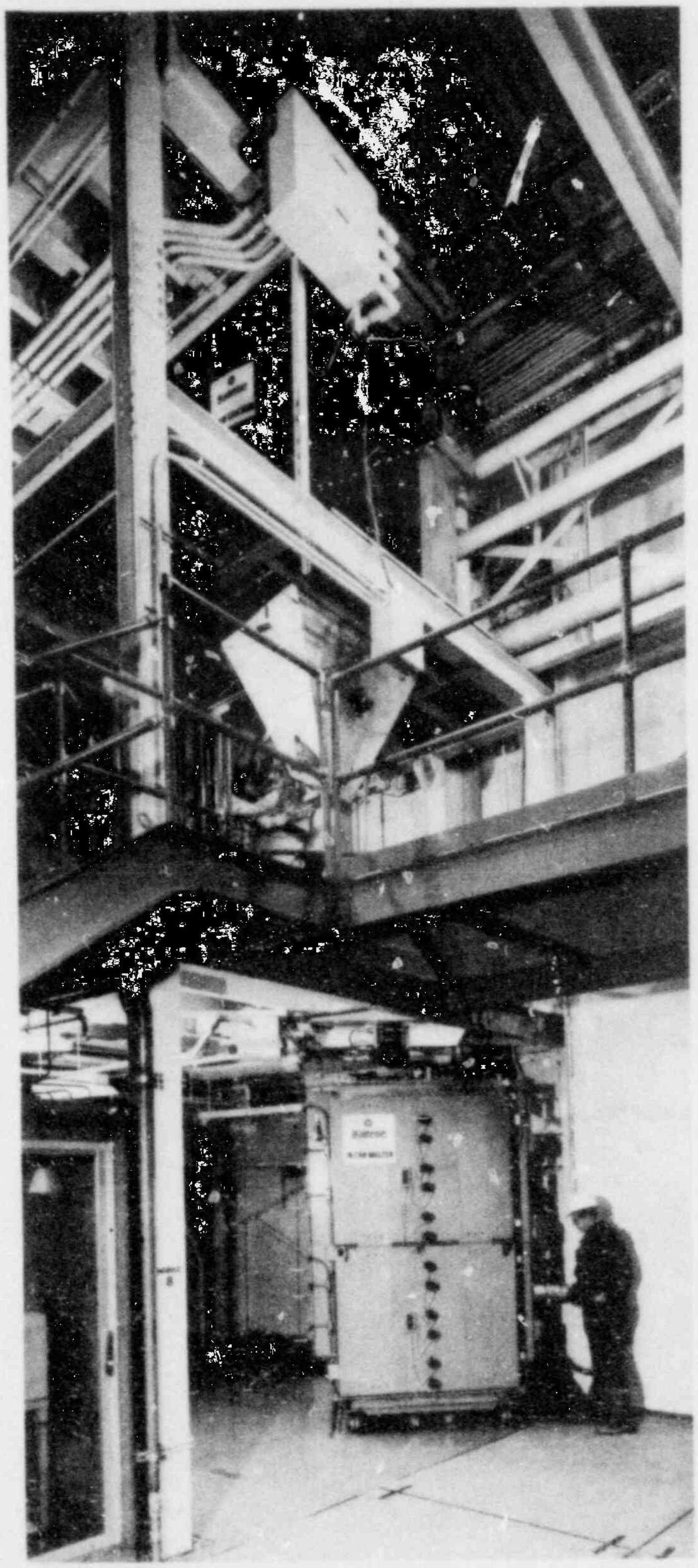
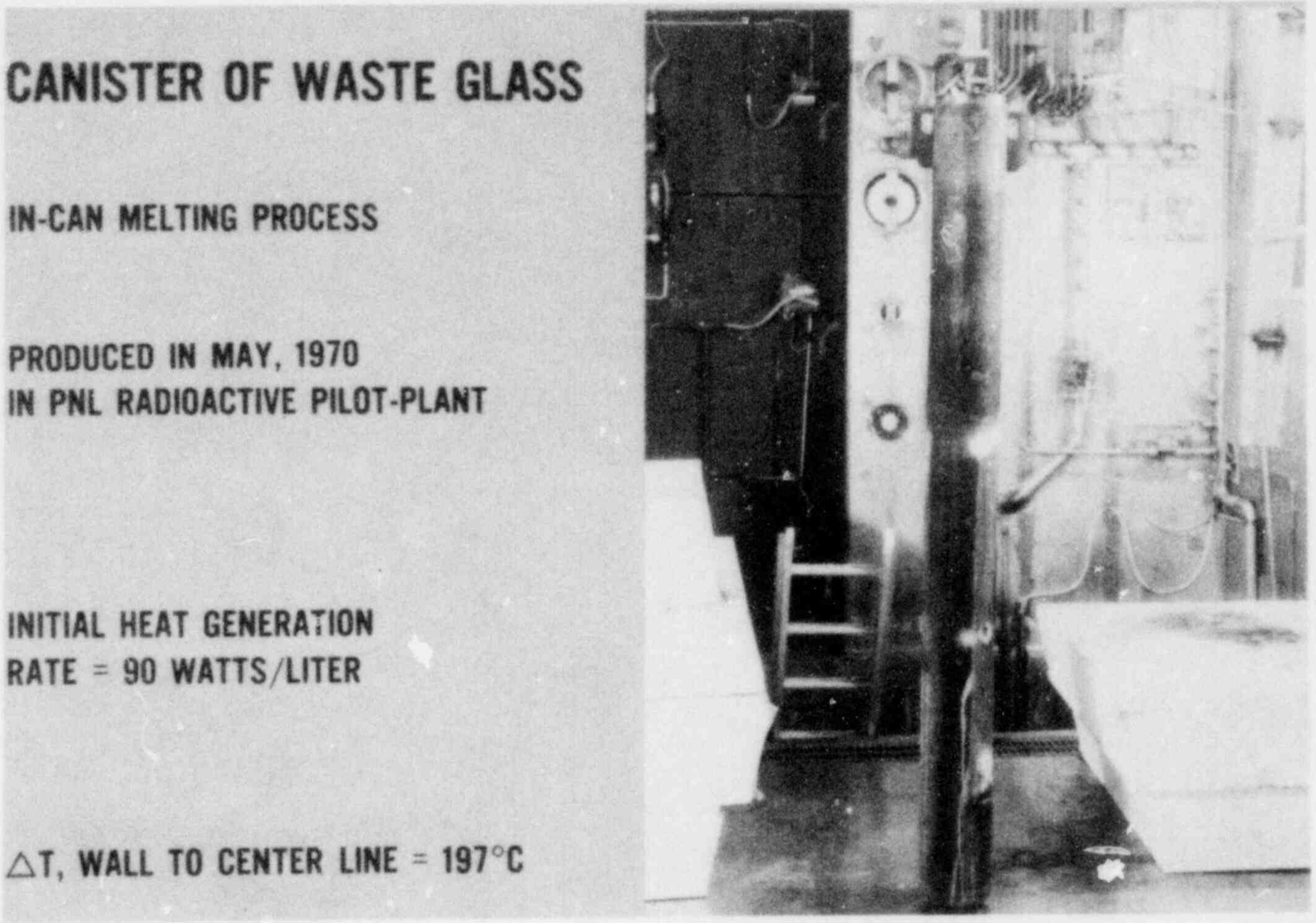


Figure 3. In-Can Melting Process Pilot Plant



CANISTER OF WASTE GLASS

IN-CAN MELTING PROCESS

PRODUCED IN MAY, 1970
IN PNL RADIOACTIVE PILOT-PLANT

INITIAL HEAT GENERATION
RATE = 90 WATTS/LITER

$\triangle$T, WALL TO CENTER LINE = 197°C

Figure 4. Radioactive Waste Glass Canister Photographed through Lead Glass Window

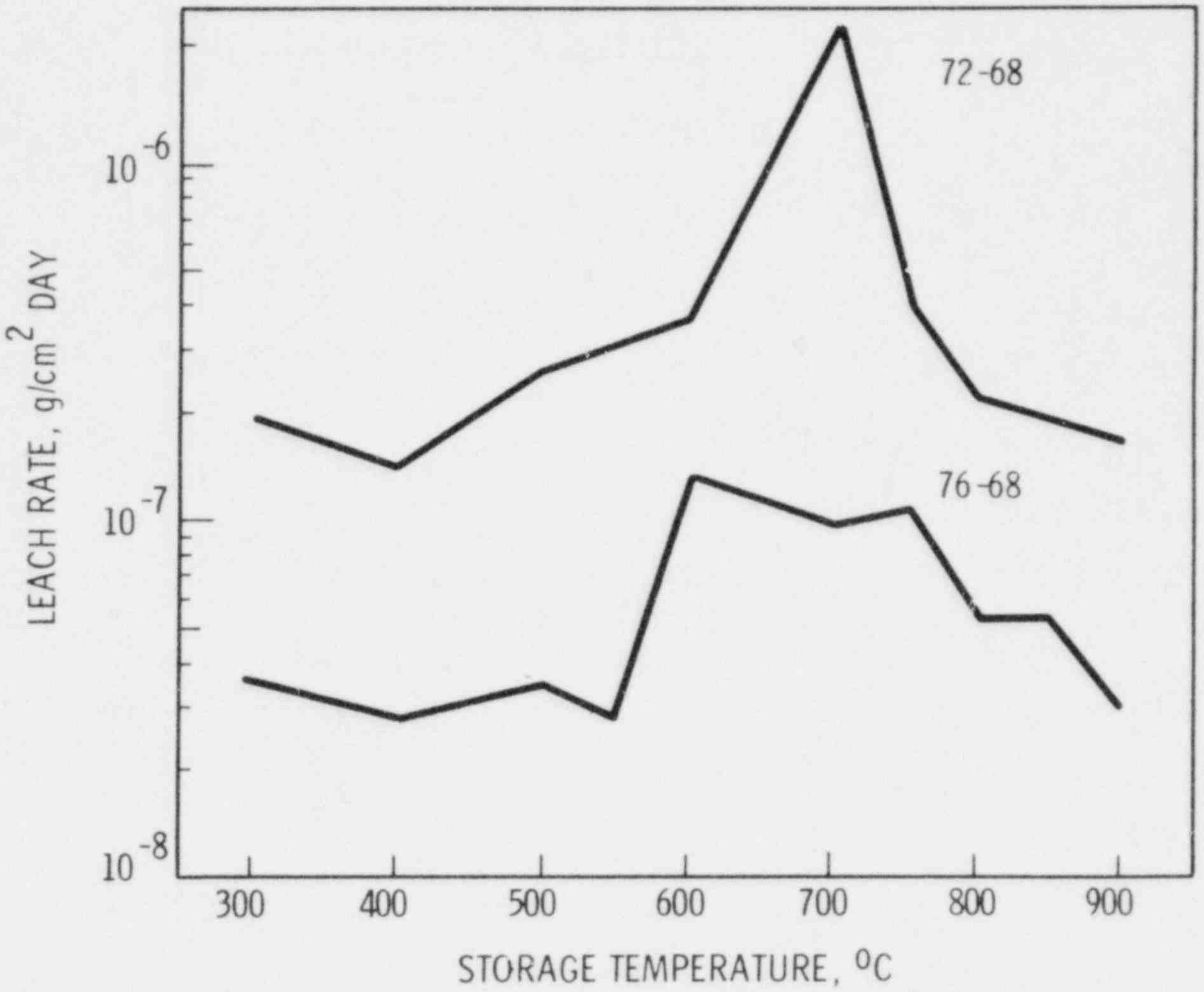


Figure 5. Effect of Devitrification on Leach Rate

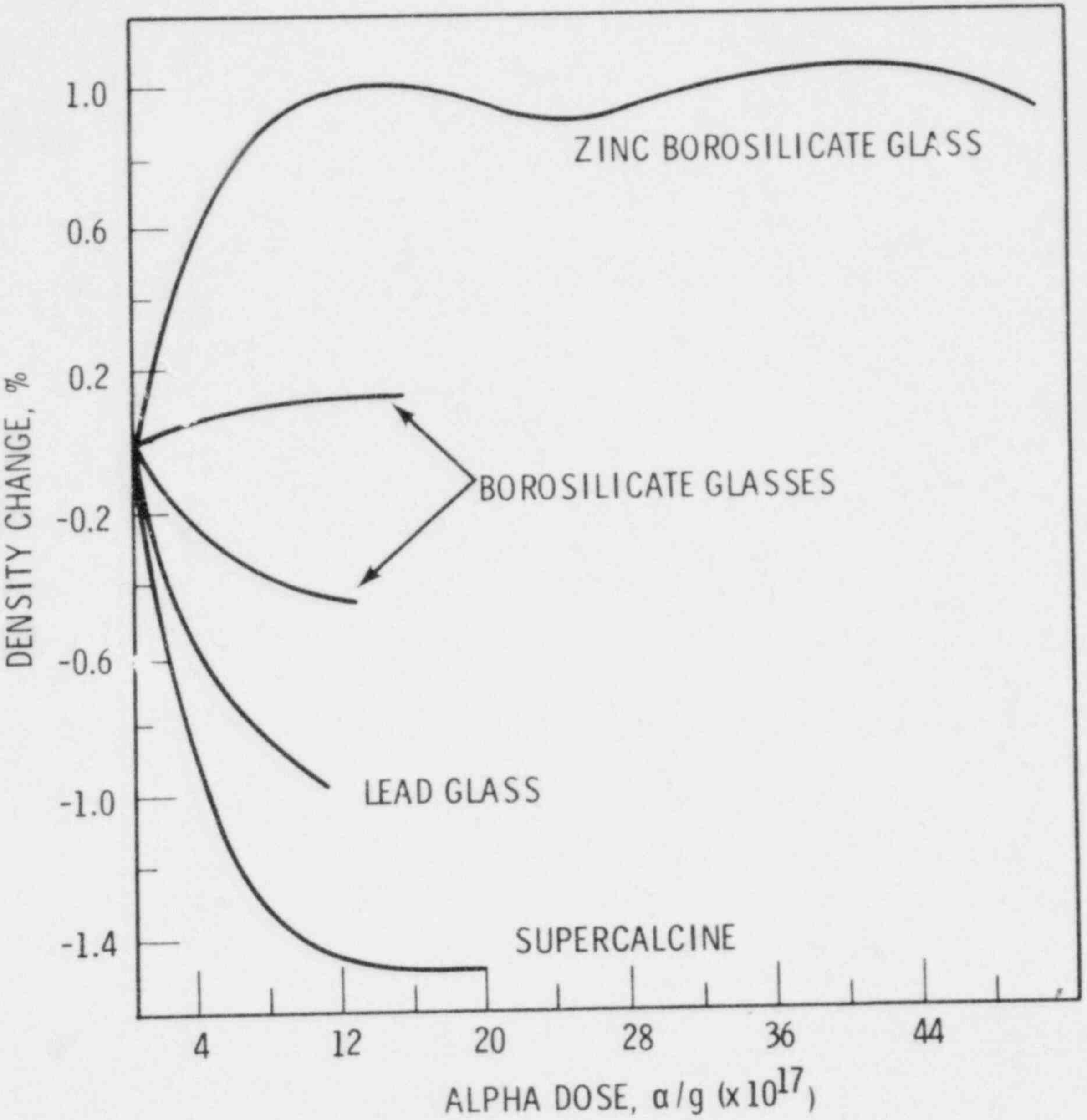


Figure 6. Radiation-Induced Density Change in Solidified Waste Forms

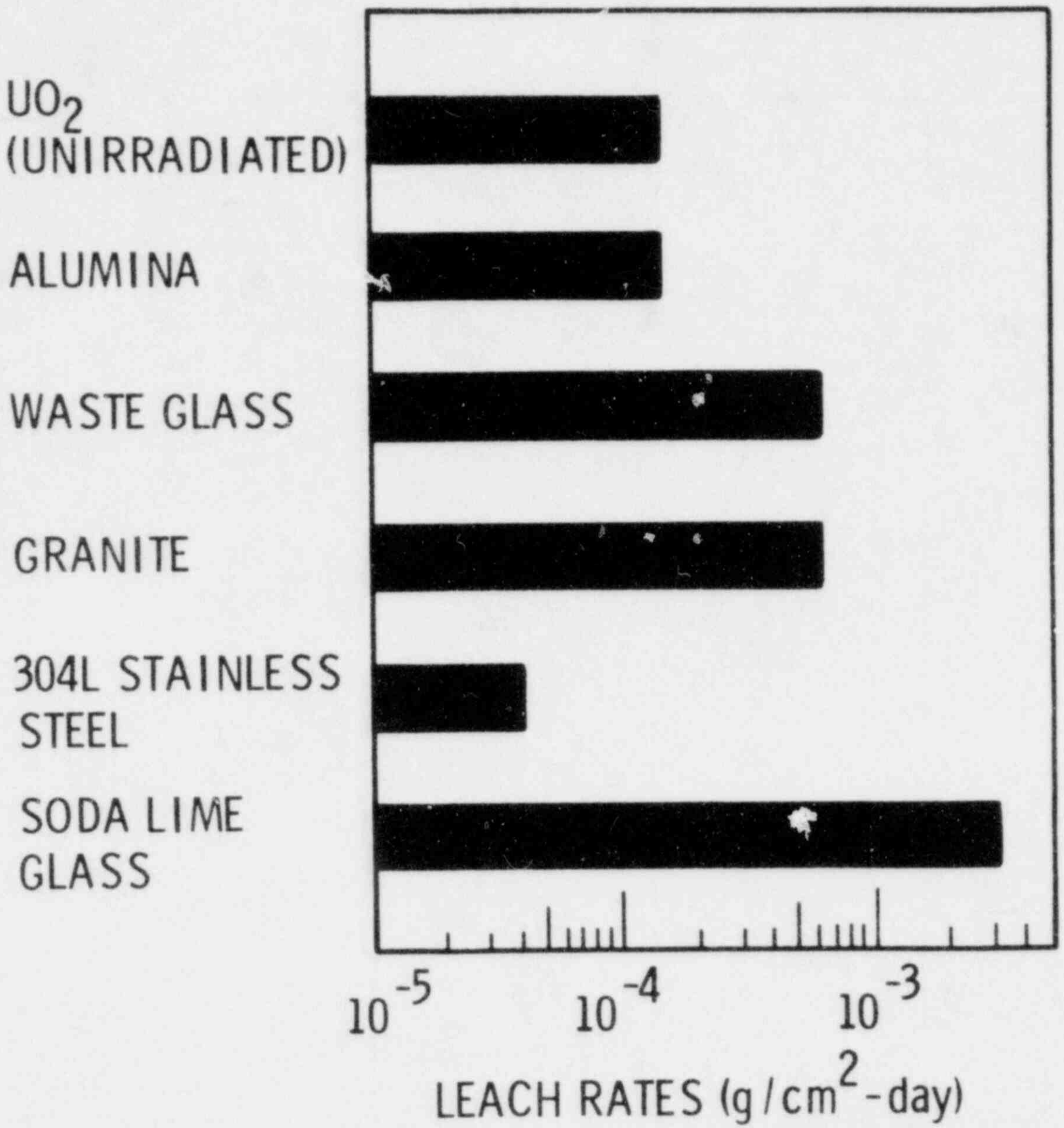


Figure 7. Leach Rates in 250°C Salt Brine Based on Weight Loss

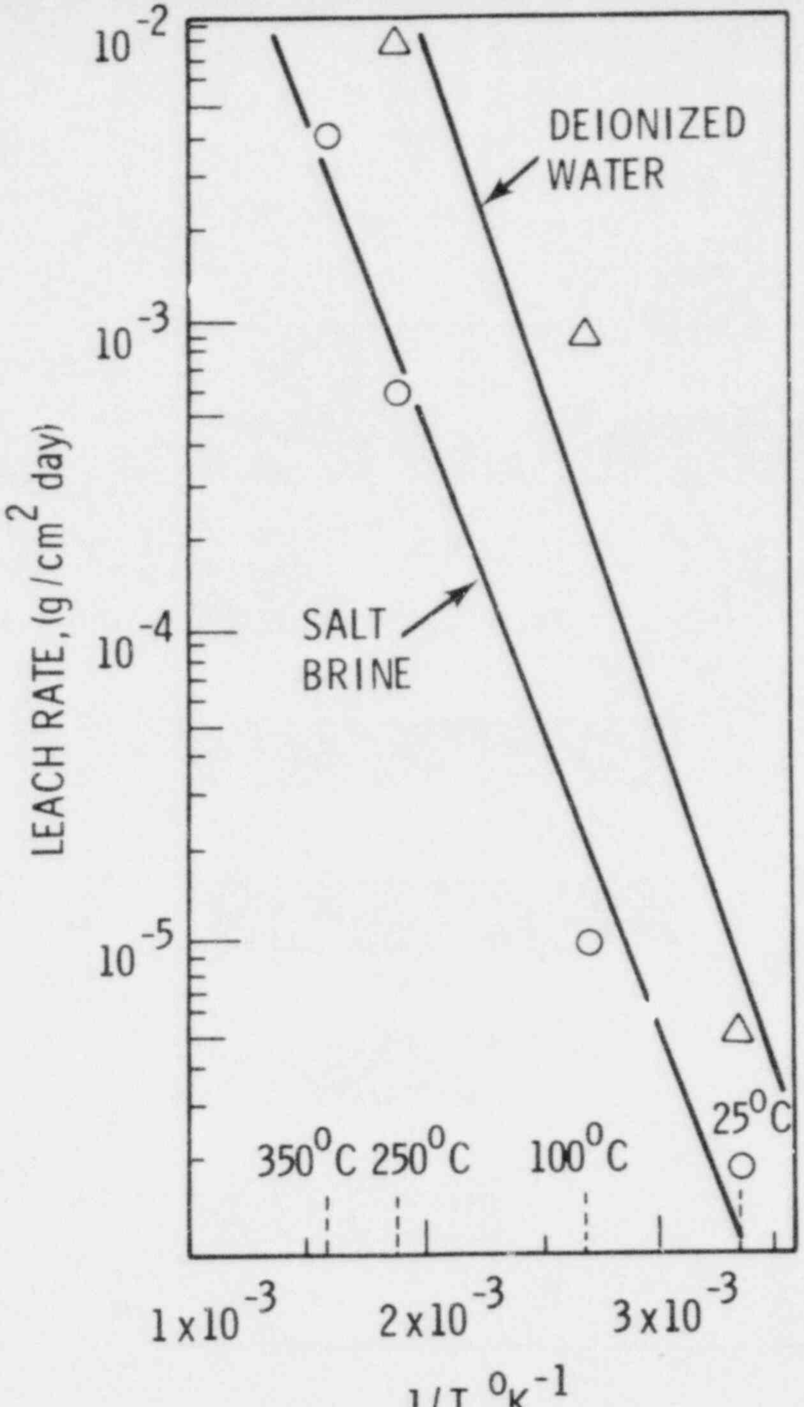


Figure 8. Leach Rate of Waste Glass ~~on~~ as a Function of Temperature

Discussion Following

PHYSICAL PROPERTIES OF WASTE GLASS

Presented by John E. Mendel

Bob Watt - Los Alamos, private citizen
Question:
You mentioned several possibilities, one of them to maintain temperature controls and one of them to maintain dry conditions. From the calculations presented in various places, I think the duration of such activities would be several centuries. Does that agree with your thinking?

Mendel
Response:
Well, the temperature drops quite rapidly in the first 500 to 1,000 years; it does not reach the ambient temperature for several thousand years. It is just a 10 degree difference or so.

Watt
Question:
You have answered the question; the control period which we are talking about is many centuries. In general, I believe, one of the conditions that one should not plan on is social institutions having any kind of significant control for more than one century. Do you see that as a serious problem?

Mendel
Response:
No, I do not think that is a serious problem, because most of these techniques I mentioned could be installed and be in place within that time period--less than 100 years.

Watt
Question:
Would they continue to operate without human care?

Mendel
Response:
Yes. Engineered barriers, systems included in the barrier to either absorb water or be impermeable to water--those kinds of systems would be installed during the hundred years or so and then the system could last for at least 500 years.

Fred Schmidt - University of Washington
Question:
A geologist in Australia whose name is Ringwood has made an alternative suggestion instead of using glass or sequestering material. If you are familiar with it, could you just make a spot judgment as to what you think of his proposals?

Mendel
Response:
In essence, I do not believe his proposal is much different from the supercalcine concept that has been under investigation at Pennsylvania State University for some time under subcontract to PNL. As I indicated, I believe that this hydrothermal stability is really the only area where alternative waste forms have a potential. The problem is whether you can do it practically and do it very soon. The complexity of the waste compositions makes it difficult to design minerals that will contain all of the constituents in the waste.

Eugene N. Cramer - Southern California Edison Company
Question:
For several years, at least at Hanford, the defense waste has been separated so the cesium and strontium is stored under water in the form of a titanate. Is there any ongoing effort to design a waste form specific to this cesium and strontium?

Mendel
Response:
There has been some work. The cesium and the strontium are not being stored as a titanate; they are being stored as chlorides and fluorides. There is some work going on at Hanford to either develop glass compositions for the cesium and strontium or other waste forms.

Cramer
Question:
Is it premature to discuss that?

Mendel
Response:
It is premature for me to discuss that, because it is being done by Rockwell and I am not up to date on the status of their work.

Larry Penberthy - Penberthy Electromelt International, Inc.
Comment:
I can answer the question on cesium and strontium. Well over 100,000 tons of soda lime, that is, sodium calcium silicate glasses, are being made every day. The cesium and strontium are counterparts of sodium and calcium. And hence, no special glass structures is required.

Robert Williams - EPRI
Question:
Having heard John Mendel's assessment of the systems approach to waste engineering and the many compromises that have gone into selection of glass, both because of the practicality of production and its tolerance for variation in waste composition as an input stream, I would like to ask Fred Donath if he would concede that glass is an adequate first generation waste form for our waste disposal systems. I was not sure where he stood by the end of his presentation here this morning.

Fred Donath - University of Illinois
Response:
I am already on record in the APS study as stating that glass is an acceptable first generation waste form. I think that the point I made in response to a question after my presentation was that glass may have many different possible applications in the waste isolation system. And I only drew attention to another possible, totally different type of philosophy of deliberately designing a glass that would break down to provide different types of components which might be more stable in the long term. But in terms of the short term and initial emplacement and concern over transportation and placement, glass certainly is acceptable.

Williams
Comment:
Thank you, I just wanted to make sure that the record reflected that point.

Bernard Cohen - Argonne National Laboratory
Question:
Could you be a little more explicit on methods of keeping the waste dry, and of also controlling the temperature?

Mendel
Response:
The methods of controlling the temperature involve the distribution of the canisters, how far apart they are, and how much heat is in each canister. If you are making glass, this can be done either by simply diluting the glass or by longer interim storage on the surface before you place it in the repository. As far as the methods of keeping the repository dry, again, one method certainly involves selection of the repository. This gets to the question of location of aquifers and so forth. Another technique is using ventilation, leaving the repository open for a longer length of time, and using forced ventilation to dry the repository out. In a non-salt repository, there is a good likelihood that the heat from the canisters will tend to keep the repository dry for some length of time.

STABILITY OF FIXATION SOLIDS FOR HIGH-LEVEL RADIOACTIVE WASTES[+]

by

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STABILITY OF FIXATION SOLIDS FOR HIGH-LEVEL RADIOACTIVE WASTES

Abstracts

Mechanisms which control the rate of release of toxic materials from both amorphous and crystalline solids used for the fixation of high-level radioactive wastes are reviewed. The expected chemical and structural stabilities are evaluated and compared under typical repository conditions such as temperature rise, α-radiation, transmutation and an aqueous environment. Experimental results are presented which evaluate the stability of glass materials against crystallization. The results of the evaluation show that high-silica glasses offer the best combination of good chemical and structural stability and very low corrosion rates. Borosilicate glasses give higher corrosion rates but still have good chemical and structural stability. The crystalline ceramics exhibit good resistance to chemical corrosion at high temperature but are expected to undergo extensive structural damage under the conditions of α-emission and transmutation. It is shown that this damage leads to increased release rates of toxic materials and raises grave doubts about the use of crystalline materials for radwaste fixation.

Summary

This paper presents an evaluation of the factors which influence and control the release of toxic substances from fixation solids used in the disposal of high-level radioactive reprocesser wastes. The evaluation is comparative and considers the relative expected performance of the various solid forms proposed, including crystalline media such as the supercalcines and synrocs and amorphous media such as borosilicate and high-silica glasses.

The rate of release of toxic materials from fixation solids is a function of the specific dissolution rate of the solid, the exposed surface area and the elapsed fixation time. All three factors, as demonstrated here, have a strong influence on the rate of release. The specific dissolution rate of a material is a function of its chemical composition, its physical state (polycrystalline, amorphous or partially crystallized), its microstructure, its temperature and the chemical nature of its surroundings, specifically the bath which contacts its surface. Since the materials contain radioactive isotopes, some of these conditions may change with time (physical state, temperature, etc.). These changes are discussed in detail below.

The mechanisms of dissolution of solids in aqueous media have been shown to cause variations in the dissolution rate with time. These mechanisms consist of the formation and possible subsequent peeling and cracking of a hydrated layer or depleted layer on the

outside surface of materials. These may result in a cyclic variation in leach rates, with cycle periods from several months to several hundred years. These mechanisms are discussed in detail, here, and extrapolation methods are presented which allow setting meaningful long term limits for maximum dissolution rates.

The exposed surface area of the fixation solids affects the rate of release of toxic materials to the same degree as the specific dissolution rate. In fact the release rate is a function of the ratio of dissolution rate to average particle radius. Therefore a decrease in particle radius of a factor of 1000 by breakage will increase the release rate as much as would an increase by the same factor in the specific dissolution rate. Most materials can be designed to expose a minimum surface area initially. However, changes in exposed area depend upon the physical stability of the material and are expected to occur with time during the storage period. Changes in exposed area result from local stresses in the materials and produce microcracking. These phase changes occur as a result of α-emission and radiation damage, transmutations, and long term exposure to weathering conditions and high temperatures. Cracking can also occur in the fixation media as a result of the formation of hydrogen and helium gas internally as a product of radioactive decay. Increases in surface area by factors of 10^3 to 10^6 are possible.

In comparing the relative performance of the various fixation media let us first consider chemical stability, since this is determined by the material's initial state, and does not appear to be altered drastically by radiation or transmutations. The chemical durability of solids varies greatly with chemical composition. In the selection of fixation materials, however, this variation has been recognized and most proposed solid forms have been selected to optimize chemical durability. Most materials fall within the range of dissolution rates of 10^{-4} to 10^{-11} g/cm^2 day, at room temperature. In general, the initial physical state of the material (crystalline versus amorphous) does not have a large effect on the initial chemical durability of the solids. We find that chemical composition has a more pronounced effect and that materials of a specific general composition exhibit similar specific dissolution rates whether crystalline, amorphous, or partially crystallized. For example, at room temperature, the borosilicate glasses or partially crystallized glasses have dissolution rates of 10^{-4} to 10^{-7} g/cm^{2}day and the crystalline ceramics of synroc and the supercalcines are at 10^{-4} to 10^{-6} g/cm^2 day. On the other hand, the high silica glasses are at 10^{-9} to 10^{-11} g/cm^{2}day whether completely amorphous or partially crystallized. These similarities in behavior only occur initially. If storage conditions allow the material to heat up, changes in specific chemical durability will take place. Under α-emission and transmutation, however, the major effect appears to be a change in surface area through cracking rather than a change in specific chemical durability.

Looking first at the effect of temperature rise, we find that the specific dissolution rate of materials in water behaves as an activated process. This means that temperature increases are extremely detrimental to the chemical durability of materials. With an activation energy of only 9 kcal/mol, which is generally a lower limit, the dissolution rate will increase by a factor of 10 between 20° and 70°C and by a factor of 30,000 between 20° and 600°C.

The concern with the temperature dependence of dissolution rate arises from the high thermal output of commercial solidified wastes. It is possible under some storage conditions proposed for sealed mines that the temperature of the storage medium will exceed 600°C. This is highly detrimental to the chemical stability of all fixation media. In this case, the crystalline ceramics exhibit a smaller degradation than the borosilicate glasses. However, neither material is sufficiantly resistant. This problem is not unavoidable, and in fact it is possible and desirable to select storage sites which are not sealed and can be cooled through air circulation. Additional precautions such as aging the wastes or spent fuel before processing and fixation and reducing loading levels can insure that the ambient temperature of the waste solids remains below 80°C. The use of cladding containers with lifetimes exceeding 50 years is also possible and will reduce the corrosion at high temperatures.

The chemical nature of the bath in contact with the fixation solid has a large effect on the dissolution rate. It is, of course, desirable to select repository sites where the ambient bath is as non-corrosive as possible. Of all possible storage sites considered, salt mines offer the most corrosive bath to all materials except possibly for titanium, since the bath will form HCl and HF acids as a result of the irradiation from the radioactive wastes. Granite mines with cooling systems and air recirculation appear to offer a repository site more suited to the long term survival of both the amorphous and crystalline fixation materials.

While the effect of high temperatures can be avoided by design, the effect of chemical and structural instability cannot. There is a large effect on chemical durability arising from the presence of microstructure with phase or grain boundaries. When phases or grains differ markedly from each other structurally, the interface energy is generally high, which enhances diffusion along the boundary and dissolution of the material through the boundary. This effect is expected to be small initially in polycrystalline materials, where the grains differ only in orientation, but can become significant when different phases or crystals are formed as a result of structural instability of the material.

The structural stability of the fixation materials is of equal importance to the chemical stability, since it controls the amount of surface area exposed to the external environment. In the case of glasses, several tests have been conducted with borosilicate compositions identical to those proposed for fixation and containing Am and Cm to accelerate the α-radiation damage. Little structural change was observed in the samples, and the chemical durability or dissolution rate of the materials remained unchanged.

Tests on borosilicate glasses loaded with fission products (25% by weight) showed no cracking and no degradation in dissolution rate over a storage span of 11 years, which is the time period for high rates of transmutation. Therefore the oxide glasses have demonstrated good structural stability under actual and simulated storage conditions, i.e., while undergoing α-emission and transmutation.

The question of physical stability of the metastable amorphous state over very long periods of time has been studied. The results, which are presented in this paper, are based on actual data and well established phase transition theory. They show that if the ambient temperature is 50°C below the glass transition temperature of the material, the projected times to crystallization in a dry environment are much longer than storage times. This is the case regardless of specific composition for the borosilicate and the high-silica glasses. The presence of water in the glass has the effect of lowering the viscosity, which requires an increase in safety margin of 75 to 100°C below the glass transition temperature of the water-free glass.

The question of structural stability of the crystalline forms proposed for disposal is not as clearly answered, since the actual systems have not been tested. There are, however, a number of similar minerals and man-made ceramics from which some conclusions may be drawn. Due to α-emission, minerals containing uranium have in general undergone a metamictic phase transition to an amorphous state with high stress development and microcracking. These minerals contain some of the basic elements of the proposed ceramic fixation media and have shown an increased susceptibility to metamictization when silica and rare earths are present. Rare earths are essential components of the radwaste fixation media, and silica is often used as a major component of the ceramic host. It is expected that under actual fixation conditions, the additional presence of Am, Cm and Pu, which have a higher α-emission than uranium, will further aggravate the damage. In many cases, the studied natural minerals exhibited fracture surfaces as close together as fractions of microns. The increase in effective surface area associated with a fracture structure consisting of cracks several microns apart is of the order of 10^6 times. In the unlikely event that recrystallization occurs instead of metamictization, grains will be formed with high interfacial energy and will undergo rapid dissolution and end up as powder also with a large associated increase in area.

The expected effect of transmutations in crystals can be evaluated from basic crystallographic concepts, some phase diagram studies of similar systems, and a valence change experiment on a system containing some of the basic elements of synroc. Combined, these analyses show that transmutation from Cs^{+1} to Ba^{+2} and from Sr^{+2} to Zr^{+4} will cause large structural damage which will likely result in a metamictic phase transition and in powdered samples. Again the expected result is similar to that of radiation damage and the surface area will increase by large factors.

Unfortunately, these results are obtained by inference. We suggest that tests be conducted on the crystalline ceramic waste forms containing the α-emitters and some fission products. However, the clear conclusions of the evidence available cause concern about the physical stability of all crystalline waste forms in the presence of α-emission and transmutation.

The final question of structural stability of waste forms concerns the presence of internally formed hydrogen and helium gas. We have not at this time estimated the rate of gas formation. Therefore, the only conclusions possible are based upon the measurements of diffusion of these gases through materials. The results show that amorphous materials, due to their open structure, have a higher coefficient of gas diffusion for hydrogen and helium than do crystals. Therefore the glasses will be less likely to suffer damage from internal pressure build up.

Unlike the problem of temperature rise in the repository due to the thermal output of waste materials, which can be adjusted by suitable cooling, the problems of α-emission, transmutation and gas formation are an inherent part of the radioactive decay process and cannot be alleviated by reporitory design. Therefore, we see that there are no ideal materials for the disposal of radioactive wastes. However, with careful control over composition and thermal loading conditions, some glass candidate materials such as the high-silica glasses offer the combination of high-chemical durability below 100°C, high chemical stability and high structural stability essential to the suitable fixation of high-level radioactive wastes in solids for long time periods. The borosilicate glasses offer high structural stability. However the best chemical durability achieved is 1000 times lower than in the high-silica glasses. The crystalline ceramics show moderate chemical durability at room temperature and a smaller degradation of this with increasing temperature than glass, but they are not likely to exhibit the necessary structural stability during storage and therefore cannot be considered suitable candidates at this time.

An interesting aspect of the long term stability of the amorphous state was recently present by J.A. O'Keefe, B.P. Glass and S. Alterescu, who evaluated the stability of geological, lunar and ancient man-made glasses. They find from lunar glass evidence that in general, for a wide range of compositions, the amorphous state is stable over long time periods, of the order of 3 to 4 billion years, at temperatures from a few degrees to several hundred degrees Kelvin when no water is present. When water is present in the environment glasses with low silica concentrations are found to dissolve and reprecipitate over long time periods, as in ancient man-made glass. However if the content of network formers such as silica and alumina is above 80%, as in the North American tektites, the glass have survived in aqueous environments without structural change for over 35 million years. These glasses demonstrate extremely low dissolution rates and exhibit losses of less than 10 microns from their surface after 35 million years at the bottom of the ocean, despite the expected corrosive action of sea water. The reasons for this high structural and chemical stability appear to be the high silica content of the glasses and the low ambient temperatures (< 50°C).

Acknowledgments

The authors gratefully acknowledge the contributions in private discussions of: J.A. O'Keefe, from N.A.S.A.-Goddard Space Center, R.S. Roth, from N.B.S., and D. Gottfried from Geological Survey.

I. INTRODUCTION

The suitability of various fixation media for the safe disposal of high-level radioactive wastes is determined by the chemical and structural stability of each material under disposal conditions. The primary concern is with the release of radioactive nucleides to the environment by chemical leaching of the fixation medium. The release of toxic materials from solids is a function of the dissolution rate, surface area and time. Therefore, while it is desirable to use materials with very low dissolution rates, it is necessary to also minimize surface area.

Dissolution rates are determined by the chemical composition of the material, by the physical state (i.e., crystalline, amorphous, partially crystallized), by the microstructure (grain size, grain boundaries, interfaces) by the ambient temperature and by the chemical nature of the medium in contact with the surface of the material. This requirement of chemical stability has long been recognized and there is sufficient data at present to draw conclusions regarding the relative performance of the various fixation media.

The performance of different fixation media in maintaining a minimum external surface area may be evaluated by determining their structural stability and their tendency to break up into small pieces or powder during the storage period. Conditions which will affect the structural stability of materials during storage are particle radiation such as α-emission from the actinides, transmutations of the fission products and actinides, and internal gas formation (H_2, He). The behavior of some radwaste glass candidates has been investigated with tests on real and simulated wastes. The effect of transmutations on physical and chemical properties of a borosilicate glass was measured by loading the glass with actual radioactive waste materials.[1] Long-term radiation damage was evaluated in borosilicate glasses through accelerated tests using Am and Cm isotopes which have a short half-life and therefore emit a high α-dose.[2,3] Unfortunately, similar tests are not available for the crystalline ceramic waste forms. In our evaluation of their expected performance, we use evidence from phase diagram studies on similar compounds and crystals and from analyses of mineral samples containing low levels of uranium and thorium. The evidence from mineral samples however must only be taken as an indication of the best possible behavior of waste solids since the minerals investigated do not contain the short-lived isotopes of Am, Cm and Pu which emit high α-doses and are likely to cause far more damage than uranium or thorium. In this vein, we recommend that suitable tests be undertaken soon, using real loading levels and the entire spectrum of α-emitters present in the wastes.

The effect of time, temperature and water on the rate of crystallization of glasses will be discussed in detail. The results are based on experiments described in this paper. The time and temperature extrapolations presented are based on the well established formalism of physics of phase transitions and on the analysis of the behavior of very old geological samples and minerals.

Finally, we will show data on geologic model glasses to demonstrate the general long-term behavior of amorphous materials and to test the predictions of long term structural stability in aqueous environments.

In this paper, all the attention will be focused on the waste solids and not on the geologic repositories. We will only discuss properties of some geologic sites in so far as they affect the waste fixation solids.

As a final restriction, we are only evaluating the properties of crystalline ceramics and glasses as waste forms. Other forms such as concrete and calcines have such a high initial dissolution rate[4] that their long term chemical and structural stability is of no consequence since they will totally dissolve in the short term.

II. STORAGE CONDITIONS

After the waste materials have been incorporated into the structure of the fixation medium, certain unusual conditions will be created. These must be considered first in order to determine the physical and chemical stability problems of the fixation media during extended storage. The storage conditions considered are as follows:

1. High heat output in commercial wastes.
2. Emission of various particles including α-particles from within the storage media.
3. Transmutation of the radio isotopes into new elements.
4. Gas production (Hydrogen and helium).
5. Presence of an aqueous environment in the repository.

A. Thermal Output

The large production of heat in commercial wastes is due to the decay of the fission products and has a relatively rapid exponential decrease. Temperatures of several hundreds of degrees for over a hundred years have been estimated for commercial wastes deposited in sealed mines.[5] While the actual temperatures reached will vary depending on the properties of the repository, it has been proposed that the thermal output problem may be solved, if desired, by cooling the repositories, by reducing waste loading levels, and by aging the wastes above ground for 10 to 30 years. A workable scheme has been developed to maintain waste media temperatures at and below 80°C.[6] If cooling is not desired, the large thermal output of commercial wastes will cause a temperature rise in the fixation media. Their properties and stability must be investigated as a function of temperature in the range of 80 to 600°C to determine if the decrease in stability with increasing temperature for each material warrants the expense of cooling the wastes to maintain relatively low temperatures such as 80-100°C.

B. Radiation

The radio isotopes present in the fission products and actinides in the wastes emit all forms of radiation including elementary particle, α-particle and photon emission. Of these the most potentially damaging is the emission of α-particles and its associated nucleus recoil.

The potential effects of α-particle and nucleus recoil damage on physical and chemical stability at high radiation levels must be assessed. This problem is not significantly reduced by long term surface storage and therefore is an inherent part of the storage condition. Some reduction of the effect is possible by decreasing the concentration of actinides in the waste media.

C. Transmutations

As the radioisotopes decay with time, they lose nuclear particles which results in a change of their elemental form and therefore their valence, their bond states and configurations and their equilibrium coordination numbers. For example, Cs^{137} decays by the emission of an electron to Ba^{137}. Cesium is a monovalent element while barium is divalent and needs to form two atomic bonds to remain in equilibrium. Sr^{90} which is divalent decays similarly to Y^{90} which rapidly decays to Zr^{90} which is tetravalent. The formation of new bonds or dangling bonds and the decrease in nuclear size strongly affect the structural equilibrium and the stable coordination of the atoms. The actinides also decay to new elements, however, due to their high valences and their large number of possible valence states, it is difficult to predict what will happen. Some authors have suggested that transmutation effects in the actinides are relatively less severe than for the fission products,[7] but others suspect that the naturally occuring metamict minerals containing actinide elements may be a result of transmutations of the actinides rather than radiation damage.[8] Aging of the wastes for long time periods before fixation in solids can help reduce the effect of transmutations of the fission products. The effect from actinides is not known.

D. Gas Production

The emission of protons and α-particles forms hydrogen and helium gases, within the fixation medium. A survey of gas diffusion in solids can be examined to determine potential problems. The formation of these gases may have an influence upon waste loading levels and the design of canisters.

E. Aqueous Environments

If the wastes are stored on earth, whether on or below ground level, it is very likely that they will rest in an aqueous bath at some time during the storage period. The nature of this bath regarding temperature, trace element content, acidity, etc., will be determined by the geological fixation site. However all these parameters can be varied to desired values by the proper choice of burial site and backfill. In this case, the material property of importance is the chemical durability of the fixation material in an aqueous environment.

III. CHEMICAL STABILITY

A. General

The chemical stability of the disposal materials is related to its tendency to dissolve in its aqueous environment. One of the major drawbacks of the use of salt mines for repositories, from the standpoint of the fixation materials is the highly corrosive aqueous environment formed. The liquid present will consist of water containing HCl and HF formed by radiation and can dissolve all glass, ceramic and most metallic materials except possibly for titanium. Therefore in considering the chemical stability of the various disposal fixation media, since the geologic repository has not been selected and may vary from site to site and from country to country, it is necessary to consider simple aqueous solutions to be only used as guidelines in evaluating the various materials. These would consist of neutral, clean deionized water, and water buffered at a low, acidic pH (2.3) a close to neutral pH (5.7) and a high, basic pH (9.5). This work is presently undertaken for the International Standards Organization.[9] Data is available on some materials soaked in neutral, clean deionized water.

In general at room temperature, the proposed fixation media exhibit release rates of 10^{-2} to 10^{-4} g/cm^{2}d for cement; 10^{-4} to 10^{-6} g/cm^{2}d for the multibarrier supercalcines; 10^{-4} to 10^{-7} g/cm^{2}d for the borosilicate glasses; and 10^{-9} to 10^{-11} g/cm^{2}d for the multibarrier high silica glasses.[4,10] In comparing <u>initial</u> chemical durability at room temperature, differences appear according to chemical composition. There do not appear to be large differences due to the physical state of the material, whether it is totally crystalline, totally amorphous or partially crystallized. As the temperature is raised to 100°C, we find that the leach rate or material dissolution rate increases, somewhat like an activated process. The activation energy is generally 9 to 15 kcal/mole.[11] The increase in rate is shown in Table 1. It is quite obvious that with an activation energy of 15 kcal/mol, the material is totally dissolved in a very short time at temperatures near 600°C regardless of the chemical durability at room temperature. If the activation energy is higher, then, the temperature for rapid total dissolution will be lower.

Table 1. Increases in Dissolution Rates with Temperature

Temperature	Dissolution Rate (15 kcal/mol)	Dissolution Rate (9 kcal/mol)
20°C	1	1
40°C	5	3
70°C	40	10
100°C	240	30
200°C	10^4	3×10^2
400°C	2×10^6	6×10^3
600°C	2×10^7	3×10^4

Experiments conducted on borosilicate glasses and ceramic samples at 400°C in aqueous environments have borne out these calculation and have shown that glasses will dissolve and reprecipitate as crystals under these conditions. Reprecipitation obviously occurs in cooling and the results do not necessarily indicate that the precipitated products have a greater chemical stability than the glass. A comparison of the behavior of supercalcines and borosilicate glasses shows that the former have a greater stability at the higher temperatures, although as shown in Table 1, the activation term is overwhelming and both will dissolve far too fast to offer real containment capabilities, at high temperatures.

Careful examination of Table 1 and the high temperature results of dissolution measurements on glasses and ceramics indicates that aqueous environments at high temperatures are not desirable conditions for storage of fixation materials. It is possible either to avoid self-heating of the wastes by suitable cooling measures as chosen by the Swedish Waste Disposal (KBS) Report,[6] or to prevent the waste fixation media from resting in an aqueous environment when the temperatures are above 100°C. The former solution is more likely and the waste fixation solids may be maintained below 100°C for more than 100 years by either cooling the repositories through air or water circulation, aging the wastes before fixation or decreasing the loading levels and increasing the thermal conductivity of the waste material-canister system.

B. Effect of Layer Formation on Long-Term Predictions

In evaluating the dependability of chemical durability tests conducted under short term laboratory conditions in establishing well founded upper limits for the prediction of long term corrosion rates of the various materials used in nuclear waste fixation, one must be very careful to consider the possiblity of cracking and peeling of the depletion of hydration layer. For example, it has been shown that materials, when undergoing dissolution, release different components of the composition at different rates.[13] The alkali metals having a high ionic diffusivity in general are released at a faster rate than the matrix is dissolved. In return, protons or hydroxyls from the bath penetrate into a surface layer. Thus are formed a depletion and a hydration layer on the surface of the material during exposure to corrosive environments. This process is crucial to the evaluation of long term dissolution rates because these layers as they grow become stressed due to swelling or contraction and may crack or peel from the material, thus exposing a new fresh surface to the corrosion environment. As a result, calculations of material release rates based on an extrapolation of short-term leach rates may be too low by many orders of magnitude. The effect is two-fold. First, as most materials are exposed to aqueous environments, the leach rates have been observed to decrease in time.[13,14] This decrease which is in fact a manifestation of the formation of a depleted of hydration layer will continue until the layer peels off and the leach rate will return to its initial value, with a resulting cyclic variation in leach rate, between a high initial value and a low value prior to the layer peeling. This gives a higher effective leach rate than predicted by the extrapolation of the lowest leach rate observed. The differences are clearly related to the length of the cycle time. Second, the material in the cracked or peeled layer has a high surface area and very small size. Its dissolution will be rapid, therefore, it must be assumed to be disseminated to the bath when cracking or peeling occurs. In this case, the thickness of the layer determines the magnitude of the increase in effective release rate.

The mechanisms and rate of formation of these layers have been investigated in detail for some glasses,[15] but there is little work available on the behavior of crystalline materials. In glasses, the formation of a hydration layer generally occurs simultaneously with the depletion of alkali ions. This is sometimes complicated by crystallization occurring in the layer. The final effect is the same however, as the crystallization leads to cracking and peeling. We do not know what happens in crystalline ceramics.

It is generally recognized in studies of corrosion of that in the case of relatively durable alkali-containing silicate glass dealkalization due to selective leaching during the first stage of attack leads to the formation of a silica-rich protective layer.[15] Under steady-state conditions, this layer achieves a constant thickness when the rate of diffusing out of alkali ions through this layer has slowed down until it is equal to the rate of dissolution of the siliceous network of the protective layer.

If a leaching test is carried out on a glass sample until such steady-state conditions are achieved, i.e., until the rate of both alkali and silica dissolution are constant and the ratio of alkali-to-silicate in the dissolving material is equal to the corresponding ratio in the solid glass, it can be expected that the steady-state rate of dissolution will furnish a reliable basis for long-term prediction of durability, because under steady-state conditions the dealkalized layer reaches a constant composition, a constant thickness and a constant level of stress due to hydration and swelling.

On the other hand, with certain glass compositions the stress may rise during the build-up of the dealkalized layer to such high levels that the layer will crack and even peel off before the rate of dealkalization has become equal to the rate of network dissolution. An excessive increase in stress is particularly likely if the hydrated layer undergoes crystallization, promoted by the lower viscosity of the hydrated layer and possibly by a reduction of size of the crystallizing unit of structure in this layer as compared with the solid glass. If excessive stresses can develop one can expect to see that the rate of dissolution or weight loss of the glass will decrease during the initial stages of the leach test due to the build-up of the protective layer; however, instead of stabilizing at a level which will correspond to the steady-state conditions, i.e., at a level controlled by the dissolution of the network, the rate will rise abruptly due to cracking and partial or complete peeling off of the protective layer. This sequence can be expected to be repeated continuously, with the rate of dissolution showing a series of sharp increases followed by gradual decays. The effective rate of corrosion should in this case be obtained by integration over a period corresponding to a representative cycle.

When cyclic variations in dissolution rate are not observed in the course of a leaching test, i.e., the dissolution rates are not observed to increase at any time interval during the test, the dissolution rates obtained in the final stages of the test can be used for long-term evaluation of the chemical durability of the specimen only if the criteria for a steady-state situation are met, i.e., the rates of dissolution of both the major component such as silica and alkali have leveled off and the composition of the dissolving material is identical to that of the solid glass.

However, practical problems may render continuation of the test until steady-state has been established difficult, if not impossible. The major difficulty is the time it may take for the dealkalized layer to grow until it reaches its maximum thickness and begins to regenerate at a constant rate.

Corrosion experiments were conducted in our laboratories specifically to investigate the layer formation problem. Two glasses were chosen. One was a borosilicate glass containing only sodium oxide as added component. This allows for a very high coefficient of ionic diffusivity and is used to represent an example of low layer stability. The second glass was Pyrex Brand which contains more components including other alkali and alumina. These components lower the ionic diffusivity of the glass and would tend to reduce the problem of layer formation. Actual radwaste glasses contain many components including the alkali metals Na, Rb, Cs and the alkaline earths Sr and Ba which interact with each other to reduce the ionic diffusivity in glasses. This tends to reduce the layer formation problem in glasses. The behavior of crystalline ceramics is not known. We are presently conducting tests of layer formation of both borosilicate and high silica glasses to determine their behavior.[15]

Measurements on a borosilicate glass containing only sodium (0.44% Na_2O) have been carried out for a period of 20 days at 22°C in distilled water (pH 5.7). The results of these measurements are presented in Fig. 1 and in Table II. It can be seen that after 8 days the rate of silica dissolution becomes approximately constant at a level of 5 ng/cm^2d (the accuracy during the later stages of the test is low due to the extremely low levels of dissolved silica concentration). The rate of sodium dissolution during the 20 day test period is approximately 0.5 ng/cm^2d, very close to the analytical detection limit for sodium. Between the first day of the test and the end of the 20 day period the rate of silica dissolution decreases by a factor of 8, while the rate of sodium leaching is reduced by a factor of more than 400. Correspondingly, the $Na:SiO_2$ molar ratio in the dissolved material drops from 14:1 during the first day to 3:1 after 9 days and to about 0.2:1 after 20 days, while the corresponding molar ratio in the glass is only 0.009:1. In terms of layer thickness, at the end of 20 days, assuming the concentration of sodium throughout the rod to be uniform, a surface layer 662 nm thick has been completely dealkalized while the thickness of the dissolved silica layer is only 1.5 nm.

The results of the experiment on the corrosion of Corning 7740 glass (Pyrex) are qualitatively similar to the results obtained for the sodium glass, but in the case of Pyrex the initial rate of specific sodium leaching is lower and this rate falls off less steeply in the couse of the test. The test on Pyrex has been carried out at an elevated temperature of 70°C. Parallel tests have been carried out in distilled water (pH 5.7) and in a buffered pH 5.7 solution, and the results of these two tests are identical within experimental error. The test period is 90 days. After 5 days the rates of both silica and sodium dissolution become stabilized at levels of 61 ng/cm^{2}d SiO_2 and 10 ng/cm^{2}d Na. The rate of silica dissolution decreases by a factor of 2. The rate of sodium dissolution by a factor of 8.3, and consequently the $Na:SiO_2$ ratio decreases from an initial value of 3.5:1 to a plateau value of 0.75:1. The corresponding ratio in the solid glass is 0.096:1. In terms of layer thickness, at the end of 90 days a 145 nm thick layer has been dealkalized while the equivalent thickness of dissolved silica is only 15.4 nm.

Both the tests reported above show that the dissolution rates of both sodium and silica, as well as the ratio of sodium to silica in the dissolving materials, decline steadily in the course of exposure without showing any sign of rising again. However, in both cases the build-up of the hydrated layer has not been completed at the end of the test period. In the case of pyrex glass at 70°C the rates of both sodium and silica dissolution have become nearly constant after a 5 day period and in the case of the sodium glass, silica dissolution also appears to approach stabilization after 8 days, but in both cases the ratio of sodium to silica in the dissolved material is still higher by an order of magnitude than the ratio in the solid glass. The rate of silica dissolution, although it shows only a small drop during the course of the test compared with a much larger drop in the case of sodium, is still too low by the end of the experiment relative to the rate of leaching of sodium. The only case where steady-state rates have been approached is that after 5 days, and up to at least 90 days of exposure, the rates of dissolution of both sodium and silica are observed to be constant with a sodium-to-silica ratio of 0.16:1 in the dissolved material compared with 0.096:1 in the solid glass.

The finding that extremely long periods are required for the establishment of steady-state conditions is in agreement with results obtained in zinc borosilicate radwaste glass, where the rate of corrosion is observed to decline by about one order of magnitude during a period of 100 days of immersion in a neutral solution, and is still declining at the end of this period.[14] The observed rates of corrosion in this case are considerably higher than in our experiments, leveling off at about 650 ng/cm^{2}d at 22°C and at about 7500 ng/cm^{2}d at 70°C. In the case of Na_2O-CaO-SiO_2 and K_2O-CaO-SiO_2 it has been demonstrated that as long as the mole fraction of CaO is below 10% the silica to alkali ratio in water extracts remains low compared to the ratio in the solid glass even when dissolution becomes linear with time.[13] In the extreme case of the low-durability glass $3K_2O:17SiO_2$ potassium is leached out in strong preference to silica throughout the course of the attack until the entire glass becomes completely dealkalized.[17]

It has been concluded above that in the case when a periodic abrupt rise in corrosion rate, indicative of rupture of an overstressed hydration layer, is not observed during the course of a leaching test, it is necessary to carry out the test until steady-state criteria have been met and the layer has been regenerated at least once in order to make certain that such rupture will not occur in the long term. However, the experimental evidence described above shows that the achievement of steady-state conditions in the case of durable glasses and neutral leachants may take extremely long periods. In particular, the data obtained for the soda glass at 22°C appears to show that regeneration of a leached layer will take much longer than 20,000 days (the apparent thickness after 20 days divided by the silica dissolution rate at this stage). In the case of pyrex at 70°C the corresponding time is at least 900 days.

The question now arises as to whether it is possible to take into consideration a possible rupture of the hydration layer, without observing it experimentally and without reaching steady-state, in establishing meaningful upper limits for predicted long-term rates of corrosion. In order to do that, one can make a worst case assumption, i.e., assume that rupture would have occured if the exposure to the leachant was carried out for a slightly longer time than the actual test period. Assuming that such rupture would occur periodically, the upper limit for corrosion is then estimated by integration over a period corresponding to one hypothetical cycle of rupture and renewed build-up of the layer, and this period is taken to be equal to the actual time of the test.

A further question is how high can the corrosion rate rise during such a cycle, i.e., how much material can be lost from the glass when the rupture occurs. We will cast the following discussion in terms of the rates of loss of only sodium and silica. Experimental evidence shows that the alkali metals behave like sodium and the other elements like silica to a first approximation.[18] Four hypotheses are possible:

1. <u>The rate of dissolution after the termination of the actual test will remain constant or continue to decrease indefinitely.</u> According to this model, the build-up of the hydrated layer will continue until steady-state conditions are established without becoming over-stressed and without rupturing. In this case, the long-term upper limits for the rates of dissolution of sodium, silica and any other components of the glass are directly obtained from the respective observed rates at the end of the actual test.
2. <u>The rate of dissolution immediately following the rupture will return to its maximum value at the beginning of the test</u>

and then decline in the same manner which has been observed during the actual test. The corresponding physical model is that of a gradually thickening protective layer, with a resulting decline in dissolution rate. When the layer becomes overstressed, it cracks, loses its protective capacity and leaves an exposed pristine surface which is similar to the original surface. In this case, the rate of dissolution of both sodium and silica during one hypothetical cycle are calculated by integration of the respective observed dissolution rate over the time of the actual test.

3. During a rupture, an extra amount of silica will dissolve, which will be equivalent to the amount of sodium leached during the previous cycle. According to this model, every time a sodium atom is leached away from a Si-O-Na group it leaves behind a labile hydrated silanol group, which has a much larger tendency to dissolve away than a network Si-O-Si group. As soon as the protective layer is cracked, the silanol groups can pass into the solution. The assumption of greater solubility of the hydrolyzed Si-O-Na group compared to that of the network is supported by the large body of evidence (see Refs. 13,17) pointing to the fact that the kinetic patterns of silica dissolution are in many cases very similar to those of sodium leaching during the same test even though the rate of silica dissolution may be low compared with that of sodium with respect to the solid glass composition.

Alternatively, it is possible to visualize such a result assuming that during leaching the Si-O-Na bond is broken, both fragments break away but while sodium passes into the bulk of the solution hydrated silanol is trapped and becomes loosely adsorbed on the network of the dealkalized layer (possibly as silica gel). As soon as this layer is ruptured, the silanol groups dissolve away.

In case 3 the upper limit of the amount of silica dissolved during a hypothetical cycle is therefore taken to be equal to the molar quantity of sodium leached away during the buildup of the layer, and is calculated by integration of the observed dissolution rate of sodium over the time of the actual test.

4. During a rupture, the extra amount of silica lost will be equal to the entire silica content of the leached layer. According to this mechanism, when the stress in the growing hydration layer becomes excessive the entire layer may peel off and break away either as a solute or as solid fragments. One way of estimating the dissolution rate during such a cycle is to assume that the rate of dissolution of silica remair effectively constant at its initial high value; however, this estimate is not reliable because of specific characteristics of the original surface before immersion and because of the possibility of silica re-adsorption even at the initial stages. To

estimate the rate of dissolution in case (4) it is therefore preferable to use the entire silica content of the dealkalized layer. In this case the thickness of layer is calculated from the integrated sodium leaching data during the actual test. Since the concentration of sodium in the glass is low, such an estimate is higher than the one obtained in case (3) where the leaching of one Na atom is assumed to lead to the loss of only a single SiO group.

The results of estimates based on models (1), (2), (3) and (4) together with the observed rate of dissolution at the end of the actual test, are shown in Table 2.

Table 2. Estimates* of the Long-Term Rate of Corrosion Assuming Rupture of the Leached Layer

	Sodium Glass 22°C, 20 days nm/d	Corning 7740 70°C, 90 days nm/d
Observed rate at beginning of test	0.19	0.28
Observed rate at end of test		
Case 1	0.032	0.16
Case 2	0.064	0.163
Case 3	0.535	0.174
Case 4	33.1	1.611

* (A triangular, rather than exact graphical, integration was carried out; this results in slightly increasing the calculated upper limits).

One observation regarding the two different samples is that while in both cases the rate of dissolution of silica has decreased by a similar factor before appearing to level off, and while the final sodium-to-silica ratio in the dissolved material relative to the solid glass is comparable, the rate of sodium leaching has dropped in the course of the test on the sodium glass factor of 424, while in the case of the Pyrex sample the corresponding decrease is only by a factor of 8.3. This is the reason why even the highest estimate (Case 4) for the matrix dissolution rate is higher than the observed rate only by a factor of 10, in the case of Pyrex, while in the case of the sodium glass the corresponding estimate is higher than the observed rate by a factor of 1000.

One possible reason for the much higher initial rate of release of sodium from the sodium glass is a non-uniform concentration profile of sodium across the sample, with a high concentration of sodium in the outer layers of the original surface. In general, such variations in the composition of the surface relative to inner layers of the glass will lead to large discrepancies between the observed final rate of dissolution and the estimates of the upper limit of this rate based on the extent of hydration. Surface nonuniformities can be minimized by mechanical grinding or chemical etching and the concentration profiles verified prior to the beginning of the test. The proposed methods of estimating upper limits of rate of dissolution in the case of excessive leaching stress are also inapplicable to phase-separated or graded-composition glasses.

The results obtained in the corrosion test on pyrex show that in this case the highest estimates for the long-term dissolution rate, based on the assumption of periodic complete destruction of the entire hydration layer, are higher by only a factor of 10 than the final dissolution rates observed during the test period. In order to further narrow down the additional extent of corrosion due to possible crystallization and/or overstressing and cracking of the leached layer, it is necessary to gather more experimental data on several aspects of the problem including:

a. Accurate corrosion tests on glass samples with various durabilities pretreated to ensure uniformly flat composition profiles across the sample. Accurate data on representative components of the radwaste solid such as Na, Cs, Sr, Si and at least one actinide should be obtained for the longest possible test periods.

b. Dissolution tests on glass compositions which are likely to show the phenomenon of periodically enhanced corrosion due to rupture of the leach layer. Analysis of the used leachant has to be carried out on total silica and sodium removal both in solution and in solid fragments. The results can be used to test the models offered above for estimation of excess matrix dissolution.

c. Composition effects. Since several multivalent elements, such as Ca and Ba are known to reduce the extent of selective alkali leaching (see Ref. 13,15) the presence of such components may reduce the danger of the buildup of an excessively thick leached layer. Systematic studies of the effects of various components on the rates of hydration as well as the rates of dissolution have to be carried out.

d. Characterization of the composition structure, thickness and sharpness of the hydrated layer at different stages of the exposure.

e. Attempts to estimate the characteristic stress relaxation time in the hydrated layer. If it can be shown during

> any stage of exposure that further buildup of stress due to hydration and possible crystallization becomes so slow as to be comparable with the stress relaxation time, then the possibility of rupture can be discounted. This is the case even if steady-state conditions have not yet been reached. Experimental studies along several of these lines are carried out at present in our laboratory.

In conclusion, we have shown that layer formation during leaching can be detrimental to long term dissolution predictions. Short-term tests must be conducted to determine the extent of layer formation and its effect on steady-state leaching. If steady-state is not achievable during the short-term tests, we have shown how one may predict effective release rates for the long term. The results can change the actual rate of release of materials. For example, we have shown how a sodium glass may exhibit a dissolution rate in the long term which is 1000 times that actually measured in the laboratory. In the case of glasses used for fixation, due to the lower ionic diffusivity, we expect changes by a factor 10 at most, as was shown to occur in Pyrex glass. Tests are presently under way on borosilicate and high silica storage glasses. We suggest that similar tests be conducted on the polycrystalline ceramics if they are to be considered as serious candidates for radwaste fixation.

C. Fixation Capability Based on Leach Rates - Effect of Composition

In order to determine the relative safety of various materials regarding their performance as fixation solids, from measurements of their respective leach rates, a calculation may be conducted to evaluate, as a function of storage time, the amount of each radioactive isotope accumulated in an aqueous bath surrounding a fixation medium as shown below. This will give a better basis from which to evaluate the comparative effects of various leach rates.

The amount M_i, of each radioisotope, i, present in the waste which is accumulated in the surrounding medium may be calculated as a function of storage time, t, and initial concentration in the waste, M_{oi}, by the following expression:

$$\frac{M_i}{M_{oi}} = \alpha_i \, e^{-t/\tau_i} \left(\frac{2Dt}{\rho r_o} - \frac{D^2 t^2}{\rho^2 r_o^2}\right)$$

$$+ \alpha_j \left(\frac{2Dt}{\rho r_o} - \frac{D^2 t^2}{\rho^2 r_o^2}\right) \left(\frac{\tau_j}{\tau_1 - \tau_j}\right) \left(e^{-t/\tau_j} - e^{-t/\tau_i}\right)$$

where the isotope i is the decay product of the isotope j; D is the effective matrix dissolution rate (i.e., the rate of release of silica in the discussion above); ρ is the density of the fixation medium; r_o is the radius of the cylindrical fixation medium; τ_i and τ_j are the mean lifetimes of isotopes i and j respectively; t is the storage time, and α_i and α_j are the fractional concentrations of isotopes i and j in the dissolved material. Generally, α_i and α_j are unity, unless a multibarrier protection system is used at which point α_i and α_j take on the value of the fractional concentrations of the isotopes in the barrier until it is dissolved and then revert to unity when the barrier is totally removed.

At present, storage conditions and loading levels are still uncertain and subject to change, therefore, in the calculations to follow, we will assume two types of thermal conditions. First we will consider a room temperature storage for the entire disposal period and second a disposal period with samples at 100°C for the initial 100 years. The calculations are conducted for two specific isotopes: Cs^{137} and Pu^{239}. Cs^{137} is chosen to represent the short-lived isotopes (half-life of 30 years) and Pu^{239} is chosen to represent the long-lived isotopes (half-life of 24,400 years) in the waste solutions. Pu^{239} is expected to be the worst case, since in addition to its long life, it is also a decay product of Am^{243} with a half-life of 7,400 years. The calculations for room temperature storage were made using 3 different dissolution rates obtained following model 1 in Section B above: 1×10^{-5} g/cm^{2}d which represents a typical value for borosilicate glasses and supercalcine solids, 2×10^{-7} g/cm^{2}d which is the best borosilicate glass value, and 5×10^{-10} g/cm^{2}d which represents the best high-silica multi-barrier glass.

In the calculation, samples are assumed to be cylinders 1 cm in radius which is the expected shape of most samples including the borosilicate glass samples following breakage during cooling after fabrication.[14]

The values of constant assumed in these calculations are repeated in the figure captions. The results are plotted in Figs. 2 and 3 for Cs^{137} amd Pu^{239} assuming room temperature dissolution rates. The graphs clearly show that the accumulation of Pu^{239} is much higher than that of Cs^{137}. At a dissolution rate of 1×10^{-5} g/cm^{2}d, the maximum dissolved Cs^{137} accumulated in the bath after 40 years is 8% of the original amount loaded. Pu^{239}, after 800 years, reaches a maximum near 90% of the initial loading. The dissolution rate of 2×10^{-7} g/cm^{2}d which is the best achieved with borosilicate glasses is improved in its safeguard against Cs^{137} reaching a maximum of 0.1% of the initial amount. However, it is not effective in the fixation of Pu^{239}. After 20,000 years the accumulated dissolved Pu^{239} reaches an amount which is 70% of the initially loaded amount. Levels of 1% are reached in 200 years. It is obvious from these data, that at dissolution rates above 2 x 10^{-7} g/cm^{2}d the fixation of Pu^{239} and other long-lived isotopes is not obtained over long time periods.

Figures 2 and 3 also show the fixation characteristics at room temperature of the best high-silica multibarrier glasses with a dissolution rate of 5 x 10^{-10} g/cm^{2}d. The maximum accumulations achieved are 0.1 ppm (10^{-5} percent) for Cs^{137} and 80 ppm (8 x 10^{-3} percent) for Pu^{239}. These levels are extremely low and can be considered to offer safe fixation of both short-lived and long-lived radioactive isotopes.

The second storage condition considered here begins with an initial temperature of 100°C for 100 years followed by a drop to room temperature for the remainder of time. The dissolution rates of the borosilicate glass and supercalcines are near 10^{-4} g/cm^{2}d while the high-silica glass has a rate below 2 x 10^{-6} g/cm^{2}d at 100°C. Calculations were made using these two rates for the first 100 year period to evaluate the resulting decrease in safety.

The accumulation of released Cs^{137} in the environment surrounding the glass fixation materials for storage at 100°C is shown in Fig. 4. The dashed curve represents the dissolution rate of 10^{-4} g/cm^{2}d while the solid curve represents the high silica glass. The accumulated Cs^{137} released to the environment by the borosilicate glass reaches a maximum after 30 years of 40% of the total amount loaded in the glass, clearly posing a serious hazard. The high silica multibarrier glass, however, only peaks at 0.03% and remains well within safe limits.

A calculation of the rate of release of Pu^{239} from the borosilicate glasses shows that all of the Pu^{239} will be released to the environment within 40 years. The high-silica glass, however, does not exceed a maximum accumulated level of 0.2% at any time during the storage period despite the 100 years at 100°C.

In conclusion, the chemical stability of storage media can be increased to suitable levels for safe long-term disposal of radioactive wastes by a judicious choice of composition of the solid fixation media. However, the temperatures must be kept low due to the behavior of the leaching process as an activated process. Obviously, dissolution will occur at all temperatures, but manageable levels can be maintained if the temperatures are kept below 100°C. There is a large difference between the chemical stability of various materials, however, the use of durable canisters, multibarrier storage, and minimized surface area may lower release rates to suitable levels. The high-silica glasses appear to offer the best chemical stability.

IV. STRUCTURAL STABILITY

Structural stability as applied to solids for waste containment refers to the ability of the materials to remain in a given physical state and to oppose changes from that state. Phase transitions such as immiscibility, crystallization of amorphous materials, recrystallization or metamictization* of crystalline materials, and phase decomposition are demonstrations of structural instability. These transitions generally form phases with different physical properties such as coefficient of thermal expansion and specific volume, and therefore are accompanied by large volume changes which stress the material and often lead to microcracking. The formation of powder or microcracks in a material can increase the total exposed surface area by 1000 to 1,000,000 times. The effect that this has on the rate of release of toxic materials from a fixation medium is shown in the equation above. The direct effect of powdering or cracking is to reduce the effective size of the particles formed. This is represented as r in the equation. Examination of the equation reveals that the amount of accumulated isotopes is proportional to the ratio of dissolution rate to particle radius, therefore a 1,000 fold decrease in radius is identical to a 1,000 fold increase in dissolution rate.

If cracking does not occur, the phase transitions result in the formation of new interfaces with high surface energies which results in a highly accelerated chemical attack at the interfaces, with a similar increase in release rate as when powdering occurs. Below, we present discussions of the sources and forms of instability in crystalline materials such as the newly proposed supercalcines of McCarthy[19] and Ringwood[20], and the sources and forms of instability in amorphous glasses such as the borosilicate glasses and the high silica glasses.

A. Crystal Instabilities

The major potential sources of instability in crystals are transmutations arising from the radioactive decay of the waste materials and the radiation damage of α-particle emission and its associated nucleus recoil.

1) Transmutations

As transmutations occur in the fission products, new crystalline forms are generated. Since the new elements have a different valence and a different size from their parent elements, they will likely require a different equilibrium nearest-neighbor configuration and coordination. In ionic crystals, each coordination state is associated with the ratio of the cation to anion radius as shown in Table 3. Since the materials proposed for waste fixation are oxides, the anion radius for O^{2-} will be: 1.40A. The

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*Metemictization is the transformation of crystalline materials to an amorphous state.

Table 3. Dependence Coordination States on Cation/Anion Radius Ratios.

Coordination No.	$R\hat{c}/R\hat{a}$	$\Delta R\hat{c}$	$1/2\ \Delta R\hat{c}$
2	0 - 0.155	0.22A	0.11A
3	0.155 - 0.225	0.10A	0.05A
4	0.225 - 0.414	0.26A	0.13A
6	0.414 - 0.732	.45A	0.22A
8	0.732 - 1.00	.38A	0.19A
12	1.00		

maximum radius change calculated for each range of sizes corresponding to the same coordination number is shown in the $\Delta R\hat{c}$ column. However, since good stability is achieved when the radius ratios are in the middle of the range, the best estimate of a maximum allowable ionic radius change is $1/2\ \Delta R\hat{c}$ of $1/3\ \Delta R\hat{c}$. The ionic radius change of the transformation from Cs^{1+} to Ba^{2+} is -0.34A while the change from Sr^{2+} to Zr^{4+} is -0.33A. Both of these are significant size changes and must cause a large change in local coordination in the crystals based upon the size change alone! Therefore as a result of the changes in valence and ionic radii, new crystals will be formed.

These new crystals can be accommodated in the original structure by the formation of a solid solution. Solid solutions may be of two forms, substitutional and interstitial. A substitutional solid solution results when the solute atoms take up the position of the solvent atoms in the crystal lattice. If the respective atomic radii differ by more than 15% the range of solubility is very small. However, even for differences in radii as low as 8%, solid solutions do not cover a wide range of compositions until the two atoms have the same valence and the compounds have the same crystal structure. The cesium-barium pair has a difference of 24% and the strontium-zirconium pair is at 29%. Therefore a substitutional solid solution is out of the question. Interstitial solid solutions involve atoms where the interstitial atom is very small such as H, B, C or N, and therefore are not applicable here.

Since solid solutions cannot be formed, recrystallization or metamictization will occur. The extent of structural damage resulting from recrystallization depends upon the volume change at the transition, the respective initial and final crystal structures and the temperature of the material. For example, a material may recrystallize at high temperatures but will either become amorphous or break up into fine powder if the transition occurs at room temperature.

Experiments have been conducted by R.S. Roth et al. on the systems K-Al-Si-O and Ca-Al-Si-O.[21] These systems readily simulate the radwaste fixation conditions with the substitution of K for Cs and Ca for Ba. Both the radius change of 0.34A and the valence change are identical to the Cs-Ba transformation. In addition, this system is well suited for a first-step simulation of proposed systems of supercalcine since it contains both Al and Si which are the major components of many of the supercalcine ceramics. It was found that the system does not allow for the formation of solid solutions over any range at low temperatures (see Fig. 5).[22] A solid solution was only formed at one composition between the K crystals and the Ca crystals, however, when there was a concurrent substitution of Al for Si giving the following: $KAlSi_3O_8$ + $CaAl_2Si_2O_8$. The Al/Si ratio therefore had to be changed from 1:3 to 2:2. In the waste storage condition, however, this concurrent Si to Al exchange cannot take place. Under conditions of fixed Al/Si ratio, no solid solutions could be found and the materials formed were weak and readily crumbled to powder.[23]

Further evidence of the effect of transmutations on crystalline ceramic materials is provided also by Roth et al.[24] They studied the effect of the valence change, Ce^{3+} to Ce^{4+} on the structure of cerium titanates (note some Ringwood Synroc compositions are primarily titanates) tantalates and niobates. The authors observed large changes in the respective crystal structures, and the build up of hign stresses. They concluded that the presence of cerium in the phases of minerals structurally related to sheelite and fergusonite but found naturally occurring in the metamict state without the presence of radioactive elements gives a strong indication that metamictization resulted from decomposition at low temperatures associated with the slow oxidation of Ce^{3+} to Ce^{4+}. Metamictization of crystals is generally accompanied by a large volume change (increase) and microfracture due to the build-up of local stresses.

It is therefore evident that the occurrence of transmutations in the crystalline ceramic waste forms is extremely destructive to the structure through the formation of new crystals when the transformations are at high temperatures or through metamictization or powdering when the transformations are at low temperatures (i.e., several hundred degrees below the melting point). In either case the rate of release of toxic materials will increase drastically. For example, powdering will increase the exposed surface area from 1,000 to 10^6 times. Metamictization will either lead to powdering or will form a structure of microcracks as shown in Fig. 6 for Zircon[25] where the cracks are fraction of a micron apart. This will result in similar increases in exposed surface area as powdering. Recrystallization is unlikely to occur since the temperature will not be sufficiently high, however, if it does occur it can lead to powdering or the formation of highly energetic grain boundaries which raises the rate of chemical dissolution by many orders of magnitude before the material breaks into a powder.

Since transmutations cannot be avoided in the storage process, this is a serious problem for radwaste disposal in crystalline ceramic solids which must receive consideration and must undergo thorough testing. The problem may be somewhat reduced for transmutations of the fission products by the storage of spent fuel for extended time periods beyond 30 to 50 years before fixation in crystalline ceramics. The problem of transmutations of the actinides which is less well defined at present cannot be alleviated.

2) Radiation Damage

The major potential sources of radiation damage in radwaste fixation materials are the emission of α-particles by the actinides and the associated collisions and nucleus recoil. The α-doses at the proposed loading levels are near 2×10^{18} particles/cm^3 over the first 100 years with a quarter occurring in the first 10 years. Each primary collision is absorbed by 100 to 1,000 displacements in solids. Therefore, there is a significant amount of lattice rearrangement.

Experiments to test the α-radiation damage of oxide ceramics with typical structures for nuclear waste fixation have not yet produced results. However, minerals containing actinides can provide an excellent basis for the present evaluation of the long-term effect of α-radiation damage on the structure of crystalline solids. In general, minerals which contain α-emitters in concentrations as low as or below those proposed for the fixation media, have undergone severe metamictization over long periods of time. The conditions which appear to favor metamictization are:[26]

a. The original structure is weakly ionic and possibly susceptible to hydrolysis.

b. The structure contains one or more ions that are readily susceptible to changes in ionic states.

c. The crystal generally contains α-emitters.

Crystals of structures similar to quartz, zircon, gaddolinite, thorite and scheelite are very susceptible to metamictization. These represent some typical crystal structures proposed for the supercalcine materials and the results should warn us of this potential danger. Further, the transformation to a metamict state appears to be enhanced by the presence of silica or by the presence of rare earths, even in low concentrations.[27] Both of these are essential components of supercalcine ceramics. A detailed evaluation of the susceptibility of natural minerals to metamictization is present in a paper by Rodney C. Ewing[28] in this issue.

The evidence from mineral sources however shows only a part of the problem and one cannot assume that geologic minerals which contain uranium and do not exhibit metamictization such as Huttonite will be structurally stable when used for radwaste containment. The reason is that these minerals only contain uranium which has a long half-life and therefore a low α-dose. However, the waste materials include Pu, Am and Cm all of which have isotopes with shorter half-lives and will subject the fixation materials to a much higher dose of α-particle emission and radiation.

In conclusion, the results clearly show that a large number of crystal structures including many similar to those proposed for supercalcines are unstable under α-radiation and nucleus recoil, and that the presence of elements which are an essential part of the radwaste solution, such as the actinides and the rare earths, will greatly enhance the transformation. As the crystal undergoes metamictization its specific volume increases leading to a large density of microcracks in its structure. As was shown above, microcracking is extremely detrimental to the fixation performance of materials since it can drastically increase the exposed surface and lead to high release rates of toxic materials. In the supercalcine approach, the formation of crystals further aggravates the problem since it requires the concentration of actinides and rare earths in localized volumes which are the same size as the α-particle penetration range. This increases the local concentrations and reduces the time to metamictization.

The problem of α-radiation cannot be alleviated by storing the unprocessed wastes in cooling vessels above ground for a long time since the actinides have half-lives of the order of thousands of years. Therefore, this is a storage condition which must be evaluated thoroughly with accelerated tests using Cm^{244}, Pu^{238} or Am^{241}, as was done for some glass candidates.[1,2,3]

3) Thermal Output in an Aqueous Environment

The supercalcines will experience higher local thermal production than glasses due to the segregation of materials caused by the crystal precipitation process, but the average value will equal glasses with the same loading levels. Below 100°C, the supercalcines appear to exhibit a similar chemical durability to the borosilicate glasses. The supercalcines appear to have a better durability than borosilicates at higher temperatures; however, they also undergo chemical degradation at high temperatures in an aqueous environment. Therefore high thermal output and its associated temperature rise when cooling is not present will not affect the crystalline oxides as adversely as the borosilicate glasses.

B. Instabilities in Oxide Glasses

The potential sources of instability in glasses are also transmutations, and α-particle damage as in the crystals. Glasses, however, are thermodynamically metastable with respect to a crystalline state. The metastability arises from kinetic hindrance, which corresponds to a marked decrease in diffusion coefficient with lowering temperature. The amorphous glasses are therefore prevented from crystallization at room pemperature by two processes: nucleation of the crystal phase and growth. The kinetic or growth hindrance is often the most effective of the two constraints as nucleation generally can occur at temperatures where little growth is possible. As the temperature is raised, nucleation and growth of crystals will take place and the material crystallizes. There are, however, many glass compositions which exhibit great difficulty in crystallizing.

Below, we will discuss the tendency of glasses to crystallize as a function of ambient temperature and report data taken on a typical borosilicate glass for radwaste fixation. Lifetimes or times to crystallization will be estimated. Then we will discuss the effect on structural stability of transmutations in glasses and the results of experimental investigations of α-radiation damage and gas diffusion in glasses. Finally, we will describe the properties of some geological glasses known as Tektites and compare their performance characteristics to those expected for glass fixation media.

1) Crystallization of Nuclear Waste Disposal Glass

a. Background

Products of glass crystallization are considerably more dense than the parent glass. Because of this stresses develop during crystallization, which can eventually lead to fracture and exposure of increased surface area to environmental attack. Therefore for nuclear waste disposal glass it is vital to have reliable estimates of how long it takes for a given volume fraction X of glass to crystallize well below the glass transition temperature, T_g.

In approaching this problem we note that a glass is formed from a melt which experiences two failures as it is cooled. First, it fails to crystallize at the liquidus temperature (T_M), and second, it fails to retain the equilibrium liquid structure below T_g. Both failures take place because of kinetic reasons. In Fig. 7 is shown schematically the temperature dependence of a typical properties, volume V, or enthalpy H, during cooling.

The time scale of crystallization of a good glass former at a temperature T_1 well below T_g is orders of magnitude longer than the human lifetime. Hence values for the extent of crystallization at such a temperature can be obtained only by calculation. We will use a method which has proven extremely successful in kinetic problems in glasses and liquids - the time-temperature superposition principle. This principle rests on the assumption that the form of the kinetic laws governing processes in liquids and glasses is temperature invariant; changes in temperature merely alter the time scale of the process. We can determine the rate of crystallization of a glass at a high temperature where it can be conveniently measured experimentally. If we know the temperature dependence of the kinetic parameters governing crystallization rates, we can then calculate the crystallization rate at a lower temperature where it cannot be measured.

b. Theory of Crystallization

The time t required for crystallization of a volume fraction X of a glass or liquid is given approximately by[29]

$$t = (3X/\pi I_V u^3)^{1/4} \tag{1}$$

where u is the crystal growth velocity and I_V the overall crystal nucleus formation rate. I_V is the sum of the homogeneous and heterogeneous nucleation rates, $(I_V^{Ho} + I_V^{He})$. According to the kinetic theory of crystallization[30,31]

$$u = (fD/a_o)[1 - \exp(-\Delta G_V \bar{V}/kT)] \tag{2}$$

$$I_V^{Ho} = (N_V D/a_o^2)[\exp(-16\pi\gamma^3/3kT\Delta G_V^2)] \tag{3}$$

$$I_V^{He} = A_V N_s \nu[\exp(-16\pi\gamma^3 g(\theta)/3kT\Delta G_V^2)] \tag{4}$$

where f = fraction of crystal surface sites at which atoms can be added or removed

D = coefficient of diffusion across liquid-crystal or liquid-nucleus interface

a_o = molecular diameter

ΔG_V = Gibbs free energy difference per unit volume between liquid and crystal

$\bar{V}$ = molecular volume

k = Boltzmann constant

N_V = number of molecules per unit volume

γ = crystal-liquid interfacial tension

A_V = surface area of nucleating substrate per unit volume

N_s = number of molecules per unit area of substrate

ν = frequency factor

$g(\theta)$ = numerical factor which depends on crystal-liquid-heterogeneity interfacial tensions

ΔG_v is proportional to $(T - T_M)$, so that at sufficiently low temperatures the expressions in brackets in Eqs. (2) - (4) become unity. Since we are considering crystallization well below T_M, we shall henceforth assume that this low temperature condition is satisfied. The diffusion coefficient and frequency factor may be approximated by the Stokes-Einstein equation:

$$D = a_o^2 \nu = kT/3\pi a_o \eta \tag{5}$$

where η is the shear viscosity. Introducing these two assumptions into Eqs. (2) - (4) we get

$$u = fkT/3\pi a_o^2 \eta \tag{6}$$

$$I_v^{Ho} = N_v kT/3\pi a_o^3 \eta \tag{7}$$

$$I_v^{He} = A_v N_s kT/3\pi a_o^3 \eta \tag{8}$$

Substituting these into Eq. (1) we get

$$t = KTX\eta \tag{9}$$

where K is a constant. The shear viscosity η of a silicate melt typically changes by an order of magnitude every 20°C in the glass transition region, so that the explicit dependence of t on T in Eq. (9) is negligible compared to its implicit temperature dependence arising from η. Hence if a time $t(T_{ref})$ is required for volume fraction X to crystallize at a reference temperature T_{ref} where the viscosity is $\eta(T_{ref})$, then the time $t(T)$ for the same amount of crystallization at some other temperature T with viscosity $\eta(T)$ is given approximately by

$$t(T) = t(T_{ref})\eta(T)/\eta(T_{ref}) \tag{10}$$

Eq. (10) is an example of the time-temperature superposition principle. To calculate $t(T)$ for a given glass we thus require two pieces of information:

a. the time $t(T_{ref})$ for crystallization of the volume fraction of interest at a sufficiently low temperature that the terms in brackets in Eqs. (2) - (4) become unity, and

b. the shear viscosity temperature dependence in the range T_{ref} to T.

In the following sections we shall describe the acquisition of this data for a typical nuclear waste disposal glass and its application to the calculation of crystallization times at storage temperatures.

c. Experiments and Results

i. Sample

The glass studied was a simulated nuclear waste disposal glass (SNWDG) received from Battelle Pacific Northwest Laboratories. It was formed by blending 67% borosilicate glass frit with 33% Purex-type waste calcine (Type PW8a-2) from a low temperature spray calciner. The blend was melted in a stainless steel container for 2 h, cooled to room temperature and crushed. The frit and calcine compositions are given in Tables 4 and 5.

ii. Heat Capacity and Electron Microscopy Studies

Determinations of the time $t(T_{ref})$ required for crystallization of a given volume fraction of the SNWDG and rough determinations of the viscosity temperature dependence in the glass transition region were obtained by measurements of the heat capacity C_p in the glass transition region. The C_p determinations were conducted over the temperature range 427 to 627°C at a heating rate of 20 K/min using a Perkin-Elmer Model DSC-2 differential scanning calorimeter (DSC). Glass samples of approximately 35 mg encapsulated in gold sample pans were used. Single crystal Al_2O_3 was used as a heat capacity standard.

Typical C_p results are shown in Fig. 8. Detailed explanations of the shapes of the C_p curves are given in previous papers from this laboratory[32-34] and will be discussed only briefly here. At high temperatures (above 600°C in Fig. 8) the time scale for rearrangement of the liquid structure is sufficiently fast at the applied heating rate (20 K/min) that the system is in thermodynamic equilibrium and exhibits the equilibrium liquid heat capacity C_{pe}. At low temperatures (below 475°C in Fig. 8) the time scale for rearrangement of the structure is so slow that it does not occur on the experimental time scale and so makes no contribution to C_p. At low temperatures the system thus exhibits a lower, solid- or glass-like heat capacity C_{pg}. Generally the heat capacity exhibited by a glass and that exhibited by the corresponding crystal differ very little, if at all. The intermediate temperature region (475 to 600°C in Fig. 8) in which during heating C_p rises fairly rapidly above the glass-like value C_{pg}, passes through a maximum, and then assumes the equilibrium liquid value C_{pe} is called the glass transition region. The complicated behavior of C_p in this region is due to structural relaxation effects explained in the previously cited papers[32-34] and need not concern us here.

If a part of a glass has crystallized, the crystalline portion will make no contribution to $(C_{pe} - C_{pg})$, the part of the high temperature heat capacity associated with structural rearrangement in the

Table 4. Frit Glass Composition Used in Forming Simulated Nuclear Waste Disposal Glass. SNWDG is 67% Frit.

Component	SiO_2	B_2O_3	Na_2O	ZnO	CaO	TiO_2
wt %	59.70	14.20	11.20	7.95	3.00	4.45

Table 5. Calcine Composition Used in Forming Simulated Nuclear Waste Disposal Glass. SNWDG is 33% Calcine.

Oxides	kgs Oxides/MTU
Na_2O	14.057
Fe_2O_3	29.008
Cr_2O_3	1.151
NiO	1.471
P_2O_5	1.342
K_2O	1.141
SrO	1.059
ZrO_2	4.944
MoO_3	6.375
CoO	0.304
Ag_2O	0.088
CdO	0.097
TeO_2	0.725
BaO	1.567
Rare earth mixture	21.307

liquid. Thus the fact that C_{pe} for the SNWDG heat treated for 330 h at 870°C is lower than C_{pe} for the SNWDG "as received" indicates that during its high temperature heat treatment the melt underwent partial crystallization. We thus propose that the decrease in $(C_{pe} - C_{pg})$ can be used as a measure of the extent of crystallization. That is the fraction of glass, 1 - X, in a partially crystallized sample given by

$$1 - X = \frac{(C_{pe} - C_{pg})_t}{(C_{pe} - C_{pg})_o} \tag{11}$$

where $(C_{pe} - C_{pg})_t$ refers to a glass heat treated for time t at temperature where crystallization may occur, and $(C_{pe} - C_{pg})_o$ refers to the uncrystallized (as received) glass.

To test this method for determining the amount of crystallization samples of the glass encapsulated in gold DSC pans were heat treated in a furnace at 870°C for times ranging from 162 to 564 h, after which C_p was measured in the range 427 to 627°C. The same experiment was also carried out for heat treatment for a single time interval, 162 h, at 800°C. Measured values of C_{pg}, C_{pe} and $(C_{pe} - C_{pg})$ are given in Table 6. The statistical scatter in the C_{pg} values for the "as received" and heat treated samples is sufficiently large that the C_{pg} values for all the samples in Table 6 can be considered identical within experimental error. For samples with a given heat treatment, random errors which led to a large measured value of C_{pg} in a given DSC scan also tended to give a large value of C_{pe}, so that the statistical scatter in the $(C_{pe} - C_{pg})$ values is generally smaller than the scatter in the C_{pg} or C_{pe} values.

The slow crystallization of the SNWDG at 870°C is reflected in the decrease $(C_{pe} - C_{pg})$ with increasing heat treatment time. The % glass in these samples, calculated from Eq. (11), is plotted versus heat treatment time in Fig. 9. It appears that even after some 600 h at 870°C the fraction of sample crystallized has not reached its equilibrium value for that temperature.

Shown in Fig. 10 is a replica electron micrograph of the SNWDG after 120 h of heat treatment at 870°C. Crystallized regions appear as the isolated, light colored regions in the micrograph. Comparison of the areas of the crystalline regions and areas of the glassy regions in Fig. 10 indicate that 88% of the sample is glassy, i.e., that 12 volume % of the material crystallized in 162 h at 870°C. This point is plotted in Fig. 9 and falls within experimental error on the curve determined from C_p data, showing that Eq. (11) is a reliable way to determine the amount of crystalline material in a glass.

Having established this, we determined $t(T_{ref})$ to be used in calculations involving Eq. (10) by heat treating a SNWDG sample for 40 h on the DSC at 627 C, i.e., $t(T_{ref}) = 40$ h and $T_{ref} = 627$°C.

Table 6. Heat Capacities C_p (cal/g K) of Simulated Nuclear Waste Disposal Glass. C_{pg} Measured at 467°C, C_{pe} at 597°C.

History	No. Det'ns	C_{pg}	C_{pe}	$C_{pe} - C_{pg}$
as received	14	0.243 ± 0.007	0.348 ± 0.007	0.105 ± 0.004
162 h @ 870°C	2	0.235 ± 0.001	0.329 ± 0.003	0.093 ± 0.003
330 h @ 870°C	2	0.236 ± 0.002	0.317 ± 0.001	0.082 ± 0.004
402 h @ 870°C	3	0.228 ± 0.003	0.307 ± 0.005	0.079 ± 0.003
564 h @ 870°C	2	0.229 ± 0.001	0.303 ± 0.001	0.074 ± 0.001
330 h @ 800°C	2	0.240 ± 0.008	0.327 ± 0.009	0.087 ± 0.001
40 h @ 627°C	4	0.231 ± 0.002	0.339 ± 0.003	0.108 ± 0.001

This comparatively low value of T_{ref}, about 50°C above the glass transition region, was picked for two reasons: (a) it shortens the temperature region over which viscosity needs to be known for extrapolation to lower temperatures, and (b) for silicate glasses the temperature of maximum nucleation rate, below which the terms in brackets in Eqs. (2)-(4) can be set equal to unity, is close to or about 50°C above the glass transition temperature.[35,36] The (C_{pe} - C_{pg}) value for the sample treated for 40 h at 627°C is given in Table 6 and within experimental error is equal to (C_{pe} - C_{pg}) for the "as received" glass. More precisely, taking two standard deviations as indicative of the maximum upper and lower bounds on these two (C_{pe} - C_{pg}) values, we calculate via Eq. (11) that at the very most 7% of the glass could have crystallized in 40 h at 627°C. 7% crystallization or less is too small to cause fracture of a glass. Hence we may take 40 h as a "safe time limit" (STL) for exposure of the glass to a temperature of 627°C, if fracture due to crystallization is to be avoided.

The behavior of the C_p curves in the glass transition region reflect the response of the property enthalpy H to the structural relaxation process, as explained in detail elsewhere.[32-34] The rate of approach of enthalpy (or any other property) to equilibrium is controlled by a mean structural relaxation time, τ, whose temperature dependence is found experimentally[32-34] to be equal to that for the shear viscosity η:

$$d\ln\eta/d(1/T) = d\ln\tau/d(1/T) = \Delta H^*/R \qquad (12)$$

where ΔH^* is the activation enthalpy for structural relaxation and viscous flow and R the ideal gas constant. The more slowly a melt is cooled through the glass transition region, the lower the temperature at which the V or H vs. T curve breaks away from the equilibrium liquid curve (cf. Fig. 7). This in turn results in a decrease in the so-called limiting fictive temperature T_f (defined in Fig. 7) with a decrease in cooling rate q. The interdependence of these two quantities is given by:[33]

$$d\ln q/d(1/T_f) = -\Delta H^*/R \tag{13}$$

We cooled a sample of the "as received" SNWDG on the DSC through the glass transition region (627 to 427°C) at a variety of rates q ranging from 1.25 to 40K/min. After each cool C_p was measured while reheating the glass over the same temperature range at 20 K/min. The value of T_f attained by the glass at a given cooling rate was calculated from the C_p data obtained during reheating using the expression:[33]

$$T_f = \int_{T>>T_g}^{T<<T_g} \left(\frac{C_p - C_{pg}}{C_{pe} - C_{pg}}\right) dT \tag{14}$$

In Fig. 11 is shown the semi-logarithmic plot of q vs. $1/T_f$. The slope gives via Eq. (13) an activation enthalpy $\Delta H^* = 159$ kcal/mol.

iii. Shear Viscosity Measurements

Shear viscosity of the "as received" SNWDG was measured over the temperature range 525 to 700°C (viscosity range 10^7 to 10^{13} P) using a Perkin-Elmer Model TMS-1 thermomechanical analyzer as a parallel plate viscometer.[37] In this method the rate of compression (dh/dt) under a load of mass m of a cylindrical sample positioned between two parallel plates is monitored; the viscosity is given by

$$\eta = \frac{2\pi m g h^5}{3V(2\pi h^3 + V)(dh/dt)}$$

where h is the sample height, g the acceleration due to gravity and V the sample volume. Our sample had dimensions 0.572 cm diameter, 0.833 cm height. Changes in h of as little as 2×10^{-6} cm could be detected.

The experimental viscosity data are shown in the form of an Arrhenius plot (log η vs. 1/T) in Fig. 12. It is typical of both organic[38] and inorganic[39] melts to exhibit linear Arrhenius plots (i.e., constant activation enthalpy ΔH^*) at high viscosities near the glass transition region. At higher temperatures and lower viscosities, however, the Arrhenius plots curve upward, corresponding to an apparent decrease in ΔH^* with increasing temperature.

In Fig. 12 the linear region covers the temperature range 525 to 590°C. In this region η is well described by the equation

$$\ln \eta(P) = A + \Delta H^*/RT(K) \tag{15}$$

with $A = -60.01$

$\Delta H^*/R = 7.178 \times 10^4 K$

The linear portion of the line through the data is the graph of this equation. The value of ΔH^* (=143 kcal/mol) from viscosity measurements is, as expected, in reasonable agreement with ΔH^* (=159kcal/mol) assessed from the dependence of T_f on cooling rate.

d. Calculation of Viscosity and Safe Time Limit at Low Temperatures

log η responds to the structural relaxation process in the same fashion as do properties such as volume V and enthalpy H. In recent detailed treatments have been developed for calculating the time-temperature evolution of glass properties due to structural relaxation.[34,40] In addition extensive experimental studies have been carried out on the effect of structural relaxation on shear viscosity of silicate glasses in and below the glass transition region.[41-44]

For our purposes in the present section, it is sufficient to note that if a melt is cooled at a constant rate the shape of the log η vs. 1/T plot resembles the shape of the V or H vs. T plot, as is shown in Fig. 7. That is, as the melt departs from structural equilibrium in the glass transition region during cooling, the measured viscosity becomes lower than the equilibrium liquid viscosity, and well below Tg the log η vs. 1/T plot is linear with a slope considerably less than that for the equilibrium liquid. Experimentally the activation enthalpy for the glass viscosity well below T_g is approximately half the activation enthalpy just above the glass transition region i.e.,

$$d\ln \eta/d(1/T)\big|_{T<T_g} \approx 0.5\, H^*/R = 0.5 d\ln \eta/d(1/T)\big|_{T>T_g} \tag{16}$$

Note from Fig. 7 that the low temperature glass viscosity line can be considered to have departed abruptly from the equilibrium liquid line at the limiting fictive temperature T_f. Consequently the location of the glass viscosity line depends, via Eq. (13), on the cooling rate. In Fig. 13 we show an Arrhenius plot over a temperature range extending down to ambient temperatures of the viscosity of the SNWDG cooled at a typical rate of 3K/min. The glass viscosity line (curve B) has been made to depart from the equilibrium liquid line (curve A) with an activation enthalpy of 71 kcal mol (= $0.5\Delta H^*$ from Eq. (15)) at a temperature of 508°C (= T_f for q=3 K/min from Fig. 11). The safe time limit t(T) for volume fraction of crystallization $X \leq 0.07$ can now be calculated from Eq. (10) using the data from Fig. 11 and from the previous section with

$$T_{ref} = 627^{\circ}C$$

$$t(T_{ref}) = 40\ h = 0.0046\ yr$$

$$\eta(T_{ref}) = 6 \times 10^{8} P$$

The log t(T) vs. 1/T plot for the SNWDG cooled at 3 K/min is the same as that for log η vs. 1/T except for a shift in scale; the log t(T) scale is shown on the right side of Fig. 13. The STL for avoidance of fracture due to crystallization of the SNWDG at ambient temperature is about 10^{35} yr, considerably longer than the estimated remaining lifetime of the solar system (5×10^{9} yr). Even at a temperature of 450°C the STL is about 10^{4} yr, much longer than the estimated 10 yr period that the glass might experience this temperature due to self-heating during storage.[45] Note that changes in the glass cooling rate q by a few orders of magnitude on either side of the 3 K/min rate for which Fig. 13 was constructed will change only the temperature T_f at which the glass STL curve departs from the equilibrium liquid curve. Since T_f for a given q must be selected from Fig. 11, it should be clear that such changes in q affect the calculated STL by a negligible amount on the scale of Fig. 13.

e. Discussion

i. Effect of Low Temperature Structural Relaxation on Safe Time Limit

Fig. 13 gives the STL at each temperature for the case in which the viscosity is constant at the initial value attained during the 3 K/min cool. In fact, if a glass is cooled to a temperature well below T_g and then held isothermally, properties such as V, H or log η will not remain constant. Rather, because of structural relaxation the property will move in time toward the equilibrium liquid value at that temperature. In the present case this means that the viscosity will increase with time, thus increasing the STL at a given temperature above the values given in Fig. 13.

Of importance here is the fact that the time required for the viscosity of a glass to approach its equilibrium value is much shorter than the time required for an appreciable fraction of the glass to crystallize. For example, from typical structural relaxation times measured for silicate glasses in the glass transition region[46] and the temperature dependence of the viscosity of the SNWDG, we estimate via Eq. (12) that at 627°C the viscosity of a non-equilibrium SNWDG melt would relax by 99% of its initial deviation from equilibrium in roughly 0.2 s. This is to be compared with the 40 h required for a volumeefraction of crystallization $X \leq 0.007$. The STL values in Fig. 13 thus undoubtedly underestimates the actual STL's by an appreciable number of orders of magnitude.

ii. Previous Work on Glass Crystallization at Low Temperatures

Turcotte and Wald[45] have studied crystallization in a zinc borosilicate SNWDG of somewhat different composition than the one studied here. These results are summarized in Fig. 14, which shows the fraction of Zn_2SiO_4 crystallized from their glass as a function temperature for various different heat treatment periods (1 to 365 da). For a given time period the fraction crystallized initially increases with decreasing temperature, passes through a maximum in the 600 to 700°C region, and then falls to extremely small values at around 500°C. The reason for this behavior is the opposing effects of the ΔG_v and η terms in Eqs. (2) - (5) on the fraction crystallized X in a given time period. The former term tends to increase X with decreasing temperature, while the latter term tends to decrease it. Turcotte and Wald's data of Fig. 14 are thus taken in a temperature region where the terms in brackets in Eqs. (2) - (4) cannot be set equal to unity and in and of themselves cannot be used for reliable estimation of crystallization times at very low temperatures.

Kny and Nauer[31] have recently reported calculations of the extent of crystallization of alkali silicate glasses at ambient temperature (300 K). For dry $Na_2O \cdot 2SiO_2$ glass they estimate that heterogeneous mucleation could lead to crystallization of a fraction $X = 10^{-6}$ in as little as 1×10^6 yr. From Eq. (1) this corresponds to crystallization of a fraction X = 0.07 in 1.6×10^7 yr.

The 28 order of magnitude discrepancy between this crystallization time and the one calculated by us in Fig. 13 is not due to the difference in compositions of the two silicate glasses. Rather it is because Kny and Nauer used the unrealistically low but commonly quoted value of 10^{20} P for the ambient temperature viscosity of their glass. A silicate glass which is stressed at ambient temperature will show a time dependent strain which frequently corresponds to an apparent shear viscosity of around 10^{20} P. This apparent viscosity is due, however, not to irrecoverable viscous flow, but to recoverable delayed elastic effects. If the stress is removed from the glass, the strain disappears in the same time it took to develop.

Our method of extrapolating glass viscosity to ambient temperature, on the other hand, is based soundly on experimental viscosity measurements[41-44] in which great care was taken to ensure that delayed elastic effects made no contribution to the observed values of η. The equilibrium viscosity of the Na_2O - $2SiO_2$ melt has been measured close to the glass transition region;[35] $\eta = 10^{13}$ P at 415°C and $\Delta H^* = 94$ kcal/mol. If we assume that the glass viscosity curve during a 3 K/min cool effectively departs from the equilibrium liquid curve at about the 10^{13} P temperature with half the equilibrium liquid activation enthalpy (as in Fig. 13 and as observed experimentally for a soda-lime-silica glass[44]), then we calculate that the 300 K viscosity of Na_2O - $2SiO_{22}$glass is 2×10^{32} P. This corresponds to a time of

3×10^{19} yr for 7% crystallization, in considerably better agreement with our 10^{35} yr estimate for the SNWDG at ambient temperature.

iii. Effect of Water on Safe Time Limit

Of the possible variations in composition of borosilicate nuclear waste disposal glasses which might affect markedly the viscosity and the STL the only one of importance is variation in the water content. This might come about if the calcine were imcompletely dried and sufficient melting time was not allowed for escape of the water from the melt. Experimental measurements[47] on B_2O_3 and alkali borate melts showed that in the glass transition region 1% H_2O in the melts decreased η by 2-3.5 orders of magnitude, ΔH^* by 40-50%, and the glass transition temperature by 40 to 50°C. If we take 1% as reasonable estimate of the maximum amount of H_2O that might occur in the SNWDG, the 3 K/min cooling rate T_f might be lowered to 460°C and ΔH^* to 100 kcal/mol. This would give STL values of about 10^{24} yr at 25°C and 10^3 yr at 450°C, still very much on the safe side.

iv. High Silica Glasses

A high silica waste disposal glass, which should have considerably improved chemical durability compared to borosilicate waste disposal glass, has a T_g of around 750°C and ΔH^* of around 140 kcal/mol at T_g. This means that the STL for high silica glass is likely to be even greater than that for the SNWDG studied here.

2. Transmutations

The generally disordered structure of oxide glasses enables them to better withstand than crystals the ionic size and valence changes associated with transmutation. Valence changes in glasses, particularly of the transition metals, have been studied and show no structural effects. The effect of transmutations and α-radiation on vitrified wastes was investigated at Harwell on Fingal glass containing 25% waste oxides and stored in a vault for 11 years.[1] The glass showed no change in chemical durability from that of a freshly prepared version. Its structural integrity also was not affected and the samples appeared intact. Some devitrification was observed in the aged radioactive sample, however, it was not known whether this devitrification arose during fabrication or aging. The effect of devitrification on the chemical durability of this glass was investigated and could not be detected.

In conclusion, experiments show that glasses since they are amorphous and have less well defined local coordination than crystals, can readily accommodate the ionic size and valence changes which result from nuclear transmutation. Therefore, glasses appear to offer a more viable alternative than crystals when the storage condition of transmutation is considered.

3) Radiation Damage

A number of glass compositions have undergone accelerated α-radiation damage tests. Borosilicate glasses were prepared with Am^{241}, Pu^{238} and Cm^{244} in order to simulate a 1000 year expected dose for waste materials in periods of only 1 to 2 years.[2] Tests showed no change in mechanical properties and chemical durability. The formation of He gas was not a problem and did not cause a change in brittleness. Tests with Cm isotopes show that no significant change can be expected of borosilicate glasses even after storage periods of 10,000 years.[3]

While both expansion and contraction of glasses have been observed under high levels of α-radiation, the glass compositions used for the fixation of radwastes have exhibited little dimensional change. It is clear, therefore that tests must be conducted on the specific alternative compositions for glass fixation media. However, the data to date shows that glass exhibits good structural and chemical stability under simulated α-radiation storage conditions.

V. TEKTITE GLASSES

When amorphous materials are proposed for fixation of nuclear wastes over periods of several hundred thousand years the question of thermodynamic stability with and witnout an aqueous environment becomes important. The oldest artificial glasses are less than 4,000 years old, and while their leach rates are typically a few microns per year, their age is only a small portion of the total storage period for glasses used in the fixation of radwastes. Information about the behavior of glasses over longer time periods come from lunar minerals, volcanic glasses and Tektites.

Glass minerals (beads) found on the moon demonstrate that the metastable amorphous state is long-lived (4 billion years) at temperatures from a few to several hundred degrees Kelvin (Fig. 15).[48] However, the lunar surface provides a dry environment. These data experimentally confirm the conclusions of IV B on the rates of crystallization of glasses.

Volcanic glasses (obsedians) can be found up to 60 million years old without traces of crystallization. Their chemical durability or hydration rate is at a few microns per hundred years. However, because of their high water content: 1000 to 10,000 ppm of water, and their low silica content (60%), they do not present the best behavior achievable. Low water content (100 ppm) and high concentration of glass formers such as silica and alumina (70 to 90%) as may be produced industrially at this time[10,49] are found in Tektites collected both from the earth's surface and the bottom of the ocean.[50] These tektites show a complete lack of devitrification over 35 million years and leach rates below 0.5A per year. For example, Bediasite Tektites from Texas were melted 35 million years ago and show no sign of devitrification.[51] Some of these samples have interior voids a few millimeters in diameter which contain some neon, helium and oxygen but no argon. Since argon is more abundant in air than either neon or helium, but has a lower coefficient of diffusion through glass, it can be concluded that the structure of the glass around the void has remained impermeable and therefore free of microcracks or interface boundaries for 35 million years.

North American microtektites have survived for 35 million years in the Gulf of Mexico and the Caribbean at depths of 2 to 4 km and show neither traces of crystallization nor dissolution greater than 10μ in depth over the 35 million years spent at the ocean bed (Fig. 15).[52]

The high chemical and structural stability exhibited by the North American tektites is a result of their composition and in particular, their high concentration of glass formers. (See diagram Fig. 17.[50]) The composition of tektites found on earth is shown in Table 3 with their estimated age. It is clear that one common property is the high content of silica and alumina combined. The fact that they were found at this time is primarily an indication of low dissolution rate. Since they are totally amorphous, the high-silica and alumina contents also help prevent devitrification in an aqueous environment. The North American Crystalline Spherule is an example of good durability in partially crystallized glass, however, the lower silica and alumina content explains the devitrification. Therefore, this is clear evidence that glasses can remain amorphous in the presence of water over long time periods and can be fabricated to exhibit extremely low dissolution rates also in the presence of water at room temperature. The critical characteristic for this chemical and structural stability is high content of silica and other glass formers. Since the radiation field (α-emission and transmutations) does not appear to affect its properties, a glass material with high glass former content proves to be an excellent candidate for the fixation of radioactive wastes if the temperature is maintained near room temperature or below 100 to 200°C.

Table 7. Tektite Compositions and Age[50]

		SiO_2	Al_2O_3	TiO_2	R_2O	RO	Total Formers	Total Modifiers
Australite	700,000	70	14	1	4	10	85	14
Indochinite	700,000	73	13	1	4	9	87	13
Aouelloul	18,600,000	85	6	1	2	3	93	6
North American Microtektite	34,000,000	64	17	1	5	12	82	17
Georgia Tektites	34,000,000	84	10		4	3	94	7
Lybian Desert Glass	28,000,000	98	1		0.5	0.5	99	1
Moldavites	14,000,000	84	8		3	5	92	8
Ivory Coast	1,000,000	68	17		4	11	85	15
Bediasite	34,000,000	76	13	1	4	5	90	9
North American Crystalline Spherule	34,000,000	58	5		1.5	33	64	35

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Expanded Figure Captions

Figure 1. Corrosion tests on borosilicate glasses in water

A - dissolved SiO_2 from sodium glass at 22 C
B - dissolved Na from sodium glass at 22 C
C - dissolved SiO_2 from Pyrex at 70 C
D - dissolved Na from Pyrex at 70 C

Figure 2. Accumulated Cs^{137} in the ecosphere resulting from the dissolution of the fixation medium, given as a percentage of the amount initially stored in the medium. The dotted line represents a fixation solid with a dissolution rate of 1×10^{-5} g/cm^{2}d. The dashed line represents the best borosilicate data with a dissolution rate of 2×10^{-7} g/cm^{2}d. The solid line represents the high-silica glass with multibarrier protection and a dissolution rate of 5×10^{-10} g/cm^{2}d.

Figure 3. Accumulated Pu^{239} in the ecosphere resulting from the dissolution of the fixation medium, given as a percentage of the amount initially stored in the medium. The lines are drawn as in Fig. 2.

Figure 4. Accumulated Cs^{137} in the ecoshpere resulting from the dissolution of the fixation medium, given as a percentage of the amount initially stored in the medium. The dashed line represents borosilicate glasses with a dissolution rate of 1×10^{-4} g/cm^{2}d at 100°C. The solid line represents high-silica glasses with multibarrier protection and a dissolution rate of 2×10^{-6} g/cm^{2}d.

Figure 5. Phase diagram of the K_2O-CaO-Al_2O_3-SiO_2 system. Reprinted from Ref. 22.

Figure 6. Illustration of microfracture patterns in Zircon. Reprinted from Ref. 25.

Figure 7. Schematic plots of volume or enthalpy versus temperature and of logarithm of viscosity versus reciprocal temperature for (1) equilibrium liquid, (2) glass formed by cooling of equilibrium liquid, and (3) crystal.

Figure 8. Heat capacity versus temperature measured at a heating rate of 20 K/min for "as received" simulated nuclear waste disposal glass and (Δ) SNWDG heat treated for 330 h at 870°C. Prior to C_p measurements glasses were rate cooled at 20 K/min through the glass transition region.

Figure 9. Percent of glass remaining in SNWDG after heat treatment at 870°C versus heat treatment time.

Figure 10. Replica electron micrograph of SNWDG heat treated for 120 h at 870°C. Bar represents μm.

Figure 11. Arrhenius plot of cooling rate versus glass fictive temperature for SNWDG.

Figure 12. Arrhenius plot of shear viscosity versus temperature for SNWDG.

Figure 13. Extrapolation of shear viscosity η and safe time limit log t(T) for 7% crystallization or less of SNWDG to low temperatures for a cooling rate of 3 K/min. (A) equilibrium liquid curve, (B) glass curve.

Figure 14. Wt % Zn_2SiO_4 crystallized versus heat treatment temperature for various heat treatment periods for zinc borosilicate SNWDG of Turcotte and Wald 45.

Figure 15. Glass spheres from lunar fines. Reprinted from Ref. 48.

Figure 16. SEM of a test of an arenaceous Foraminifer found 3.5 km below the ocean surface, containing a North American Microtektite 35 million years old. Reprinted from Ref. 51.

Figure 17. Phase diagram showing the composition of many of the tektites in Table 7. Most contain a large silica concentration. Reprinted from Ref. 50.

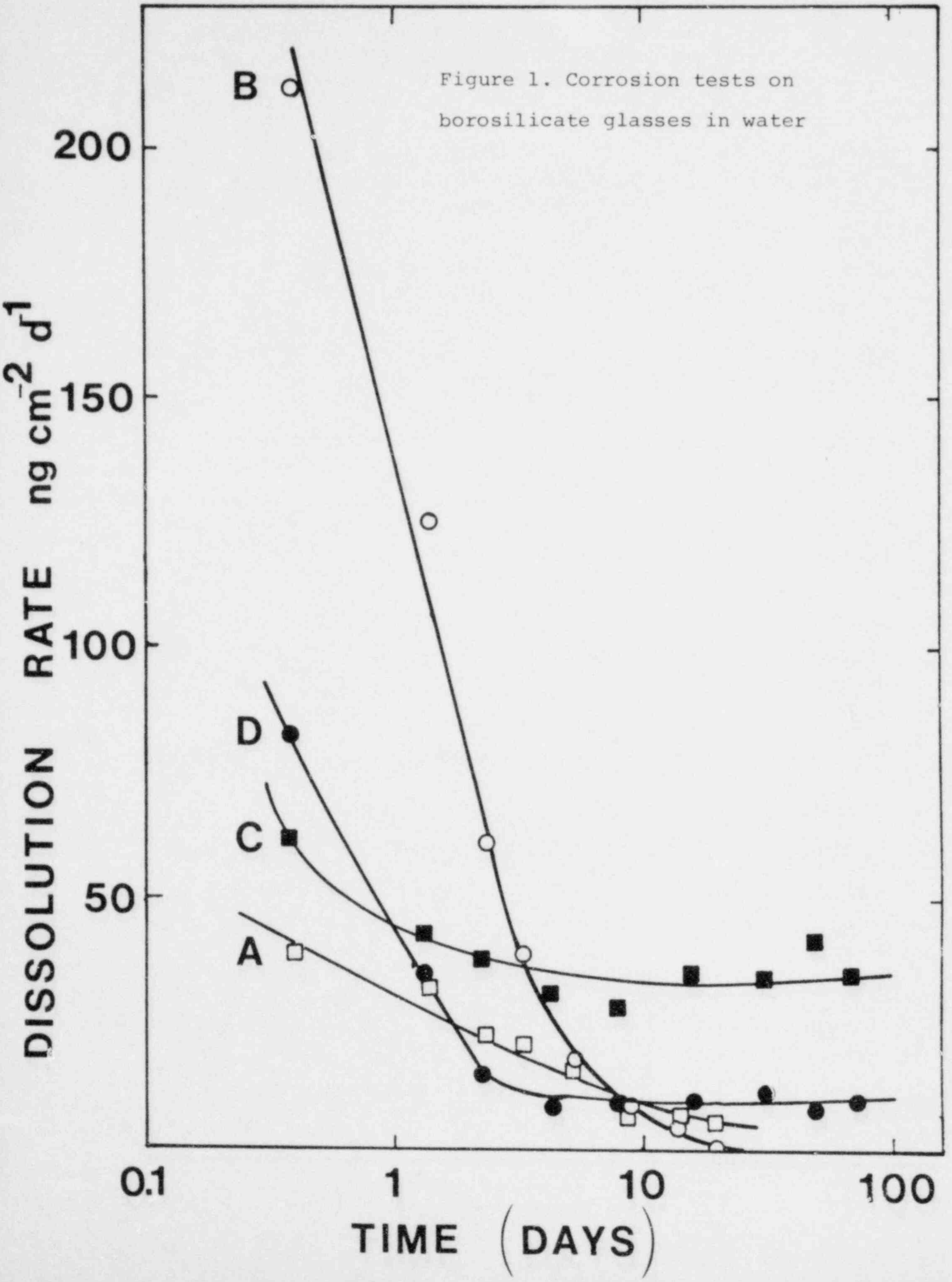


Figure 1. Corrosion tests on borosilicate glasses in water

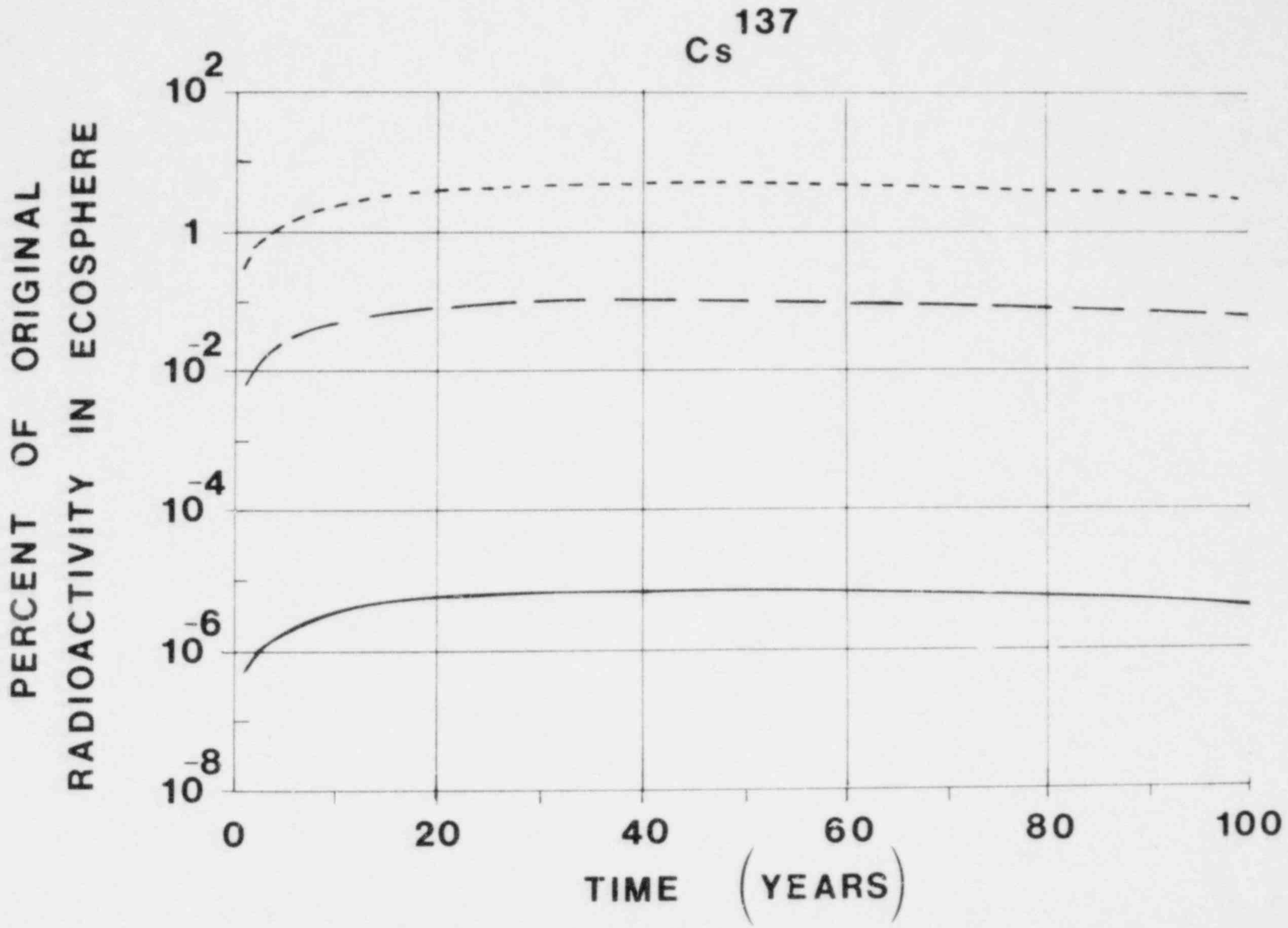


Figure 2. Accumulated Cs^{137} at 20°C

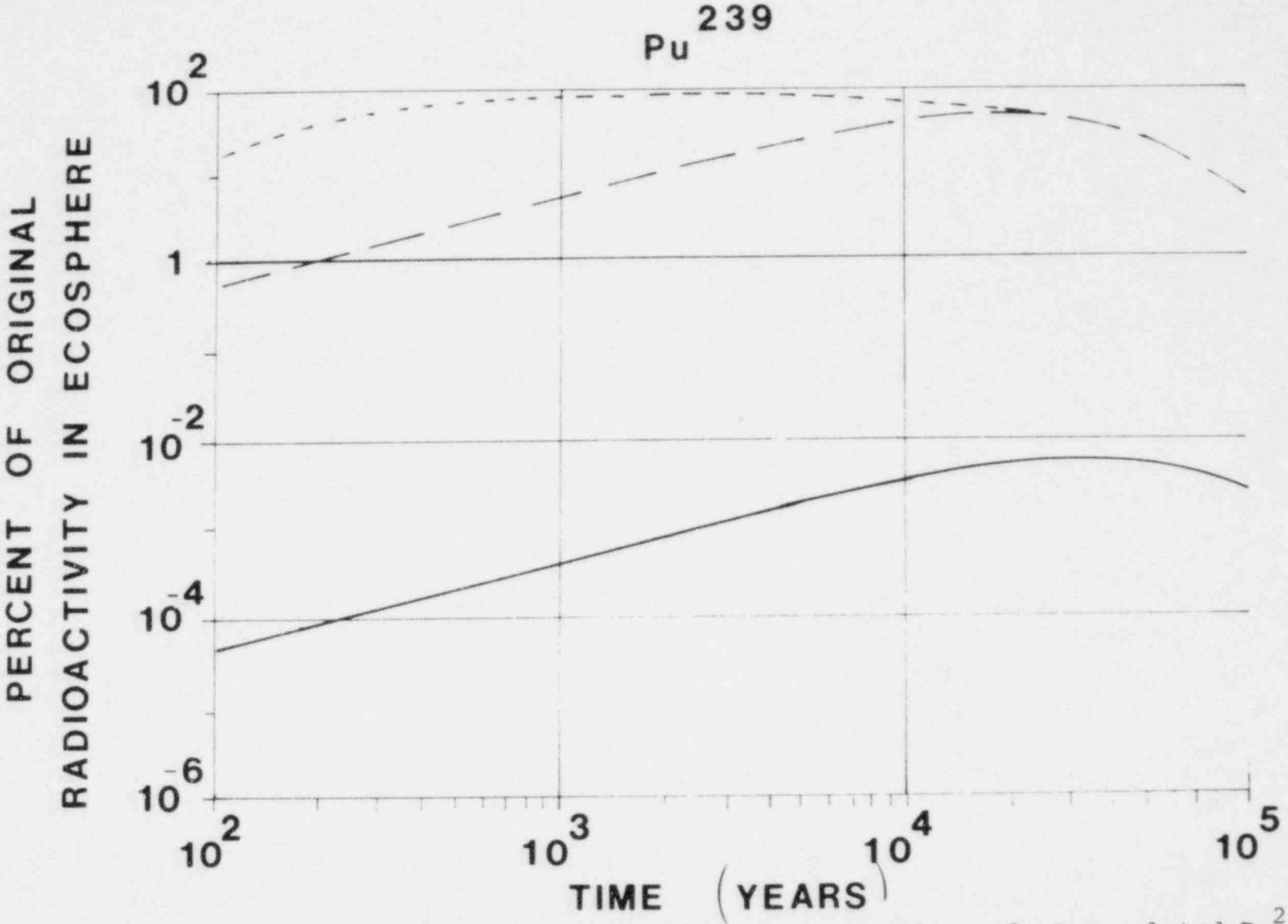


Figure 3. Accumulated Pu^{239} at 20°C

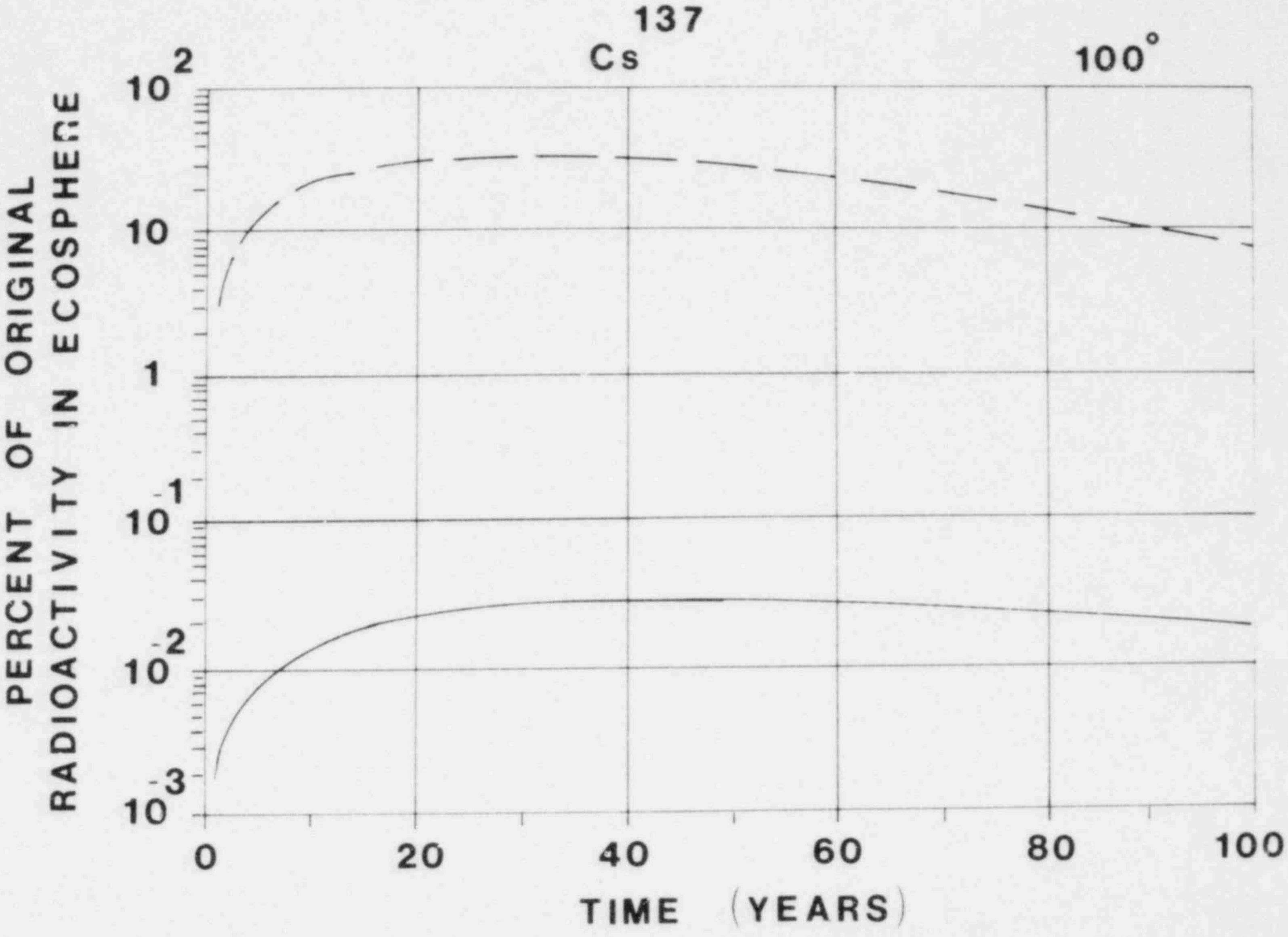


Figure 4. Accumulated Cs^{137} at 100°C

K_2O-CaO-Al_2O_3-SiO_2

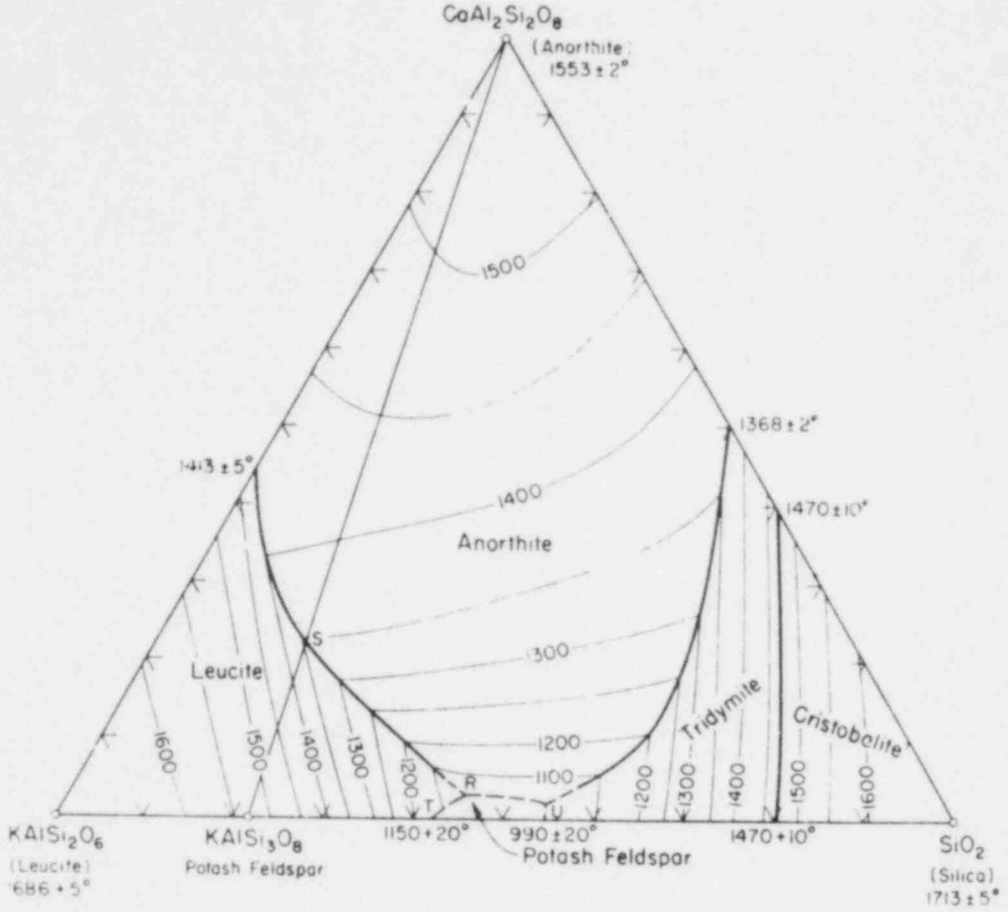


Figure 5. Phase diagram of the K_2O-CaO-Al_2O_3-SiO_2 system.

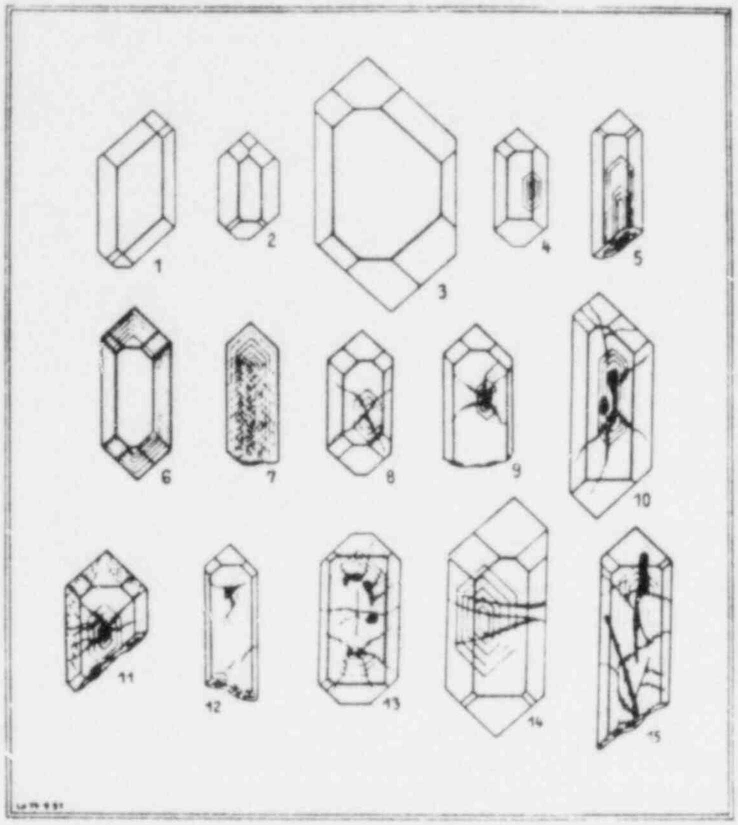


Figure 6. Microfracture in Zircon

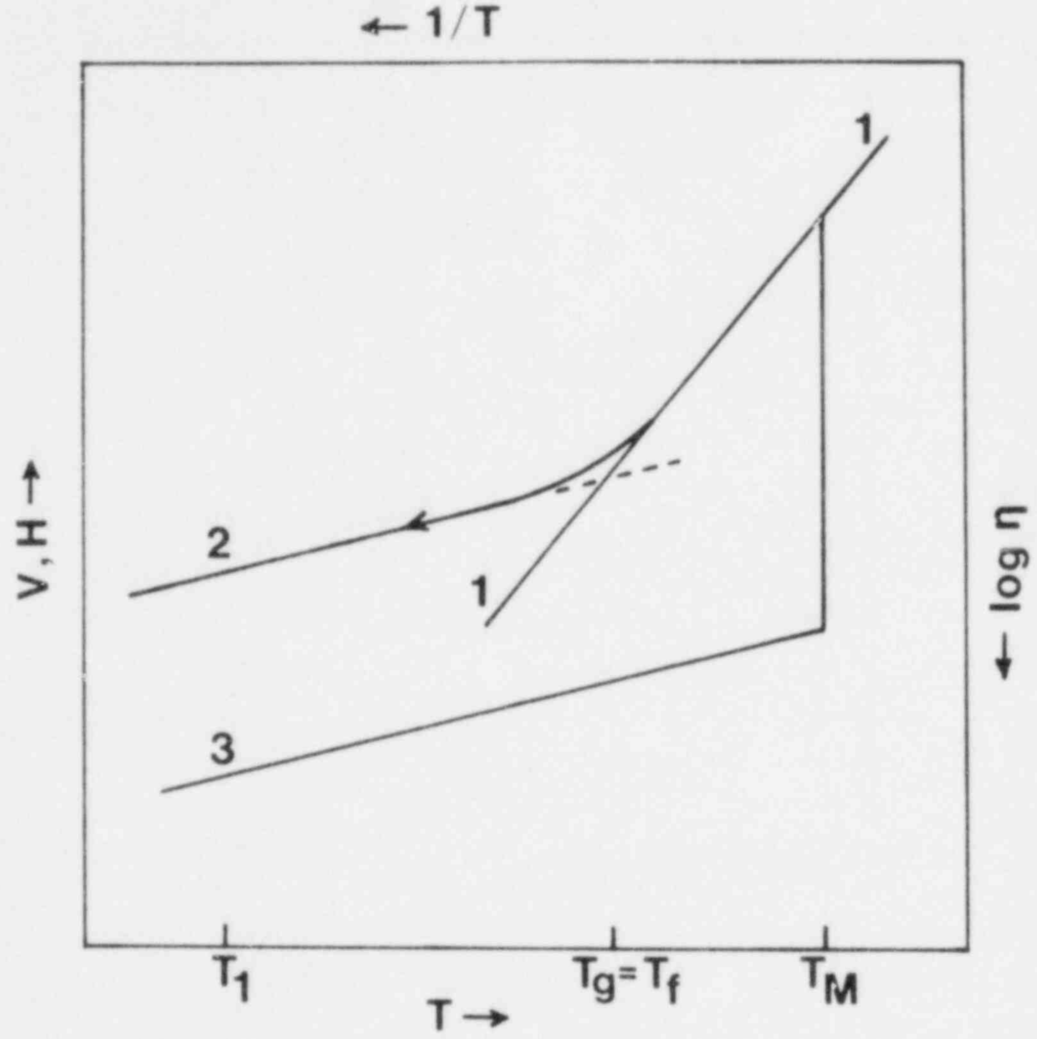


Figure 7. Plots of volume or enthalpy versus temperature

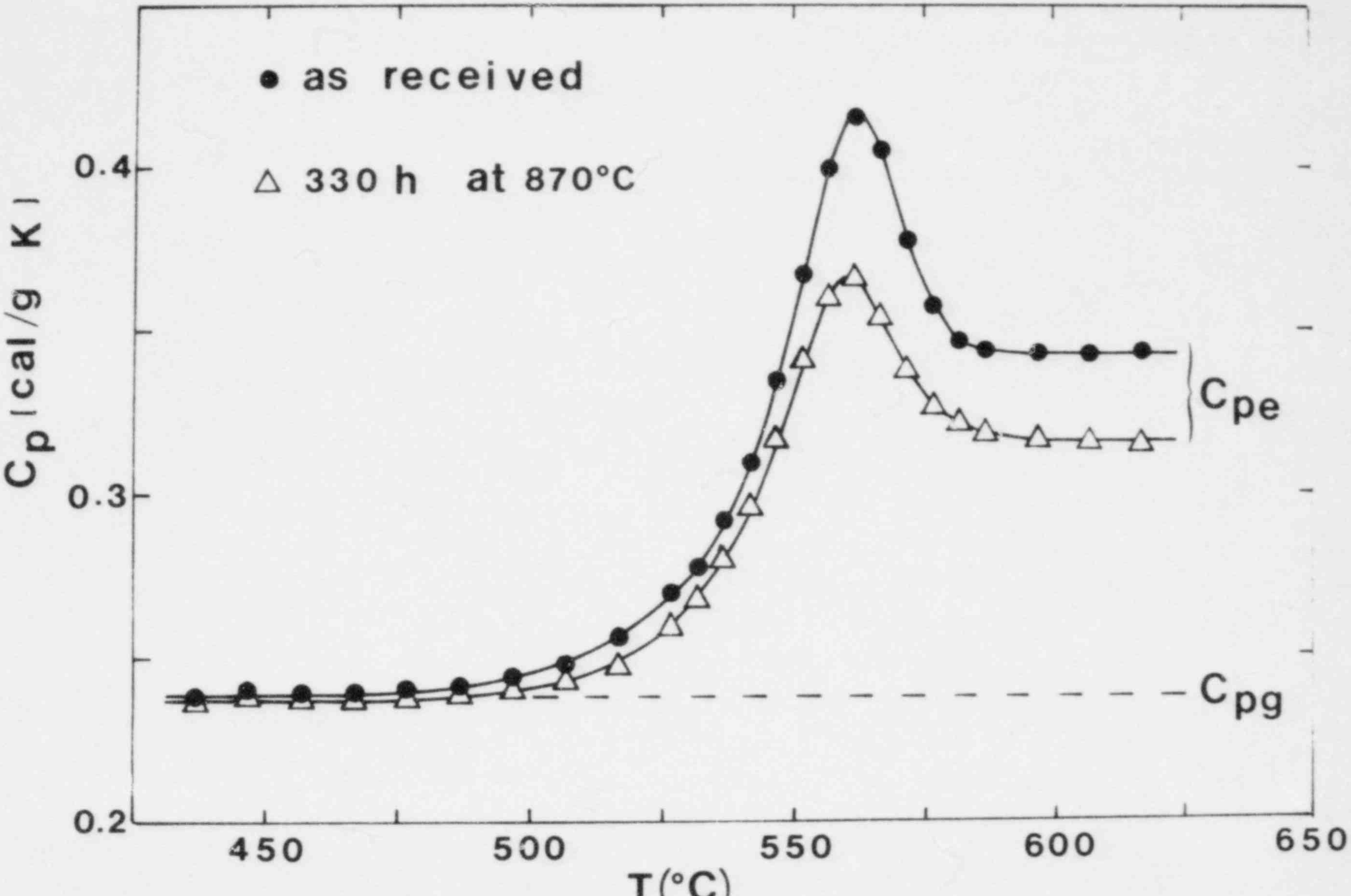


Figure 8. Heat capacity versus temperature

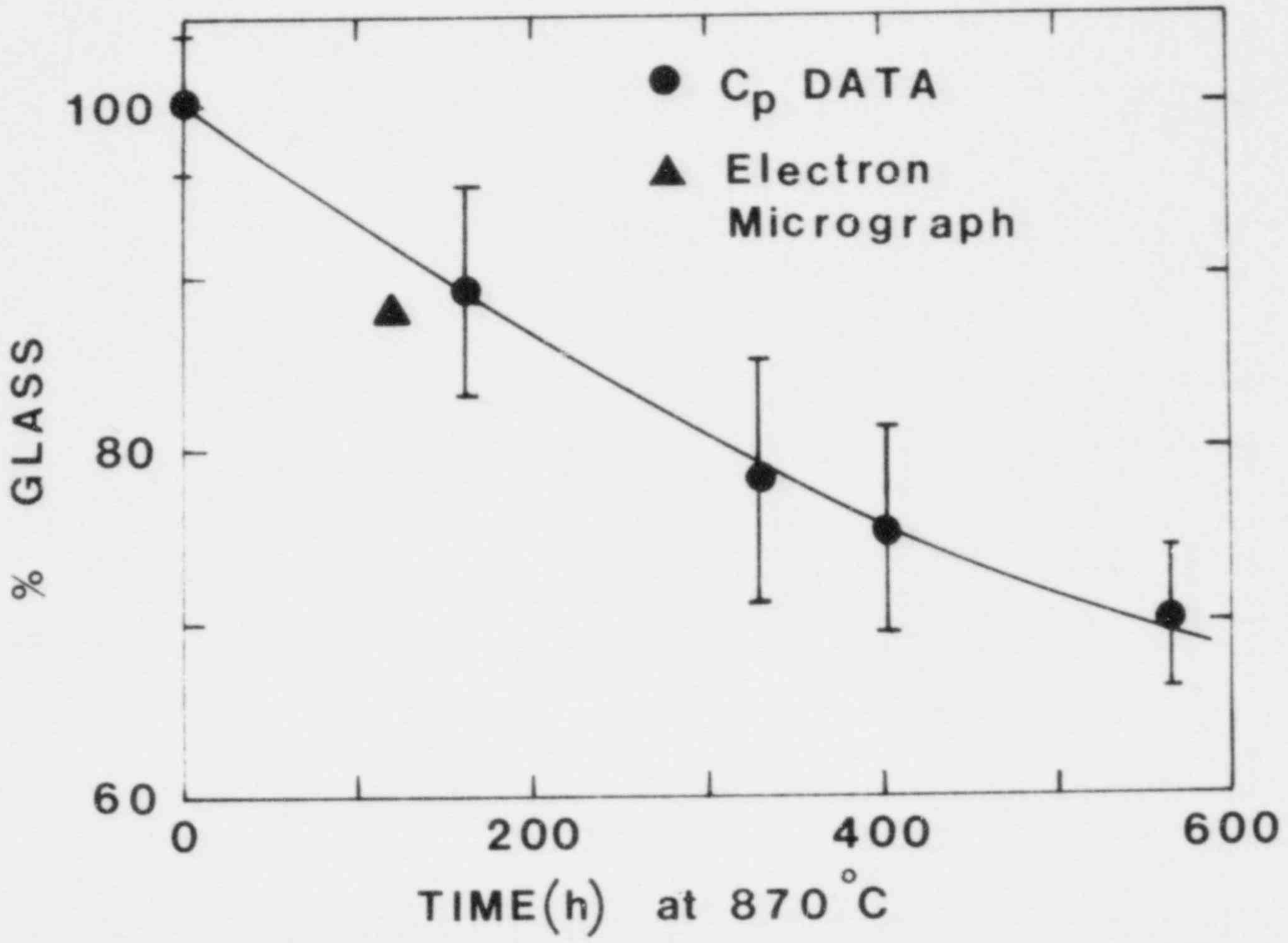
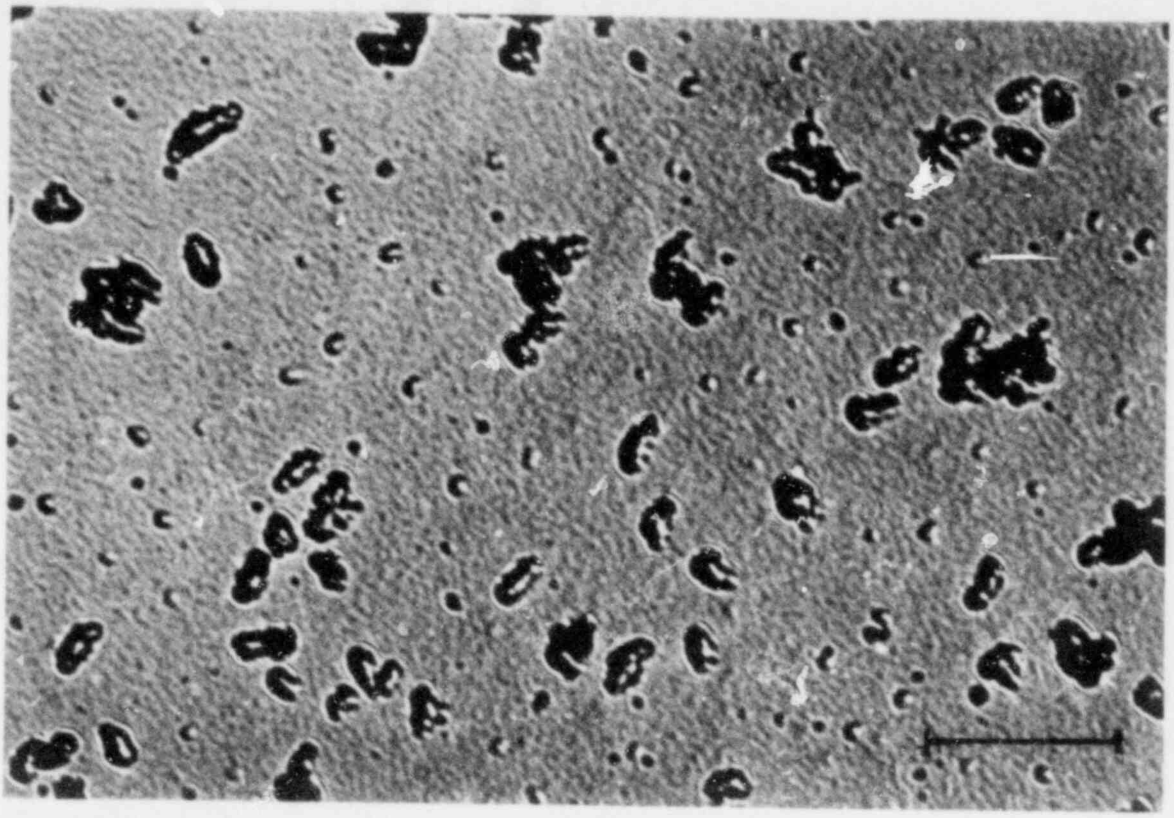


Figure 9. Percent of glass remaining in SNWDG after heat treatment at 870°C versus heat treatment time.



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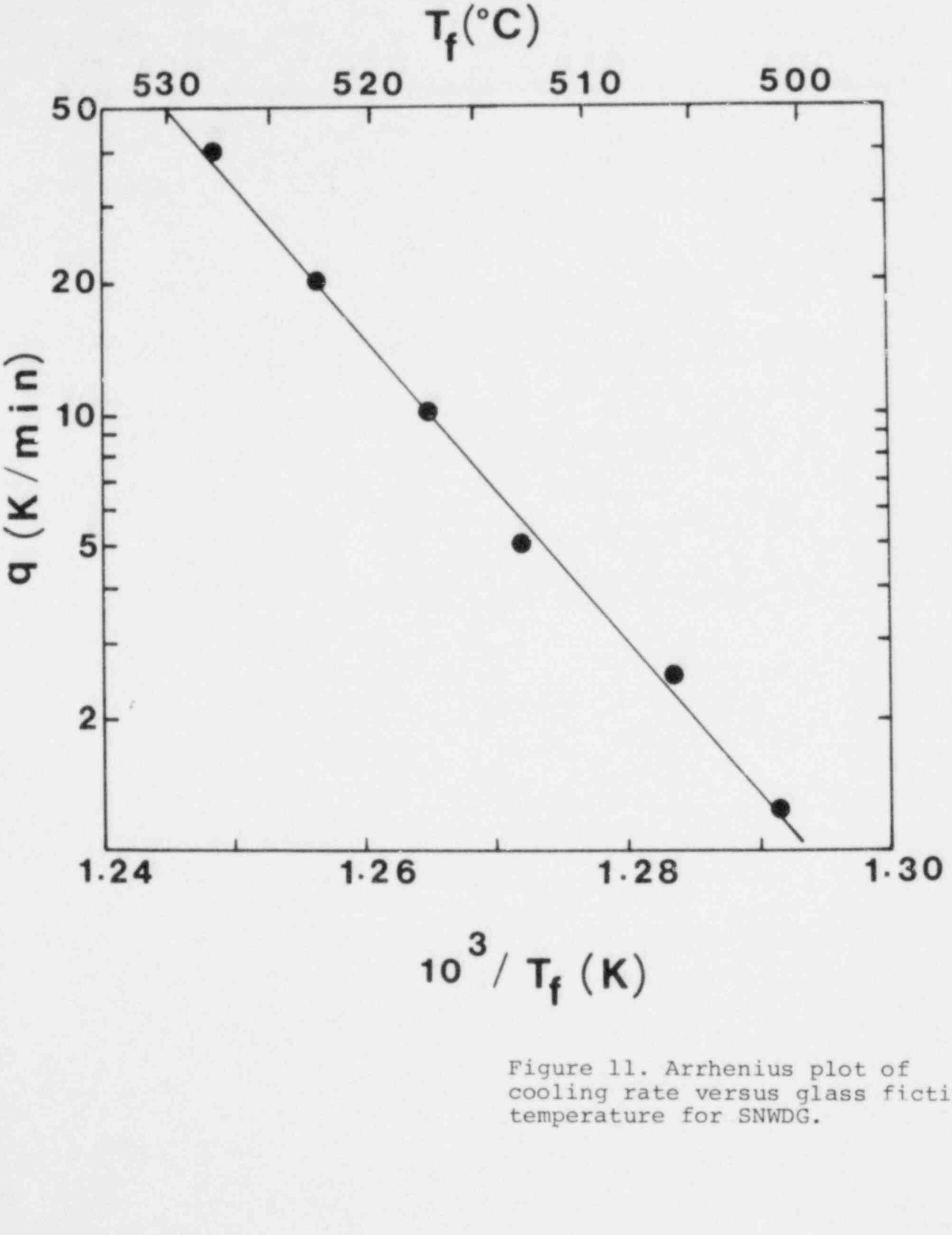

Figure 11. Arrhenius plot of cooling rate versus glass fictive temperature for SNWDG.

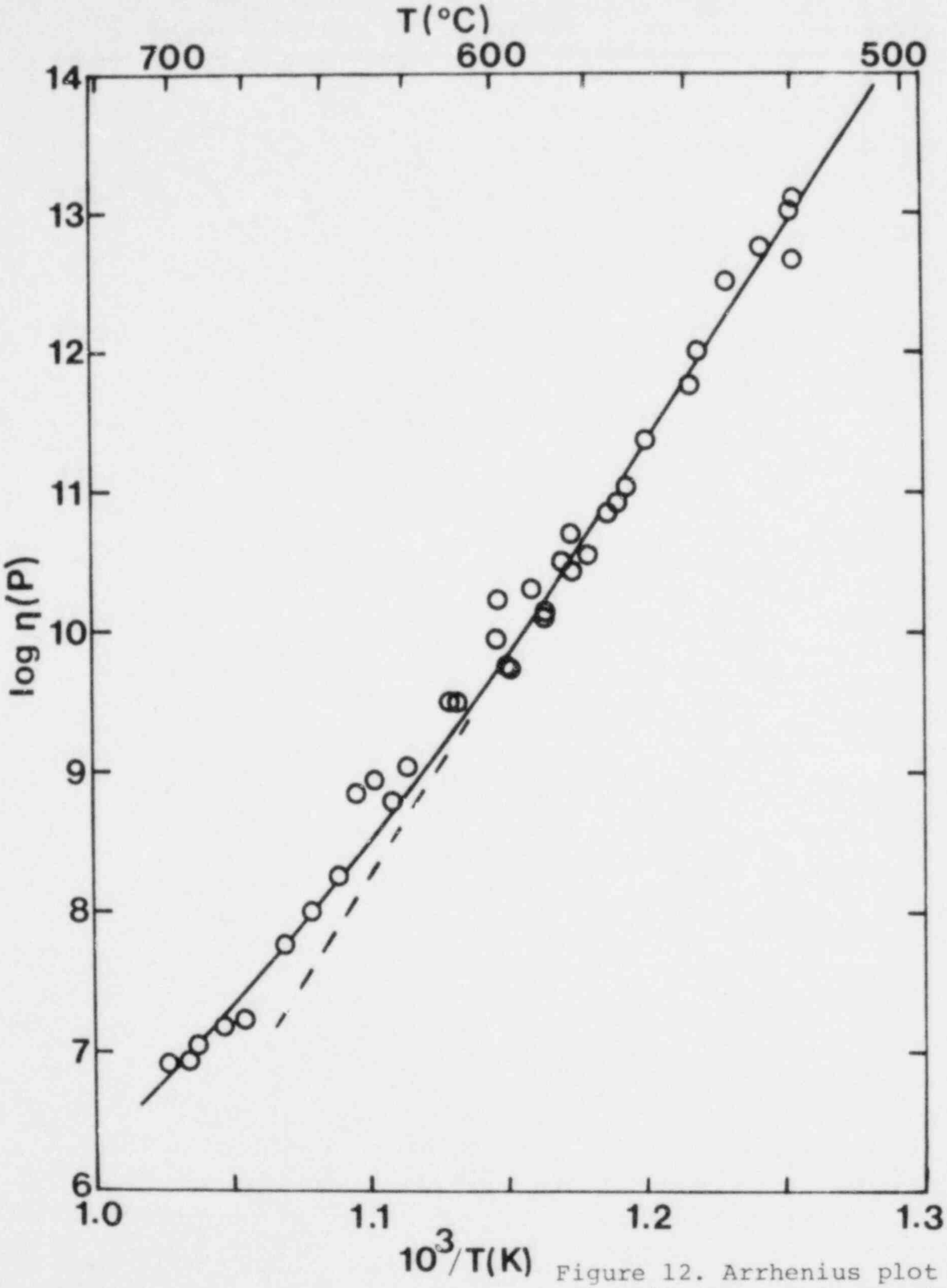

Figure 12. Arrhenius plot of shear viscosity versus temperature for SNWDG.

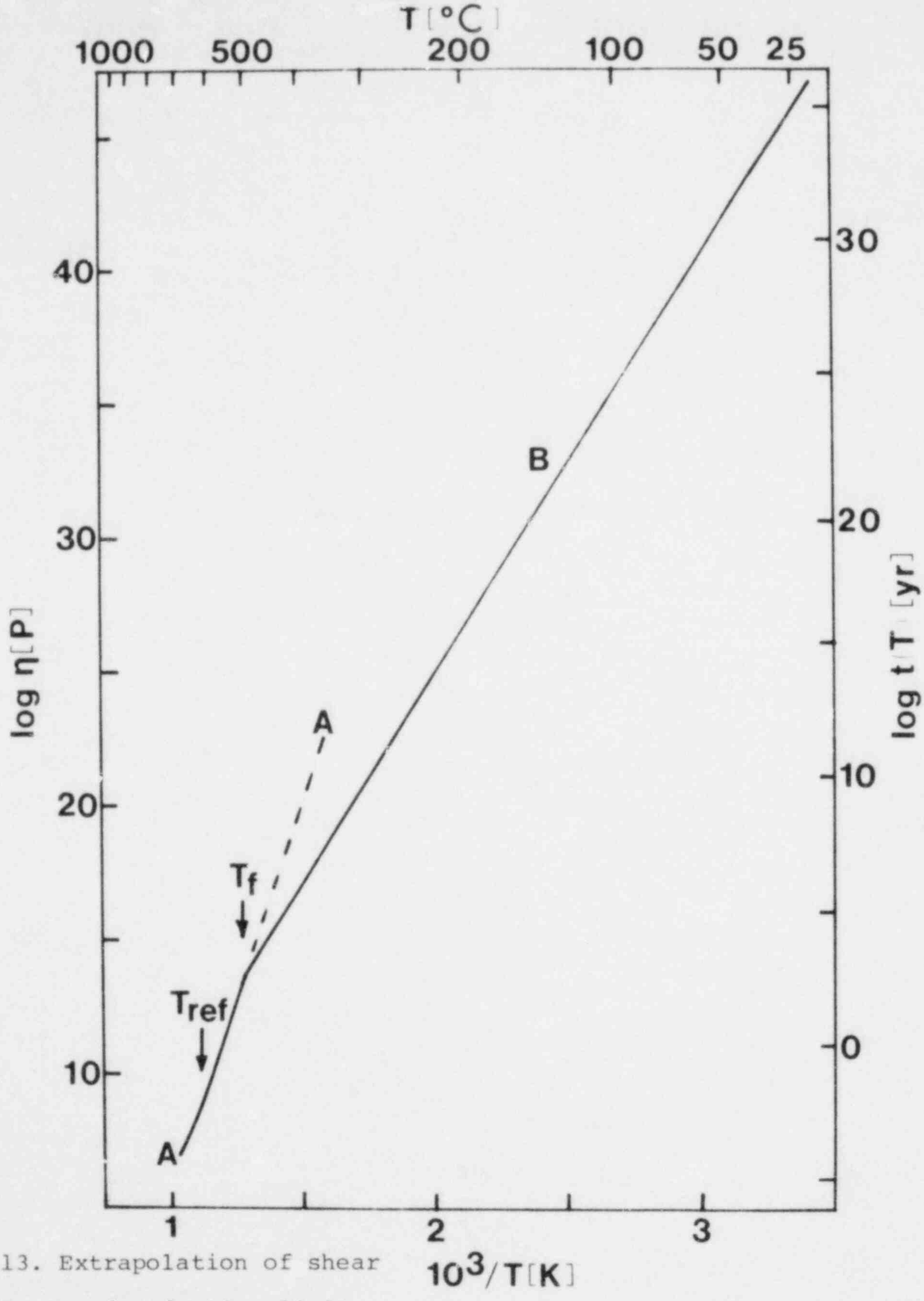

Figure 13. Extrapolation of shear viscosity η and safe time limit

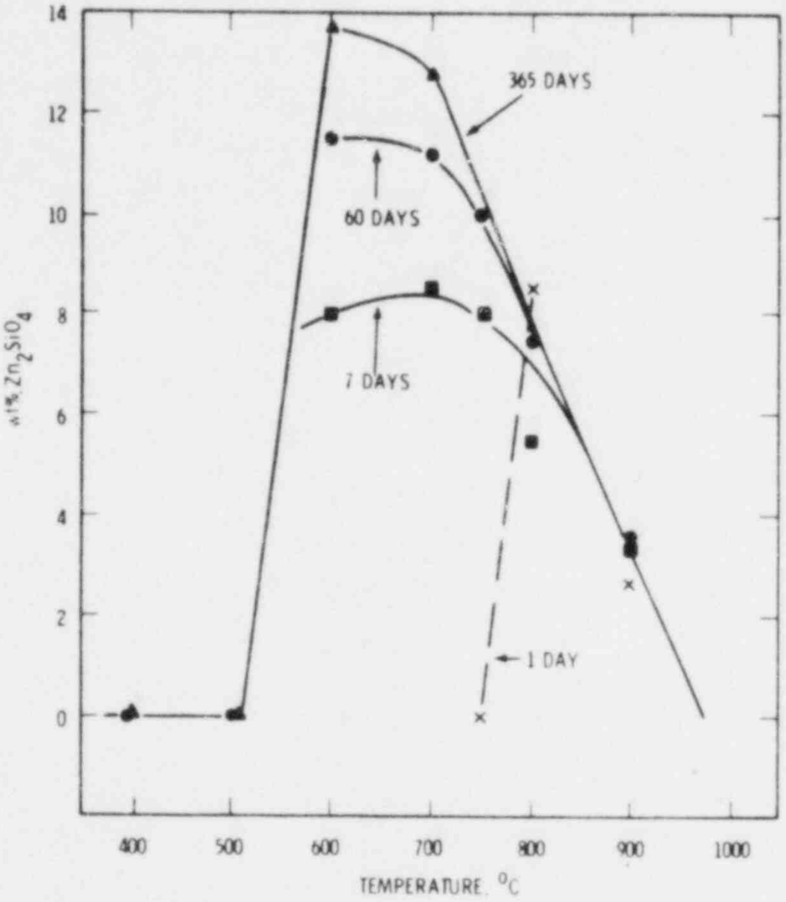

Figure 14. Wt % Zn_2SiO_4 crystallized versus heat treatment temperature

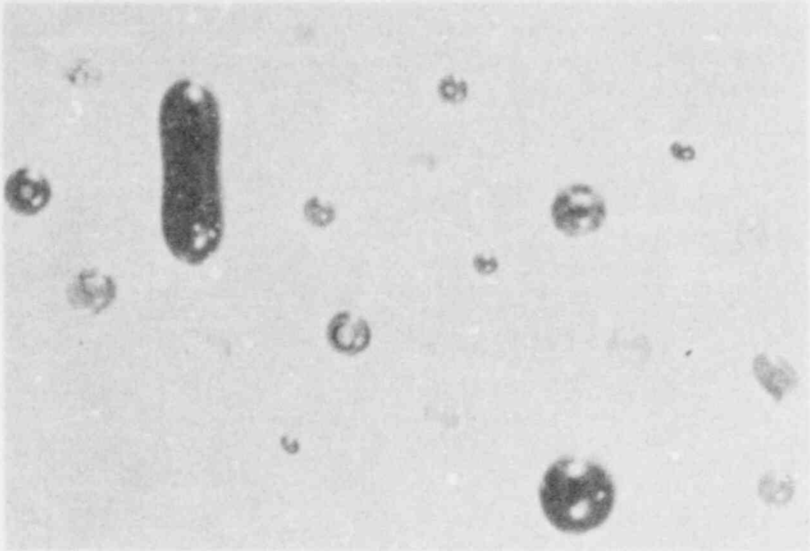

Figure 15. Glass spheres from lunar fines.

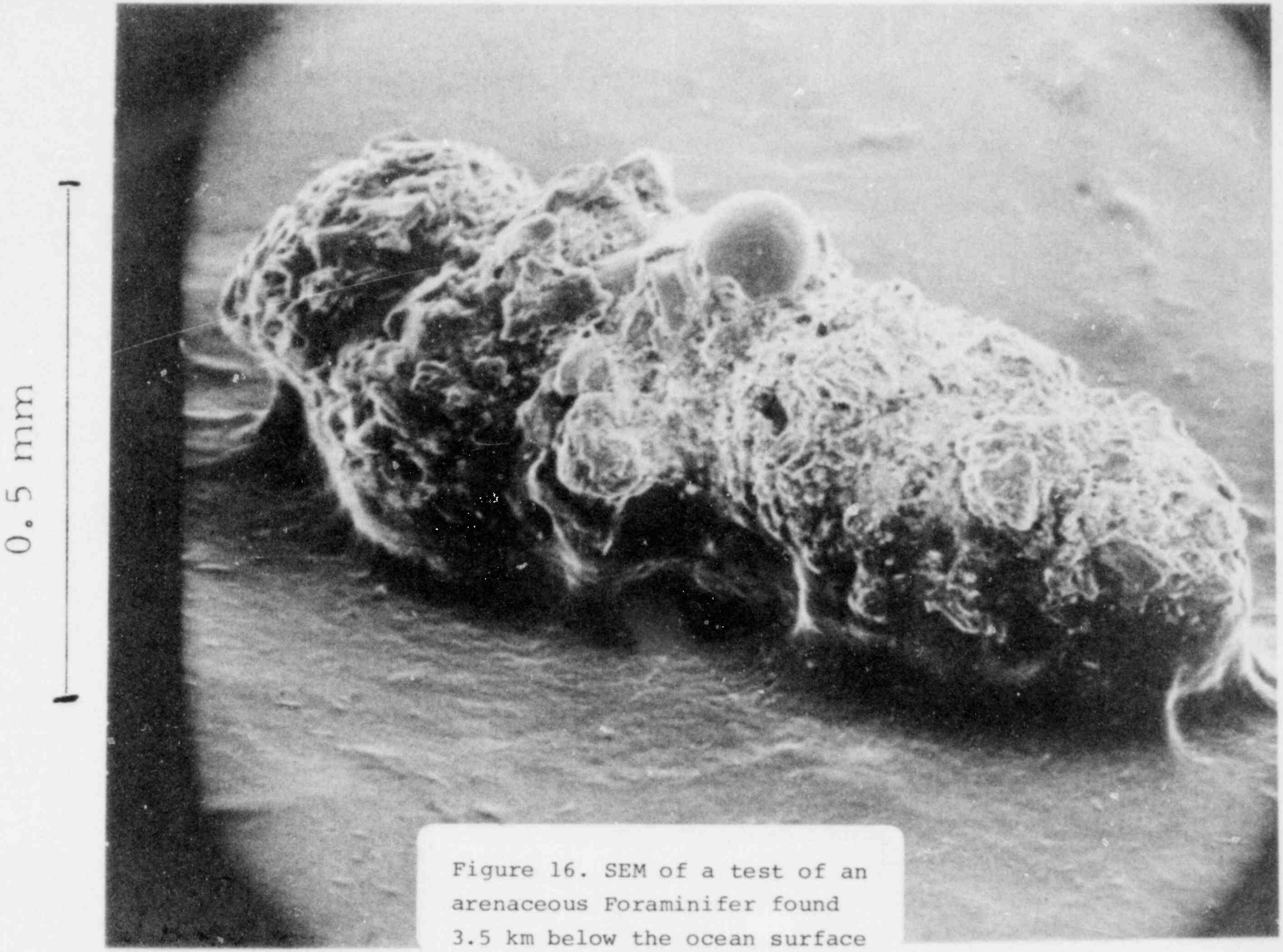

Figure 16. SEM of a test of an arenaceous Foraminifer found 3.5 km below the ocean surface

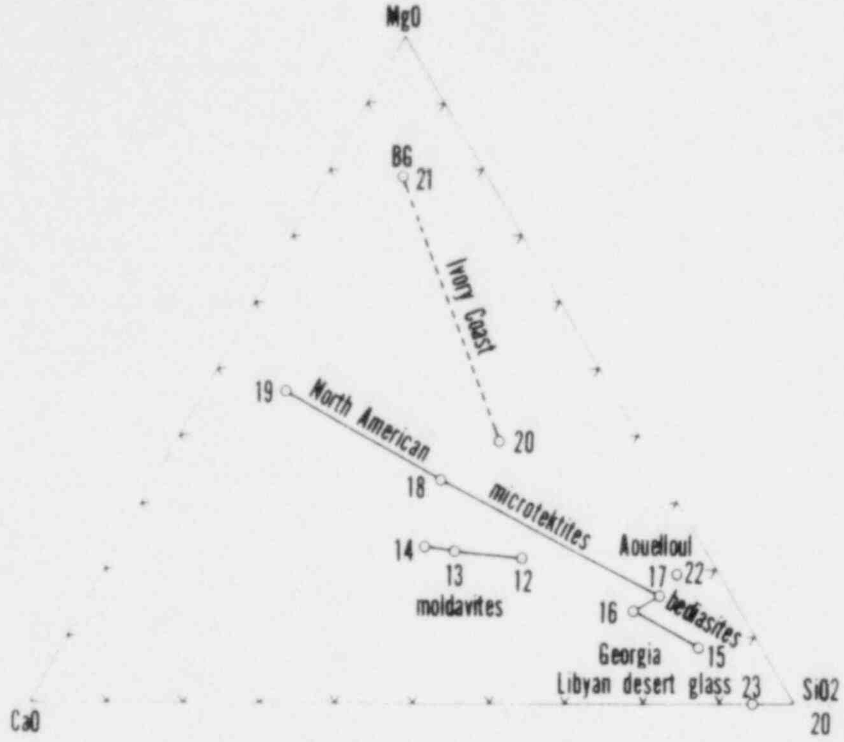

Figure 17. Phase diagram showing the composition of the tektites

Discussion Following

STABILITY OF FIXATION SOLIDS FOR HLRW

Presented by Pedro B. Macedo

Gregory McCarthy - Pennsylvania State University
Question:
Do you have, besides the Battelle studies, any other a priori evidence that glasses are more forgiving to radiation effects than crystals with similar loadings or greater loadings, etc.? I have not seen a great deal of information and we have looked very hard in the peer-reviewed literature.

Macedo
Response:
I would like to point out a couple of things. One, if you look at metamict transitions, the material that has high radiation and long geological time ends up being vitreous (or amorphous, if you do not want to call it glassy). The second thing I want to point out is that there has been a significant amount of work done by the ISO (International Standards Organization, Test Number ISO/TC/85/SC5N28) on radiation damage in glasses. They have found that we really do not have a problem there. We are continuing to work on leaching studies, but the ISO material unfortunately has not reached the open literature. It represents laboratories from all over the world. Also see reference 1 of my paper.

McCarthy
Comment:
This is very important and encouraging and we look forward to seeing those reports. I should point out, and you will hear a great deal more of this from Professor Ewing, that while zircon and quartz and perhaps several dozen other materials in nature are indeed very susceptible to metamictization from radiation effects, nature provides us with hundreds of other examples of crystals which are not susceptible to it. Several of them, fortunately, are known to contain actinides and to have radionuclide loadings similar to or greater than any conceived for nuclear waste storage. So the case from nature for metamictization, even if it were proven a problem, is indeed very good.

Macedo
Response:
I would like to point out to you that the metamictization has to do with the total alpha particle energy absorbed by the solid and not the composition. A crystal could, for example, tolerate 100% uranium replacement, but the alpha particle activity of some of the actinides are sometimes 10,000 times higher than uranium. So you would have to have an impossible 5,000 percent uranium replacement to be able to simulate the nuclear waste loading.

Donald Cameron - Atomic Energy of Canada - Whiteshell Nuclear Research Establishment
Comment:
I would like to emphasize this question of radiation stability of

crystalline phases with a personal example from another field. In the early 1970's, Dr. Schulson and I proposed using the intermetallic compound Zr_3Al as a pressure tube material. This material should be more creep resistant than either of its two component parts, zirconium or aluminum. We were looking for creep resistance. We did all our out-reactor tests and the material was superb. The creep resistance was excellent, the oxidation resistance was good, strength was good, ductility was good. We then exposed it to radiation, in the reactors. It became amorphous. It grew. It achieved zero ductility. Its fractured toughness was lousy, and the creep resistance was poor. So I would emphasize very strongly not to design material forms on the basis of thinking pertaining to non-radioactive environments. You have to consider the radioactive environment and do the test to demonstrate the effects of radiation.

John P. Sokol - Westinghouse Electric Corporation
Question:
This is, in a way, related to the questions about Ringwood's work in Australia. His work has been entirely with non-radioactive materials and my question is (and I think I know what you are going to answer) that when we discuss these glass forms and talk about new waste forms, shouldn't we clearly point out--in this conference and in everything else people write--that some of these forms have been tested (such as glass) with radioactive materials and some of them have only been tested with non-radioactive constituents? Shouldn't you do radioactive tests of all these forms before you can really make judgments about their suitability. After all, the proof is in the pudding.

Macedo
Response:
I want to point out two things: one is that your comment is absolutely correct; second, is that you have to be very careful how you do this testing, because the results are very dependent upon the level of loading. It turns out that one of the problems which I did not spend much time on is that the glasses do fall apart in a water environment unless you keep the temperature low. So if you lower the level of loading to 10 percent, as the Swedes do, you have a good chance of survival in an aqueous environment. The same possibilities are useful in keeping crystals together. However, you can have a crystal which is very stable with uranium present but the addition of a small amount of rare earth causes the structure to become unstable. Our nuclear wastes are loaded with rare earths.

M. K. Murphy - Ontario Research Foundation
Question:
You said you showed one of the slides of the PNL glass which is phase separated. Now when one talks of leachability of the glass (PNL glass), is it related to the amount of phase separation or is it only homogeneous glass?

Macedo
Response:
It turns out that the phase separated PNL glass is closed spheres. Closed spheres are not a real bad problem in leachability. It is when you have an interconnected structure that the situation is difficult. I have not done a leach study as a function of heat treatment, but most of the PNL numbers that are published deal with glass which has already been phase-separated. They have done leach rate studies as a function of annealing and have found that the leach rate increases by a factor of ten.

Rodney Ewing - University of New Mexico
Comment:
I would like to make several comments. You talked about using natural analogs to predict what might happen in a waste form and you referred to tektites. I would simply caution anyone doing that to be aware that it is very difficult because the natural analogs will have very different thermal histories as well as perhaps having existed in very unusual environments. In the case of lunar glasses, of course, water is not available. If you looked at other glasses, say volcanic glasses, which are exposed to water you could make a strong case for the early devitrification, crystallation, and alteration of a glass waste form on the surface of the earth. Tektites are an example where this apparently does not occur.

Another comment is that it is not entirely useful to categorize materials as being stable, metastable, or unstable. Putting them into these categories, that is, saying the material is metastable in particular, does not mean that over the long run it will not be there and will not perform its job. Perhaps the best example would be diamonds, which is definitely a metastable phase, but which persists for long periods of time.

Macedo
Response:
I agree with most of your comments. The important thing is that in the case of tektites, they were in an aqueous environment. The bottom of the sea is beautiful; we know exactly what the temperature was, we know it was in contact with water, we know the salinity of water, and the amount of water it was in contact with. I do agree that tektites are different in composition than Battelle's glass. They are very similar in composition to the Catholic University nuclear waste glass.

Alexis Parks - Boulder, Colorado, private citizen
Question:
A question about lowering the temperature: Is this a temperature lowering by mechanical means and if so, for what length of time?

Macedo
Response:
The source of heat in nuclear waste is strontium and cesium primarily, and the two of them have a decay time (life time) on the order of 30 years. So the Swedes have proposed, for example, cooling for twenty years after processing the canisters. In this way they hope to keep the temperature below 80°C.

Parks
Question:
What if there is a mechanical failure within that system?

Macedo
Response:
In this system the canisters are not deep. They are relatively high up. There is a certain large relaxation time to this building so that the temperature increase will occur relatively slow. You can have mechanical failure of a week or a month before you get major damage. If you do get damage and water does come into the building, because we are not deep, the boiling point of water is 100 degrees C and you are basically controlling the exposure to the material to below 100 degrees C where glasses behave well.

LARGE SCALE WASTE GLASS PRODUCTION

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ABSTRACT

The Marcoule Vitrification Plant (so called A.V.M) started up in June 1978.

The process is based on the french continuous technique and supplies a final glass through two steps : a calcination one, operated in a rotary kiln and a melting one in a metallic pot.

The plant was designed to cope with a maximum flow-rate of 36 l/h of fission products solution that it converts into 15 to 18 Kg/h of glass.

Every day a container loaded with approximately 360 Kg of glass is sealed and outside decontaminated, then it is stored in a nearby air cooled disposal facility.

The amount of the released radioactive materials is very low : the liquid wastes are concentrated and fed back. The possible solid wastes will be cut and put in container in order to be melted afterwards.

The first active campaign which lasted 26 days gave rise to 8.4 tons of glass corresponding to 18 m^3 of fission products solution and 530 tons of spent fuels.

No activity **was** noticed in the stream exhausted from the gas off treatment equipment. A similar plant devoted to the LA HAGUE reprocessing plant is presently in design and ought to be running in 1985.

LIST OF FIGURES

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LARGE SCALE WASTE GLASS PRODUCTION

HISTORICAL BACKGROUND

The research and development of the solidification of high level radioactive wastes has been under investigation in France for over 20 years.

First radioactive glasses and synthetic micas were made in 1958 [1]. Glass blocks weighting 5 to 15 Kg and having specific activity of about 1000 Ci/l were achieved in 1963 by a gel technique in graphite crucible for examination purpose. In the meanwhile, processes of industrial interest were under development : a batch and a continuous one [2] [3] [4] [5] [6] [7] [8]. The first in operation was the batch one, a pot vitrification technique which lies in performing drying, calcination and vitrification in the same vessel, a metallic pot heated by induction. In 1969, a pilot plant called PIVER using this process was operated under fully active conditions at Marcoule Nuclear Center. Until 1973 it has processed wastes solutions from spent natural uranium fuel yielding 12 tons of glass of a maximum activity of 3000 Ci/l.

Because of the successful operation of PIVER, it was decided in 1972 to built an industrial vitrification plant at Marcoule. The continuous process was chosen in preference to the pot technique, as it was found to be more flexible, cheaper and easier to scale up for higher throughputs. A plant called AVM was built and started up in active operation in June 1978 [9].

BASIC PROCESS

The process lies in performing the vitrification in two stages.Fig 1.The first one is a calcination. The feeding solution is introduced in a rotary kiln in order to be transformed into solid form. The calcined products are then mixed with suitable raw materials in an electric furnace to make the wanted glass.

The glass is poured at stated intervals in containers which are transfered to a disposal facility. The off gas released during the fabrication are processed in a specific off gas treatment equipment.

MARCOULE VITRIFICATION PLANT (A.V.M.)

Glass involved in the vitrification process.

The main liquids to be vitrified at Marcoule fall in 3 types related to the reprocessing of MTR spent fuels, military and commercial natural uranium spent fuels (graphite gas reactor system).

Table 1 gives the characteristics of these wastes. As it is impossible to determine any single glass dealing with the various composition of the wastes, 3 different groups of glass compositions, all of borosilicate type, have been selected after researches carried out in cold and hot laboratories [3] [4] [6] [10] [11] [12] [13].

The characteristics of the glasses are plotted in Table 2. The examination of the glasses were carried out in respects of the behaviour of the structure under irradiation and thermal conditions and their physical and chemical properties connected to the technology of fabrication and radioactive hazards in a final disposal.

Description of A.V.M.

The vitrification plant, designed jointly by C.E.A and S.G.N was built for the sake of COGEMA (1) in order to solidify all the solutions of fission products generated by the local reprocessing plant, including those already in storage for over 20 years.

A.V.M is located close to the storage tanks. The construction which started up on summer 1974 ended on January 1977 with the first non radioactive run and gave rise to the actual radioactive operation on June 1978.

The plant is made up of two different parts : the so called plant and a nearby storage facility.

The building made of reinforced concrete and partially countersunk is 22 meters long, 18 meters wide and 33 meters high, 14 meters of which beeing underground.

Figures 2 and 3 show a vertical section and a cross section. The main part is the vitrification cell which is 10.5 meters high, 12.5 meters long and 3.5 meters wide. Its walls made of concrete are totally lined with stainless steel. Their thickness is 1.55 meters. It contains the chief equipment of the process : feeding device, calciner, melting furnace, dust trapping column and condensor. It encloses also the apparatus ensuring the welding of lids of the glass containers and the cutting of used metallic materials.

Every part of the equipment located inside the cell was designed to

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(1) Compagnie Générale des Matières Nucléaires

be removed for taking off or refitting by means of the following devices :

- a 20 KN bridge-crane which supplies the whole cell and ensures the needed tools to be sustained.
- specific tools in the range from a mere hook to a more elaborate tool as an electrical screw driver. The principle of the dismantling of the calciner is showed as an example by figure 4.
- eight couples of master-slave manipulators distributed on the operating side and twinned with eight windows.

The vitrification cell is connected to :

- a solution storage cell which comprises two 10 m^3 buffer tanks.
- a decontamination cell which also plays a part in the transfer of the glass to the storage area.
- a maintenance cell which is used in addition to drain the equipment in and out and as a garage for the bridge-crane.
- a gas off treatment cell (showed on the cross section of the figure 3) which contains a column for the recombination of nitrogeneous stream and another one as a washing column which collects also the gas issued from various breather tubes.

Surrounding the main cell, there are (as plotted in figure 3) : the container supplying room,the medium frequency power generator room, and the control room.

The glass storage facility is close to the vitrification cell. It is laid out in order to provide conditions of safety, to give rise to a low operational cost and to make possible any further retrieval.

It has been designed as a "clean" one to avoid filtration after a rather long-term disposal when the natural convection cooling is applied in substitution of the forced air cooling.

The facility is made of 3 engineered vaults made of concrete which are underground. The vaults are stuffed with impervious stainless steel barrier. The one meter high containers are piled up in ten meters high vertical pits fitted in the vaults.

Two vaults are presently equipped with respectively 80 and 60 metallic pits. The third one is in stand by (with 80 pits). The 2 0 pits take a ground surface area of 415 m^2 and correspond to the need of Marcoule until 1990. A further extension is available.

The ventilation has been designed in order the maximum temperature of the forced air is not in excess of 100°C when the maximum specific power (50 W/l) is applied to the glass. The reason is to limit the temperature of the concrete at 60°C and those of the glass at 500°C (forced air cooling) and 600°C (natural convection)at the center line.

Each vault is equipped with its own ventilation device. The stream flows first along the walls of the vaults to cool the concrete and then is injected at the bottom of the pits to flow in the annular space which is located between the wall of the pit and the container (figure 6). The total flow-rate is 80 000 m^3/h.

Every pit is fitted with a throttle valve which can lessen the stream according to the directions of a thermocouple located in the valve stand.

An absolute filtration is operated on the exhausted air. This one is drained out to a stack fitted in each vault.
Practical experience has already pointed out this filtration is not necessary.
Due to the level of the steady temperature, the inside frames of the vaults are wholly metallic and the upper biological shielding lies in metallic caissons filled with concrete.

The storage facility is hence totally underground. It is capped with a metallic shed in which the handling of the containers is operated.
A 350 KN bridge crane ensures the transfer of the containers put in shielded casks from the way out of the vitrification building to any storage pit.

Vitrification plant operation

The plant runs continuously by all day round with a staff composed of a score of workers distributed in 5 shifts of 3,plus five persons.
Figure 5 pictures the diagram of the operation.

The solutions coming from the liquid storage tanks are transfered in 10 m^3 batches in the 2 A.V.M tanks. These tanks are cooled and mechanically stirred. The solutions are sampled for analysis and eventually chemically adjusted to cope with the composition of the raw materials.

A double air-lift exhauts them to the vitrification cell into a metering device which is able to feed the calciner with a flow-rate in the range of 30 to 36 l/h according to the concentration of the liquid.

At this step, a chemical additive is introduced at a rate of 2 l/h. This additive is an organic product (azodicarbonamide - Trade mark = Ferupore -) the aim of which is to prevent caking on the wall of the calciner and to improve the size distribution of the calcined product. A solution issued from the first cleaning gas equipment is also fed back at a flow-rate of 4 l/h . Consequently the total liquid flow-rate can vary from 36 to 42 l/h.

The calcination is operated in a rotary kiln made up of a metallic tube 3.6 meters long, 0.27 cm diameter and 12 mm thick, made of uranus 65. It is electrically heated along 2.5 m by a 4 zones furnace. The power is 25 KW for each of the two first zones devoted to the drying and 10 KW for each of the two others related to the calcination. In fact a total of 40 to 45 KW are actually used.
The tube is set with a 3 % tilt and rotates at a speed of 30 rpmn. The two ends are fitted with an end-fitting where is fixed the device which ensures the tightness. This device comprises a graphite ring.

The feeding solution is injected continuously through the upper end-fitting. The consequent calcined product (8 to 9 Kg corresponding to 30 l of solution) falls straight in the melting furnace through the lower end-fitting. A loose rod, located inside the tube makes the calcination easier and gives contribution to avoid caking.

The calcined product is partly granular partly powder and still contains 20 % of the initial nitrates of the solution.

The lower end-fitting is also used for the connection to the melting furnace and to feed the raw material in the form of a primary glass (frit). The frit is fed at a mean rate of 9 to 12 Kg/h at stated intervals in 400 to 600 g batches through a lock chamber.

The melting pot is a metallic cylinder 1.7m long, 0.35 m diameter and 1/4 inch thick made of Inconel 601. A drain tube is fitted at the bottom.

The heating is supplyied by a medium frequency induction (10 KHz) furnace which is made up of 4 main induction coils.

A variable voltage can be applied to each coil. The voltage depends of the glass level which is controlled in measuring the temperature at several places. The available power is 100 KW but the actual need is only

60 KW. The through-put is about 15 Kg/h of glass melted at 1100 - 1150°C. The pouring is initiated every 8 hours by heating the cold glass plug located inside the drain tube. Every eight hours, 120Kg of glass are cast.

The gas elaborated in the melting furnace and the calciner is drained out through the upper end-fitting. They are composed of steam, nitrogen compounds generated by the denitration and an amount of dusts the main part of which beeing soluble in nitric acid. For this reason the first step of the gas off treatment is a counter current washing in a "deduster". The used liquid is continuously recycled in the calciner (Figure 8).

The stream flows then in a condensor and in a standard equipment composed of : an absorption column, a washing column, an absolute filter and a fan ensuring the wanted negative pressure.

The glass is cast in metallic containers made of refractory stainless steel. They are 50 cm diameter and 1 m high. They receive 3 casts. The weight of the glass is measured during pouring.
One container loaded with 360 Kg of glass (150 liters) is thus yielded per day. This is equivalent of about 800 liters of fission products solution.

Some hours after filling, the container is shifted to the welding area where it is covered with a lid welded with a plasma torch. The cleaning is operated one day later by washing the surface with high pressurized water (200 bars).

To this purpose, the container is put in a tank. Then a moving cylindrical hose washes it from top to bottom.

The decontamination is checked by injecting air flowing around the container and measuring a possible air contamination. A further checking is operated in rubbing the wall of the container during its transfer to its storage pit and counting.

The process of the liquid wastes depends of their specific activity.

- The condensate and used liquids issued from the first column are estimated as highly radioactive liquids and are recycled to the fission products solutions concentration unit in order to be finally fed back and vitrified.

- The used liquids of the washing column and of the container decontamination (500 1/d) have an activity below 1 mCi/m^3 and are therefore deemed only as dubious wastes and transfered to the low-level wastes treatment plant. They are in a way the only liquid wastes released by A.V.M.

The solid wastes are possibly generated by any failure or by the removing of predeterminated life-time implements or vessels. The latter includes especially the vitrification pot which has to be removed every 2000 hours.

The wastes are able to be submitted to a previous decontamination in the vitrification cell by dipping in a special tank. It is also possible to cut them partially to shorten their overall size, they are then either transferred to the maintenance cell to be conditioned in concrete in drums or put in containers similar to the glass ones.

The latter is the case of the pot vitrification which is, when used, put in a container. This one is welded and disposed in a particular storage pit prior to be conditioned by melting as the major part of the metallic wastes will be later on.

The glass storage cooling system facility does not need, when it runs normally, any workers. The air stream must be only fed back according to the temperature of the exhauted air when a pit was just filled. Control is automatically operated. The main items involved in it are as following :

- pressure drops in the loops, in order to manage the flow-rate at various points.

- air flow-rate at the stack level

- presence of liquid in the bottom of the vaults

- temperature of in and out airstream and temperature of concrete at hotest places.

- activity of the stream before and after filtration.

The safety related to a possible fan failure is provided in duplicating fans and electric current supplying generators.
In spite of these safety devices, if the cooling were stopped, the storage heat capacity could give the possibility to keep for 3 hours the temperature below the permissible ones, viz. 60°C everywhere in the concrete of the frame and 650°C everywhere in the glass.

If the failure is extended over 3 hours, the vaults can be cooled by natural convection. The values of the temperatures when the steady state is reached are plotted on figure 7.

Outcomes and performances

From January 1977 to April 1978, cold running tests have been achieved. Their target was :

- to vitrify simulated solutions similar to the 3 types stored at Marcoule. During this period of time, 18.1 m^3 of solution were vitrified to yield 8.8 tons of glass (see table 3).

- to perfect automatized devices and to look for better safety conditions in case of failure of various feedings(raw material, electric current, air, steam etc....).

- to achieve every available remotely handlings to check the feasability of each operation. These tests required over 10 000 hours of working time.

The plant was gradually put in active condition in increasing the radioactivity of the feeding solution. The first campaing using concentrated fission products solutions started up on June 28, 1978 and ended on July 24, 1978 for staff vacation reasons. The processed solution was an old one of 30 Ci/l of specific activity generated by the reprocessing of SICRAL type spent fuel (concentration 35 l/ton).

An other campaign related to the reprocessing of the same type of solution was initiated at the end of September 1978 and stopped 1000 hours later, to remove the pot vitrification. This was a scheduled operation due to the age of the pot (over 2000 hours).

After the remplacement of the pot, a third campaign began, involving 6 to 8 times more active solutions.

The whole performance of the plant is shown on Table 4.

The composition of the solution vitrified in the course of the 2 first campaigns is plotted on Table 1.

A total volume of 50 200 liters were processed during a 1644 hours feeding time. This corresponds to 1400 tons of spent fuels giving rise to 23.4 tons of glass disposed in 70 containers lodging 330 Kg to 360 Kg of glass each. The factor of volume reduction is 5.4 as it was foreseen. The loading factor of the plant was 98 %.

Water was substituted to the fission products solution during 2 % of the feeding time at the same flow-rate.

The reason is the failure of the ancillaries equipment and troubles related to the raw material feeding device.

Feeding, calcination and melting experience

Every equipment ran satisfactory.
The liquid feeding is very accurately ensured by a metering wheel. This one was set at 30 l/h for the 1st campaign and 33 l/h for the 2nd one. The linear expansion of the rotary tube has kept the same value ($\simeq$ 13 mm). The inside pressure ($-$15 cm water) was also very stable.

The raw materials feeding device is the more overworked one of the plant. It has run during the 2 campaigns almost 40 000 times, introducing over 18 tons of frit. Some troubles obliged to stop the fission products solutions for a total of 16 hours (out of 1650).
It must be noticed that as a non radioactive equipment, its removing is very easy. Nevertheless, the use of a more liable device, presently under testing, has been planned.

The melting of the glass in the pot was operated, in keeping the temperatures of the wall below 1130°C. The casts initiated every 8 hours drained out 110 to 120 Kg of glass during 15 to 20 minutes feeding time viz.at a mean flow-rate of 350 Kg/h.

210 casts were performed in 70 containers (3 casts in each). The containers were filled at 76 % during the 1st campaign and 84 % during the 2nd one, in order to cope with the increasing of the feeding flow-rate. Figure 9 pictures the steps of the filling behaviour of a container related to a liquid feeding flow-rate of 33 l/h.

Welding, decontamination and transfer of the containers to the storage facilty.

The welding is operated some hours after the last cast. This operation did not suffer any difficulty except two occasions where an additional pouring has be done.

Every container was washed with 450 liters of pure water under a 200 bars pressure during 3 minutes. The radioactivity of the used water was found out below 2.10^{-4} µCi/ml which in the value of the limit detection. There was no activity in the air stream injected around the container previously to the transfer to the storage area.

The 70 containers were piled up in 7 storages pits.
The released thermal power from each pit is 1 Kw that is not high enough to make possible any alteration of the temperature of the cooling air between the injection and the exhaust levels.

Gas off treatment data

- The efficiency of the recombination of nitric acid and nitrates reached over 90 % in the condensor and over 82 % in the first column. This meets the data from the non-radioactive campaign.

- About the non radioactive cations, no insoluble dust was noticed in the liquid of the deduster. Chemical analysis of this liquid and of the condensate pointed out an average draining out of 5 % and a trapping efficiency of 96/98 %. This also meets the results of the non radioactive runs [14].

- Table 5 gives the most important information related to the released nuclides. Figures 10,12 and 13 show the activity of Ru, Cs and Sr germane to one curie of every element processed, collected in various places of the equipment and the decontamination factor of the apparatus. Attention must be paid to the large quantity of the 106 Ru carried by the off gas (38.7 %) and the poor corresponding efficiency of the deduster (DF = 2.3) which gives rise to a content in the condensate of 17 % of the initial Ru.

In spite of that fact, the ruthenium volatilization does not appear as a shortcoming since the condensate and the wastes generated by the recombination column are recycled to the fission products concentration unit (see table 5). The only ruthenic waste which is taken into account by the plant is the used liquid generated by the washing column, Ru concentration of which is not in excess of 10^{-4} % of the initial Ru. Similar values were found out in the pilot plant ATLAS which is an half scaled A.V.M equipment.
The following table shows the comparison of the data.

	escaping of the calciner	fed back through the deduster	content in the condensate
A.V.M.	38 %	22 %	16 %
ATLAS	50 %	30 %	20 %

- Some ways to overcome this were looked for. The use of sugar in substitution of ferupore seems to lessen the problem.

Figure 11 shows the marked effect of the use of sugar upon the volatilisation of Ru that reduces total draining out of the calciner to 2 % and the content in the condensate to less than 1 %.

- About 137 Cs (see figure 12), rather high volatility and poor efficiency of the deduster are noticeable. This results call for confirmation and will be checked in the course of the next campaign. The same remark is to be applied to 144 Ce.

- 90 Sr on the other hand (see figure 13) appears to behave like non volatile element.5.2 % of Sr is released from the calciner, 96 % of which is fed back. Consequently the balance, 0.2 % is found in the condensate.

In any case, the chief liquid waste which is composed of the 10 l/h of the used water of the washing column contains nothing but :

10^{-4} % of the initial Ru
10^{-7} % of the initial Cs
5.10^{-6} % of the initial Ce
7.10^{-8} % of the initial Sr

This ought to be considered satisfactory and to be credited to the good decontamination factors of the recombination column and the condensor.

Gaseous wastes

In order to evaluate the decontamination factor of the gas off treament equipemnt, some samples were taken in various places of the line (see figure 10, A, B and C locations). They were not able to give rise to any value owing to the very small activity of the off gas, but they gave the possibility to assume minimum values to A and C points (see figures 10 and 12)and as following .

	A point	C point
Ru DF	$> 3.10^6$	$> 1.2.10^7$
Cs DF	$>1.8.10^8$	$> 1.2.10^9$
Ce DF	$>8.6.10^6$	$> 2.10^7$

The measurement at A point was done by counting the gas sampled in 60 cm^3 capsules. To improve the accuracy,1liter capsules were used at C point, but the activity was nevertheless too small.

As the stack control pointed out, the activity of the stream was smaller than the normal background, it is assumed that the ruthenium decontamination factor was at least 10^9. The next campaign which will involve more active solutions (30 times more for Ru) should give the possibility to reach the real value of Ru DF.

Findings

The A.V.M running has been very satisfactory during the 70 days working time. No contamination occurence happened and the contamination rate of the cell atmosphere varied from 0 to 60 counts per second that is an indication of a very low level contamination.

LA HAGUE NEXT VITRIFICATION PLANT

A vitrification plant, assigned to vitrify fission products solutions of La Hague current reprocessing plant, is presently in design. Another one is scheduled to vitrify the fission products solutions generated by the next reprocessing plant which will be located on the same site.

Scaling up to cope with the need of a 800 t/year reprocessing plant could be done according to the diagram shown in figure 14 with the following assumptions :

- the spent fuels are reprocessed after 3 years cooling time
- the fission product solutions are concentrated at a rate of 500 l/t that sets a specific power of 7 w/l (at the time of reprocessing).

The vitrification plant will have then to face up solutions of a specific power of 5 to 6 watts per liter that will give rise to 25 to 30 watts per liter of glass, taking into account a reduction volume factor of 5.

Two processing lines will be necessary. Each line will be composed of one calciner connected with a melting furnace. The rotary tube might be heated by induction in order to shorten the time needed to reach the steady state and to shut off. This heating device could by the way, when used, becomea less bulky solid waste than a resistance furnace.

Every calciner will be fed at a flow-rate of 50 l/h with a 500 l/t concentrated solution. Every connected melting furnace will produce 25 Kg of glass per hour.

The whole through-put of the plant will be 600 m^3 per year with a loading factor of 250 days a year.

The glass could be cast in 50 cm diameter cylindrical containers by 200 Kg batches running. After welding of a lid, tightness test and outside decontamination, they will be transfered to a storage facility to be cooled for 2 years by forced air and further on by natural convection.

The arising liquid wastes (mainly condensates), will be concentrated and recycled to the storage tanks to be vitrified. The only generated liquid wastes will be dubious ones which will be directed to the low level processing unit on site.

The gross decontamination factor of the plant about the off gas could reach 10^{11} for ruthenium and at least matching values for the other nuclides.

CONCLUSION

The commission of A.V.M. has opened the industrial development era for the continuous vitrification process.

The very good results which have been obtained about the running aspect of the plant, as well as the very small level of the activity of gaseous and liquid wastes, indicate that the problem of the management of fission products solutions is going to be overcome.

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R. BONNIAUD - C. SOMBRET - F. LAUDE
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R. BONNIAUD - A. REDON - C. SOMBRET
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R. BONNIAUD - A. JOUAN - F. LAUDE - C. SOMBRET
Seminar on radioactive effluents from nuclear fuel reprocessing plant. KARLSRUHE - 22,25 Novembre 1977.

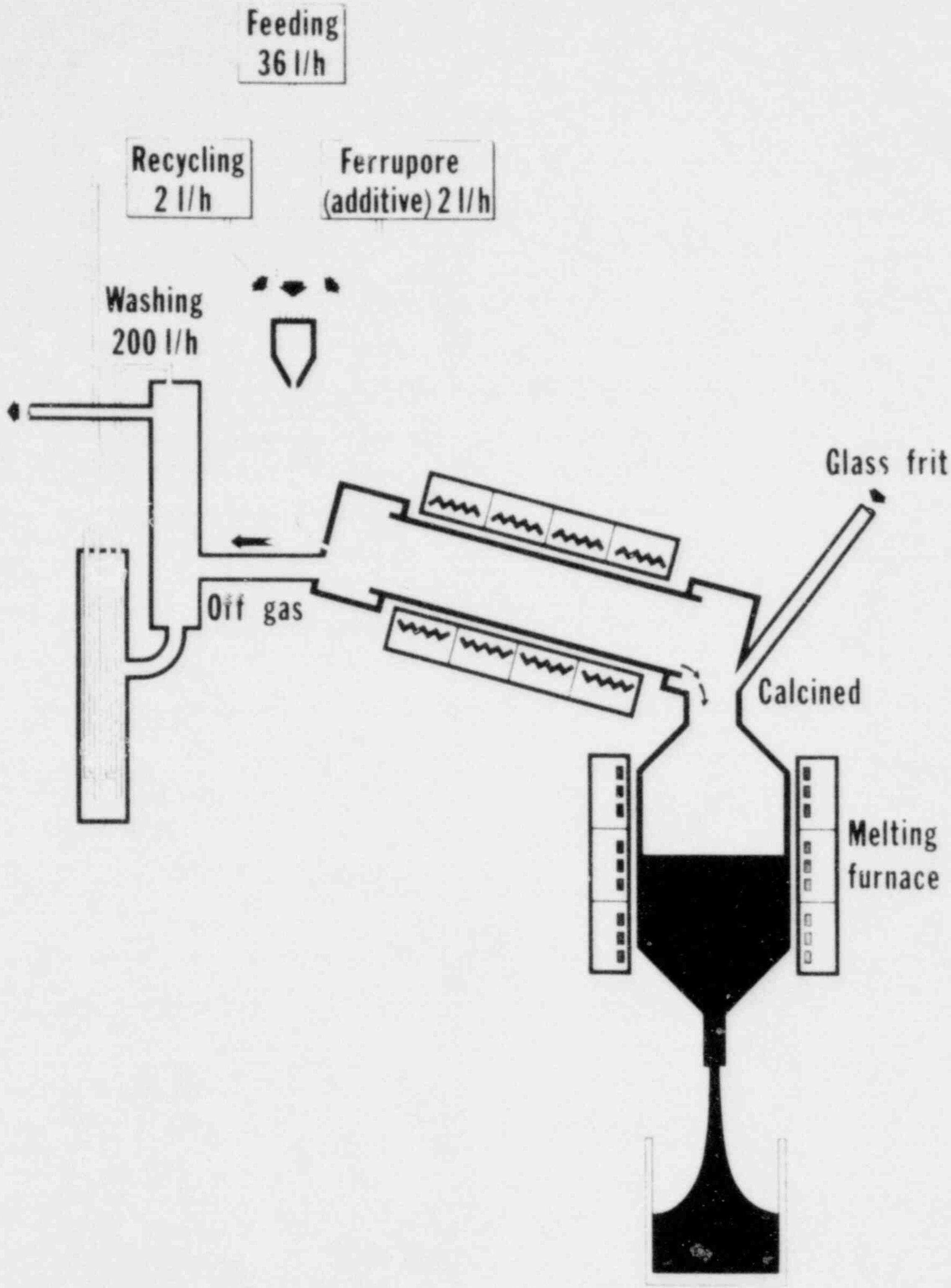


FIG. I CONTINUOUS VITRIFICATION PROCESS

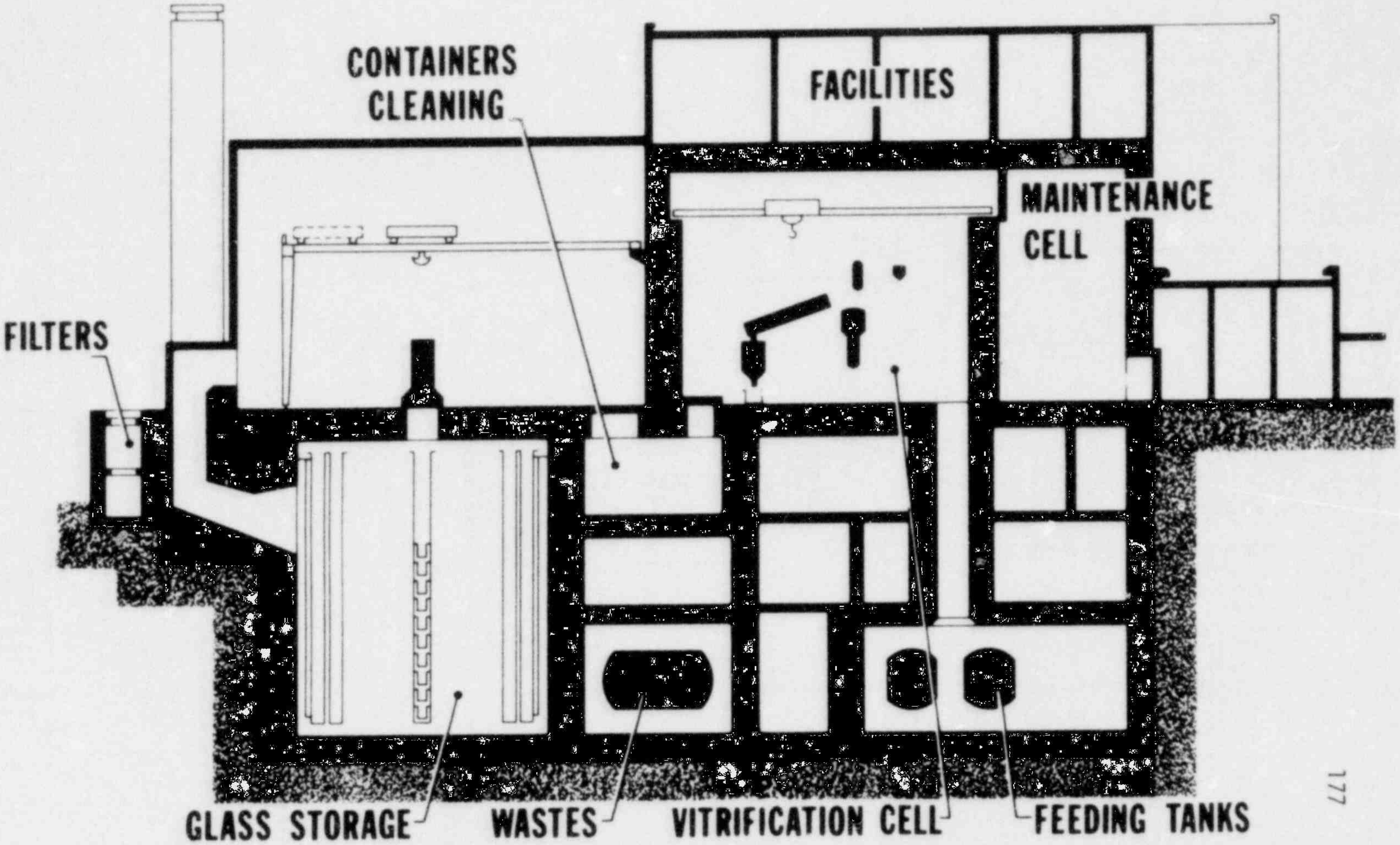


FIG. 2 AVM VERTICAL SECTION

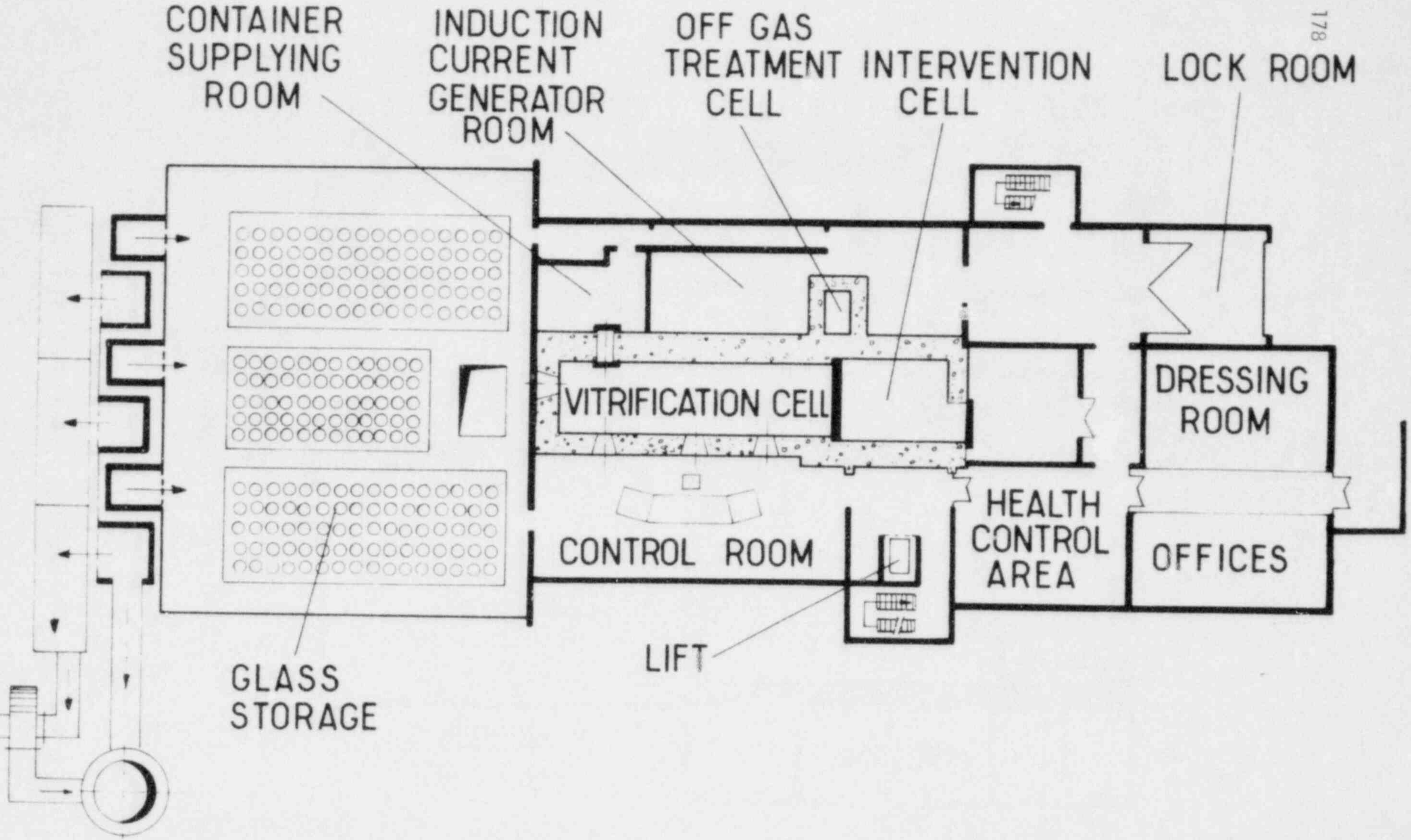


FIG. 3 AVM HORIZONTAL SECTION

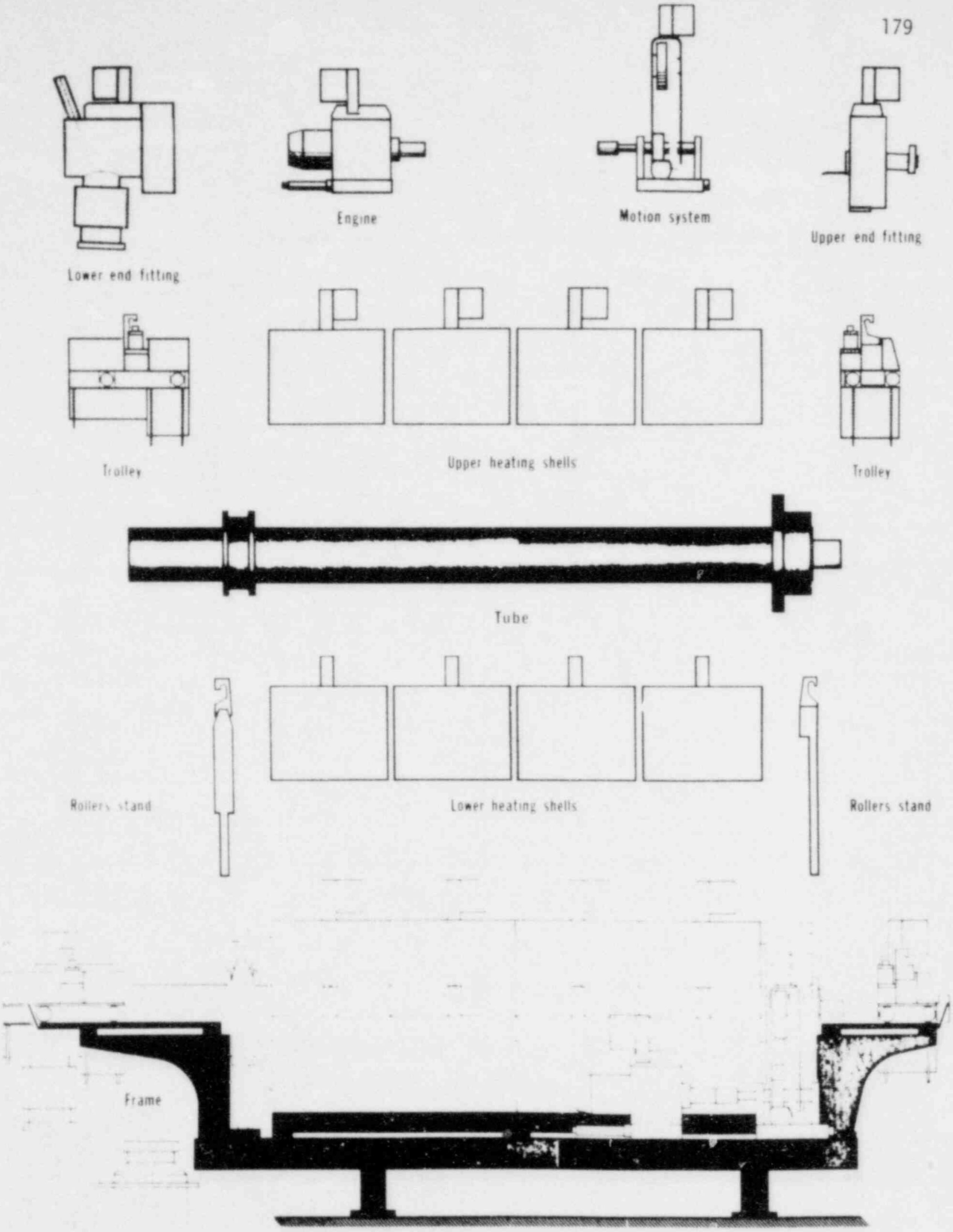


FIG:4. CALCINER DISMANTLING PRINCIPLE

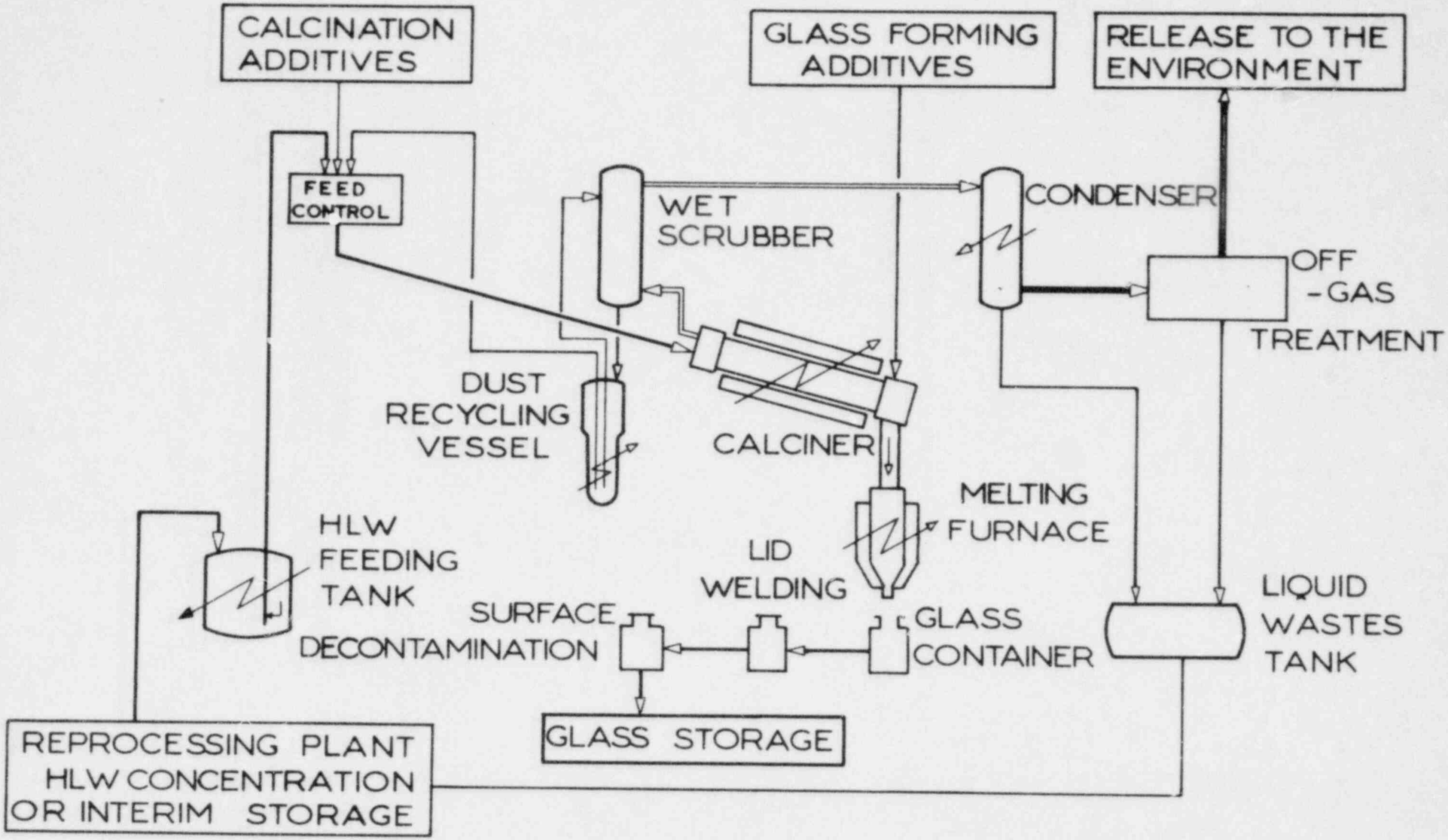
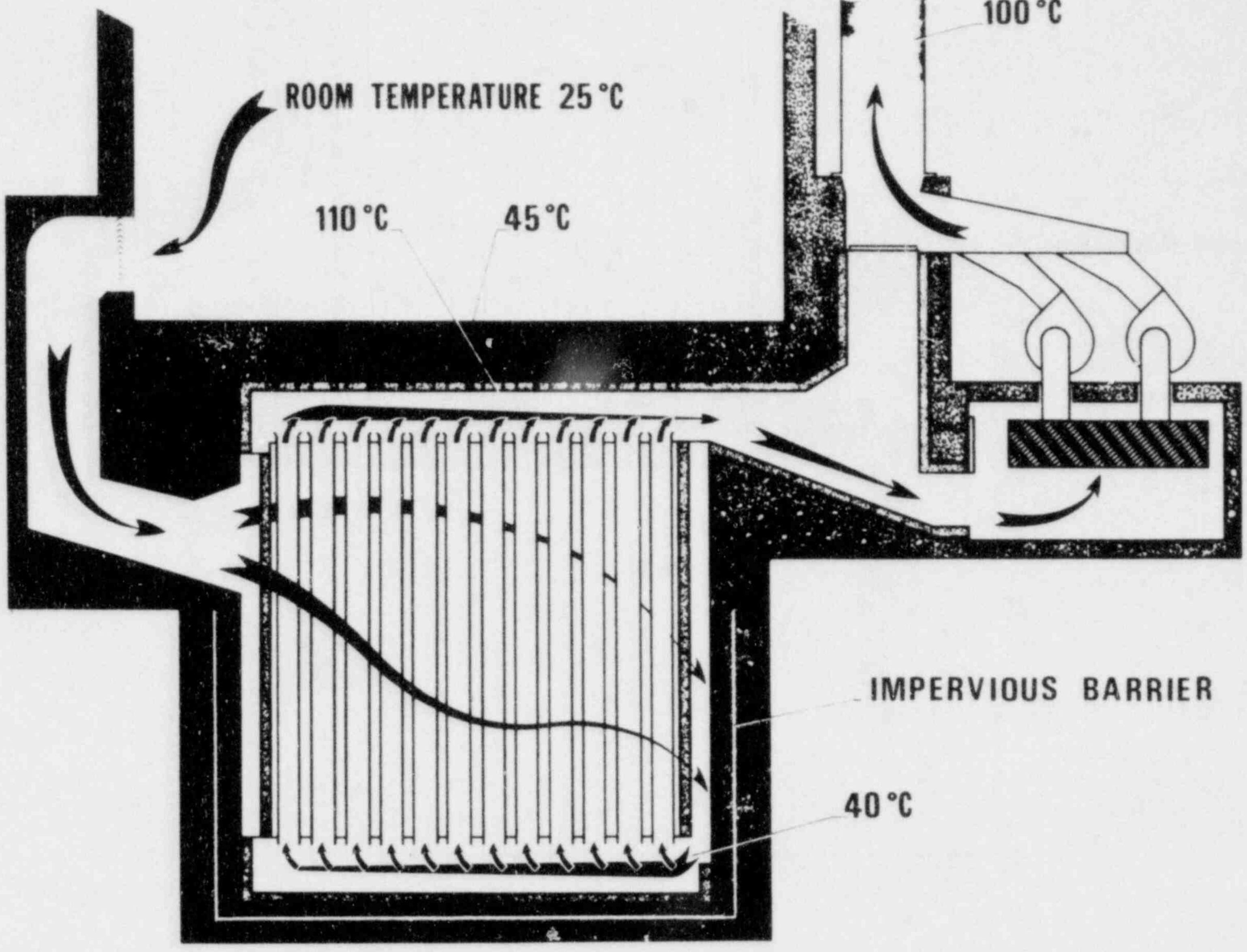


FIG.5 MARCOULE VITRIFICATION FACILITY

FIG. 6 AVM GLASS STORAGE

FORCED AIR COOLING



NATURAL CONVECTION AIR COOLING

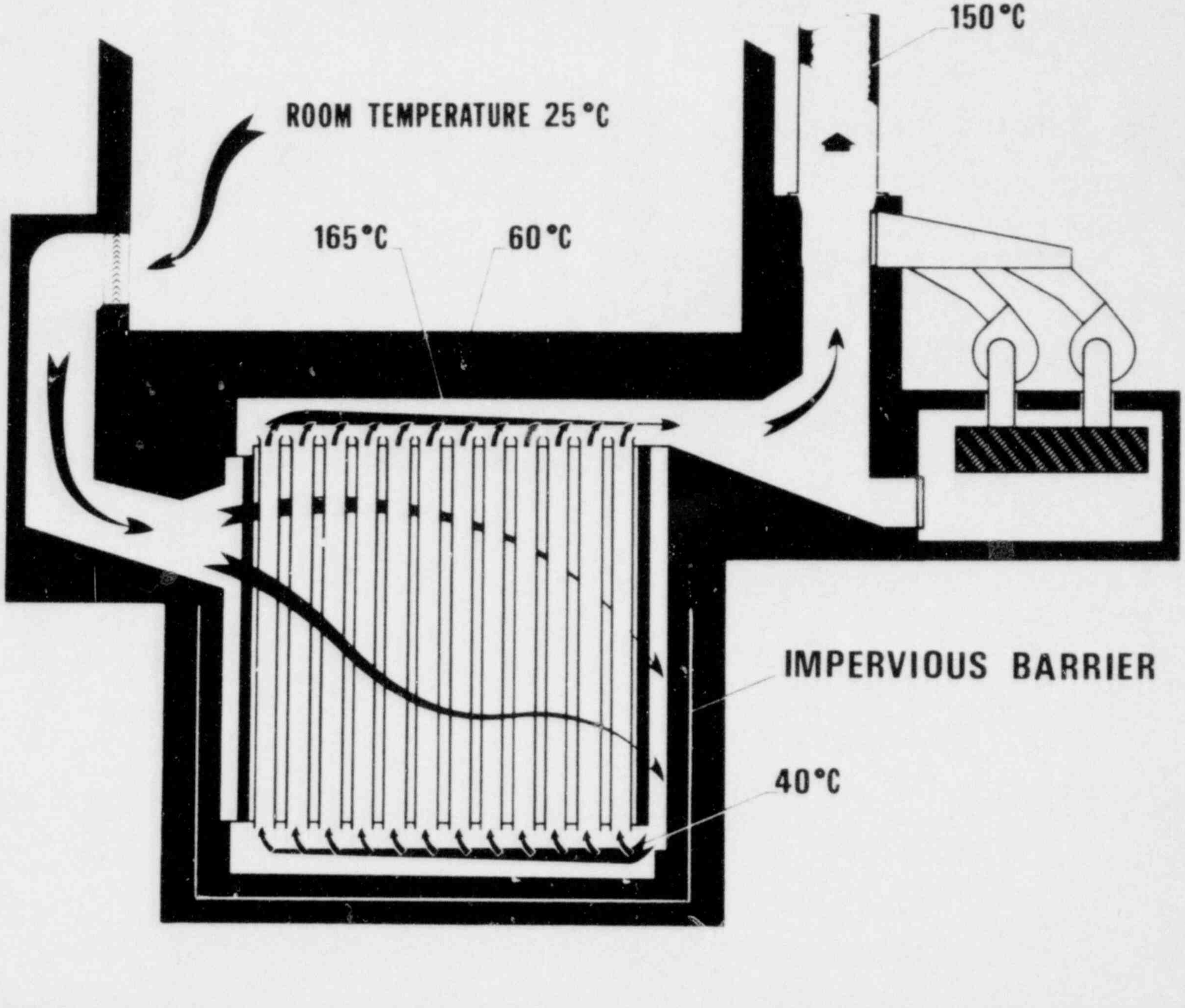


FIG. 7 AVM GLASS STORAGE

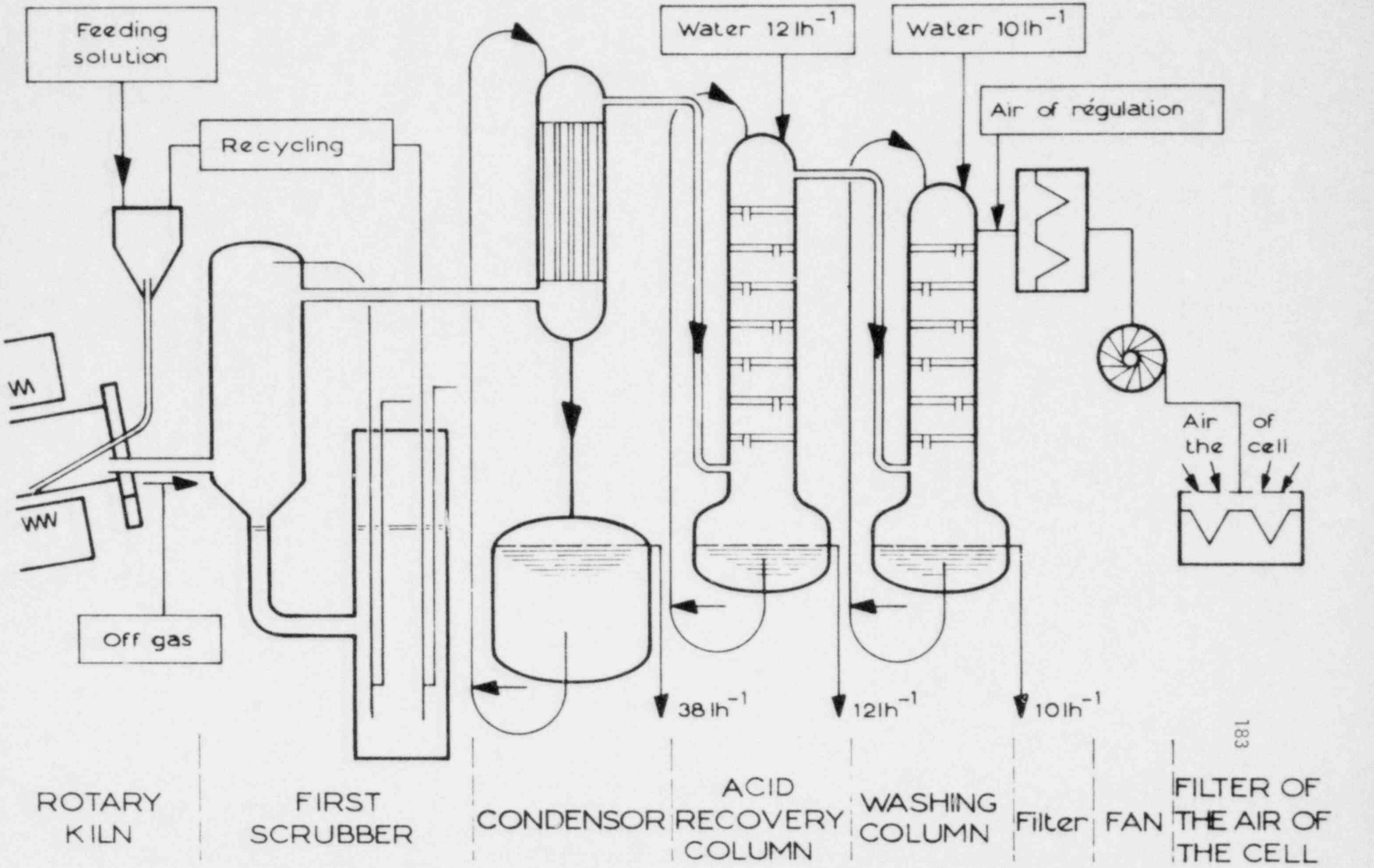
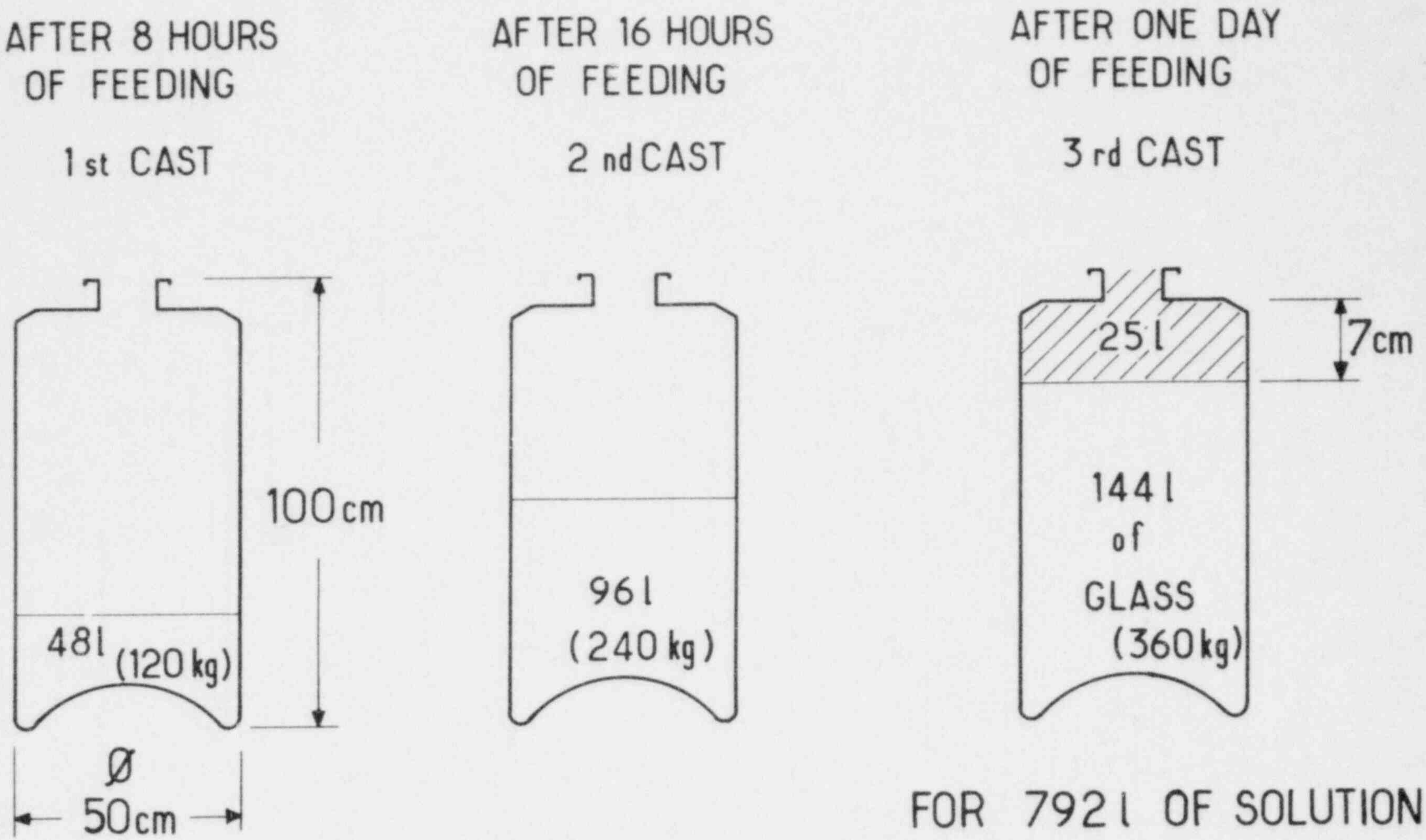


Fig:8_OFF GAS TREATMENT OF THE A.V.M.



FACTOR OF REDUCTION OF THE VOLUME
792 / 144 = 5.5

FIG. 9 FILLING OF THE AVM CONTAINER

Vitrification of sicral G solution (feeding rate 33 l h^{-1})

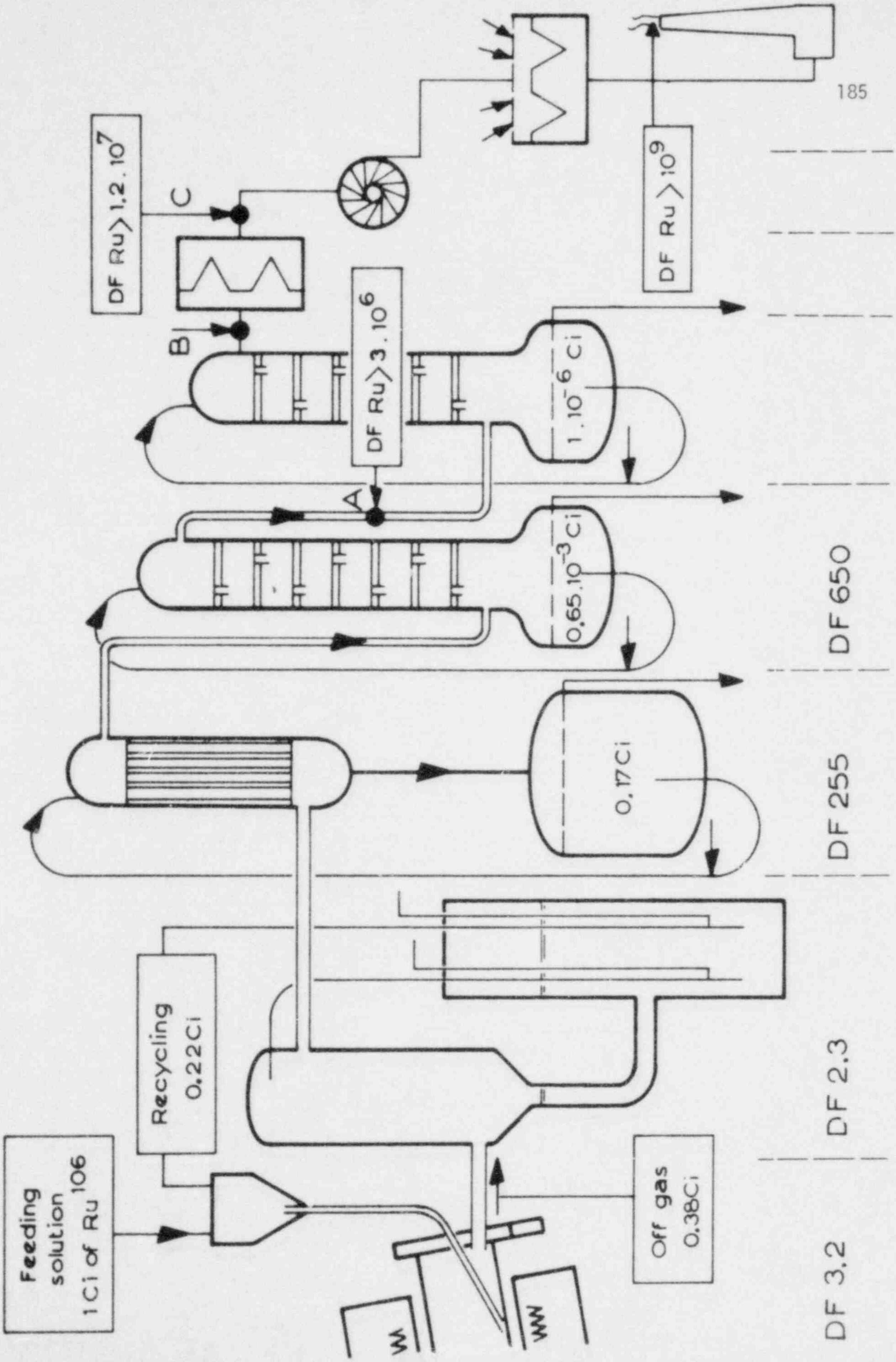


Fig:10_ Efficiency of the off gas treatment for the Ru^{106}

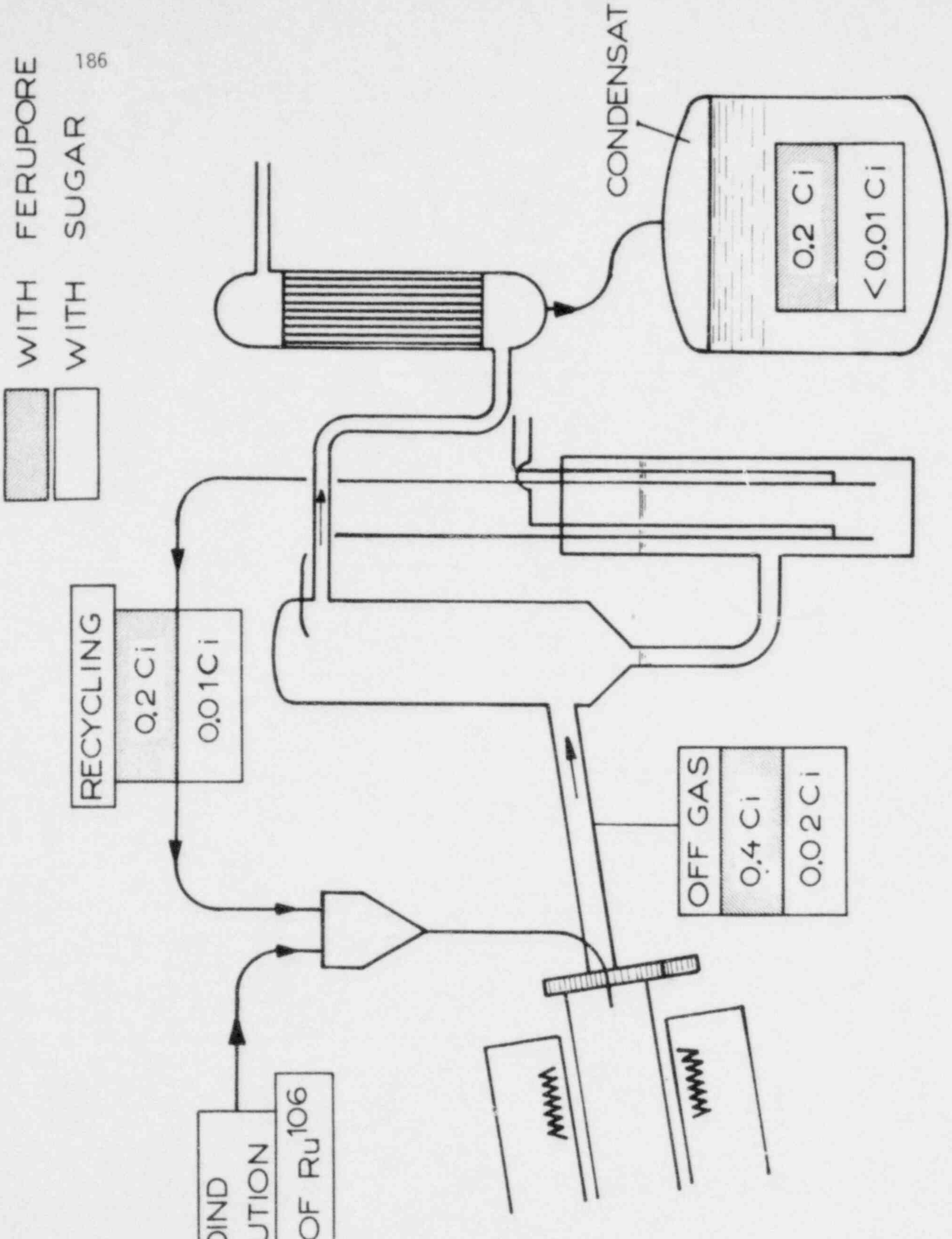


FIG. 11 EFFECT OF THE ADDITION OF SUGAR ON THE Ru VOLATILITY

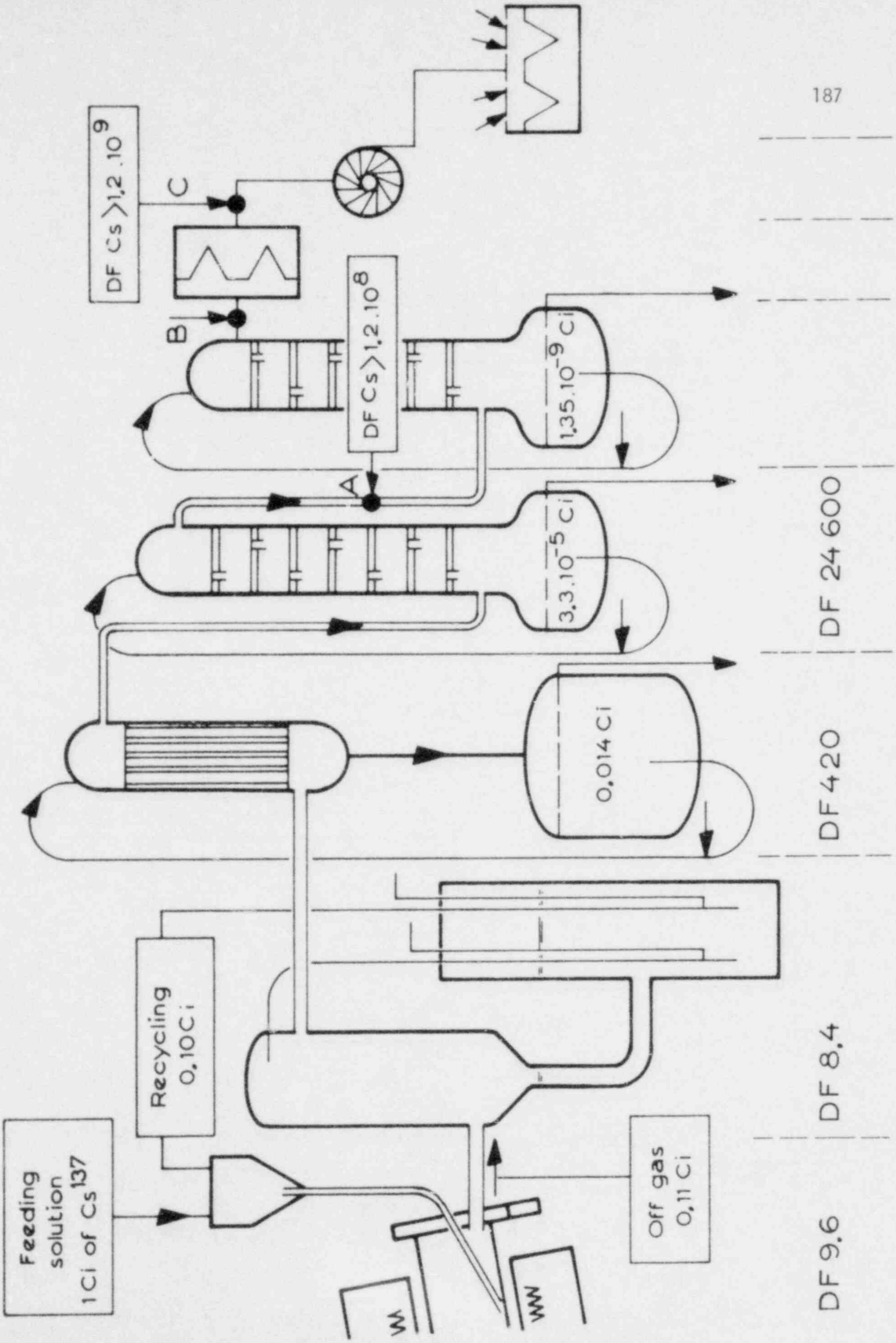


Fig:12 - Efficiency of the off gas treatment for the Cs^{137}

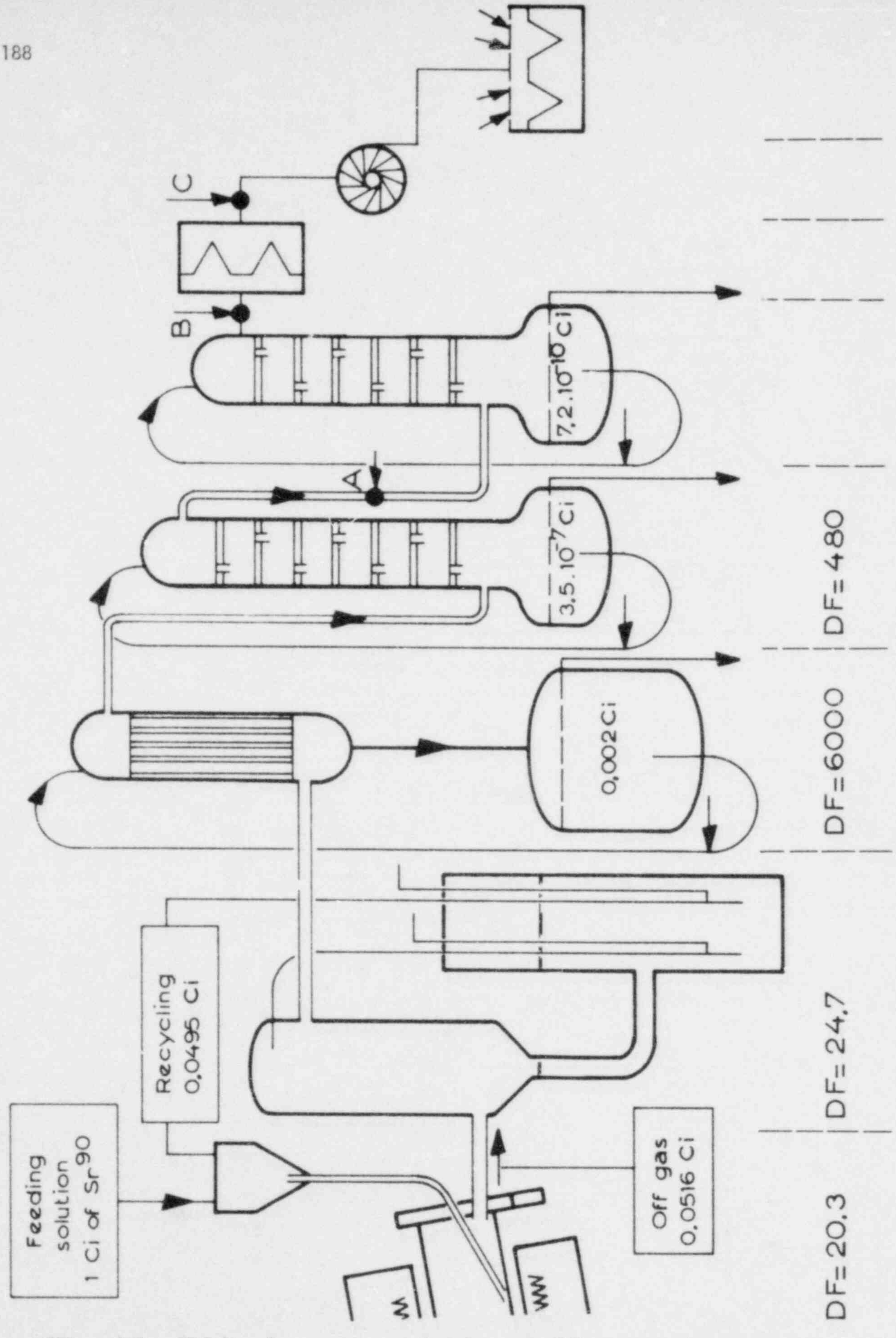


Fig:13. Efficiency of the off gas treatment for the Sr^{90}

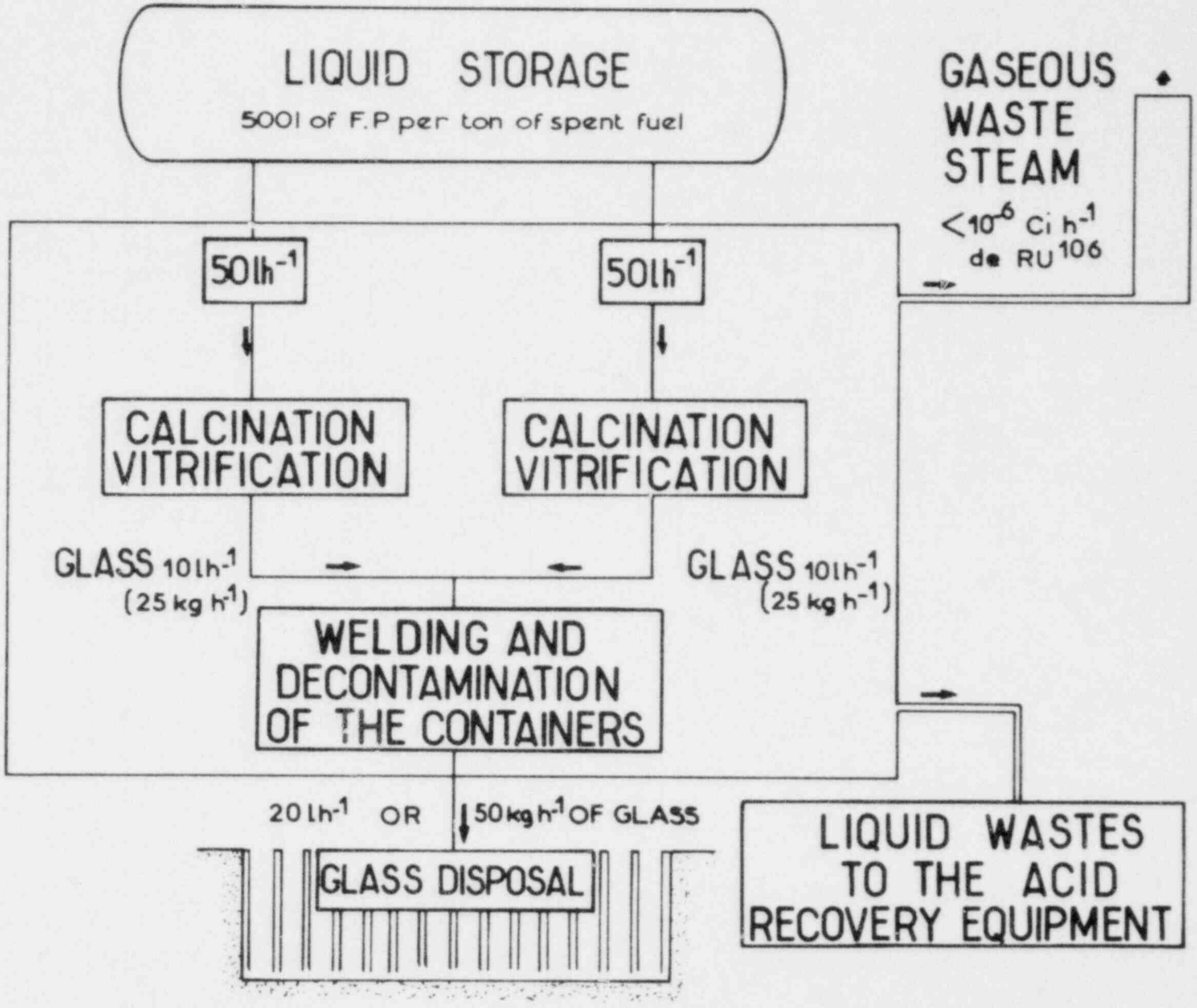


FIG. 14 DIAGRAM OF "LA HAGUE" VITRIFICATION PLANT (UP3 800 t/year)

Table 1 : CHARACTERISTICS OF MARCOULE HLW

		Commercial GG spent fuels	Military GG spent fuels	M.T.R. spent fuels
Burn up		4000 to 5000 MWd/t	1000 to 1200 MWd/t	500 MWd/Kg
Chemical composition (g/l)	F.P.	35 to 40	20 to 25	very low
	U	2.5 to 3.5	1.5 to 2.5	very low
	Np	$\simeq$ 0.2	$\simeq$ 0.1	very low
	Pu	$\simeq$ 0.02	$\simeq$ 0.02	very low
	Al	8 to 12	30 to 35	81
	Cr	$\simeq$ 0.4	$\simeq$ 1.5	$<$ 0.5
	Fe	6 to 10	15 to 17	0.5 to 2
	Ni	$\simeq$ 0.3	$\simeq$ 1	$<$ 0.5
	Na	4 to 6	19 to 23	1 to 3
	F	--	$\simeq$ 8	$\simeq$ 12
	Mg	2 to 3	4 to 5	--
Acidity		1.0 M	2.0 M	- 1.8 M (depleted)
Specific activity after 2 years cooling time (Ci/l)		1600 to 1700	500 to 1000	low
Specific power after 2 years cooling time (W/l)		4 to 5	2 to 3	low
Concentration (l/t)		$\simeq$ 100	30 to 40	12 000

Table 2 : CHARACTERISTICS OF MARCOULE GLASSES

		Commercial GG spent fuels	Military GG spent fuels	M.T.R. spent fuels
Example of composition (Weight %)	SiO_2	42.5	40.0	37.0
	Al_2O_3	8.5	13.0	23.5
	B_2O_3	17.5	16.0	16.5
	Na_2O	14.0	17.0	19.5
	MgO	1.0	2.0	-
	Fe_2O_3	1.6	5.0	0.2
	F	1.4	2.0	1.8
	$NiO+CrO_3$	0.5	1.0	0.2
	FP oxides	13.0	4.0	1.3
Current volume reduction (related to the concentrated liquid)		7.0	5.4	3.5
Volume of glass per ton of fuel		13 to 15 litres	5 to 6 litres	3.4 m^3
Specific gravity of the glass		2.50	2.61	2.43
Viscosity at 1100° (Po)		150	100	430
Thermal conductivity at 100° (W/m.°)		1.25	1.25	1.25
Range of the leaching rate (1) ($g/cm^2/d$)		$10^{-7}/10^{-6}$	$10^{-7}/10^{-6}$	$10^{-7}/10^{-6}$

(1) Leaching operated at room temperature with tap water

TEST WITH SIMULATED SOLUTION	WORKING TIME	VOLUME OF SOLUTION TREATED	WEIGHT OF GLASS	NUMBER OF GLASS CONTAINERS FILLED
Military GG Spent fuels (low burn up)	365 h	10.0 m^3	5.0 t	15
M.T.R Spent fuels	231 h	6.6 m^3	3.25 t	10
Commercial GG Spent fuels (high burn up)	52 h	1.5 m^3	0.55 t	2
TOTAL	648 h	18.1 m^3	8.8 t	27

TABLE 3 : COLD TEST OF THE AVM PLANT

		WORKING TIME	VOLUME OF SOLUTION TREATED	WEIGHT OF GLASS	NUMBER OF GLASS CONTAINERS FILLED
FIRST RUN	COLD PERIOD	97 h	2.4 m^3	1.15 t	3
	HOT PERIOD	649 h	19.2 m^3	8.96 t	28
SECOND PERIOD		994 h	31.0 m^3	14.44 t	42
TOTAL WORKING TIME		1643 h	50.2 m^3 *	23.4 t	70

* Which are generated by the reprocessing of 1400 tons of uranium spent fuels

TABLE 4 : FIRST AND SECOND HOT RUNS OF A.V.M.

	% OF THE ELEMENTS				
	ESCAPED FROM THE CALCINER	RECYCLED IN THE CALCINER	IN THE CONDENSATE	IN THE ACID RECOVERY COLUMN	IN THE WASHING COLUMN
^{106}Ru	38.7	22	16.7	0.07	10^{-4}
^{137}Cs	11.5	10.1	1.4	$3.3\ 10^{-3}$	$1.3\ 10^{-7}$
^{144}Ce	5.9	4	1.9	$0.4\ 10^{-3}$	$0.5\ 10^{-5}$
^{40}Sr	5.2	5	0.2	$3\ 10^{-5}$	$0.7\ 10^{-7}$

BACK TO THE FP CONCENTRATION
AND VITRIFICATION

TABLE 5 : EFFICIENCY OF THE OFF GAS TREATMENT
RESULTS OF THE A.V.M FIRST RUN

Discussion Following

LARGE-SCALE WASTE GLASS PRODUCTION

Presented by Claude Sombret

Thomas Cochran - Natural Resources Defense Council
Question:
We had heard rumors. I do not know if these are true or not. I would like for you to comment on the validity of them. In the early hot tests that you ran you were experiencing difficulty with the glass fracturing when it was cooled down. In your talk you did not comment on the analysis of the hot glass after the vitrification process. Would you comment on observations you have made on that and whether or not you do have fractures?

Sombret
Response:
I must confess we did not have the possibility of taking samples of the hot glass and we did not have any idea of the state of the glass inside the container either. This is not a large problem, because this is our defense waste. The main problem for us in France is commercial wastes generated by the reprocessing of LWR reactors. We have in design now the AVM vitrification plant. In that plant we shall manage to get some samples of glass in order to perform chemical analyses and also to have a device to check the tightness of the containers. But we can imagine the state of the glass in the container by performing some cold (non-radioactive) tests under the same thermal conditions.

Cochran
Question:
But you have not looked at any of the hot glass?

Sombret
Response:
Not the hot glass, no. We have already performed simulated cold tests.

Cochran
Question:
How do you plan to handle very high burn-up fuels? I notice you only went to 400 megawatt days per metric ton, and yet the light water reactors are planning to move up towards 50,000.

Sombret
Response:
We hope to build an AVM plant in 1982 or 83. We hope it will be in operation in 1984 or '85.

Cochran
Question:
For the high burn-up fuels, do you plan to dilute them by another factor of 10? I speak in terms of the designs that the U.S. light-water reactor program uses.

Sombret
Response:
Yes, we use exactly the same, because we use the American system in France. So we plan to use what you saw in the picture which depicted the diagram related to the LWR plant. In France, we have two reprocessing plants. The one which will be used for reprocessing of the LWR waste is located in La Hague. Today, presently, we have in La Hague a facility which is designed only for 400 tons per year. And in the future we will have two other plants. One which is devoted to 800 tons and another one for 800 tons also.

Cochran
Question:
That was not my question. My question was when you go to higher burn-up by a factor of 10, do you, in order to meet your thermal loading limitations, plan to dilute that waste by a factor of 10?

Sombret
Response:
Yes, in the picture I showed you, the maximum specific power of the glass will be 35 to 40 watts per liter. We can cope with the thermal release by cooling the glass containers by air. But we could imagine cooling the glass with water, it is not impossible. Formerly, we had in mind a glass containing maybe 20% of fission product oxide, which would give a very high specific power. In that case, that maximum power could rise to maybe 80 or 90 watts per liter of glass. In that way it would be necessary to cool by water, but if we use only 12, 13, or 14 percent of fission product oxides in the glass we could solve the cooling problem with air only.

Donald Lorenzo - Oak Ridge National Laboratory
Question:
I was wondering if you would explain a bit more why fluorine appears in some of your waste, and what effect it has had on your glass system and the product glass?

Sombret
Response:
The fluorine is used in Marcoule, not in La Hague. It is a process specific to Marcoule. It is used to avoid foaming on the interface of liquid/liquid separation in the reprocessing of the spent fuels. Therefore, in order to avoid corrosion of the material we add aluminum

to complex the excess of fluorine. We have a lot of aluminum and fluorine in the waste, but the amount of fluorine is not very high, and so the content of fluorine is below 1.5 percent. You know the well-known effect of fluorine in glass: the first effect is to decrease the viscosity of the glass. This is not a problem for us because we like to allow viscosity in order to transfer the glass very easily from the glass melting furnace to the container. We want to have less than 600 poises at 1100 degrees C , which is a maximum value for our process. So if we have fluorine, this is not a problem from that standpoint. But the other well-known effect of fluorine upon the vitreous structure, is to give rise to devitrification, especially in the form of sodium flourate. But the quantity of fluorine is not sufficient to produce this type of crystal. We have carried out some tests, leaching tests in our leaching cell, and there is no effect from fluorine on the leachability of the glasses.

Lorenzo
Question:
The aluminum adequately complexes the fluorine so you do not see any corrosive effects in your off-gas system, calciner or melter?

Sombret
Response:
That is correct.

Barry Naft - NUS Corporation
Question:
Could you comment on what specific quality control or process control procedures you use to meet your glass specifications?

Sombret
Response:
This is a good question. The specific composition of the glass has been set up in a laboratory, of course, so we need to have the desired composition of the final glass. The first thing, which is very difficult, is to know the chemical composition of the liquid. You know how people in charge of management of fission product solutions are. Sometimes they make the transfer of the liquid from a storage tank to another one. So it is very difficult to know even the average value of the chemical in that vessel. But this is the reason for which we transfer the liquid by batches of 10 cubic meters in AVM and we perform chemical analysis from this liquid. Of course, we can not change the composition of the raw material, because we order the raw materials in quantities of tons. We then address the chemical composition of the liquid stored in the AVM tanks. Of course, if there is a lack of sodium we add a little bit of sodium nitrate and so on in order to have the right composition we expected. By the way, we control the composition of raw material and we weigh the glass during the casting; they are the only way we have to control the specific quality of the glass.

SURFACE LEACHING OF GLASSES AND GLASS-CERAMICS

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Department of Materials Science and Engineering
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Gainesville, Florida 32611

Abstract

An experimental approach is presented which enables one to predict the stability of glass and glass-ceramic waste forms for long periods of time. The method is based upon a theoretical correlation of changes in thickness of leached layers with given changes in ratio of surface area (SA) exposed to a specific solution volume (V). The validity of this method is established by comparing results for a range of silicate glass compositions with varying $SiO_2/M_2O + MO$ ratios with measurements on 200, 300, 400 and 1700 year old buried glasses and the weathering of various geologic silicates. The effect of crystallization on leaching is examined by comparing rates of attack on polycrystalline and glassy materials of equivalent compositions. Effects of surface passivating agents on slowing down leaching mechanisms are related to overpack design and selection of storage location. Results of the above variables on leaching are applied to understanding the behavior of a BPNL zinc-boro-silicate glass (72-68(PW-4b-7(2.9)73-1) with simulated waste loadings.

Introduction

The primary objective of this paper is to describe where we stand with respect to developing a scientific methodology which will enable the long term prediction of the leaching of a nuclear waste form in contact with water and the geologic storage environment.

Leaching is a primary factor in establishing long term stability. The results of leaching studies of nuclear waste storage forms are summarized in the following section. Because of large variations in experimental procedures used in leaching studies, scientific comparisons are difficult. For example, various laboratories have used either powders, grains, or bulk surfaces in obtaining data. The aqueous media has been changed at various sequences for analysis. Various temperatures, pressures, water quality, and duration of experiments are reported. Results are often based upon weight loss or single ionic tracers. Variations in the heterogeneity of samples have often been present and are seldom reported. Likewise comparison of leach rates under hydrothermal conditions with data from low temperature exposures may not be valid and the ratio of surface area of sample to the volume of reaction solution often is not described.

Thus, only a few generalizations from the earlier literature should be emphasized. Leach rates reported for room temperatures vary from 10^{-4} g/cm^{2}d to 10^{-8} g/cm^{2}d depending upon waste form and method of measurement. Leach rates increase rapidly with temperature and decrease with time; the mobile species Cs and Sr have the highest leach rates; actinides have lower leach rates; and hydrothermal conditions tend to alter surface reaction mechanisms and leach rates.

The introduction of new instrumental analytical approaches makes possible the development of a scientific methodology for long range prediction of leaching. Neutron activation studies recently reported by Flynn (1) show that release of individual ionic species can be followed at very low concentrations, and the ion beam spectrochemical analysis of White and co-workers (2) show that chemical profiles of ionic species can be mapped on the sample surface. Data shown in the bulk of this paper will also show that Auger electron spectroscopy, SIMS, infrared reflection spectroscopy, and SEM-EDXA analysis together with solution analysis can provide the data base we need to achieve long range predictive relationships.

Previous Leaching Studies

The leachability of radionuclides from the different nuclear waste forms is of extreme importance in the determination of the suitability of the chosen form of containment. A widely used method of obtaining leach rates involves the use of a Soxhlet apparatus with a continuous reflux of distilled water. The leach or corrosion rates of various materials are compared in Fig. 1 which shows that BPNL 72-68 borosilicate waste glass composition (3) is similar to durability to other stable materials. Cesium concentrations determined by this method and converted to a bulk leach rate show that over a period of one year, the leach rates dropped nearly an order of magnitude from 10^{-6} g/cm^{2}d to 10^{-7} g/cm^{2}d. BPNL 72-68 which has been devitrified at 700°C showed an increase in Soxhlet leach rate of nearly an order of magnitude.

Another BPNL borosilicate glass composition, 76-68, containing 13 wt % fission product oxides was treated with ten fold excess by weight of water in a sealed Au capsule at ∿300°C and ∿300 bar for one to four weeks (4). The pressure and temperature were chosen to simulate the upper range of conditions to which the glass might be exposed upon burial in some geological formation. After one week the glass spheroids contained numerous cracks and several areas of discoloration, and after 2-4 weeks the samples had broken into several fragments. Approximately 5 wt % of Cs originally in the glass was in solution after one week and the interior of the Au capsule was covered with crystals of acmite ($NaFeSi_2O_6$) as well as Na-Cs-weeksite $(Na, Cs)_2\ (UO_2)_2\ (SiO_5)_3\cdot 4H_2O$.

In other experiments (4) carried out at high temperature (150°-200°C) and pressure (∿300 bar), simulated calcine was treated under hydrothermal conditions with a shale and a basalt. Cs and Na in the calcine quickly reacted with aluminosilicate minerals in the rocks to produce Na-pollucite, $(Cs, Na)\ AlSi_2O_6\cdot xH_2O$. This is a desirable reaction since the Cs is fixed in a form thermodynamically stable with its environment.

De and co-workers (6) prepared several borosilicate glasses containing 15-60 wt % fission products. A few of these glasses were melted, crystallized and the product reduced to a powder (grain size 0.0315-0.05 cm). Two grams of the powder was boiled in distilled water for one hour and the loss of alkalies from the glass determined by titration. The leaching rates were found to be 8-12

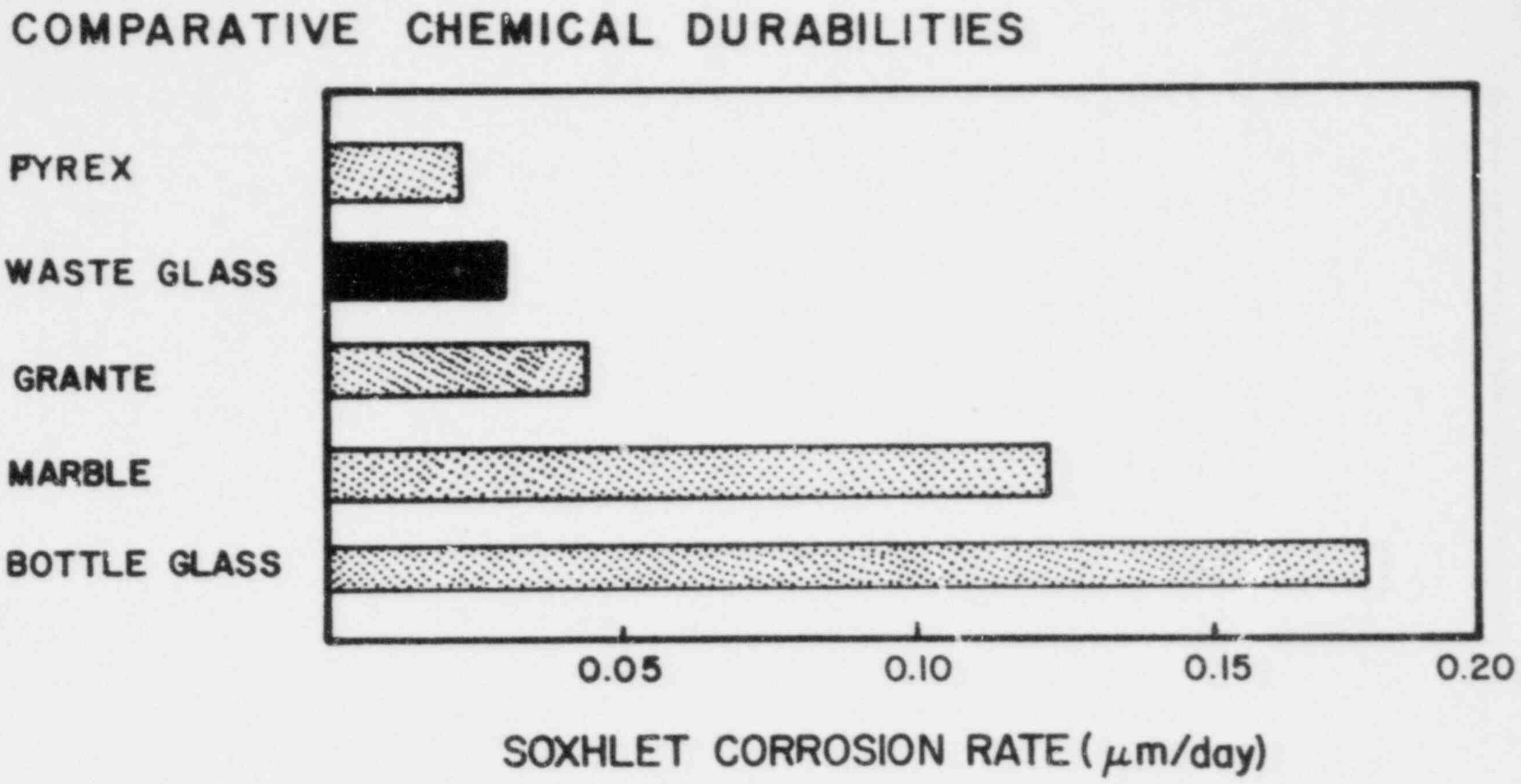


Fig. 1. Comparison of corrosion rates of waste glass and other durable materials in a 99°C, distilled water soxhlet test (13).

μg/cm^{2}d and did not vary drastically from their glass counterpart which had leaching rates 3-10 μg/cm^{2}d. SEM investigations showed preferential leaching in the residual glass phase in the glass-ceramic, while the large pollucite crystals which were formed during crystallization remained completely unattacked.

Soxhlet extraction of a 50 wt % waste loading of a quartz-calcine mixture was in the range 5-20 wt % which is unacceptable (7). Addition of a small amount of glass frit allowed incorporation of 20-30 wt % waste loading which led to reduced leaching. One particular composition (HP-41) showed only 1-1.4% weight loss after 72 hours of Soxhlet extraction. The concentration of Cs in the extracted solution was 6 μg/ml in 300 ml of leachant (this is equivalent to 6-9% of the Cs in the sample). The test was continued for 10 days after which time 17% of Cs in the specimen was leached into solution. After 3 and 10 days leaching, the crystalline phase showed no difference from the unleached specimen. The X-ray diffractogram of the 3 day leached specimen gave indications of the presence of cristobalite which is the residue remaining after leaching of Cs from the Cs-silicate glass.

Watson et al. (8) have developed a method for incorporating high level liquid wastes in a nepheline syenite glass. A laboratory study of leaching rates from blocks of the glass proved to be satisfactory and was therefore extended to an in-field study (9-13). A burial site was chosen below the water table in a sandy permeable soil of pH 6, a mean temperature of 6°C and a total solids content of 30 ppm (Fe 5 ppm; Al 5 ppm; Ca 3 ppm; SiO_2 10 ppm; with lesser amounts of Na, K and Mg). Relatively larger amounts of radioactivity as Sr^{90} was released the first year, but since then the amount leached has levelled. Continuous studies over a period of two years (1961-1963) showed average leaching rates of Sr^{90} of 0.06 μc/d i.e., 1 part in 10^{10} of Sr^{90} present leaving the sample of block glass each day. Assuming no diffusion of Sr^{90} into the glass, calculations showed the mean daily erosion per unit surface area of glass was 6.5×10^{-9} g/cm^{2}d. During the years 1970-1977, the leaching rate of Sr^{90} remained constant at 5×10^{-11} g/cm^{2}d. The concentration of Cs diminished rapidly with distance from the block indicating it was strongly fixed on the soil. In contrast, the concentration of Sr was high close to the blocks, diminished along a 5.5 m path, and rose to a peak concentration at 7.3 m. Beyond this, the Sr concentration decreased until the front was reached at 11.8 m. This suggests that Sr was only temporarily held on the soil and was eluted by the passage of ground water containing reduced concentrations of Sr.

Soxhlet leach results from a titanate ceramic and zinc borosilicate glasses studied at Sandia Laboratories (14) showed the former to be the most durable. After three months of extracting at 95°C, there was no detectable Cs in the leachant. After three weeks there was no detectable Sr, but in the second month an appreciable amount of Sr appeared and by the third month the amount of Sr leached declined to only 2 μg/g. No explanation was offered for this unusual behavior.

A crystalline ceramic prepared by casting a melt of ortho-and pryophosphates showed increased water leachability of 10-100 times that of high level waste borosilicate glasses (15). In another borosilicate composition, Cs and Sr were found to leach at similar rates from the as-formed glass while leach rates of both were increased ten fold by devitrification (16). The data were obtained using IAEA suggested methods (17).

A high level waste supercalcine (72-2) formulated by McCarthy (18), was prepared by firing at 1110°C for 1 hr and subjected to Soxhlet leaching. The product was seen to undergo strong physical weathering as well as dissolution. A small amount of clay was added to a batch of 72-2 before cold pressing and firing to give a product with a six fold decreased leachability. If the same formulation, without clay, was prepared by hot pressing, the Soxhlet leachability was even less than high level waste glasses.

Moore et al. (19) have prepared a grout consisting of Portland cement, fly ash, Attapulgite -150 clay, Grundite clay and delta gluconolactone and incorporated simulated nuclear wastes. Leach studies using the method prepared by IAEA (17) or a modification of that method, showed that the cumulative fraction of Cs leached as a function of time was significantly dependent on the sampling frequency. Curing time of the grout also had a marked effect on the cumulative fraction of a leached species--longer curing times led to a decrease in the fraction of Cs leached. In addition, leaching of Cs was greater if curing was carried out in a dry atmosphere as opposed to a humid one. For all specimens studied the cumulative fraction leached followed the order Cs > Sr > Cm > Pu, and the amount of each species leached found to be dependent on the leachant composition in the order: distilled water > tap water > grout water.

A comparison of the leaching results obtained for grout to previous work relating to the leaching from glasses (20) showed that calcines have the highest and glasses the lowest leach rates for alkali and alkaline-earth elements (see Figs 2 and 3). The comparison shows that bitumens, cements and grouts can have leach rates as low as those for glasses (10^{-4} - 10^{-7} g/cm^{2}d for Cs and Sr; 10^{-6} - 10^{-9} g/cm^{2}d for rare earth and actinide elements). For a given waste product, the leach rates for rare earths and actinides are a factor of $\sim 10^3$ less than for alkali or alkaline-earths. The data obtained for the grouts indicate that the total fraction leached varies with t the square root of time.

In addition to Soxhlet extraction with atomic absorption and emission, neutron activation has recently been used in the study of leach rates (1). Radioactivity was induced in elements of interest in simulated waste forms, and γ-rays and β-rays detected using GeLi detectors or gas proportional counters, respectively. A coupling with radiochemical separation is carried out when necessary. Leach rates of 10^{-9} - 10^{-10} g/cm^{2}d for specific elements can be obtained in one week using a one gram sample. This study showed that different leach rates for several elements for a variety of waste forms as a function of temperature, time and leaching media were observable but not dramatic.

The leaching process in nuclear waste glasses have also been determined indirectly by measuring compositional profiles of different elements in the glass by sputter induced optical emission, also known as ion beam spectrochemical analysis (IBSCA) (2). The use of IBSCA has revealed that Li, Na and K all had identical profiles which suggests a common leaching mechanism. In addition, there was a pile up of Ca and Mg at the surface and very little variation for Si and Al. Since the density of Si and Al apparently remains constant throughout the sample after leaching, it appears that the aluminosilicate layer remains intact during leaching under neutral conditions.

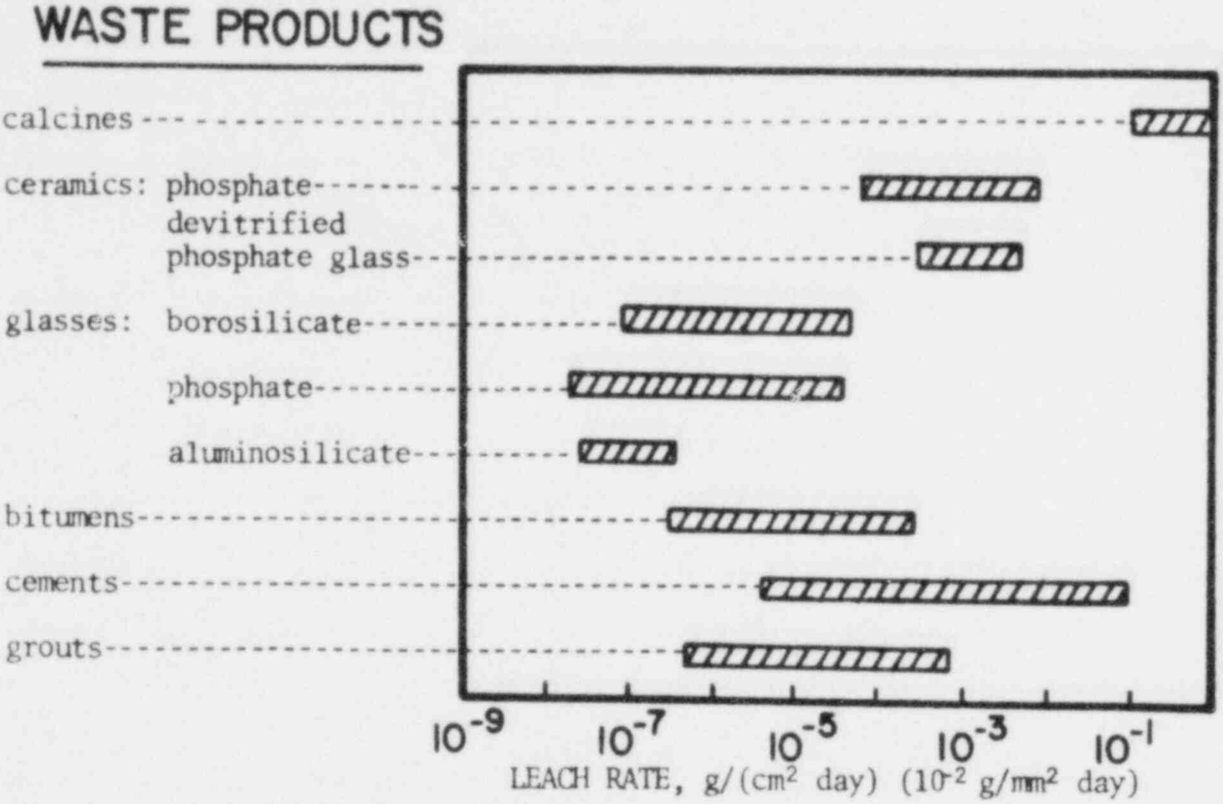


Fig. 2. Comparison of leach rates for alkali and alkaline-earth elements from various waste products (20).

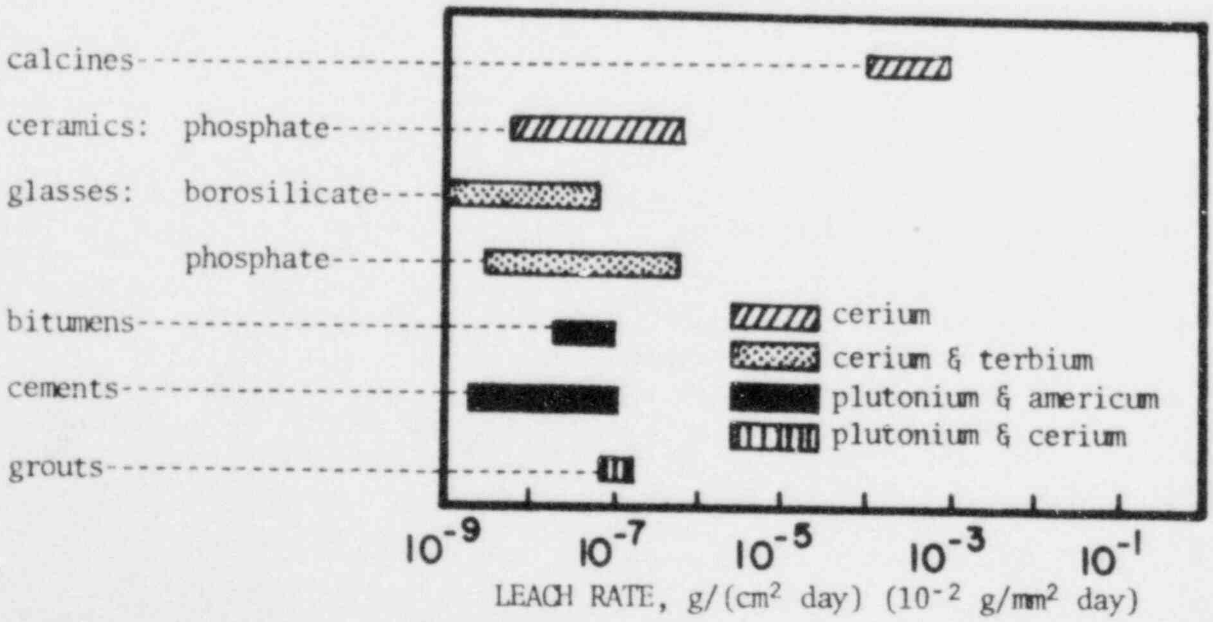


Fig. 3. Comparison of leach rates for rare-earth and actinide elements from various waste products (20).

Determination of the amounts leached from a solid over a long period of time is often carried out by fitting the data to various functions and extrapolating the results (17,19,21). The expressions used are based on mass transport theory which assumes that diffusion through the solid is the only or rate limiting process. These expressions fit leach test data over the midrange of time but for longer times other mechanisms such as dissolution of the matrix or reversible and irreversible chemical reactions are overlooked. An attempt has been made (22) to model the system using mass transport theory which takes into account diffusion as well as one of the following: 1) surface concentration of mobile species which is time dependent, 2) initial concentration of mobile species which is a function of position in the specimen, 3) dissolution and precipitation of mobile species, or 4) dissolution of matrix material.

Numerous other types of materials such as the fresnoite glass-ceramic ($Ba_2TiSi_2O_8$) (23) and a β-spodumene glass ceramic (24) have shown decreased leachability when compared to nuclear waste glass. A synthetic rock, Synroc (25), composed of some or all of hollandite ($BaAl_2Ti_6O_{16}$), cubic zirconia (ZrO_2-Ca, Ti ss), perovskite ($CaTiO_3$), celsian ($BaAl_2Si_2O_8$), "kalsilite" ($KAlSiO_4$) and leucite ($KAlSi_2O_6$ ss) has shown low porosity and high resistance to alteration and leaching in geological environments. This also appears to be superior to borosilicate nuclear waste glass.

A multibarrier means of storage involving vitreous beads (26) or a supercalcine ceramic core (27) in various metal matrices have been examined in distilled water, dry salt and brine solutions. The metal matrix serves as added improved resistance to impact as well as the environment. A different multibarrier approach (28) has been taken by the Swedish nuclear power industry. Unreprocessed fuel is loaded into canisters made of copper. The space between the fuel and the canister walls is filled with lead, and each canister deposited in its own tunnel which is lined with compressed bentonite. When contacted with water the bentonite swells to ten times its own volume and, if constricted, becomes compressed and seals the tunnel.

This summary is by no means a complete survey of the literature but gives an indication of some of the types of materials being considered for nuclear waste storage and the information gathered so far. Interpretation of leach rates is an extremely complex matter because of the many factors involved such as variation of the rates with time and temperature, sample form, preferential leaching of certain elements, flow rate of leachant, and the pH and composition of the leachant. Preliminary studies have shown that leach rates in ground water are greatly decreased from that in deionized water which is commonly used in laboratory experiments. Feasible temperature and pressures used in laboratory corrosion studies are far removed from the actual temperatures and pressure to which the waste glass will be exposed. In addition, the total amount of a species leached from the glass is a function not only of leach rate but also of the surface area which could easily be increased by fracturing due to thermal or mechanical shock.

Another parameter which must be considered is the effect of radiation on the behavior of glasses and other waste forms. Unfortunately, leaching tests are usually carried out independently of irradiation effects. However, irradiation tes with high-level gamma ray irradiation have shown that the effect on the leaching rate from nepheline syenite glass is minimal (12).

A Proposed Method for Long Range Prediction of Leaching of Nuclear Waste Storage Materials

It is clear from the above review that a science based, comparative method of predicting the long term leaching of alternative nuclear waste forms (NWF) is needed. The method being developed in our laboratory is summarized in this section. Scientific evidence being accumulated to make the eventual long term predictions is summarized in subsequent sections of this paper.

Figure 4 is an illustration of the leaching predictive method being developed. The ordinate of the graph represents a leaching index that can be measured quantitatively for a variety of materials. The thickness (d) of a leached surface or the concentration (C_i) of a specific ion leached from a surface are examples of measurable leaching indices. Although weight change is a possible index for leaching studies it is not preferred for several reasons: 1) surface reactions can lead to a sequence of loss and gain in weight due to combinations of solution and reprecipitation from solution onto the surface of a material; 2) the initial weight of many analog materials discussed below is not known; 3) leaching data of radioactive species is more important than overall weight loss.

The abscissa of Fig. 4 is log time and represents the years of storage of a NWF, years of simulated storage condition, or years of burial, etc. of analog materials.

The scientific hypotheses underlying the use of a graphical method for predicting long term leaching behavior of nuclear waste forms are as follows: 1) it is assumed that mechanisms of surface reactions of a given NWF can be related to the mechanisms of surface reactions of other materials of similar or related composition; 2) kinetics equations valid over a range of measured time can be extrapolated to longer times by use of the kinetics constants as long as the mechanisms of surface reactions controlling the kinetics do not change during the extrapolated period; 3) comparisons can be made of predicted extents of leaching of a variety of materials using measured leaching kinetics and the measured leaching indices from equivalent or the same materials removed from long term burial conditions; 4) such comparison studies on "NWF analog materials" provide verifiable evidence that surface reaction mechanisms do not change over long time periods under certain specified conditions of storage; 5) simulations of varied geologic storage conditions of candidate NWF materials can be created in the laboratory or in field trials; 6) leaching indices from the candidate NWF materials and analog materials measured during simulated laboratory or field trial conditions can be compared with the measured indices from the long term burial of the analog materials to obtain "worst case" and "best case" storage acceleration factors; 7) specifications and margins of safety for cumulative radioactivity loss from leaching of NWF's can be based upon the kinetics extrapolations and comparisons with analog materials obtained using hypotheses 1-6.

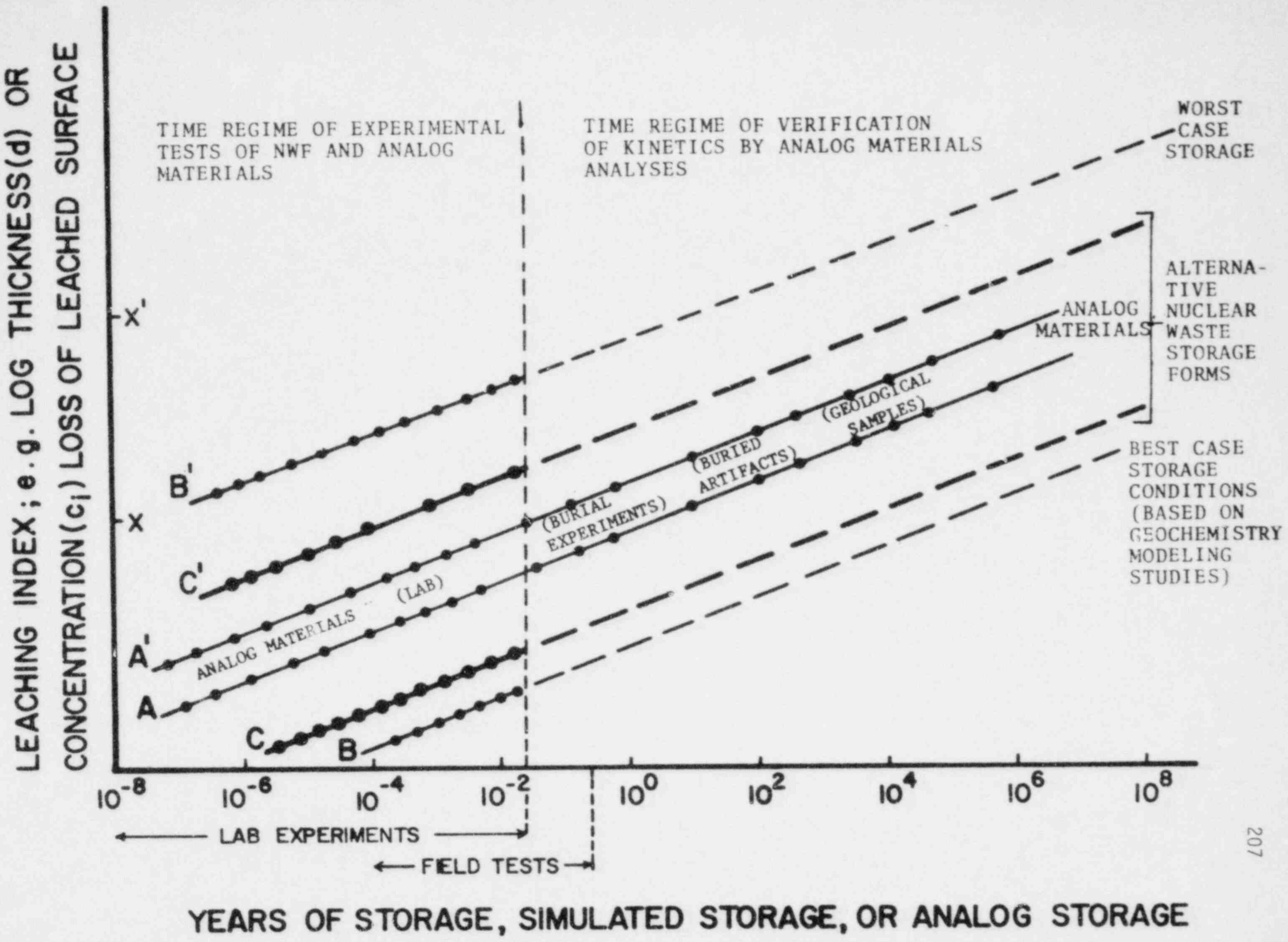


Fig. 4. A methodology for predicting long term stability of nuclear waste storage forms.

Several graphs are presented in Fig. 4 to illustrate the use of the long term predictive method described. The lines in the center of the figure, marked A and A', represent a range of leach rates measured on analog materials. Data points are shown. It is evident from lines A and A' that data points for leach indices of analog materials, such as thickness of leached layers, can be obtained over an enormous range of time. For periods up to 2×10^{-2} years it is very easy to conduct highly controlled laboratory leaching studies. Field tests involving burial in various geologic sites can be conducted realistically for periods of several years. Results obtained from samples acquired from highly accurately dated museum, restoration and archeological locations include a time range from tens of years to approximately 2×10^{3} years. Measurements from geologic field samples with reasonably accurate datings extend from 10^{4} to 10^{6} years.

Therefore, curves A and A' illustrate that for a wide range of compositions of materials the predictions of laboratory kinetics studies conducted from 10^{-8} to 10^{-2} years can be compared with measurements made on the same materials exposed to buried environments for 1 to 10^{6} years. It is obvious that the environments of the buried analog materials are not equivalent to those to be encountered in the long term storage of NWF materials. However, curves B and B' in Fig. 4 illustrate that a range of possible storage conditions anticipated for NWF materials can be simulated in the laboratory. If such storage environment simulations are based upon geochemistry computer modelling studies it is conceivable that "best case" and "worst case" extrema can be investigated with results such as B and B'. The magnitude of difference in leach rates on analog materials observed between low temperature surface burial, non-radioactive conditions (A and A') and the "worst case - best case" conditions that include elevated temperature, radiation, and water chemistry effects, etc. can provide the basis for adjusting the kinetics equations to include various combinations of environmental terms. Confidence in the extrapolation of the "best case - worst case" laboratory data from the analog materials to long times is based upon the scientific kinetics relationships. As long as mechanisms of reactions remain unaltered in the more severe environments, the curves of B-B' remain parallel to those of A-A' and the extrapolations of B-B' are valid. If there is a potential for mechanisms to change under the more severe storage conditions it is assumed that the changes can be induced during the laboratory range of experiments. Our data obtained on glass NWF samples to date, described below, indicates that this assumption appears reasonable.

The final set of comparisons in the methodology involves obtaining laboratory kinetics data on candidate NWF materials under the same non-severe conditions as the analog materials of A-A' and under the simulated severe storage conditions of B-B'. Thus, extrapolations of the laboratory leaching results of the NWF materials, C and C', to long times are directly based upon the comparison of the kinetics relationships between the analog materials and the NWF materials verified by the measurements from the 1 to 10^{6} year buried analog materials.

The concentration of radioactive constituent leached for a given period of time under the environmental condition tested, or the storage condition planned is represented by the ordinate values in Fig. 4. Therefore, it should be possible to specify an acceptable level of cumulative loss of radioactive species from a NWF, i.e., a fixed value on the ordinate based upon biological tolerance levels and projected distribution rates under various storage conditions, and predict the time required for that value to be reached using the intersection of the appropriate kinetics curves of Fig. 4. For example, if distribution rates are projected for a geologic storage site it might be predicted that a leaching loss represented by X on Fig. 4 is acceptable. In such a case the kinetics analysis shows that "best case" response of a given NWF, represented by curve C, would be acceptable for 10^4 years. However, a "worst case" response, C', would not be acceptable beyond 10^{-4} years. Addition of an overpack to adsorb the loss of radioactive species before they could enter the geologic distribution system could well increase the acceptable loss level to a value of X'. In such a case, under "best case" reactions the NWF, curve C, would be acceptable for greater than 10^8 years and even under "worst case" conditions an acceptable response could be predicted for 10^5 years. In this manner the relative merits of alternative geologic storage sites, overpack compositions, multibarrier concepts, alternative nuclear waste forms, and variations in leach rate kinetics for different NWF's can be compared quantitatively. Since it is impossible to test such combinations of variables for other than very short periods of times the confidence in such a predictive approach rests upon the scientific accuracy of the kinetics measurements and relating the kinetics results to the durability of glasses, ceramics, and geologic materials of related compositions that have been buried for long periods of time.

A brief synopsis of some of the experiments being conducted to produce the predictive methodology described above follows. Because of our previous efforts to understand the durability of glasses and the technology potential of glass as a nuclear waste encapsulant the bulk of the following discussion will be devoted to glass. However, the predictive methodology described above and the types of experiments summarized below are relevant to glass, polycrystalline, glass-crystalline, and composite waste forms.

Types of Glass Surfaces

It is vital to recognize that a glass surface is usually markedly different in composition from the bulk. Consequently, the leaching of a glass NWF is largely a function of the surface composition and the rate of change of the surface under a given set of environmental conditions. It is known that surface composition differences can extend many micrometers into the glass. It must be recognized, however, that the surface layers formed on a glass depend upon the bulk composition, processing history, surface roughness, and environmental history including time, temperature, pH, exposure atmosphere, and water chemistry, etc.

Various glass corrosion processes yield several different kinds of glass surfaces that may vary in composition and structure during exposure. All of the surface types obtained during corrosion are summarized in Fig. 5. There are five types of surfaces that are characteristic of a silicate glass at any time in its history (29,30). A type I surface has undergone only a thin, 50 Å surface layer hydration. No significant surface compositional change by either dealkalization of silica network dissolution has occurred and hence the surface composition is nearly the same as the bulk composition. Nearly pure vitreous silica exposed to neutral pH solutions exhibits a Type I surface.

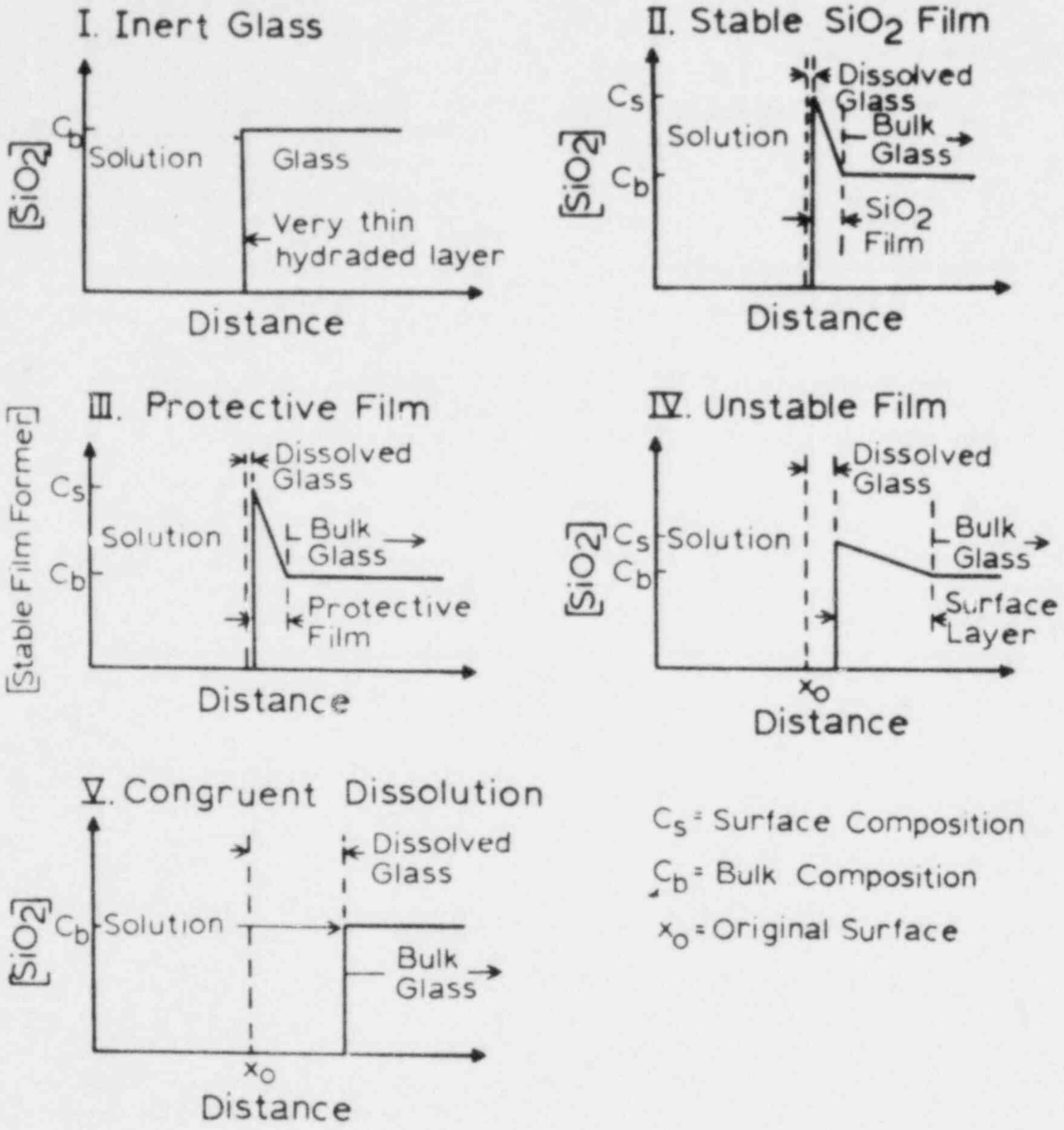


Fig. 5. Five types of surfaces produced during corrosion.

A Type II surface possesses a silica-rich protective film due to selective alkali ion removal. Dealkalization of alkali-alkaline-earth silica glasses with low concentration of alkali results in a Type II surface. A glass with this type of surface is reasonably durable, especially in solutions of pH < 9. The kinetics controlling formation of a Type II surface are $Q = kt^{1/2}$ because the alkali loss mechanism is diffusion controlled (31,32).

Two layers of protective surface films are characteristics of Type III glass surfaces. Adding Al_2O_3 or CaO to a glass composition can result in dual surface layers, such as alumina-silicate or calcia-silicate species on top of a silica-rich layer. Such glasses are very durable in both acid and alkali solutions. These protective films can be produced by dealkalization, surface structural modifications, or precipitation from solutions. Kinetics of formation of Type III surface are also diffusion controlled and a $t^{1/2}$ relationship exists.

Type IV glass surfaces also have a silica-rich film but the silica concentration is insufficient to protect the glass from rapid attack from dealkalization or network dissolution. Binary sodium-silicate or potassium-silicate glasses rich in alkali form Type IV surfaces and have poor durability.

A glass that is undergoing congruent dissolution with equivalent loss of alkali and silica exhibits a Type V surface. Because of the uniform attack, the surface composition of a Type V glass is equivalent to the bulk composition. Thus, there is little difference in the surface SiO_2 compositional profile between a Type V and Type I glass. However, a glass exhibiting Type V behavior is losing considerable quantities of ions into solution. Thus, chemical analysis of the corrosion solution distinguishes the two types. Also, a heterogeneous attack of the surface often results under Type V conditions and is visible by various microscopy or infrared reflection spectroscopy techniques. Silicate glasses exposed to conditions with pH $>$ 9-10 tend towards Type V behavior.

Type IV and Type V glass surface behavior is especially undesirable for nuclear waste encapsulants for two reasons:

1) The kinetics of network dissolution is linear with time, $Q = kt^1$ and therefore more rapid than diffusion controlled processes.

2) All constituents of the glass are released into solution. Since this includes the long half-lived actinides it is an undesirable mode of attack. In contrast the diffusion controlled processes generally result in the loss of the more mobile species such as Cs or Sr from the glasses.

Higher valence ions within the glass structure often tend to concentrate within the silica-rich film formed on the glass surface complexing structurally with Si-O-Si bonds. This behavior results in a Type III protective dual film surface. Such a condition tends to occur for the complex zinc borosilicate nuclear waste encapsulant glass 72-68 developed by BPNL laboratories . Figure 6 shows a compositional profile of the glass surface after hydrothermal corrosion in

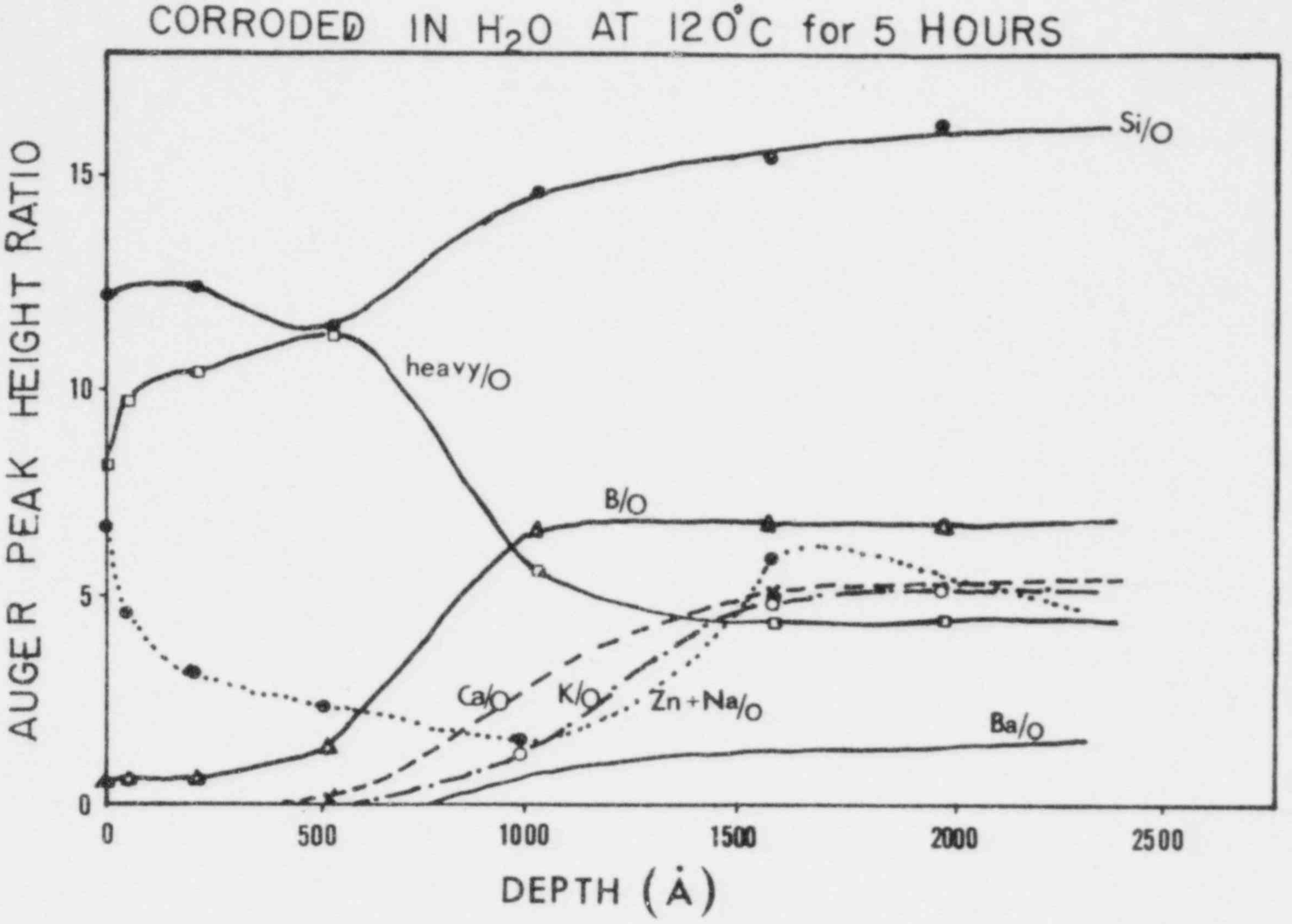


Fig. 6. Depth compositional profile for BPNL glass 72-68(PW-4b-7(2.9)73-1).

water at 120°C for 5 hours at 15 psi. The Ca, K, and Ba ions have been depleted to depths of 500 to 800 Å. The heavy elements, simulating long-lived radioactive constituents have accumulated in a surface layer. As long as this layer continues to exist, the kinetics of diffusion remain slow and the glass remains durable.

Kinetics Transitions

Under certain environmental or projected storage situations, conditions can exist whereby a glass NWF can undergo transition from a protective Type III surface to a rapidly deteriorating Type IV or Type V surface. Static leaching conditions are especially severe in this regard. This is because loss of alkali or alkaline earth species from the glass to an aqueous media occurs by means of hydrogen ion or hydronium ion exchange (33). The net effect is a gradual increase in the OH^- concentration of the static solution and a corresponding increase in solution pH. The progressive increase in solution pH for BPNL glass 72-68 under static leaching conditions at 120°C, 15 psi in distilled water is shown in Fig. 7.

At some value of pH, dependent upon the concentration of network formers in the glass, the protective silica-rich surface film begins to break down and the glass network begins to be attacked, e.g., Type IV and V behavior results. By use of Auger electron spectroscopy-Ar ion milling analyses of surface changes of BPNL glass 72-68 in combination with infrared reflection spectroscopy, it has been shown (34) that the transition pH from $t^{\frac{1}{2}}$ kinetics and diffusion controlled reactions to t^1 kinetics and network dissolution controlled reactions is at pH ∿ 8.5 for BPNL glass 72-68.

That such a transition time exists has now been demonstrated for a wide range of glass compositions (30). Its importance lies in the fact that three parameters must therefore be known for glasses, glass-ceramics, and probably polycrystalline ceramics as well in order to construct long term predictive curves such as in Fig. 4: 1) You must measure the kinetics constant of the diffusion controlled regime over the range of environmental and storage conditions of concern; 2) The kinetics constants for the network dissolution regime must be measured; and 3) The time for transition between $t^{\frac{1}{2}}$ to t^1 must be determined for the conditions of interest.

Kinetics Dependence on Surface Area to Solution Volume (SA/V)

Recent research findings (35) show clearly that a geometric parameter, the ratio of glass surface area exposed to the solution volume in contact with the glass surface ($cm^2/cm^3 = cm^{-1}$), is a primary variable in controlling both reaction kinetics and transition times. This importance is amply illustrated in the (SA/V) dependence of the time changes of pH of BPNL glass 72-68 shown in Fig. 7. The transition from $t^{\frac{1}{2}}$ kinetics, below pH = 8.5, to t^1 kinetics, above pH = 8.5, occurs very rapidly at high (SA/V) ratios and progressively more slowly at low (SA/V) ratios.

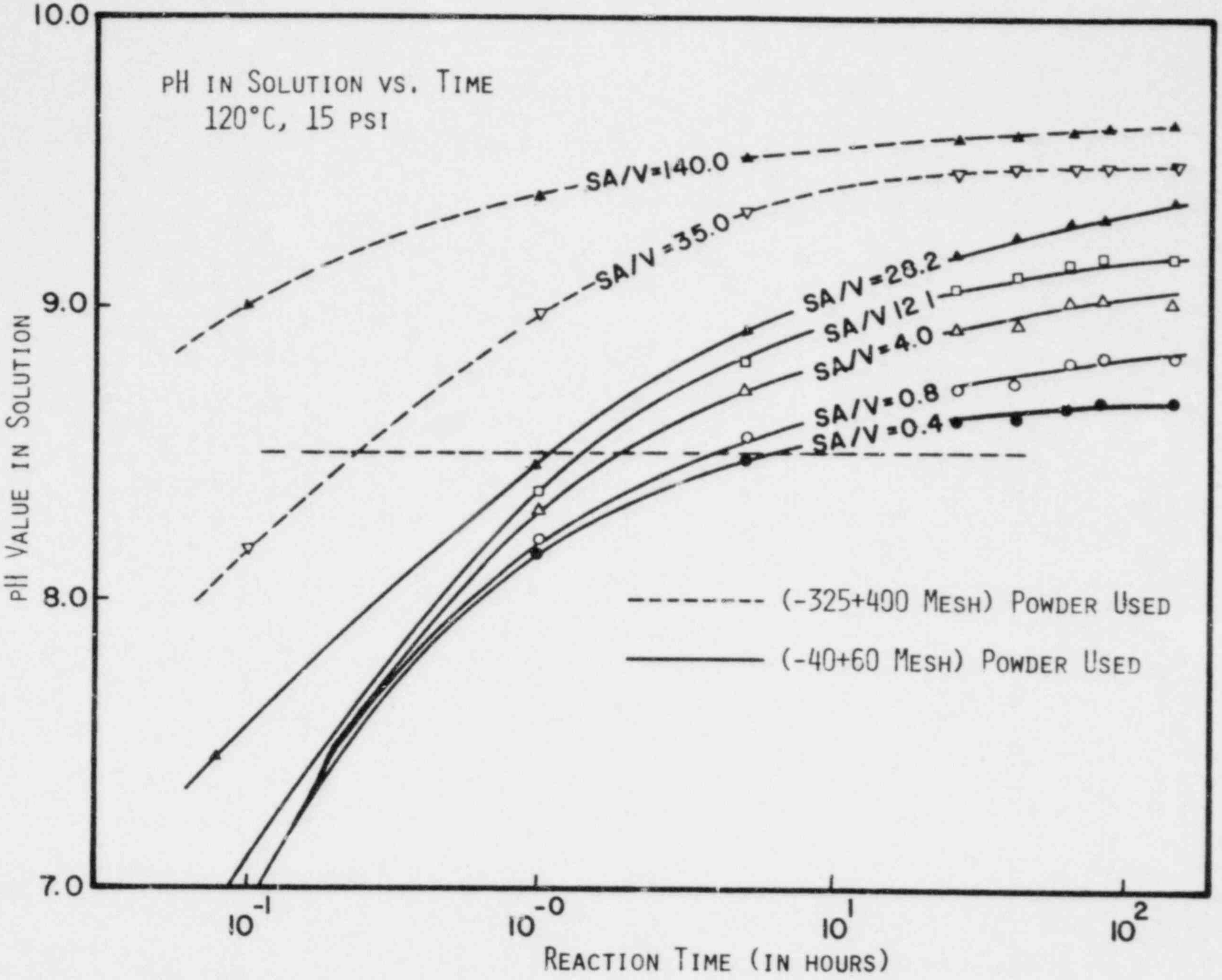


Fig. 7. Solution pH versus exposure time for various surface area-to-solution volume ratios (SA/V).

Thus, increasing the (SA/V) ratio of a static leaching experiment has the highly useful effect of accelerating the transition time without altering reaction mechanisms. Kinetic theory (36) shows that one can plot the logarithm of the time for the kinetics transition as a function of log (SA/V) and obtain a straight line such as shown in Fig. 8. The ordinate on the graph in Fig. 8 represents the time required for the solution in contact with the various NWF to reach a specific pH. This pH corresponds to the time where a changeover in corrosion kinetics occurs and hence is referred to as t_c. The value of pH at which a changeover in kinetics takes place is dependent on several properties including composition and microstructure. In general this pH is between 8.5 and 9.5, but can be measured by monitoring solution ion concentrations as a function of solution pH. The pH at which certain species are in solution in the same ratio as in the glass is the pH at which network dissolution is rate controlling (i.e., $Q \simeq kt^1$). It is assumed that the longer the t^1 kinetics can be suppressed, the more stable the NWF will remain. For a specified (SA/V), higher values of t_c indicates longer times of expected stability. The graph in Fig. 8 illustrates changeover times for several materials over a wide range of (SA/V). It can be seen that the transition to network dissolution occurs very rapidly for binary alkali silicate glasses at high (SA/V) values. For example, at (SA/V) = 1.0 cm^{-1}, less than 10 minutes are required for changeover in a 33 mol % Na_2O - 67 mol % SiO_2 glass at 25°C. This time can be increased by decreasing the percent Na_2O. Additionally, as illustrated by the 33 mol % Li_2O - 67 mol % SiO_2 (33L) system, the changeover time can also be increased by a suitable nucleation-crystallization schedule. Environmental storage temperature assumes an important role in the corrosion behavior. As the temperature increases, t_c decreases as illustrated with the BPNL 72-68 composition.

Surface Passivation

Aqueous solutions containing certain species, especially aluminum, have a strong inhibiting effect on glass corrosion (36-38). Experiments performed in our laboratory have shown that the presence of Al^{+3} ions in the corrosion solution retards the most damaging form of corrosion, namely network dissolution (39). The rate of selective leaching or ion exchange is relatively unaffected by the presence of Al^{3+} in solution. Figure 9 shows the rate of Si^{4+} being leached into solution as a function of time for a simple 33 mol % Li_2O - 67 mol % SiO_2 (33L) glass. As expected, the Si^{4+} concentration increases in solution with increasing exposure time. The only mechanism by which this network forming ion can go into solution is through network dissolution (i.e., breakdown of Si-O-Si bonds). Significantly, the rate of Si^{4+} dissolution from 33L glass in the corrosion solution containing 100 ppm Al^{3+} is lower than in the pure water. Auger electron spectroscopy and Ar ion milling revealed the presence of an alumina-rich film on the 33L glass corroded in the 100 ppm Al^{3+}. The presence of this film, resulting in a Type III surface, apparently passivates the glass surface against extensive network dissolution.

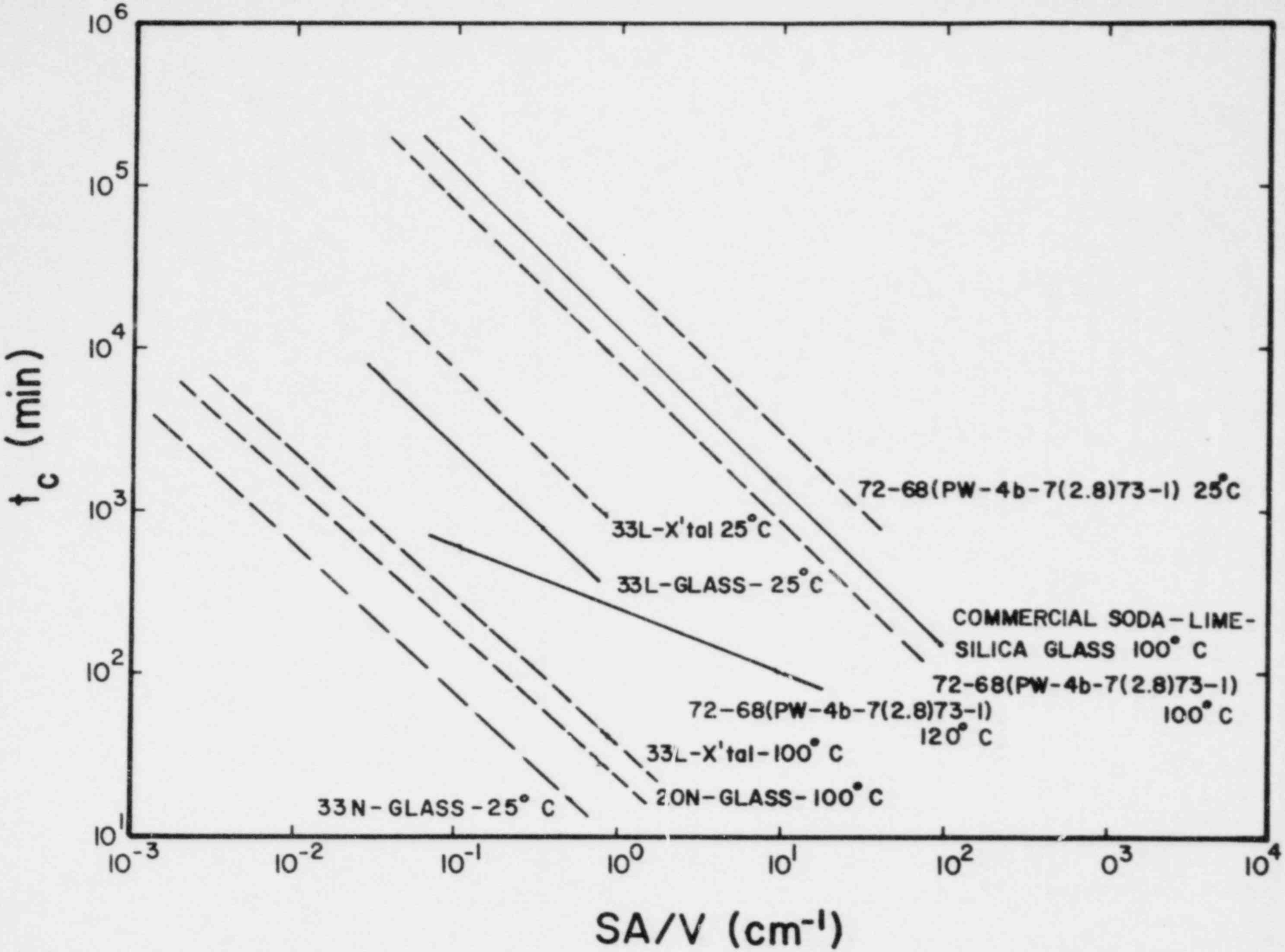


Fig. 8. Changeover time in kinetics (t_c) as a function of (SA/V) for various materials.

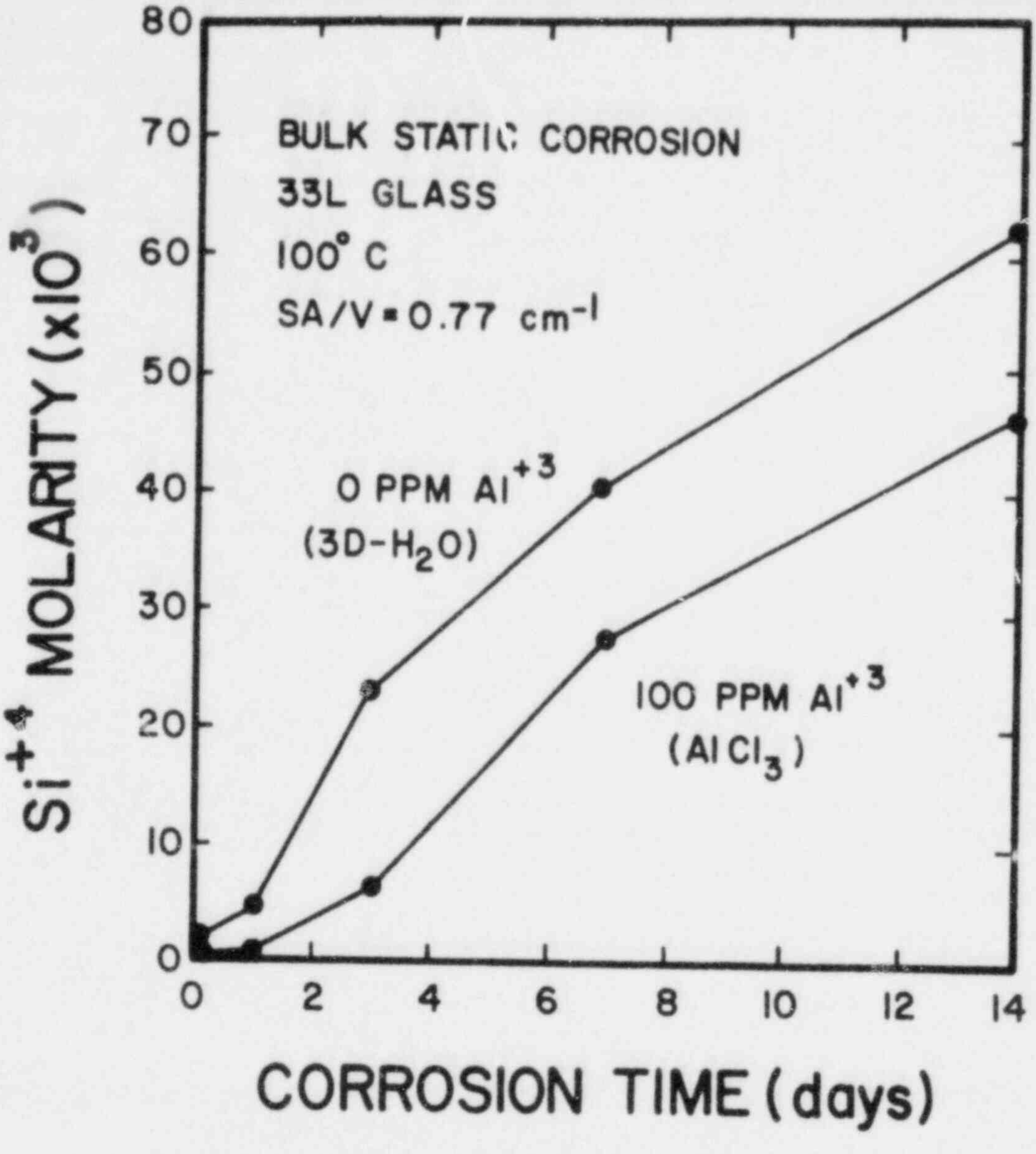


Fig. 9. Time dependence of Si^{4+} concentration in solution for 33L glass exposed to distilled water and water containing 100 ppm Al^{3+}.

Evaluation of Nuclear Waste Form Analog Materials: Prehistoric Archeological and Geological Samples

Because of the long burial times of prehistoric archeological artifacts and geologic materials we have initiated an investigation of the leaching behavior of these materials in order to use them as NWF analog materials in predictive plots such as Fig. 4. Materials covering a wide range of SiO_2 content as well as both glassy and polycrystalline nature have been chosen for study in order to compare with the alternative NWF materials being considered for waste storage. The experimental procedure for these investigations is described in some detail in the following section in order to illustrate the method used in producing the predictive relationships described in Fig. 4. It is the development of new instrumental techniques such as Auger electron spectroscopy, infrared reflection spectroscopy, the electron beam microprobe, and scanning electron microscope with energy dispersive X-ray analysis for use with glasses and other insulating materials that make quantitative kinetics studies possible (32).

Specimens approximately 1.5 cm^2 x 0.5 cm thick were sliced from the materials described in Table I. One surface from each of these specimens was polished to a 600 grit finish using SiC paper in order to eliminate previous environmental effects and to provide a standard surface on which to perform weathering experiments. The specimens were placed onto corrosion cells as shown in Fig. 10. Prior to assembly, the cavity of each corrosion cell was filled with distilled water with a pH of 6.5. The ratio of the surface area of exposed material to the volume of solution was 0.77 cm^{-1}. The entire assembly was placed into a constant temperature water bath and maintained for the duration of the experiment. As illustrated in Fig. 10, the type of corrosion cell used in this investigation permits the evaluation of synergistic interactions between various materials; for example between nuclear waste glass and geological materials. The corrosion cell also allows the environmental reactivity of a single material to be determined. This can be accomplished by placing a teflon specimen over one end of the cell. Both modes were utilized in the experiments described in this section.

Initially, the corrosion cells were used in the single material mode (i.e., comparable to placing a teflon specimen over one end of the cell).

Figure 11 shows the infrared reflection spectra before and after weathering for a tabular chert material (high crystalline) from Florida. The percent reflection is indicated on the y-axis and the wavenumber, which directly corresponds to the vibrational frequency of certain chemical bonds, on the x-axis. The percent reflection is the specular reflectance off the specimen surface compared to a mirrored surface. Also shown in this figure is the spectrum for a vitreous silica standard used for the purposes of calibration and to illustrate simularities in the spectra of materials containing SiO_2.

There are several regions of interest in the spectra shown in Fig. 11. In the spectra region from 1400 cm^{-1} to 1000 cm^{-1}, the peaks are due to the silicon-oxygen symmetrical stretch vibration and in some cases to the silica-nonbridging oxygen stretch vibrations. The well defined peaks that occur at

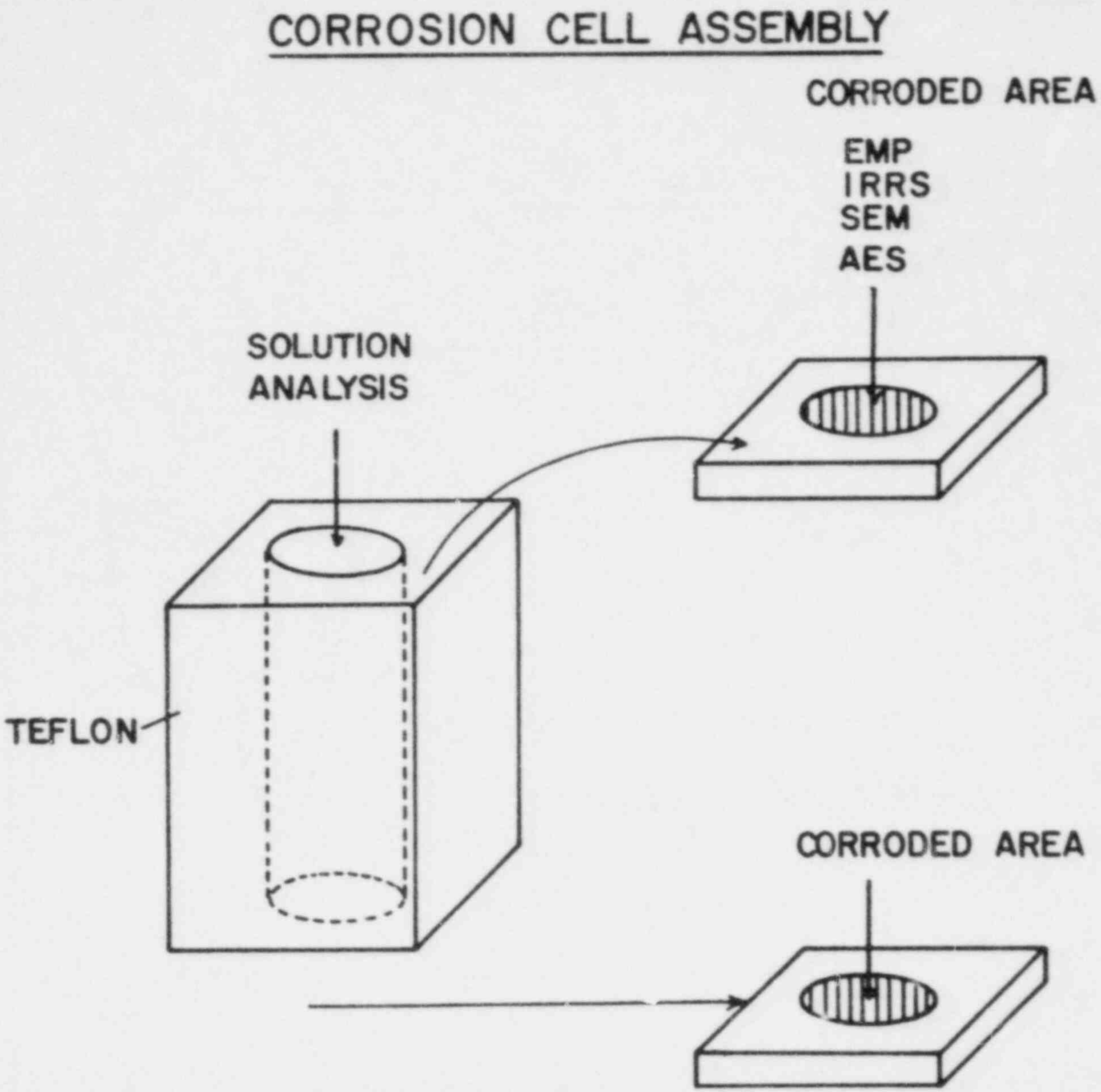


Fig. 10. Schematic of corrosion cell used for evaluating the corrosion behavior of bulk glasses.

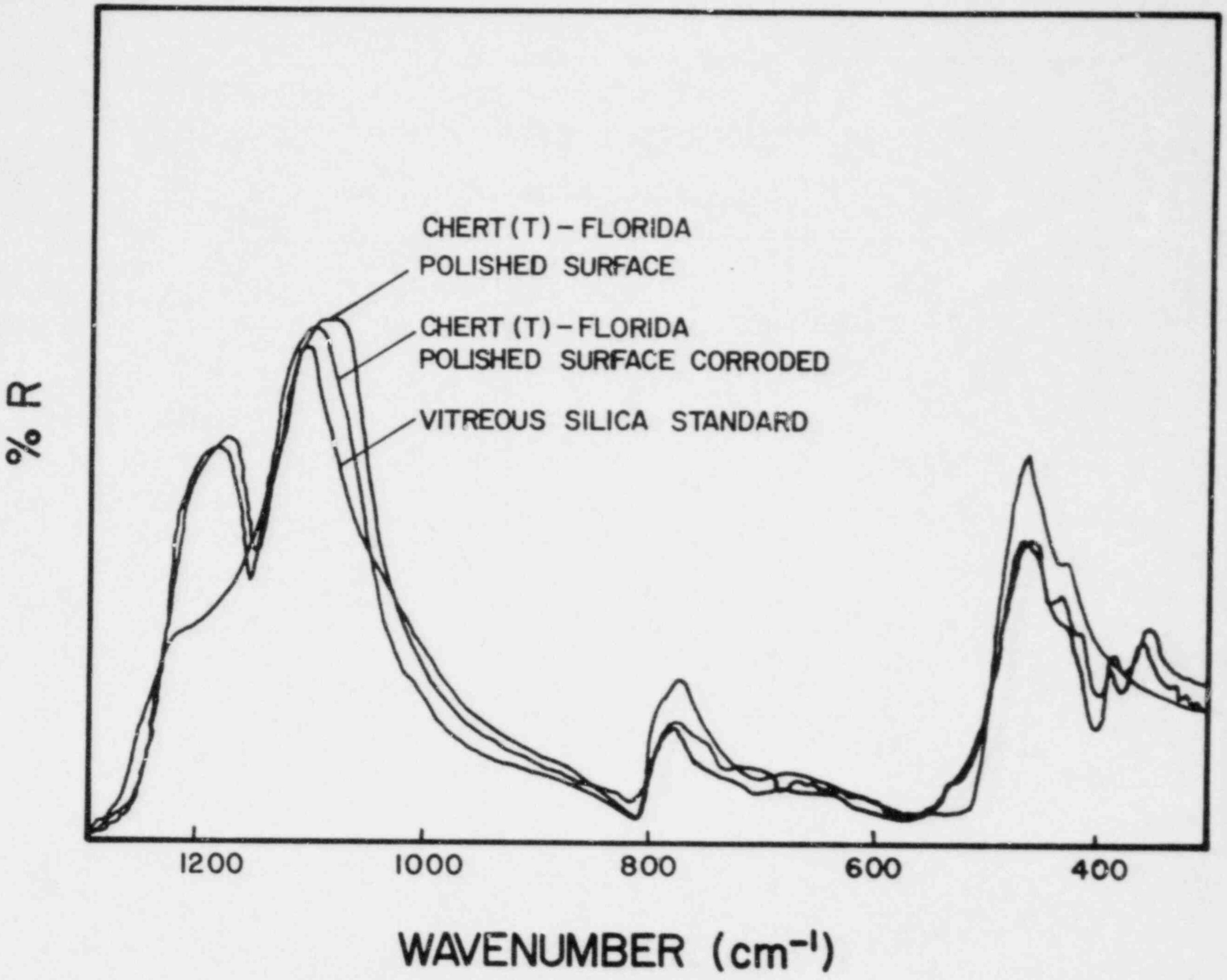


Fig. 11. Infrared reflection spectra for Florida chert before and after corrosion in the laboratory.

1200 cm^{-1} are characteristic of materials exhibiting a crystalline microstructure. Note the absence of the well defined 1200 cm^{-1} peaks in the vitreous silica spectrum. After corroding the Florida chert, it can be seen in Fig. 11 that the peaks in the infrared reflection spectra have changed slightly in both percent reflection and wavenumber position. These changes are characteristic of materials that have undergone a surface alteration. The extent of surface reaction on Florida cherts is small on laboratory weathered specimens. However, extensive reaction can occur in the natural environment over long periods of time. Electron microprobe data is presented in Fig. 12 for a Florida chert similar in composition to that discussed for Fig. 11. The data in Fig. 10 was obtained from a sectioned chert specimen buried 90 cm below the surface. Thermoluminescence analysis indicated that the specimen was approximately 30,000 years old. As illustrated, the iron is leached from the surface causing a patina to form. The thickness of this patina, which represents the depth of leaching, is $\sim$700 μm for the 30,000 year old chert specimen.

Figure 13 shows the infrared reflection spectra of an obsidian from Mexico before and after corrosion. As with the vitreous silica, there is an absence of well defined peaks at 1200 cm^{-1}. These spectra are characteristic of materials with microstructure that consist primarily of glassy phase. As observed with the chert sample, there is a change in both the percent reflection and wavenumber portion, again suggesting the alteration of the surface. This specimen was weathered under the same conditions as was the chert specimen discussed in Fig. 11. It appears that the extent of reaction is not much different for the two materials under the conditions that they were evaluated. The solution data presented in Table I also suggests nearly identical dissolution rates for the elements analyzed.

In order to determine the interactive behavior of two materials in close contact the corrosion cell shown in Fig. 11 was again used. In this experiment, a 33 mol % Na_2O - 67 mol % SiO_2 (33N) specimen was placed over one end of each of five corrosion cells. A different type of geological specimen was placed over the other end of each cell as listed in Table II. A sixth corrosion cell was also prepared containing a 33N specimen on both ends. All corrosion cell-specimen assemblies were maintained at 25°C for 66 hours.

The concentrations of SiO_2 and Na^+ in solution and the final solution pH after 66 hours are listed in Table II. The concentration of SiO_2 in the corrosion solutions exposed to the geological samples were much less ($\sim\frac{1}{2}$ or less) than that exposed to 33N only. Of interest are the relatively low concentrations of SiO_2 and Na^+ found in the solution exposed to the obsidian in comparison to the other specimens. Although additional work is required before a definitive statement can be made, it appears that the obsidian imparts a passivating effect to the corrosion solution, thus slowing down the rate of attack on the 33N specimen on the other end of the corrosion cell. The infrared reflection data presented in Fig. 14 further suggests the presence of a film on the surface of the 33N glass corroded in the same corrosion cell with the obsidian. The spectra for the 33N glasses corroded in the presence of the other geological materials is characteristic of extensive Na^+ leaching. In contrast, the spectrum for the 33N glass corroded with obsidian is nearly identical to that for 33N corroded alone. This type of spectrum is common of specimens on which total

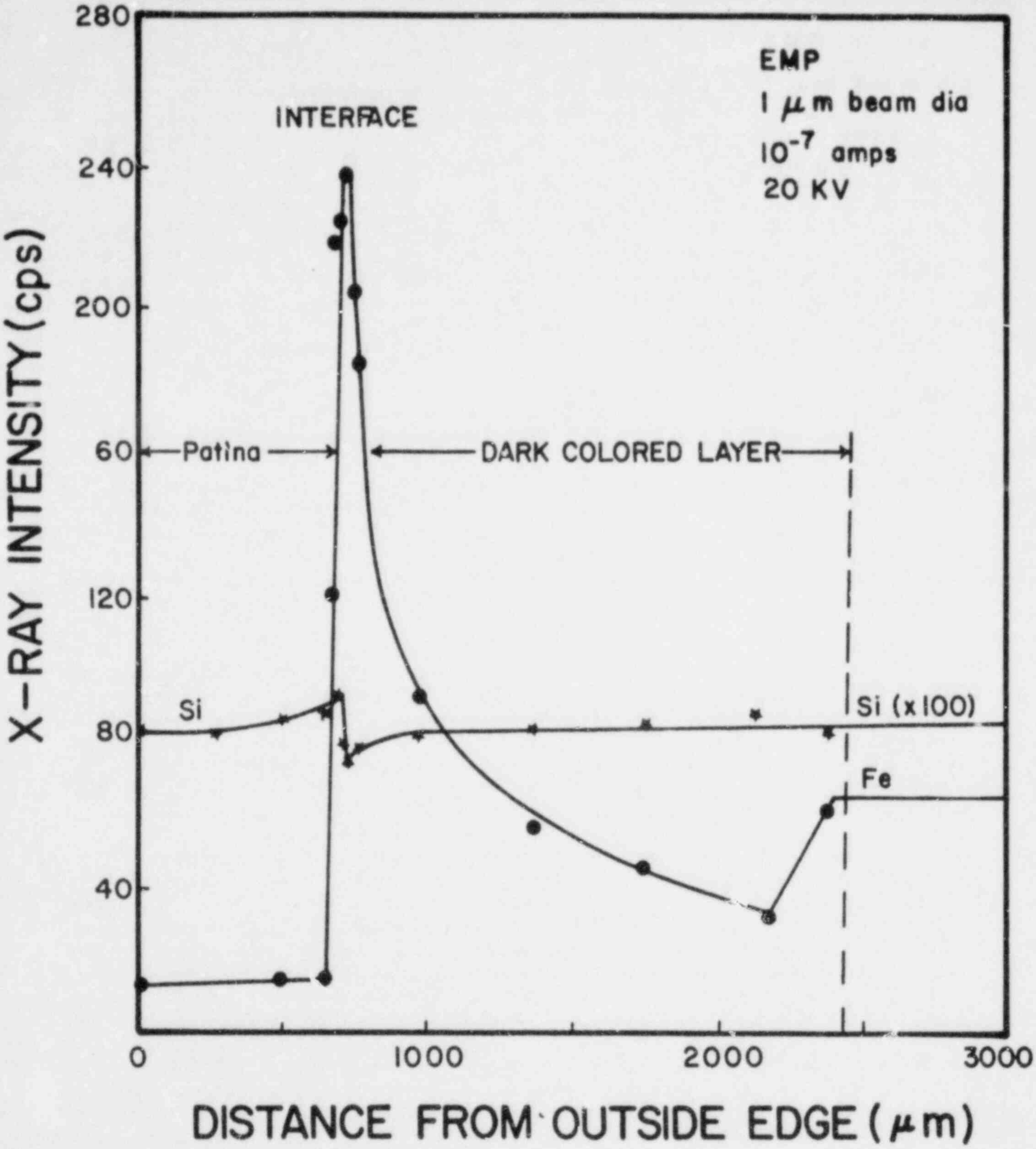


Fig. 12. Electron microprobe analysis of field-weathered chert.

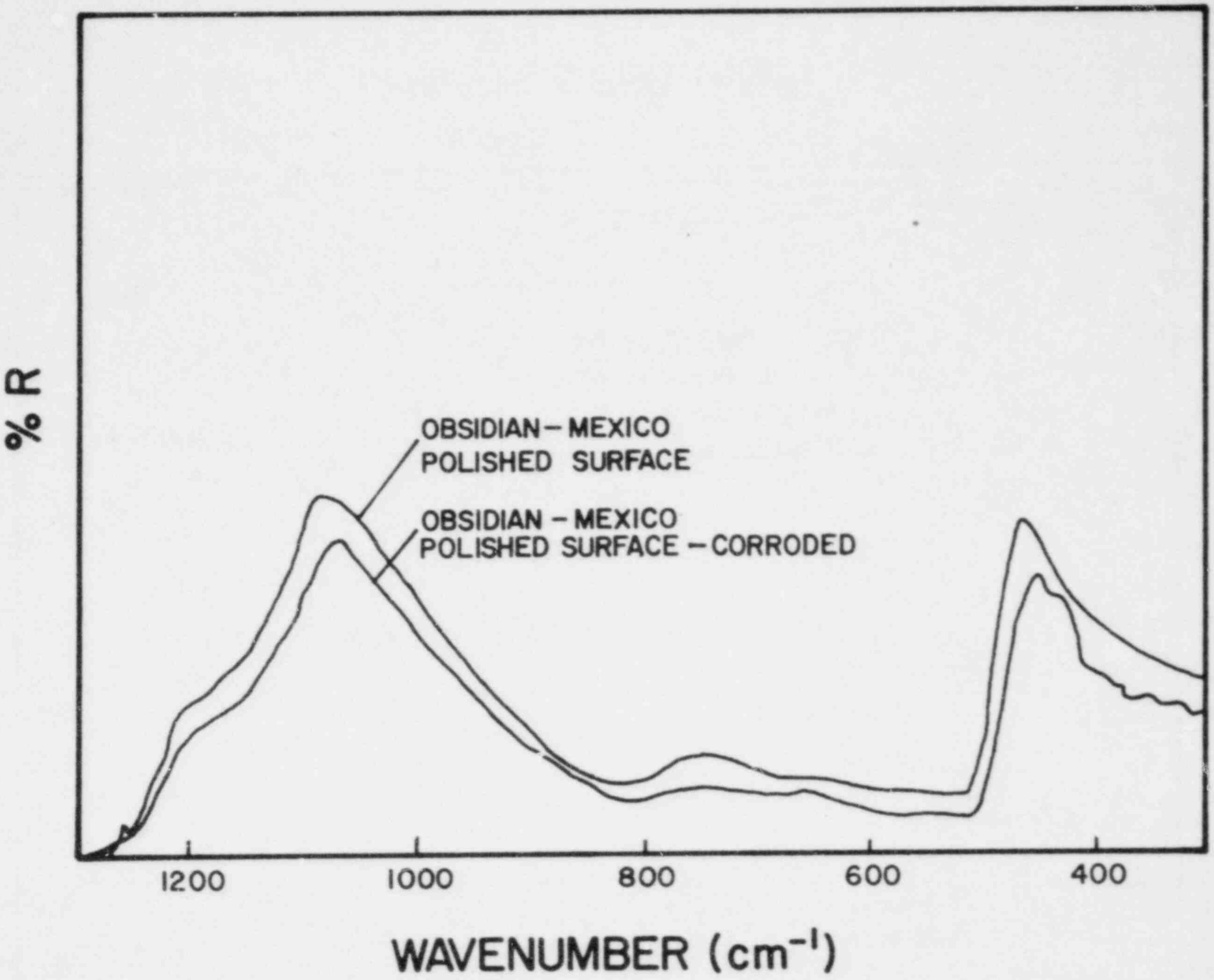


Fig. 13. Infrared reflection spectra of obsidian before and after corrosion in the laboratory.

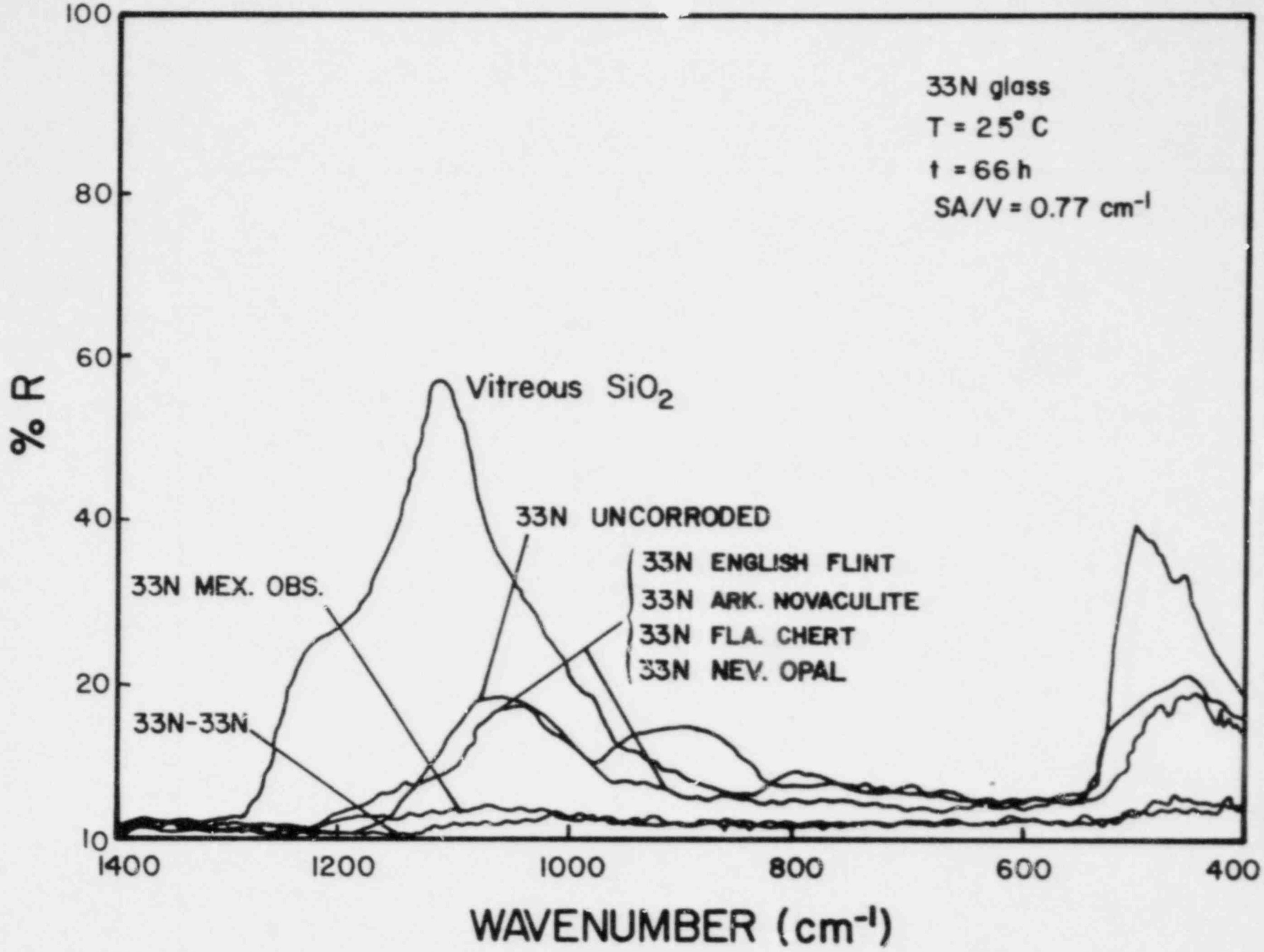


Fig. 14. Infrared reflection spectra of 33N glass after corroding in close contact with various geological materials.

Table I

Concentration of Ions in Solution After Exposing Various Geological Materials to Distilled Water for 170 Hours at 100°C

Sample	Concentration (ppm)				
	Ba	Ca	Na	SiO_2	Zn
Chalcedony (Nevada)	22.0	5.0	6.0	8.0	0.4
Jasper (Idaho)	45.0	7.3	18.8	15.3	1.8
Flint (England)	15.5	3.4	8.0	31.5	-
Flint (Wyoming)	155.0	45.0	4.8	42.5	-
Novaculite (Arkansas)	5.3	1.6	14.0	4.8	0.2
Obsidian (Mexico)	6.8	2.2	2.0	5.5	0.2
Chert (Florida)	4.6	1.6	4.2	2.3	0.1

Table II

Data for a 33 mol % Na_2O - 67 mol % SiO_2 (33N) Glass* Corroded at 25°C for 66 Hours in Water with an Initial pH = 7.1, SA/V = 0.77 cm^{-1}

Sample	Final pH	SiO_2 (ppm)	Na^+ (ppm)
33N - English Flint	11.71	1750	2100
33N - Arkansas Novaculite	11.87	2250	1350
33N - Mexican Obsidian	11.35	1450	420
33N - Florida Chert	11.79	1875	440
33N - Nevada Opal	11.53	2725	700
33N - 33N	12.21	5025	1300

---

*The 33N glasses were in close contact with geological specimens during exposure (Fig. 10).

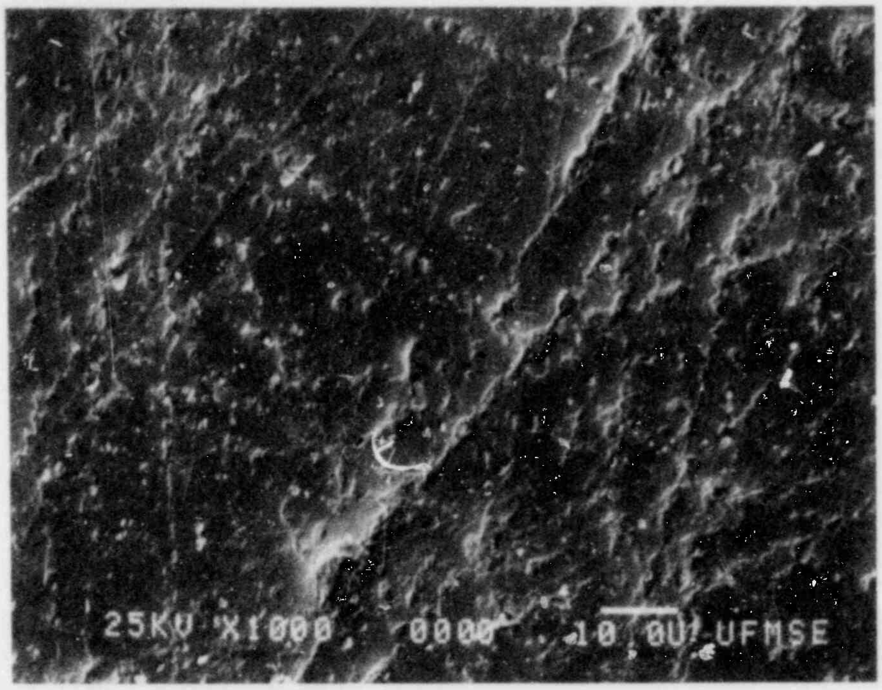
surface breakdown has occurred and on specimens where a dual passivating film has developed. The solution data suggests that the latter is the case for 33N corroded in the presence of obsidian.

Scanning electron micrographs of the obsidian and chert samples corroded in the presence of the 33N glass are shown in Fig. 15. The surface attack appears to coincide with the polish scratches on the chert specimen, whereas the attack is much more locallized on the obsidian specimen. In fact there is very little evidence of attack in the polish scratches on the obsidian.

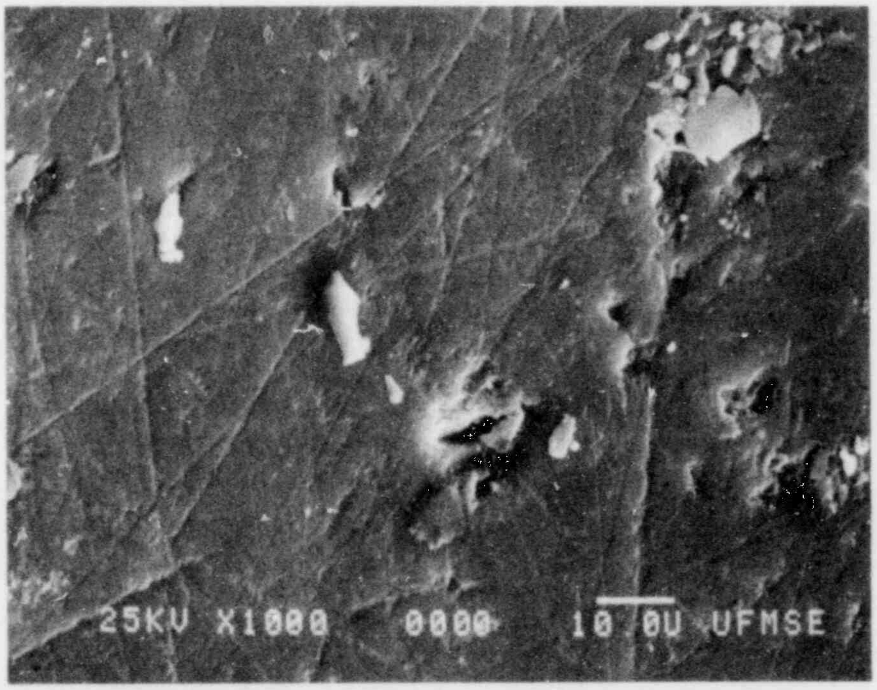
Analog Materials: Leaching of Medieval and Ancient Glasses

Many medieval and ancient glasses buried or weathered for a wide range of time are being studied as analog materials for nuclear waste forms. One series of nine glasses containing variable contents of SiO_2 (Table III) have been buried in two types of soil (pH = 4.8 and pH = 9.5) in England and removed after 1, 2, and 8-9 years. Figure 16 shows one of the authors (LLH) and English colleagues removing the 8 year burial samples from the Ballidon mine location which is a crushed lime rock burial (soil pH = 9.5) (40). A photograph of the nine samples removed from the 8 year burial is presented in Fig. 17; almost no leaching is visible. Detailed surface analyses of the thickness of the reaction layers using IRRS and AES are in progress for these samples and will be compared with equivalent analyses on the 1 and 2 year samples for the same site. Similar studies are in progress for 1, 2, and 9 year buried samples of the same composition removed from the Wareham Heath burial site (soil pH = 4.8) (41). Controlled laboratory leaching experiments on the same samples for short terms are also in progress. Reaction zone thickness obtained from this sample series will thus extend over a time range of 6 orders of magnitude when plotted as in Fig. 4. Comparison of a wide range of other glass composition studies of glass-crystal interfacial attack using glass-ceramics of varying volume fraction of crystal phase, and leaching of BPNL glass 72-68 samples with and without a clay overpack are being conducted by burying 30 samples in the Ballidon Mine location for removal in November 1979 after 1 year.

Also shown in Fig. 17 are other glass samples that have been removed from well dated archeological digs dating from 300 to 1700 years ago. Surface analyses from these glasses compared with laboratory experiments will thus cover a time range on Fig. 4 to a value of $\sim 2 \times 10^3$ years. Samples labeled A and a are two different compositions of stained glasses from the old St. Michaels Cathedral Coventry, England which are approximately 400 years old. The other samples are glasses from archaeological digs in England dating from 300 to 1700 years old. IRRS analyses at various locations on the surface of sample A have been made. The thickness of attack of the glass surface was determined by progressive mechanical polishing followed by IRRS scans revealing a total reaction thickness ranging from 6 to 12 μm. Removal of alkali from the glass is the primary mode of attack. This is determined by measuring the change in reflected intensity at 950 cm^{-1}, the location of the silicon-non-bridging oxygen-alkali molecular stretching vibration discussed in the previous section and in detail in another publication (42), in glasses of this compositional range.



Florida chert corroded in the presence of 33N at 25°C for 66 hours.



Mexican obsidian corroded in the presence of 33N at 25°C for 66 hours.

Fig. 15. Scanning electron micrographs of Florida chert and Mexican obsidian after corroding in close contact with 33N glass.

Fig. 16. Removal of glass samples from Ballidon Mine location in England after 8 years burial. Clockwise from left June Wilson, ICI Ltd., England; Walter Fletcher, Glass Research Assoc., England; Prof. Roy Newton, University of York, England; Prof. Hench, University of Florida, USA.

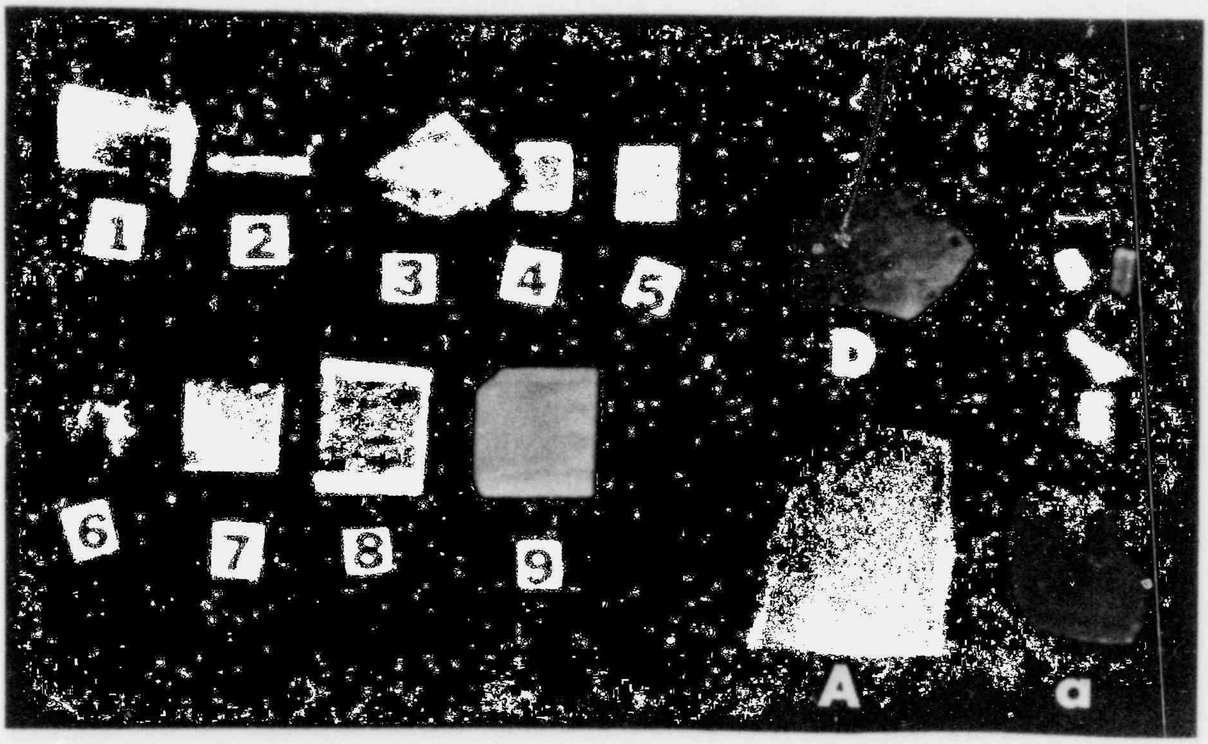


Fig. 17. Photograph of samples 1-9 (Table III) after 8 years burial in soil of pH = 9.5. Samples A & a are from old St. Michaels Cathedral, Coventry, England; Sample D is a 1670-1690 glass bottle fragment from Hangelton, England; and Samples E are ∿200 AD fragments of a Roman vase from a Welsh seacoast fortress.

Table III

Percentage by Weight in Sample No.

	1	2	3	4	5	6	7	8	9
SiO	68.5	50.1	46.5	72.7	72.7	54.3	79.1	70.1	54.2
Al_2O_3	3.6	4.3	3.5	1.1	1.1	14.4	1.8	0.8	-
Fe_2O_3	0.49	0.95	1.2	0.09	0.09	0.42	0.03	very low	
P_2O_5	-	-	4.6	-	-	-	-	-	-
CaO	7.3	18.6	21.6	9.2	9.2	17.4	0.2	9.5	-
MgO	0.5	4.7	5.4	3.1	3.1	4.4	-	1.0	-
Na_2O	18.2	2.6	0.7	13.3	13.3	0.25	4.2	10.6	8.0
K_2O	1.3	16.7	16.4	0.5	0.5	0.35	0.3	5.1	4.1
PbO	-	0.1	-	-	-	-	-	-	33.6
MnO	0.34	0.63	-	-	-	-	-	-	-
CuO	-	0.08	-	-	-	-	-	-	-
CoO	-	1.03	-	-	-	-	-	-	-
B_2O_3	-	-	-	-	-	8.0	14.3	0.6	-
F	-	-	-	-	-	0.5	-	-	-
BaO	-	-	-	-	-	-	-	2.0	-
Sb_2O_3	-	-	-	-	-	-	-	0.3	0.05
As_2O_3	-	-	-	-	-	-	-	0.06	0.1

W. W. Fletcher, "The Chemical Durability of Glass. A Burial Experiment at Ballidon in Derbyshire," J. Glass Studies XIV, 149-151 (1972).

The magnitude of change in intensity associated with dealkalization of the surface is plotted for the various locations on the sample in Fig. 18. Connecting the surface locations with nearly equivalent extents of surface leaching produces a leaching topographic map. The upper left corner shows a channel of extensive pitting due to leaching whereas a region in the middle right shows very little change, only 6-8 intensity units.

This topographic surface leaching mapping procedure provides a quantitative method for determining whether heterogeneous attack of silicate materials has occurred. Because of the possibility of heterogeneous attack due to variations in the environment in contact with a NWF surface, compositional variations within the NWF, preferential attack at phase boundaries, or differences of surface roughness, it is important to follow the area dependence of surface leaching with time using a procedure such as that of Fig. 18. Such variations in leaching of both analog and candidate NWF materials must be taken into account in constructing long term predictive curves similar to that described in Fig. 4.

Acknowledgments

The authors gratefully acknowledge Mr. Wayne Ross of Battelle Pacific Northwest Laboratories for providing samples of glass 72-68 for analysis, Dr. Barbara Purdy for assistance in obtaining the geologic samples, Prof. Roy Newton for providing buried glasses, medieval and ancient glass samples and Nuclear Regulatory Commission Contract #NRC-04-78-252, for financial assistance in pursuing this study.

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IRRS DEALKALIZATION CORROSION MAP OF ST. MICHAEL'S COVENTRY CATHEDRAL WINDOW

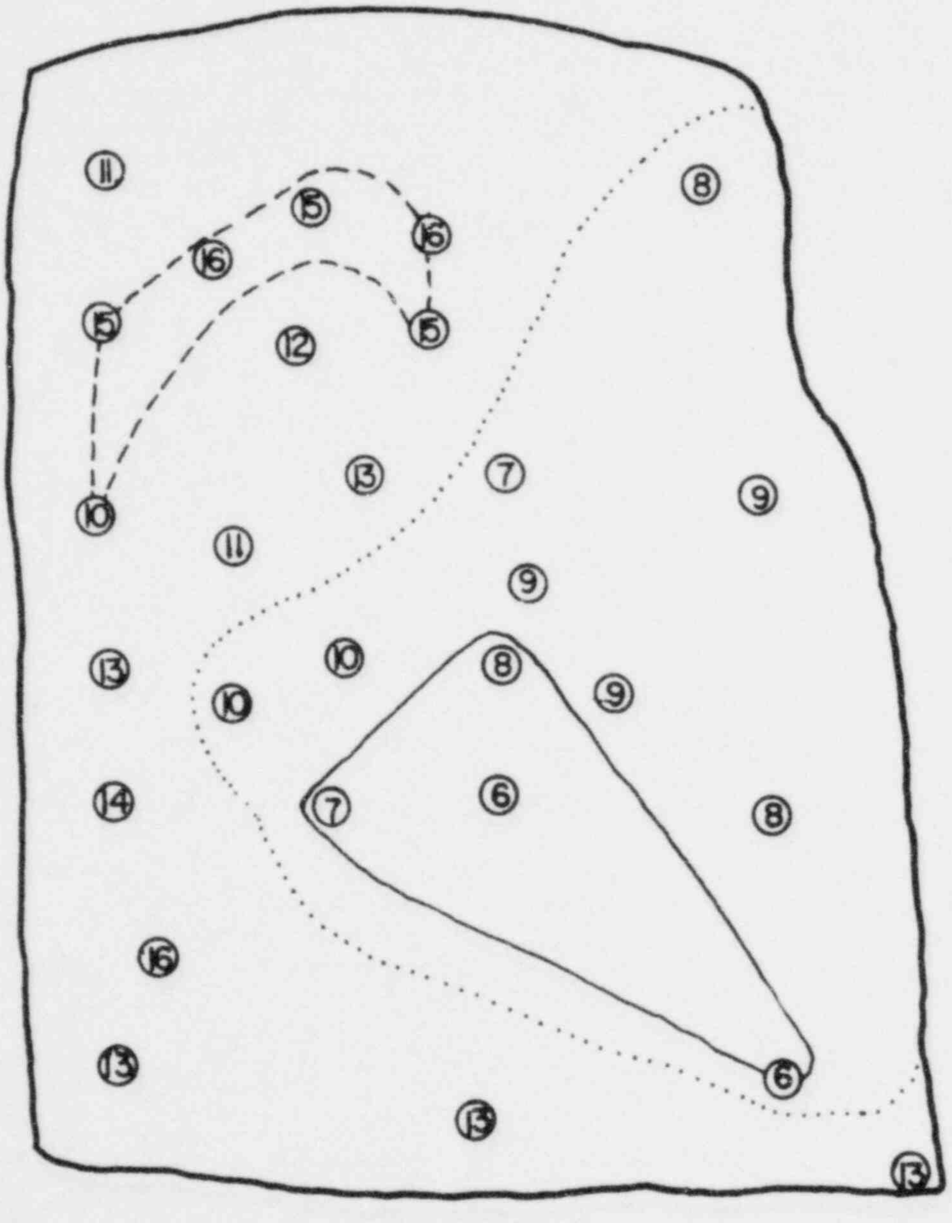

Fig. 18. An infrared reflection spectroscopy map of the areas of relative dealkalization of sample A from Fig. 17. The numbers on the map represent change in intensity at 950 cm^{-1} compared with the bulk glass surface spectra.

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Discussion Following

SURFACE LEACHING OF GLASSES AND GLASS-CERAMICS

Presented by Larry L. Hench

Pedro B. Macedo - Catholic University of America
Comment:
In terms of your talk, I just wanted to point out to the audience that there are even more complications than the ones that were already mentioned. For example, the groundwater may have a definite pH. If that happens, one has all kinds of interesting surface reactions. For example, a lot of these glasses have aluminum in them. Additions of aluminum to the glass composition will increase the chemical durability for neutral conditions. However, the aluminum addition reduces the chemical durability for both high and low pH. So one has to be very careful in terms of checking the pH and other ground chemistry. For example, one of the interesting things that we have done is to leach pyrex in acidic pH. We found that instead of the layer becoming more protective, it becomes progressively worse. In other words, the chemical durability of the glass as a function of time gets progressively worse; more and more silica comes out instead of less.

Hench
Response:
I could not agree more with the importance of small concentrations in either the solution or the glass. One of the areas that there was not time to cover is that you can put a few parts per million aluminum in the solution to which the glass is exposed and it will complex with the surface film and form a much more protective surface film and crank all these kinetics down. So there is great potential of designing passivating concepts into overpacks, for example, without having to give all of the slow-down of leaching from the glass itself.

Heinrich D. Holland - Harvard University
Comment:
First of all, I think you have done some beautiful experiments, but secondly, I think you may be overinterpreting them. I would like to suggest two ways in which you have done this. One, you have shown that during the initial stages of alteration you have a $t^{1/2}$ relationship. This could be due to diffusion. On the other hand, it could be due to other things as well, and--as you probably know--there has been a great deal of argument about the interpretation of such $t^{1/2}$ relationships. This is particularly true because in your experiments the silica concentration varied with time over several orders of magnitude, and may in itself have affected the kinetics of the reactions. Secondly, and I think this is more serious, in your experiments you are dealing with distances of microns. The things that I believe all of us here are worried about are distances on the order of millimeters or centimeters. At this point, the only way I know for getting at these things at such

distances is to look at geologic materials. We can do that now. We can look at alteration sequences over periods of thousands of years that are reasonably well dated--say in glacial tills. We have done this. You can look to the sort of thing that Dr. Macedo referred to. Look at glasses in oceanic environments. He has looked at tektites. We have looked at basaltic glasses and it is obvious that over long periods the processes that go on are extremely complicated, the kinetics are not well understood and I would simply like to caution that taking your short-term data and extrapolating them to thousands of years may be extremely dangerous.

Hench
Response:
I could not agree more and time did not permit me to go into the data that we are getting on the geologic samples and the medieval and ancient glasses. I hoped to leave an impression in the final comments that I made that the approach that we are taking on the short-term is to try to confirm any predictions with data from samples in the longer term. That may or may not be possible. But we feel that is the only real hope there is of establishing scientific credibility to such predictive relationships.

Bob Watt - Los Alamos, private citizen
Question:
I wonder whether you studied the effects of other ions and solutions. For example, sodium, cesium--things like these that are also found in groundwaters, perhaps.

Hench
Response:
Yes, time just did not permit going into those.

Watt
Question:
What has been, and will be, studied?

Hench
Response:
We generally find that the effect of ions in solution as well as in the glass is a direct function of the field strength of the ions. At a high field strength the ions will complex with the active silica film and tend to slow down the kinetics; at low field strength the ions tend to have little effect on the early stage diffusion processes.

PLENARY SESSION II

ENCAPSULATIONS TECHNIQUES AND FAILURE MODES

ANNIE SUGIER

COMMISSARIAT A L'ENERGIE ATOMIQUE, FRANCE

CHAIRPERSON

HIGH-LEVEL WASTE CANISTER CORROSION STUDIES PERTINENT TO GEOLOGIC ISOLATION

Jeffrey W. Braithwaite and Martin A. Molecke
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December, 1978

SAND78-2111

High-Level Waste Canister Corrosion Studies Pertinent to Geologic Isolation*

Jeffrey W. Braithwaite and Martin A. Molecke
Sandia Laboratories**
Albuquerque, New Mexico 87185

ABSTRACT

The compatibility of candidate high-level waste (HLW) canister materials with deep geologic isolation environments is addressed. Results are presented which are applicable to the following repositories or test facilities: bedded and domed salt, sub-seabed sediment, and various types of hardrock. Such studies are an essential portion of the technological basis for terminal waste management. These studies will identify HLW canister or overpack materials satisfying appropriate requirements for barrier lifetime. Mechanical properties, as well as constraints on cost and consumption of critically limited materials, are also selection criteria. Lifetime objectives range from a minimum of several years for retrievability constraints up to several hundred years for retardation of near-field interactions (e.g., waste form leaching with potential radionuclide release to the geosphere) during the period of greatest HLW thermal output. A review of present and prior applicable corrosion results is presented. However, emphasis is on the results obtained from current laboratory and in situ HLW canister/corrosion programs at Sandia Laboratories. The effects of multiple variables on corrosion susceptibility and rates are briefly discussed and some applicable data given. It is possible to provide a canister/overpack barrier which can survive geologic isolation environments for periods of several hundred years.

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High-Level Waste Canister Corrosion Studies
Pertinent to Geologic Isolation

Jeffrey W. Braithwaite and Martin A. Molecke
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INTRODUCTION

Disposal of high-level wastes (HLW) in stable, deep geologic formations is presently considered the most viable method for ensuring the isolation of radionuclides contained in the waste. The dispersal of radionuclides is blocked by many barriers which include the waste form, the canister, possible chemical or physical sorptive barriers, and the geologic environment. However, because all waste forms and canister materials have finite lifetimes in contact with ground water, the geologic formation itself must be the ultimate long-term barrier for all concepts of terminal geologic isolation. The geologic environments being investigated for HLW isolation in the United States include bedded salt, domed salt, sediments beneath the deep ocean floor, and various hardrock formations. Sites receiving the most intensive evaluation recently are the bedded salt deposits in southeastern New Mexico (the site of the proposed Waste Isolation Pilot Plant), the ocean sediments in a mid plate/gyre region of the deep North Pacific, basalt formations on the Hanford reservation, and a number of hardrock formations at the Nevada Test Site.

The primary focus of this paper is on the HLW canister barrier and its impact on the overall multi-barrier concept.

Canister Lifetime Definitions

Metallurgical compatibility studies are being conducted to evaluate the adequacy of materials for use as HLW canisters and/or canister overpacks under the environmental conditions which may be encountered during geologic isolation. Adequacy of materials for HLW canisters must be assessed relative to the intended purpose of the canister. Such purposes and corresponding barrier lifetimes are as follows:

1. reprocessing and interim storage: The waste canister is optimized for waste reprocessing requirements and temporary engineered storage (up to 10 years). Studies of corrosion during these stages of the fuel cycle are not considered in detail in this report.

2. 0 to 5 years after emplacement: The waste canister can be optimized for transportation requirements and/or for mechanical properties during handling and emplacement operations in a waste repository. Rapid canister corrosion resulting in compromise or loss of this engineered barrier is not considered of major impact for this defined lifetime. This may be the most desirable canister design philosophy from an economic point of view, but assumes the geologic medium will function as the only absolute barrier.

3. 5 to approximately 25 years after emplacement: Materials may be selected to facilitate HLW canister retrieval in the event retrieval becomes necessary during the early operational phases of a geologic waste repository. Retrieval may be required as a safety guarantee to cover any unexpected conditions which may arise in a repository, or if waste buried on a terminal basis (e.g. spent-fuel assemblies in the "once-through" fuel cycle) is later viewed as a resource. It must be emphasized that an intact, non-corroded HLW canister is not an absolute requirement for retrieval. Techniques are being developed[1] to retrieve degraded waste canisters in saltbed isolation by means of overcoring.

4. approximately 300 years: If a canister material can be selected that survives throughout the major heat generation phase of the HLW, it can provide a significant retarding action against thermally driven interactions, e.g. hydrothermal leaching. The physical breach of the canister and subsequent leaching of the waste form by any intruding leachant is the source for aqueous migration of radionuclides. The major heat producers in HLW consist of fission product ^{137}Cs and ^{90}Sr, both having a half-life of about 30 years. If the waste canister remains unbreached for about 10 half-lives, 300 years (or longer), the fission product concentration and thermal output of the waste is reduced by a factor of 1000 (or more). The thermal driving force for subsequent interactions is consequently also reduced. The canister also prevents the release of any radionuclides until the radiotoxic hazard measure[2] of the ^{90}Sr and ^{137}Cs is less than the radiotoxicity of ^{241}Am remaining in the waste; this requires an intact canister barrier of 300 to 400 years after emplacement. Essentially, the fission products would be partitioned in the canister.

Westik and Turcotte[3] found that high temperature, high pressure (hydrothermal) leaching of HLW glass and supercalcine quickly solubilizes a signficant amount of fission product Cs, Rb, and Mo into the aqueous phase. They recommended that hydrothermal (leaching) conditions be avoided for HLW forms if possible. An intact canister can prevent such conditions for the necessary time. Providing this canister lifetime option as part of the overall multi- barrier system must be viewed as a desirable goal. It is not an absolute requirement, particularly if a waste isolation site can be selected with a very low probability for water intrusion during the thermal period.

Objectives:

The basic objectives of compatibility studies of candidate alloys for canisters are:

1. To determine the extent of operational phase and long-term interaction between the waste canister, the surrounding geologic media, and any intruding leachant or reactant. This includes an identification and modeling of compatibility interaction mechanisms and kinetics under geologic isolation conditions.
2. To provide information which can be used for repository engineering design.
3. To supply measured parameters for overall repository safety analysis studies. Experimental data and the formulated, predictive models should permit the assessment of consequences of all interactions.
4. To select materials which have adequate mechanical strength for handling and emplacement operations in a particular repository. Material selection criteria should also consider material costs and consumption of critically limited materials. It might be concluded that the high cost of some materials is of secondary concern if the long-term benefits of such materials are substantial. The primary concern is the required/defined canister lifetime, in conjunction with the overall safety of terminal waste isolation.

Various segments of the canister corrosion studies involve laboratory testing primarily, plus bench-scale and in situ/field heater tests. Most studies are in progress now and will be described.

Finally, confirmatory testing requires in situ emplacement of actual canistered HLW into a geologic waste repository or test facility. Such testing is now in the planning stages at Sandia Laboratories (HLW in bedded salt), Rockwell Hanford Laboratory (spent fuel in basalt/hardrock), and the Office of Nuclear Waste Isolation (HLW and/or spent fuel in various geologic formations).

Effects of Environmental Parameters on Canister Corrosion

Environmental parameters acting upon HLW canisters vary with the geology of the repository and can have a major impact on resultant corrosion rates. Several isolation environment parameters for various repository geologies are summarized in Table 1. Further discussion as to the effect of these variables on resultant corrosion rates is as follows:

Temperature: Increases in temperature generally increase the corrosion rates of metals.[4,5] However, as Shannon[6] noted for steel in geothermal brines, the corrosion retarding passivating film sometimes becomes more protective as temperature is increased and the observed corrosion rates decrease. Also, increases in temperature in an open system will cause a depletion in dissolved oxygen in aqueous solutions. This will decrease the corrosion rate of metals whose rate is controlled by diffusion of oxygen (for example, 1018 mild steel).

Pressure: The restraining pressure which an HLW canister is subjected to in a waste repository affects the corrosion rate primarily in that it influences the physical state of intruding water and the concentration of dissolved gaseous species. The lithostatic (rock overburden) pressure combined with the gas impermeability in a bedded salt repository or the hydrostatic pressure in the deep ocean sediment will prevent water vaporization even at high waste temperatures. HLW emplaced in hardrock formations will not be exposed to liquid water because of the lack of a confining pressure. These arguments, of course, depend upon the sealing and reflux properties of the formations.

Solution Chemistry: Waste canisters will be exposed to any thermal decomposition products of the geologic isolation formation (CO, SO_2, etc.) and any dissolved and gaseous species present (O_2, N_2, HCl, H_2, etc.). In general, species in solution which increase the oxidizing power of that solution (O_2, H^+, H_2S, NO_3^-, etc.) will increase the corrosion rate. The exceptions are that some alloys will not support an oxygen current, form a stable sulfide, etc. Hydrogen ions can also reduce the thickness and therefore the effectiveness of a metal's passivating layer.[4] Basic pH conditions can cause caustic stress corrosion cracking or even rapid dissolution if the metal is amphoteric.[4] Chloride ion is potentially the most aggresive of the ions in that it promotes localized passive film breakdown (which leads to pitting), and is a key constituent in causing stress corrosion cracking of many alloys.[4]. Large concentrations of chloride can inhibit the corrosion rates of many alloys by salting out dissolved oxygen and/or by adsorbing and blocking many active surface sites.[4]

TABLE 1

REPOSITORY ISOLATION ENVIRONMENTS*

Geologic Formation and Waste Type	Maximum Interface Temperature	Lithostatic/ Hydrostatic Pressure	Chemistry
Bedded Salt:			
Spent Fuel	70-100°C	18MPa	98%NaCl, 1/2% H_2O
Commercial HLW	250°C	18MPa	98%NaCl, 1/2% H_2O with potential localized intrusion of $NaCl$-$MgCl_2$ brine**
Sub-seabed Sediments: Commercial HLW	200°C	55MPa	Seawater saturated sediments (40% solids)
Hardrock, Shale, Tuff: Commercial HLW	250-300°C	Atmospheric	Air and steam for about 100 years, then possibly inundated with ground water

* does not take radiolysis into account

**due to thermally induced migration of brine inclusions

Stress: The tensile stress present in the canister wall is one of the essential requirements for stress corrosion cracking.[4,5,7] Not all alloys are susceptible to stress corrosion cracking in geologic isolation conditions. For the candidate alloys the environment-specific experimental study needs to be conducted. For susceptible alloys, the threshold tensile stress depends strongly on temperature, solution composition, and the presence of an aqueous phase.

Sensitization and Welding: Alloys containing carbon and chromium can be susceptible to sensitization. For example, sensitization in stainless steels refers to the thermally induced formation of chromium carbide at or near grain boundaries. This increases the susceptibility of the alloy to intergranular attack and intergranular stress corrosion cracking.[4,5] Welding, because of the high temperatures involved, often leads to sensitization and tensile stress in welded regions. Stainless steel 304, for example, undergoes sensitization at temperatures above 400^{0}C.

Radiolysis Products: A study of gamma-radiolysis and hydrolysis in bedded salt brines was conducted by G.H. Jenks.[8] His conclusions included the following: (1) the principal corrodant is HCl which forms from $MgCl_2$ hydrolysis, (2) 2/3 of the $MgCl_2$ present in the brine can hydolyze to produce HCl (if the HCl is removed or consumed as it is formed), (3) important radiolysis products may include small amounts of Cl_2, Br_2, HNO_3, ClO_3^-, and BrO_3^-. The chlorates and bromates will probably not be stable at the high temperatures of high-level waste. The net effect of the radiolysis products would be to increase the oxidizing power of the brine to some degree. Similar studies on the radiolysis of ground water or seawater under repository conditions have not been performed.

Water Intrusion

There exist two major sources of waters/brines for the corrosion of HLW canisters in a geologic repository (excluding intervention by man): (1) intrusion or hydrologic flow into the repository; this is of extremely high probability for both seabed-sediment and hard rock repositories and of extremely low probability for a bedded (or domed) salt repository; and (2) for a bedded salt repository, migration of brine inclusions (micrometer to millimeter in diameter) up the thermal gradient, toward the HLW canister, has been identified[9]. Since this migration (rate) is a function of the thermal gradient, brine migration into the canister vicinity would be most rapid for the first several years after emplacement. Flow would cease in less than 20 years as the thermal gradient between canisters in the repository decreases. The quantity of brine inflow per canister has been calculated (for salt) to be less than 0.4 liters/year.[30] Further determination of the actual inflow quantity and development of techniques for eliminating any potential consequences of the inflow (via venting, sorption, pre-heating, etc.) are in progress.

APPLICABLE CORROSION RESULTS FROM RELATED PROGRAMS

A substantial quantity of high-temperature aqueous compatibility information has been accumulated. Such data serve as a basis for HLW canister corrosion studies. Data are available from corrosion programs involving geothermal energy, seawater desalination, waste isolation testing (Project Salt Vault)[9], and light water nuclear reactor cooling cycles.

Project Salt Vault

A waste-isolation experiment in a salt mine which was conducted in the mid-1960's by the Oak Ridge National Laboratory, Project Salt Vault, produced results most relevant to bedded salt isolation. Conclusions from the corresponding laboratory segment of the Oak Ridge corrosion program[10], indicated that the austenitic stainless steels were sufficiently resistant to relatively dry bedded salt at typical storage temperatures to enable all critical components to be constructed from stainless steel (SS) 304L. Typical maximum general corrosion rates at 200-300^{0}C in synthetic salts with 1/2% water added were 0.02 mm/yr for SS-304L and 0.1 mm/yr for mild steels. Many expensive nickel-based alloys and titanium showed substantially better corrosion resistance than SS-304L. A major problem, however, was the observed susceptibility of the SS-304L to pitting and stress corrosion cracking in aqueous chloride environments[10]. Results from Project Salt Vault in situ heater experiments conducted in a salt mine near Lyons, Kansas confirmed this problem. Significant stress corrosion cracking of SS-304L heaters and SS-304 thermocouples occurred in regions where water condensate was present (normally on the top unheated heater sections). Only moderate rusting of similar carbon steel heaters occurred with no apparent reduction in wall thickness. Kegley and Empson[7] pointed out that four of the five necessary requirements for stress corrosion cracking (residual stress, elevated temperature, chloride ion, and parts per billion dissolved oxygen concentration) were present when the hot SS-304L HLW canisters were placed in bedded salt. The fifth, the presence of an aqueous liquid phase, may or may not be present in an actual repository because the canister thermal loading is not localized or cyclic as it was with the heaters. It was observed that brine inflow was most significant immediately after the heater was turned off and that this inflow was due to thermal shock fracturing.[9] A determination that prior exposure of the candidate metals to a ^{60}Co gamma radiation field did not affect the corrosion rates of the metals was another signficant finding of this study.

Geothermal Brines and Seawater

A significant number of studies have addressed metal compatibility in very corrosive hot geothermal brines because of the role such materials will have in tapping the vast energy source geothermal energy represents. The data collected in these studies are at least qualitatively applicable to the worst-case inundated condition for bedded salt and sub-seabed sediments. Shannon[6] has screened over 30 different alloys for resistance to high temperature brines. This screening was conducted in a refreshed autoclave apparatus. The effects of the following variables on corrosion rates were investigated and reported: temperature, salinity, dissolved H_2S, and dissolved silica. Variables making the most signficant contribution to the corrosion rate of steels were pH, temperature, and film composition. The alloys which withstood 250°C oxygen free brine best were Ebrite 26-1, SS 446, high chromium alloys, nickel alloys, titanium alloys, and zirconium. Chromium additions above 23% appear to notably improve corrosion resistance. Carter and McCawley[11] were led to similar conclusions based on their results from in situ tests in the California Salton Sea area. Banning and Oden[12] surveyed the literature and obtained a compilation of corrosion data for most alloy systems in hot brines and seawater. This survey included most of data available at that time concerning both geothermal and desalination corrosion programs. A brief summary of the major corrosion characteristics of the various candidate alloy families in hot brines and hot seawater taken from this survey plus a few related articles follow.[12,13,14,15,16]

1. Aluminum alloys: susceptible to stress corrosion, galvanic, metal ion, and pitting attack. Oxygen must be supplied to passivate.

2. Copper alloys: most alloys are immune to stress corrosion with good resistance to marine fouling and general corrosion. Oxygen discharge usually controls the corrosion rate.

3. Mild, low strength steels: hot brines are very corrosive with the corrosion rate increasing with increasing brine velocity, oxygen concentration, temperature, and other oxidants. These steels usually do not pit severely nor stress corrosion crack.

4. Stainless steels: the overall general corrosion rate is much lower than for mild steels, but the austenitic types are susceptible to pitting and stress corrosion cracking. The pitting potential is reduced in many molybdenum stabilized

stainless steels such as Carpenter 20Cb3, Nitronic 50, SS-316, and Ebrite 26-1.

5. Nickel based alloys: a few of the super alloys (Hastelloy C-276, Inconel 625) are virtually immune to damage by hot brines. As the temperature is increased, some of the high nickel alloys become susceptible to stress corrosion and localized attack. However, most of the nickel based alloys have been shown to be very resistant to hot salt stress corrosion cracking.

6. Titanium alloys: at ambient temperatures, these alloys are also immune to general corrosion, pitting and crevice attack. Pitting and crevice corrosion problems usually limit service temperature to below 250°C (above 250°C, titanium is not vastly superior to stainless steels). Many titanium alloys, such as the TIMET alloy Ticode 12 and Ti-0.2% Pd, were developed to increase the service temperature to above 250°C.

Galvanic couples can cause signficant corrosion problems. Southwell[17] investigated this problem with long term (greater than 16 yr) tests in tropical seawater and from these results made a compilation of bimetallic couple corrosion data. For example, carbon steel was shown to protect the mild steels, the stainless steels, and Monel. Incidentally, the excellent corrosion resistance of commercially pure lead was demonstrated during these tests.

Archeological Data

Archeological corrosion data are of interest when attempting to predict the long-term integrity of the canister (after the thermal output of the waste had diminished) in a seawater environment. R. F. Tylecote[18] recently reported on the archeological metal corrosion evidence gained from exploring historical shipwrecks (dated 400 to 2000+ years old). His conclusions include: (1) lead and copper or some copper-base alloys can last for over 1000 years in a submerged seawater environment; (2) a 5-10 cm casing of lead could be used for periods up to 2000 years; (3) a 1000-year lifetime could be provided with a 1- to 2 cm thick wrought copper shell, or alternately, a 14% tin bronze shell. This type of data must be used with a great deal of caution, however, because of differences in seawater chemistry which occur on the ocean floor and in sediments which have been heated and irradiated.

Retrievable Storage for HLW

Mecham, Seefeldt, and Steindler[19] comprehensively studied factors influencing the reliability of HLW canisters in retrievable storage configurations. Certainly, many of the considerations explored in their study may be applicable to waste isolation in deep geologic media. Some of these considerations include waste form characterization and associated chemical effects on canister properties, fabrication and closure of canisters, conditions and methods of control of both external and internal attack, and reliability establishment methods.

CURRENT CANISTER CORROSION PROGRAMS AND RESULTS

Several DOE funded corrosion studies related to HLW isolation canisters are now in progress. Such studies include corrosion related to waste solidification processes (internal canister corrosion), water basin storage, and compatibility of the candidate alloy with both the vitrified HLW and expected isolation environments.[15,20,21,22,23]

It has been found that corrosion effects in water basin storage are either insignificant or can be controlled by proper water process control.[20,21] However, a problem which transfers to the isolation site is the high tensile stress in the canister wall which results from glass solidification processes due to different coefficients of thermal expansion of the waste glasses and the metal canisters.

A long-term (50,000 hour) compatibility study of candidate HLW glass-metal-rocksalt interactions is being conducted at the Savannah River Laboratory.[21,22] This study includes internal canister corrosion measurements (from in-can melting of glass) as well as long-term, dry salt interaction evaluations. Very few results from the long-term interactions segment are presently available.

The compatibility of seven metals and eight alloys (Ta, Hf, Au, Ag, Pb, Ti, Cu, 1018 mild steel, 316 stainless steel, Everdur bronze, Monel, Coronze, Hastelloy C, Zircaloy-2, and alpha-brass) with 250°C concentrated brine is being studied at Pennsylvania State University to determine relative corrosion resistances.[23] The only result to date is that no catastrophic breakdown has been observed with any of the metals tested.

The Swedish Nuclear Fuel Safety Project task group has recommended the following canisters for disposal of spent fuel placed in hardrock formations:[24]

(1) Reprocessed waste will be packaged in a 6mm-thick titanium canister with a 100mm-thick lead lining.

(2) Spent unreprocessed fuel will be encapsulated with a 200mm-thick copper canister.

(3) Spent fuel assemblies might also be enclosed in ceramic alumina canisters produced by sintering under hot isostatic pressure.

Sandia HLW Metallurgy Program

The emphasis of the remainder of this paper is on results obtained in a broad scope HLW metallurgy program being conducted at Sandia Laboratories. This program addresses candidate canister and overpack metal corrosion in deep geologic isolation environments. It may be considered necessary to provide a corrosion resistant overpack in order to satisfy future lifetime design requirements. For example, the susceptibility of a SS-304L canister to stress corrosion cracking and pitting makes it unacceptable for 20-year retrievable storage in salt or sea-sediments.

The corrosion program at Sandia consists of both laboratory and field testing phases. Only the bedded salt and sub-seabed environments need to be simulated in the laboratory because the poor sealing properties of hardrock coupled with the high operating temperature at the hardrock-canister interface (200-300°C) will ensure that extensively studied air and steam oxidation processes will be dominant. The field or in situ experimental results will be used to confirm the predictive analytical models based on laboratory data (bedded salt or sub-seabed) or the high-temperature oxidation data presented in the literature (hard rock). The 70°C data presented in the Laboratory Results section on crushed salt and weld effects are also applicable to the case of spent fuel disposal in bedded salt, and to long term corrosion of the alloys after the thermal output of the waste has diminished.

A wide range of metals representing many different alloy groups have been considered as candidate commercial HLW containment materials for this program. The alloy selection was based on published corrosion results in chloride media at both low and elevated temperatures. Some of the alloys, notably copper, lead, and cupronickel, must be considered only as canister overpack materials because of their very low mechanical strength. A list of candidate metals and their chemical compositions are given in Table 2.

Sandia Laboratory Results

Most of the data to be presented resulted from coupon weight loss experiments under static inundated solution conditions. These high-temperature hydrothermal experiments were conducted for periods of two to eight weeks in SS-316 and Hastelloy C-276 autoclaves. The coupons were machined from 0.62cm plate and were sealed in either pyrex or fused quartz tubes along with an aliquot of solution (sea-sediments and crushed bedded salt were added to seawater and brine experiments, respectively). The experiments with oxygen were conducted in open ended fused quartz tubes. At the completion of the experiment, corrosion products were removed by either vapor or low pressure glass bead surface honing.

TABLE 2

NOMINAL CHEMICAL COMPOSITION OF CANDIDATE ALLOYS

Alloy	C	Mn	Si	Cr	Ni	Mo	Fe	Cu	Others
1018 Mild Steel	.18	0.75	0.25	-	-	-	Bal	-	-
4130 Carbon Steel	.3M*	0.5	.3	1.0	-	.2	Bal	-	-
Corten A Steel[e]	.1	0.4	0.5	1.0	-	-	Bal	-	.02Ti
2 1/4 Cr-1 Mo	.2	0.8	0.3	2.2	-	1	Bal	-	-
Naval Brass	-	-	-	-	-	-	-	60	39Zn,1Sn
90-10 Cupronickel	-	-	-	-	10	-	1.3	88.7	-
SS-304	.08M	2.0M	1.0M	19	10	-	Bal	-	-
SS-316	.08M	2.0M	1.0M	17	12	2.5	Bal	-	-
SS-Nitronic 50[g]	.06M	5	-	22	13	2.25	Bal	-	.2Nb,.2V
SS-20-Cb3[b]	.07M	2.0M	1.0M	20	34	2.5	Bal	3.5	-
SS-Ebrite 26-1[d]	.01M	0.4M	0.4M	26	0.5M	1	Bal	0.2M	-
Monel 400[a]	.2	1.0	0.2	-	66.5	-	1.2	31.5	-
Incoloy 825[a]	.03	0.5	0.2	21.5	42	3.0	30	2.2	0.9Ti
Inconel 600[a]	.04	0.20	0.20	15.5	76.0	-	8.0	-	-
Inconel 625[a]	.05	0.2	0.2	21.5	63	9.0	2.5	-	4Nb;0.2Ti
Hastelloy C-276[c]	-	-	-	15	59	.7	5	-	4W
Zircaloy 2	.12	-	-	0.1	0.05	-	-	-	1.5Sn,98.2Zr
Titanium, C.P.	-	-	-	-	-	-	-	-	99.5Ti
Ticode 12[f]	.012	-	-	-	0.84	0.34	.09	-	98.9Ti
MP35N	-	-	-	20	35	10	-	-	35Co

*M denotes maximum

Trademarks: [a]Huntington Alloys; [b]Carpenter Technology Corp; [c]Cabot Corp; [d]Allegheny Ludlum Industries; [e]U.S. Steel; [f]TIMET; [g]Armco Steel Corp

The inundated environment is extremely improbable for bedded salt and represents the worst-case condition of brine/water intrusion after repository closure. Sub-seabed sediments contain approximately 60% seawater; therefore, a highly corrosive inundated situation is more probable. Static conditions should prevail because large solution convections in either repository are very unlikely. Some corrosion results of both welded and unwelded coupons in more probable dry salt environments will also be presented.

A principal objective of the laboratory studies to date has been to provide preliminary scoping data and to select 6 to 8 metals for further comprehensive study from the previously mentioned list of over 20 candidate metals; the selected alloys are presented in a later section. Data gathered from tests on all of the candidate metals are presented here.

Effect of Solution Composition: The effect of two near-saturated brines along with seawater plus sea sediments on the corrosion rates of many alloys in 250°C, deoxygenated solutions is shown in Table 3. The composition of the two brines and seawater is given in Table 4[25,26]. Brine "A" is a high Mg/K/Na chloride brine and is representative of water which might intrude into the proposed Waste Isolation Pilot Plant (WIPP) site by percolation through an overlying potash zone; it is also considered tentatively representative of minute brine inclusions found in bedded-salt formations. Brine "B" is a near-saturated, predominantly NaCl brine representative of dissolved, bedded salt at the 800m horizon of the proposed WIPP site.

The interesting observation from these data is that the solution corrosiveness increases in the order: Brine B $<$ Seawater $<$ Brine A. This result is due to the differences in pH of the hot solutions, as shown in Table 5. These reported pH values were measured at 25°C after heating the solutions to the indicated temperature and quenching. These pH values are not to be taken as the actual values at temperature, but are indicative of an irreversible acid producing reaction which occurs in Brine A and seawater. This reaction is the hydrolyses of $MgCl_2$:

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

The actual pH will be somewhat higher than the values in the table due to bisulfate and bicarbonate equilibria.[6]

Localized attack on mirror polished coupon surfaces was minimal for most of the candidate alloys studied in the three solutions.

TABLE 3

CORROSION RATES OF CANDIDATE ALLOYS IN DEOXYGENATED SOLUTIONS (250°C, P = 5MPa)

Alloy	Brine A (mm/yr)	Brine B (mm/yr)	Seawater (mm/yr)
1018 Mild Steel	1.7	0.07	0.4
Corten A Steel	0.9	0.05	0.2
2 1/4 Cr-1 Mo Steel	1.0**	0.1**	0.2
Lead	0.5	0.3	0.3
Copper	0.07	0.05	0.05
Naval Brass	1.0	-	1.0
90-10 Cupronickel	0.14	-	0.07
SS-304L	0.018	0.01	0.006
SS-316L	0.015	-	0.005
SS-Nitronic 50	0.008	-	0.003
SS-20Cb3	0.007	-	0.005
SS-Ebrite 26-1	0.016	-	0.005
Monel 400	0.03	-	0.1
Incoloy 825	0.006	-	0.004
Inconel 600	0.009	0.007	0.005
Inconel 625	0.005	0.001	0.012*
Hastelloy C-276	0.007	-	0.0015
Zircaloy-2	0.001	-	-
Titanium C.P.	0.003	-	0.006
Ticode 12	0.0006	-	0.005

*pitting corrosion; **crevice corrosion

TABLE 4

REPRESENTATIVE SOLUTION COMPOSITIONS
(major ions)

Ion	Seawater (ppm)	Brine A (ppm)	Brine B (ppm)
Na^+	10,651	42,000	115,000
K^+	380	30,000	15
Mg^{+2}	1,272	35,000	10
Ca^{+2}	400	600	900
Sr^{+2}	13	5	15
Cl^-	18,980	190,000	175,000
SO_4^{-2}	884	3,500	3,500
I^-	.05	10	10
HCO_3^-	146	700	10
Br^-	65	400	400
BO_3	-	1200	10
pH	8.1	6.5	6.5
Total Dissolved Solids:	35g/l	306g/l	297g/l

Effect of Oxygen: The effect of a substantial quantity of dissolved oxygen on the corrosion rates of selected alloys in Brine A and seawater is shown in Table 6. A constant partial pressure of 1 MPa oxygen was used during the course of the experiment to maintain a high level of dissolved oxygen; this should represent an overtest of the worst-case effects of oxidizing radiolysis products on corrosion. The effect of oxygen was greater in the case of seawater than Brine "A" because of greater oxygen solubilty in seawater than Brine "A". It is interesting to note that the oxygenated corrosion rates of all alloys studied (Table 6) increased over their corresponding deoxygenated rates (Table 3). Many of these metals have been shown not to support an oxygen current at 25°C[15]; this apparently is not the case at 250°C. This effect and the unexpected discovery that Hastelloy C-276 pitted in these solutions will be investigated further using electrochemical techniques.

Effect of Temperature: The effect of temperature on the initial corrosion rate of 1018 mild steel in deoxygenated seawater and brine B was determined using linear and Tafel DC electrochemical polarization techniques. The temperature range considered was 25 to 200°C. These calculated rates were an order of magnitude higher than measured similar long-term weight loss results (Table 3). This difference resulted because the electrochemical derived value represents an instantaneous initial rate. However, useful quantities are the apparent activation energies which were calculated using these initial results. These values equaled 5 kcal/mole for Brine B and 4 kcal/mole for seawater. A more extensive study of temperature effects on the corrosion of selected candidate metals is presently in progress.

Effect of Moisture Content (Dry, Moist): An experiment was conducted in which coupons were placed in crushed salt at 200°C with 100% relative humidity present. The following corrosion rates (mm/yr) were measured at the conclusion of this test: 1018 mild steel = 0.15; SS-304 = 0.004; SS-20Cb3 = 0.004; Inconel 600 = 0.004; and Ticode 12 = 0.004. As expected, all of these rates were less than those under inundated Brine B conditions (Table 3), but still not insignificant.

The corrosion rates of 1018 mild steel and SS-304L in dry crushed bedded salt with 1/2% water added were not measurable at 25°C, 70°C, or 200°C after 5 months of exposure. At 70°C and 200°C the steel samples showed only slight surface corrosion. The SS-304L samples were marked with a few small pits. Of course, experiments such as these only confirm well known observations that relatively dry salt mines are not corrosive to even susceptible alloys like 1018 mild steel.

TABLE 5

EFFECT OF TEMPERATURE ON QUENCHED SOLUTION pH

Temperature (°C)	Seawater 25°C pH	Brine A 25°C pH	Brine B 25°C pH
25	8.1	6.5	7.2
100	8.6	7.0	7.6
200	5.5	-	6.6
250	3.9	3.4	-
270	3.3	-	6.3

TABLE 6

CORROSION RATES OF CANDIDATE ALLOYS IN OXYGENATED SOLUTIONS

(250°C and P=7MPa)
(O_2)=600 ppm in Brine A and 1750 ppm in Seawater.

Alloy	Brine A (mm/yr)	Seawater (mm/yr)
1018 Mild Steel	7.0	11.0
Copper	1.2	5.0
Lead	1.2	1.0
90-10 Cupronickel	0.4	0.7
SS-Ebrite 26-1	0.24	-
SS-20Cb3	0.1**	-
Inconel 600	-	0.1
Hastelloy C-276	0.06*	0.2*
Ticode 12	0.004	-

* pitting and crevice corrosion
**crevice corrosion

Effect of Solution Volume and Hydrostatic Pressure: Most of the coupon experiments were conducted with a solution volume/alloy surface area ratio of 2-3 ml/cm^2 and a pressure of 5 MPa (700 psi). Lowering the solution volume/surface area ratio by a factor of 10 doubled the corrosion rate of 1018 mild steel. This result was probably due to the lower observed pH of the small volume experiments (3.2 versus 4). While this effect on the more corrosion resistant alloys is unknown, it is not expected to be as great. The effect of increasing the hydrostatic pressure on a wide range of alloys under deoxygenated conditions was to increase slightly the corrosion rate. This increase, however, was within experimental error and, therefore, the determination of its signficance requires further investigation. This work is in progress.

Effect of Welding and Crevices: Welded coupons with clamped crevices made from 1018 mild steel, SS-304L, and Hastelloy C-276 were exposed to deaerated Brine B at 70°C, and 200°C. Crevice corrosion problems were nonexistent in these deaerated solutions. The 1018 steel samples exhibited general corrosion but no weld attack. The SS-304L specimens showed numerous pits around the welded areas at 70°C only, whereas the Hastelloy C-276 samples were virtually immune from attack. Corrosion rates were again unmeasurable at 70°C. Measured corrosion rates at 200°C are as follows: 1018 = 0.1 mm/yr; SS-304L = .005 mm/year; and Hastelloy C-276 = 0.0001 mm/yr. The surprising lack of pitting of SS-304L at 200°C must be due to a significant separation between the rest and pitting potentials in deoxygenated high temperature brine. This electrochemical effect will be explored in greater detail.

Field Testing Results

Full-size heater experiments are being conducted or are scheduled at the following times and places:

1. January 1978 to August 1978, in the Conasauga formation in Tennessee
2. June 1978 to December 1978, in the Eleana shale formation at the Nevada Test Site
3. Summer 1979, in bedded salt in New Mexico
4. Summer 1981, in the deep North Pacific Ocean (sub-seabed sediments)

Conasauga Experiment: The Conasauga experiment has been completed. Galvanically isolated metal coupons were attached to the bottom of an electrical heater. The heater was placed into a forced dry hole in this hardrock formation. The following metals were evaluated: SS-Nitronic 50, SS-20Cb3, zirconium, Kovar, Hastelloy C-276, aluminum 2024, 1018 mild steel, 4130 carbon steel, Inconel 600, MP35N, titanium C.P. and SS-304L. The samples were held at about 200°C for 180 days. Only surface oxidation with superficial corrosion occurred during this test indicating that thermal decomposition products of the formation are not corrosive. However, another heater was placed in a very wet hole; the SS-304L heater shell tarnished, but corrosion was insignificant. A problem did occur near the top of the heater where condensed water existed. Here, all the thin SS-304 sheathed thermocouples, which had been severely deformed to fit alongside the canister, stress corrosion cracked. In the future this thermocouple problem will be avoided by using Inconel sheathed thermocouples.

Bench-Scale Salt Block Experiment

In order to scale-up laboratory corrosion testing for the bedded-salt (WIPP) corrosion study, an electrically heated bedded-salt block (a 1-meter cube) was utilized. The salt block (halite) was obtained from a southeastern New Mexico potash mine at approximately the 300m-deep horizon. Fourteen candidate corrosion coupons were picked to represent a wide range of classes. Included were the following: (1) titanium C.P., (2) titanium-6V-4Al, (3) Hastelloy C-276, (4) Inconel 600, (5) zirconium, (6) Zircaloy-2, (7) Zircaloy-4, (8) SS-20Cb3, (9) SS-Nitronic 50, (10) SS-304, (11) 17-4 pH stainless steel, (12) 70-30 brass, (13) aluminum 6061, and (14) 1018 mild steel. These alloys are listed in order of expected decreasing corrosion resistance. One surface of each coupon was mirror polished and photographed. This would enable a qualitative visual determination of any corrosion to be made. Power was supplied to the heater for 99 days. The temperature at the bottom of the coupon hole was maintained between 100°C and 150°C for most of the duration of the experiment. Examination of all coupons confirmed what might have been expected, that is, nothing corroded. Most of the coupons and the plain carbon steel heater shell appeared exactly as they did four months earlier, except for the 70-30 brass, 1018 steel and 304 stainless steel coupons. Each of these three had a thin, nonadherent oxide film on the polished surface. The weight change was below experimental detection limits. This indicated the presence of moisture at one time or another, but the absence of pitting on the SS-304 and aluminum sample showed that the moisture was present only temporarily, most likely before startup.

Selection of Candidate Metals for Further Study

Eight candidate alloys have been selected for further comprehensive study. The selection criteria included corrosion resistance under a variety of conditions, along with metal cost and availability. The selected prime candidate alloys are as follows (listed in order of increasing corrosion resistance): 1018 mild steel, Corten A steel, lead, 90-10 cupronickel, SS-Ebrite 26-1, Monel 400, Inconel 600, and Ticode 12.

ONGOING AND FUTURE RESEARCH

The following studies are currently underway at Sandia Laboratories or are planned to commence by early FY 1980:

Bedded Salt and Sub-Seabed Compatibility Studies

1. More sensitive corrosion measurement techniques for use on very corrosion resistant alloys are needed. Techniques under consideration include ion implantation of markers, radiochemistry, and instrumental analytical chemistry methods.

2. Further, comprehensive investigations on the effects of geologic isolation environment variables on the corrosion characteristics (type of corrosion) and corrosion rate are being conducted on the eight prime candidate alloys identified. The types of investigations and variables studied are as follows:

   (a) temperature (25°C - 250°C)
   (b) dissolved O_2 concentration (0 - 1000 ppm). Electrochemical methods will be used to determine whether metals will support an O_2 current
   (c) welding and sensitization
   (d) solution composition (Brine A, Brine B, Seawater)
   (e) solution volume/surface area ratio
   (f) hydrostatic pressure
   (g) flowing vs. static solution systems
   (h) prior radiation damage
   (i) intense gamma irradiation/radiolysis product effects on the canister-salt-brine system (at low and elevated temperatures)
   (j) stress corrosion cracking susceptibility at low and elevated temperature through use of slow strain rate technique
   (k) long-term (greater than 1 year) 250°C exposure to brine and seawater.

3. Long-term compatibility studies of selected alloys will be conducted with the more probable dry bedded-salt condition. This part of the study will complement the similar ongoing program at the Savannah River Laboratory.[21,22]

4. (a) An in situ heater/corrosion test in bedded salt, in southeastern New Mexico (not the proposed WIPP site), will begin late in fiscal year 1979. This test will complement the ongoing laboratory tests, but on a larger scale. A similar heater experiment in the deep North Pacific will be conducted in late 1982.
   (b) In situ demonstration testing with actual canisters of reprocessed, commercial HLW will commence at the bedded-salt WIPP facility when the first quantities of HLW are received for experimental purposes, in approximately early 1986. Experimentation only, not terminal isolation, is scheduled for HLW in the WIPP. Corrosion testing, overtesting, and demonstrations are but a small portion of the overall in situ experimental program perceived for the WIPP. Such testing and demonstrations will help confirm previous laboratory, bench-scale, and in situ heater testing results and further verify analytical models based on such data. In situ real-waste experiments provide a real- world final test, with no assumptions or simulations, and are considered an absolute necessity for a totally conclusive compatibility evaluation.

Hardrock Studies

In situ heater experiments to verify expected environmental effects on corrosion and canister alloy recommendations will be continued.

ECONOMIC IMPACT OF CANISTER MATERIAL

Certainly, the cost of a HLW canister/overpack and the impact of that metal on available natural resources should be selection criteria. For comparative purposes only, the proposed reference high-level waste canister for the WIPP program will be assumed to be a standard canister design. This canister is a double-shell right circular cylinder with a 15-foot (4.6m) overall length and a 14-inch (0.36m) outside diameter. This canister allows for the accomodation of commercially reprocessed high-level wastes and/or spent-fuel assemblies. The selected diameter (along with the assumed vitrified HLW composition) limits the maximum canister-bedded salt interface temperature to approximately 250°C. An assumed overpack is made from schedule 10 (0.25-inch wall) pipe. The inner-waste stainless steel canister is made from 12.75-inch O.D. schedule 40 (0.406-inch wall) pipe. Obviously, these dimensions may be altered in the future, based on many dependencies or requirements. The inner canister provides the necessary mechanical strength for handling, emplacement, and for withstanding geologic overburden pressure. The effective volume of the canister is 295 liters. Kisner et al[27] projected that

10,400 m^3 of commercial HLW glass will have been processed by the year 2010 (assuming HLW reprocessing). This waste will fill 35,200 canisters, corresponding to the generation of $9X10^{13}$kwh of power. A stainless-steel inside canister will be assumed in order to meet the requirements of in-can melt reprocessing requirements. The remainder of this section will address candidate corrosion resistant overpack metals.

Comparative Reference Overpack Costs

Comparative reference overpack costs for a variety of metals are shown in Table 7. Overpack fabrication charges are not included. The very high costs of the corrosion-resistant alloys can be quite misleading because most lifetime design requirements would not require a full quarter inch of these metals for corrosion protection. Utilizing data in Table 6 for the worst-case, brine inundated, 250°C, oxidizing environment, overpack material costs were recalculated for a "1-year (transportation, handling)," "25-year (retrievability)," and "300-year lifetime" barrier. These costs, relative to the cost of a Ticode 12 overpack, are shown in Table 8.

Uniform corrosion rates generally decrease with time; this would make long-term extrapolations based on our short-term experiments somewhat conservative. However, this type of extrapolation is not well substantiated and therefore the data presented in Table 8 should be taken as semi-quantitative for comparative purposes only. Thin coatings of the corrosion-resistant alloys can be very effectively submerged arc deposited or plasma sprayed onto less expensive substrates. Clearly future design requirements or lifetime options will eventually dictate which alloys and which methods of application are most economical or desirable.

Material Requirements vs. Resource Reserves

Another important area which needs to be addressed is the impact of the materials selection on availability and total-world natural resource reserves. The annual raw material requirements for a number of alloys is shown in Table 9. These figures are based on a 20-year linear production schedule of the required 35,200 reference (1/4-inch thick) overpacks. The impact of this annual requirement on present U.S. availibility[28] and the overall 20-year requirement on world reserves[29] is shown graphically in Figure 1. The large impact on annual consumption of titantium is not as signficant as it appears. Titanium production facilities are currently not being run at full capacity because of low demand. Additionally, a full quarter inch of overpack may not be necessary, as mentioned previously.

TABLE 7

COMPARATIVE REFERENCE OVERPACK ALLOY COSTS

(all based on 1978 dollars, excluding final fabrication charges)

Alloy	$/lb	$/Overpack (0.25-inch wall)	Total Overpack Alloy Cost by Year 2010 (Million$)
A36 Mild Steel	0.26	145	5
Corten A Steel	0.31	167	6
Lead	0.81	650	23
Copper	1.88	1195	42
90-10 Cupronickel	2.54	1614	57
SS-Ebrite 26-1	2.53	1394	49
Monel 400	3.72	2180	77
SS-20Cb3	3.72	2050	72
Incoloy 825	3.62	2041	72
Inconel 600	4.11	2613	92
Titanium C.P.	5.96	1917	67
Ticode-12	7.15	2300	81
Hastelloy C-276	7.65	4860	171
SS-304L (Canister)	1.04	778	27

TABLE 8

RELATIVE ECONOMIC OVERPACK DESIGN DATA, BASED ON CORROSION RATES IN WORST-CASE INUNDATED, OXIDIZING, 250°C BRINE "A" ENVIRONMENT

	Relative Alloy Cost for Overpack Required to Provide Stated Lifetime**		
Alloy	1 year	25 years	300 years
A36 Mild Steel	0.3	7	83
Lead	0.3*	5	64
Copper	0.5*	10	117
90-10 Cupronickel	0.7*	4	52
SS-Ebrite 26-1	0.6*	3	28
Hastelloy C-276	2.0*	2	24
Inconel 600	1.1*	1.2	14
Ticode 12	1.0*	1.0*	1.0*

* minimum wall thickness 1.6mm (1/16-inch sheet)

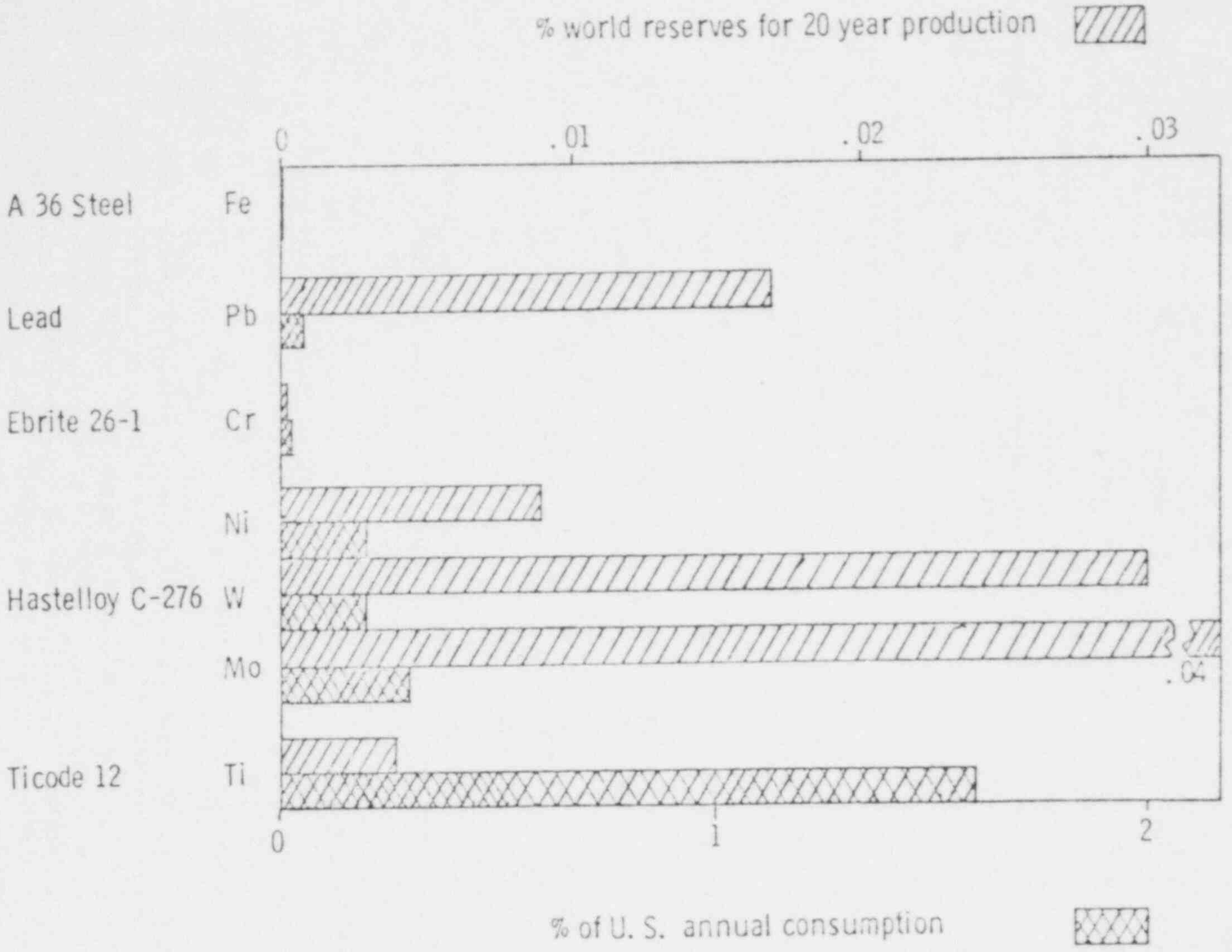
** wall thickness calculated from corrosion rate or taken as 1.6mm,* whichever is greater. Cost of 1.6 mm Ticode 12 overpack is $580 (1978).

TABLE 9

ANNUAL RAW MATERIAL REQUIREMENTS THROUGH YEAR 2010 (20-YEAR OVERPACK PRODUCTION SCHEDULE)

Alloy	Critical Component	Annual Tonnage (tons) Required
A36 Mild Steel	Fe	490
Lead	Pb	710
90-10 Cupronickel	Cu	501
SS-Ebrite 26-1	Cr	126
Hastelloy C-276	Ni	330
	W	22
	Mo	95
Ticode-12	Ti	283

Figure 1. Impact of Raw Material Requirements on Availability



It should be stressed that the most cost-effective material can only be identified after a site-specific environment is fully defined and lifetime design requirements are chosen. For example, if bedded salt repository conditions could be predicted to remain dry indefinitely, then a 1018 mild steel canister would provide a substantial period of isolation.

SUMMARY

Disposal of high-level waste in stable geologic formations is presently considered the most viable method for insuring the isolation of radionuclides contained in the waste. Although the waste canister is only one of several physical/geochemical barriers which block the dispersal of radionuclides towards the biosphere, it may play a significant role during the first several hundred years after emplacement. The compatibility of candidate waste canister materials with deep geologic isolation environments is being investigated in a series of interrelated laboratory, bench-scale, and in situ experiments. Results presented are partially applicable to bedded and domed salt, subseabed sediment, and various types of hardrock geologic waste repository or test facilities. Emphasis in this work is on bedded-salt and seabed environments.

Candidate HLW canister and overpack metals which satisfy appropriate requirements for barrier lifetime, costs, and mechanical properties have been identified using data presented. Lifetime objectives generally range from 0-5 years for transportation and handling requirements, to 5-25 years for waste retrievability constraints, and approximately 300 years for retardation of near-field, thermally driven interactions such as wasteform leaching, followed by potential radionuclide migration.

Objectives of metallurgical compatibility testing include: further defining interaction kinetics and mechanisms under appropriate conditions; providing data necessary for repository design and overall repository safety analysis studies; and, making and testing predictive analytical models based on such data. Corrosion data from the Project Salt Vault waste isolation test in bedded salt, data from geothermal brine testing, and other existing data are incorporated where applicable. The bulk of data (and emphasis) is on corrosion studies in progress at Sandia Laboratories.

Several series of laboratory tests were conducted to evaluate the effects of environmental parameters on resultant corrosion rates. The parameters represent both optimized emplacement conditions and credible, worst-case (e.g., water intrusion) boundary conditions. Variables tested include: temperature (25-250^{o}C), pressure, solution composition, oxygen concentrations, solution volume/surface area ratios, welding and crevice effects, and dry and moist salt effects. Several conclusions may be based on this data.

1. Solution corrosiveness increases in the order

   Brine B (NaCl) < Seawater < Brine A (Mg/K/Na chloride)

   These differences are probably due to a pH effect (conclusion #2).

2. The pH of seawater and Brine A decreases (from 8.1 and 6.5 at 25°C) as the solution temperature is raised (quenched, 250°C pH values are 3.9 and 3.4, respectively). Brine B pH values changed less than one unit.

3. The presence of substantial amounts of oxygen increases the corrosion rate of all alloys in seawater and in brine.

4. Localized attack (crevice corrosion and pitting) in deaerated 200°C and 250°C seawater and brine has been minimal even for 304L SS. This is surely due to a signficant separation between the rest and pitting potentials of these alloys at the high temperatures investigated. The high temperature electrochemical properties of these alloys are presently being studied. In the presence of oxygen, however, significant localized attack has been observed even in the very corrosion resistant alloys such as Carpenter 20Cb3 and Hastelloy C-276.

5. The effect of radiolysis products (due to high dosage gamma irradiation) is an area that is still insufficiently quantified. More investigation is planned.

6. The economic impact of utilizing several candidate canister and canister overpack materials is also addressed. Overpack costs were calculated for possible 1-, 25-, and 300-year design lifetime requirements under worst-case, brine inundated, 250°C oxidizing environments. The most expensive (per unit weight) alloys appear to be cost-effective for both the 25- and 300-year lifetime alternatives. Alloy requirements can be satisfied with present U.S. production capacity.

7. A wide range of approximately 20 candidate metals was initially tested for corrosion rates under appropriate simulated HLW isolation conditions. Based on these initial results, published data, and alloy costs and availability, eight prime candidate alloys were selected for further comprehensive study: 1018 mild steel, Corten A steel, lead, 90-10 Cupronickel, SS-Ebrite 26-1, Monel 400, Inconel 600, and Ticode-12.

In conclusion, it appears possible to provide an HLW canister-overpack system which can survive the potentially corrosive environments of a terminal isolation geologic facility for desired periods of time. A canister/overpack can protect the HLW form from aqueous leaching (assuming an intruding leachant) during the period of greatest waste thermal output--and greatest reactivity. The canister/overpack system can thus be a valuable segment of the multibarrier concept for HLW isolation. Studies are in progress to both further assess and then conclusively demonstrate the utility of this engineered, metallic barrier.

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Discussion Following

HIGH-LEVEL WASTE CANISTER CORROSION STUDIES PERTINENT TO GEOLOGIC ISOLATION

Presented by Jeffrey W. Braithwaite

Robert Leachman - NRC
Question:
It is conceivable, and I emphasize the word conceivable, that the licensing process might require the canister designer to certify its reliability on its own accord--not as part of a system of barriers. Is it possible to certify the canisters for the lifetime of the hazard for the fission products (namely 500 or 1000 years), for example, under the worst case conditions of salt--perhaps also the worst case conditions of basalt. If it is not possible to certify this, what more needs to be done?

Braithwaithe
Response:
I would think, with the scope of the present studies expanding as we hope they will, that it is definitely possible. I think that approximately 500 years is the limit. The DOE sponsored a symposium in Washington last year in June, and a lot of corrosion experts got together and talked that over--what was the maximum lifetime that anybody would dare sign their name to. That is what you are talking about, that thermal period plus a touch. I think that is very possible and very achievable, but no more than that.

Robert Anderson - San Jose State University
Question:
I am curious about your corrosion rates. What would happen if there was a radiation field. Would corrosion increase or decrease in a radiation field? Also, will candidate materials maintain the same order of performance in a radiation field as they do without radiation?

Braithwaite
Response:
I kind of rushed through that, but we were trying to overtest that with the oxygen. With all the materials that we tested, the corrosion rate increased by about a factor of ten when the tremendous amount of oxygen was added to these solutions. The rad[illegible] or would not effect the material's passive layer, but it will e[illegible] radiolysis products. That is what you need to worry about, what will happen to these solutions that are around the canister. We presently have that under study. We are trying to work out a joint program with the United Kingdom, also, to put autoclaves into a high gamma field and do these tests in-situ.

We currently have those tests going at a lower temperature, in approximately the range of 80 or 90 degrees centrigrade. It is a problem we are trying to further quantify, but it is the radiolysis products that you need to worry about. We think that we overtested it with that increase in oxygen that we put in. Everything seems to be susceptible to that great quantity of oxygen.

Pedro Macedo - Catholic University of America
Question:
My question was more or less asked before. I was going to ask about radiolysis. Specifically, when you have salt in the water you are going to be making HCl, and if you also happen to have fluorine in the water--because some of these salts we are talking about have fluroide--you would also be making HF. Would that not attack your passifying layer?

Braithwaithe
Response:
The pH drops quite significantly due to magnesium chloride hydrolysis at these high temperatures and produces HCl. The acidity of the magnesium brine for which I showed the corrosion results drops down to a little bit less than three. It is very acidic just due to hydrolysis, and the radiolysis will also produce more. The HCl is produced from hydrolysis, and so that should be taken care of. A low concentration of fluroide is present in the test brine, so these corrosion rates should represent realistic conditions.

Macedo
Comment:
The other element which is bad in hydrolysis is peroxide.

Braithwaithe
Response:
Certainly most theories state that peroxide is an intermediate in oxygen discharge and that peroxide formation is the slow step. Certainly when we swamp the conditions with one gram per liter of dissolved oxygen, we should have certainly seen that effect there.

Fred Schmidt - University of Washington
Question:
The Australian geologist, Ringwood, has suggested another kind of material which he claims is known to be stable against corrosion for millions of years. It is an iron nickel alloy. I guess that would even satisfy the NRC licensing requirement if it is true. Do you happen to know anything about this particular suggestion?

Donald Cameron - Whiteshell Nuclear Research Establishment
Comment:
Can I comment on that? I have some information. The material was an intermetallic compound Ni_3Fe. A recent rebuttal by J. B. Lewis in <u>Nuclear Engineering International</u>, Vol 23, No. 278, pp. 28-29, 1978, says that it will perform worse than stainless steel in most geological environments which you might encounter.

Larry Hench - University of Florida
Question:
There is an enormous variability in the welding characteristics of the lists that you presented. Are the criteria of ease of welding under remote conditions and reliability of weld one of the factors that are being considered in rating materials?

Braithwaithe
Response:
It was not in the present list. We have learned that the titanium alloy is not much harder to weld than nickel-base alloys. The technology exists that can do that. The fabricability of canisters is something that certainly needs to be looked at. Our intent and I think the intent of everybody was to limit the number of materials for which we can look at that detailed sort of thing. Yes, fabrication certainly is a consideration, along with the welding itself and its effect on corrosion. We have done some of that and it is in our paper.

Alexis Parks - Boulder, Colorado, private citizen
Question:
There is increasing scientific controversy over the use of salt or salt domes for repositories. Assume, for example, DOE is proceeding with WIPP to allow the licensing process in California and elsewhere to simply continue. If the emphasis is changing, then what percentage of the total research efforts are being applied to study canister integrity for other types of geologic media--basalt, shale and others--and what problems are associated with the other potentially more desirable media?

Braithwaithe
Response:
Martin Molecke might be able to answer.

Martin Molecke - Sandia Laboratories, Albuquerque
Response:
A large fraction of the work that is under progress at Sandia is funded by the WIPP and is specific to salt. There is also a significant seabed effort. As far as corrosion studies for granite goes, I think I probably should defer to the Swedes. Sandia is not looking at that aspect specifically. There are some in-situ tests in progress which are described briefly in the paper, however. The majority of the work in Sandia is on salt beds and seabeds, very little on other media.

Ceramic and pure-metal canisters in buffer material

by Per-Eric Ahlström, Kärnbränslesäkerhet,
Stockholm, Sweden

presented at the

Conference on High-Level Radioactive Solid Waste Forms
in Denver, Colorado, USA December 19-21, 1978.

CERAMIC AND PURE-METAL CANISTERS IN BUFFER MATERIAL

by Per-Eric Ahlström, Kärnbränslesäkerhet, Stockholm, Sweden

ABSTRACT

Within the Swedish KBS-project a great effort has been devoted to the development of canisters for the encapsulation of high level vitrified waste or spent unreprocessed fuel. The canisters will upon final disposal in deep geological formations provide an extra engineered barrier against the dispersal of radioactive nuclides in the groundwater. Comprehensive studies have been made on two types of pure metal canisters i.e. lead-titanium for the high level vitrified waste and pure copper for spent fuel. The final disposal is made in hard crystalline rock where the waste canisters are embedded in a buffer material - a clay with good long term stability. For the lead-titanium canister a mixture of quartz sand and bentonite is proposed whereas for the copper canister highly compressed bentonite is preferred. Careful evaluations predicted a lifetime of at least thousands of years for the lead-titanium canisters and probably tens of thousands of years in the actual environment. For the copper canister it is realistic to expect a lifetime of hundreds of thousands of years. Comprehensive studies have also been made of a ceramic canister of alumina for spent fuel. Through hot isostatic pressing it is possible to make a completely tight and joint-free alumina container. Alumina has a very high chemical and mechanical resistance over very long periods of time. Preliminary studies have also been made of a glass ceramic material of the beta-spodumenetype.

CERAMIC AND PURE-METAL CANISTERS IN BUFFER MATERIAL

by Per-Eric Ahlström, Kärnbränslesäkerhet,
Stockholm, Sweden

1. BACKGROUND

In April 1977 the Swedish Parliament passed a Nuclear Stipulation Law which requires that prior to the loading of fuel or operation of any additional nuclear reactor in Sweden, the reactor operator shall either:

1. produce a contract which adequately provides for the reprocessing of spent fuel and also demonstrate how and where the final deposition of the highly radioactive waste resulting from the reprocessing can be effected with absolute safety, or
2. show how and where the spent but not reprocessed nuclear fuel can be finally stored with absolute safety.

In response to the Government bill proposing the Law, the Swedish nuclear power industry decided in December 1976 to give top priority to the investigation of the high-level waste problem. The Nuclear Fuel Safety Project (KBS) was therefore organized within the legal framework of the Swedish Nuclear Fuel Supply Company (SKBF).

The KBS-project has investigated both the alternatives mentioned in the Stipulation Law. A report on the handling and final storage of high level vitrified waste was published in December 1977 /1/. This report was submitted as evidence by the utilities in Sweden in applications to load fuel to the reactors Ringhals unit 3 and Forsmark unit 1. The Swedish government rejected the applications because the geological field investigations did not prove that there was a suitable rock formation in Sweden big enough to host the total amount of high level waste. Additional drilling and field measurements are now being made in order to show a larger rock mass with the required properties.

In September 1978 a report on the final disposal of unreprocessed spent nuclear fuel was published by KBS /2/.

The Swedish nuclear power industry also has decided to continue the work started by KBS on a more long term basis. This research and development work is performed within the SKBF-company with a slightly modified organization as compared to the original project. The continued work includes studies within the geological and hydrogeological field, on buffer materials, on properties of vitrified waste, on medium and low level waste and on safety analysis. Included are the on-going studies in the old iron-mine at Stripa, which are performed jointly by KBS and University of California, Lawrence Berkely Laboratory and sponsored by the US Departement of Energy /3/.

2. GENERAL PREMISES

A general premise for the work on high level waste in Sweden during the last years has been that the final storage should be made in the precambrian bedrock (gneiss, granite) which is abundant in Sweden /4/.

The factors that will determine the suitability of a rock formation for final storage are its permeability and strength, the composition of the groundwater and its flow pattern and the delaying effects on radioactive substances when groundwater passes through fissures in the rock. Of special interest is also the risk of rock movements which could affect the pattern of groundwater flow or damage the encapsulated waste.

Assessing these factors, a depth of about 500 meters is considered to be suitable. At this depth, the bedrock contains fewer cracks and has lower water permeability than closer to the surface. This depth also gives a satisfactory protection against acts of war and such extreme events as meteorite impacts and the effects of a future ice age.

The nuclear reactors which are in operation or under construction in Sweden are all of the light water reactor type. Three of them are of the pressurized water reactor design whereas the others are boiling water reactors. At present six units are in operation, six are under various stages of construction and an additional unit was authorized by the parliament in the 1975 energy program. Thus it is expected that around 1990 about 300 metric ton (uranium weight) of spent nuclear fuel will be unloaded each year from the Swedish reactors. The burnup of the fuel will be 33 MWd/kgU for PWR fuel and 28 MWd/kgU for BWR fuel on the average. The proportions will be 25% PWR and 75% BWR fuel.

There is no capability for reprocessing of spent fuel in Sweden. The nuclear power utilities do, however, have reprocessing contracts with the operators of the British reprocessing plant at Windscale and of the French plant at La Hague. For the KBS studies the existing (or planned) French processes were used as reference in order to define the waste product. The high level-waste separated in the reprocessing is stored for some time as a liquid in stainless steel tanks. It is then solified first to calcine and then to borosilicate glass. The glass will contain about 9% fission products and about 1% actinides. Each metric ton of reprocessed uranium in spent fuel will give one glass cylinder with a glass volume of 150 liters; see figure 1. The waste cylinders will be shipped back to Sweden about 10 years after the fuel was unloaded from the reactor.

3. SAFETY PRINCIPLES FOR FINAL DISPOSAL

There are no universally accepted criteria for evaluating the safety of a repository for final disposal of radioactive waste. The bill proposing the Swedish Stipulation Law stated that "the primary consideration is whether the storage method can meet requirements for satisfactory radiation protection". Furthermore, the repository should "permit the isolation of the waste for as long time as is required for the radioactivity to decay to a harmless level".

Disposal of highly radioactive waste at 500 m depth in granite or gneiss of good quality will give a very good isolation of the radioactive substances. The water flow in such rock is very low - of the order 0.1 - 0.2 liter per m^2 and year or less /1, 2/. Radionuclides which are leached to the groundwater are strongly retarded by the rock and by clay material in the rock fissures /5, 6/. Transit time for the ground water at this depth to the biosphere is probably several thousand years.

In order to achieve the very high degree of safety expressed by the Stipulation Law it was, however, considered prudent to provide additional isolation by engineered barriers. These should give redundant safety during the time period when the waste has its largest heat generation and toxicity. The difference in toxicity between spent fuel and high-level vitrified waste is illustrated by figure 2. The residual heat from the waste follows similar curves. Considerations with respect to such decay curves and to temperature increases in the bedrock lead to the conclusion that any engineered barrier should have a lifetime of at least 500 to 1 000 years in order to provide redundancy. Furthermore the requirement on the engineered barrier is larger for spent fuel than for vitrified waste. A contributing reason for this is that the waste structure is less homogeneous for the fuel then for the glass.

Within the KBS-project a great effort has been devoted to the development of engineered barriers for the high level waste. The basic concept has been to enclose the waste in a canister with long time resistance against corrosion in groundwater. These canisters are then deposited in holes drilled from the floor of tunnels in the rock. The deposition holes, the tunnels and the shafts are backfilled with a buffermaterial. Both the buffermaterial and the canister should be considered as engineered barriers in contrast to the rock itself, which would be a natural barrier.

For the canister both ceramic and metallic materials were investigated. In the two main reports from the KBS-project /1, 2/ the proposed materials was a combination of lead and titanium for the vitrified waste /1/ and copper for the spent fuel /2/. Considerable work has also been made on a canister of alumina for spent fuel /2/. Preliminary studies were also made on a glass ceramic material of the beta-spodumene-type.

As buffermaterials the leading candidates were mixtures of quartz sand and bentonite, pure bentonite and various zeolites. The studies were at an early stage concentrated to bentonite and to the sand/bentonite mixture.

The remaining part of this report summerizes the main results of the KBS studies of buffermaterials and canisters as engineered barriers for long term isolation of high level waste.

4. BUFFER MATERIAL

The material used to backfill deposition holes and seal tunnels and shafts should possess the following properties:

- bearing capacity; to keep the canisters in place in the deposition holes and to hold back pieces of rock which may break off from the rock surface.
- plasticity; to maintain the homogeneity of the material despite minor movements in the bedrock.
- low permeability; to minimize groundwater flow in deposition holes and in backfilled tunnels and shafts.
- good thermal conductivity; to transmit the heat generated by the waste canister to the rock without the canister becoming excessively hot.
- high ion exchange capacity; to retard the migration of radioactive nuclides which may leak out from the canister.
- long-term stability against weathering, cementation or other changes; so that the material will retain the above properties throughout the service life of the repository.

Another condition is that the buffer material shall not contain components which can decisively reduce the corrosion resistance of the canister.

Tests and studies have shown that the requirements on the buffer material can be met either by pure bentonite at rather high density or by a mixture of quartz sand and bentonite. Both materials are available in the required quantities. They can also be mixed to a homogeneous material without difficulty, e.g. in an ordinary concrete mixer.

Bentonite is a naturally occuring clay which is characterized by the fact that it swells upon absorbing water. As a reference material, KBS has chosen a bentonite of the type Volclay MX-80, which is mined in Wyoming and South Dakota in the United States. (Other types of natural or synthetic bentonite can probably also be used.) MX-80 is a so-called sodium bentonite whose main constituent (90%) is montmorillonite. It has a large number of uses, for example within foundry and oil-drilling technology. The annual quantities required in the final repository comprise a very small portion of the current annual production and adequate reserves exist.

Bentonite of high density is characterized by the fact that it gives rise to very high swelling pressure when the bentonite absorbs water, if swelling is restrained. This provides a guarantee that water-bearing fissures cannot open up in the buffer material. Owing to this swelling pressure, the bentonite also penetrates into and seals fissures which may exist (or which may open up at a later time) in the walls of the storage holes.

In the KBS studies the high density bentonite is proposed /2/ to be used as backfilling material for the deposition holes for copper canisters with spent fuel, see figure 3. Further as sealing plugs in shafts and tunnels in the repository, see figure 4.

The high density bentonite is obtained by pressing bentonite powder under very high isostatic pressure, 100 MPa, to blocks of the desired dimension, see figure 5. The blocks are stacked on each other and the spaces between the blocks and the rock and between the blocks and the canister are filled with bentonite powder.

The bulk density of water-saturated bentonite is about 2 300 kg/m^3 for the blocks and about 1 750 kg/m^3 for the powder in the spaces. The mean density, when all bentonite in the storage hole has been water-saturated and swelling has ceased, is 2 100 kg/m^3. It is determined by the increase in volume which results from the fact that the joints between the blocks are filled up, the bentonite in the spaces is compressed and bentonite from the storage hole displaces and compresses the sand/bentonite fill in the overlying tunnel to some extent.

Natural deposits of bentonite which have been exposed to the temperatures, groundwater conditions and pressures which prevail in the final repository show that the bentonite can be counted on to remain stable for the period of time during which the buffer material must retain those of its properties which are vital to the function of the final repository.

The permeability of the bentonite declines with increasing density. At a density of 2 100 kg/m^3, the permeability coefficient of the bentonite is about 2 x 10^{-14} m/s. This means that the material is virtually impenetrable by water and that diffusion is a controlling meachanism for the transport of ions through the buffer material.

The blocks of highly-compacted bentonite which are placed in the storage hole prosess very high bearing capacity. In appearance and to the touch, the material resembles sopa-stone. Its shear strength is comparable to that of sedimentary rocks. Its water content, i.e. the ratio between the weight of the water and the weight of the solid material, is approximately 10% in the blocks.

Bearing capacity is a function of the material's density. The final average density of the material in the storage hole when it is fully water-saturated (water content about 20%) is, however, so high that the subsidence caused by gravity, even after one million years, is negligible. Even at a bulk density of 1 400 - 1 500 kg/m^3, when the consistency of the bentonite is comparable to that of solid modelling clay, its bearing capacity is sufficient to prevent the canister from sinking through the underlying bentonite, even over a very long period of time. This means that, even assuming improbably high material losses through fissures and the like, the bentonite still possesses sufficient bearing capacity.

Bentonite, which absorbs water under restrained swelling exerts a swelling pressure which is a function of the density of the material. The ratio between swelling pressure and density has been determined by tests for MX-80 and verified by means of theoretical calculations. At a bulk density of 2 100 kg/m^3, the swelling pressure is on the order of 5 MPa.

Its high swelling capacity in connection with water absorption gives bentonite a "self-sealing" capacity in that it is forced into fissures in the walls of the storage holes and prevents the opening of water-bearing fissures or cavities in the buffer material.

The highly compacted bentonite has also a reasonable thermal conductivity, 0.75 W/m°C at density 2 000 kg/m^3, and a substantial ion exchange capacity. More details on the properties of bentonite are given in volume II of /2/ and in several of the KBS Technical reports referenced there.

A mixture of quartz sand and bentonite has been proposed by KBS as a backfill material in the deposition holes for lead-titanium canisters with vitrified high level waste from reprocessing /1/ and also in the tunnels and shafts in both studies /1, 2/.

In order for the mixture to possess good bearing capacity and thermal conductivity as well as low permeability, it is desirable that the sand and bentonite fractions be mixed in such proportions as to provide a good (morain-like) particle size distribution.

A high bentonite content increases the plasticity and ion exchange capacity of the mixture. It also improves the material's density, since its swelling will fill the pores in the material. At the same time, however, a higher bentonite content reduces the bearing capacity and thermal conductivity of the mixture and it becomes more difficult to handle.

Tests have shown that mixtures of 80-90% quartz sand and quartz filler and 10-20% bentonite provide a good balance of the desired properties.

The sand is pure quartz sand (98% SiO_2) with a particle size distribution of 0.063-2 mm. It has a sintering point (1 400°C) which lies well above the temperature encountered in the repository.

The results of field and laboratory tests on the mixture can be summarized as follows:

- The strength and deformation properties of the mixture are approximately the same as those of a clayed moraine. The bearing capacity of the material is composed of a cohesion component and a friction component. An increase of the bentonite content increases cohesion and reduces friction.
- Permeability varies between 10^{-8} and 10^{-11} m/s when swelling is restrained. With unrestrained swelling, permeability is higher.
- Thermal conductivity is between 0.3 and 1.7 W/m°Cwhen the water content varies between 5 and 25%.
- Maximum dry solids density is 1 900 - 2 000 kg/m^3 at an optimum water content of 8-12%.
- Unrestrained swelling when the material is in contact with water leads to an increase of its original volume by 5-20%. The swelling pressure of the material under restrained swelling conditions is on the order of 30-150 kPa.

The major advantage with the highly compacted bentonite is that the water permeability is much lower and because of that all transport of ions through the buffer is governed by the diffusion. The diffusion rate in the compacted bentonite has been measured and found to be about 100 times lower than in water /7, 8/.

A disadvantage with the highly compacted bentonite is of course the cost.

As was previously mentioned some investigations of zeolites as buffer-material have also been made /9, 10/. The advantage with zeolites is that the ion-exchange capability is much better than for in particular the quartz/bentonite-mixture. Of particular interest from this point of view is clinoptilolite /10/. The studies showed, however, that there were several objections against using zeolites in the buffer material /9/. Thus cementing properties have been observed, the permeability of pure zeolites is too high, the heat conductivity is poor and too little is known about the mechanical properties in mixtures with other materials.

5. LEAD-TITANIUM CANISTER FOR VITRIFIED WASTE

For high level vitrified waste from reprocessing KBS has proposed to use a canister of lead-titanium. The titanium is a special quality with low (<20 ppm) hydrogen content. The lead is high purity oxygen free with a grain size not less than 10^{-4} m in order to minimize the creep.

The design of the canister is shown on figure 6.

The titanium shell has a thickness of 6 mm with 12 mm end plates. The lead has a minimum thickness of 10 cm.

With the grain size specified above the creep of the lead will be so slow that the lead encasement will keep its shape and dimensions for thousands of years. Even if a canister during handling is damaged by a mechanical impact, which will reduce the grain size locally, a large and rapid increase of the grain size will then occur at the temperature the canister will have in the final repository. Thus there is no risk that lead could creep out through holes or cracks in the shell /12/.

The titanium sheets are produced from slabs with hot rolling. They are then annealed, blasted and pickled. Welding shall be performed under protective gas.

The lead canister is produced by extrusion. The canister is assembled in a hot cell which provides radiation protection for the operators.

The thickness of the lead has been chosen in order to reduce the radiolysis of the groundwater that comes into contact with the canister. Calculations have shown /11/ that equilibrium concentrations will not exceed: oxygen 3 ppb, hydrogen 8 ppb, hydrogen peroxide 0.2 ppb and Fe^{3+} 3 ppm. Furthermore it may be noted that of all hydrogen formed should be adsorbed by the titanium the quantity of hydrogen formed during 10^4 years will be as low as 1.8 ppb/cm^2, which would give an additional 0.7 ppm of hydrogen in the titanium. The amount of oxidants formed will be of the same order of magnitude.

The lead-titanium canisters with vitrified waste are deposited in vertically drilled holes which are backfilled with quartz sand mixed with 10% bentonite. The maximum temperature on the surface of the canisters will not exceed 80°C.

The expected corrosion lifetime of the canister has been evaluated by a group of specialists appointed by the Swedish Corrosion Institute. They have summarized their findings as follows /11/:

"On estimation of the life of the titanium sheath a general corrosion rate of 0.25 μm/year has been taken as a conservative value, which would lead to a life of at least ten thousand years. Pitting and crevice corrosion have been considered very unlikely at the foreseen temperatures and salt contents. Further the risk of delayed fracture, due to hydrogen up-take, is considered as small but cannot be completely excluded at the present state of knowledge. For this reason the titanium sheath cannot absolutely be guaranteed an appreciable lifetime.

If the titanium sheath were penetrated due to mechanical damage or localized corrosion, the exposed lead could suffer localized attack. The corrosion rate would then be determined by the supply of oxygen from the surrounding buffer to the canister surface. Conservative calculations have shown that perforation of the 100 mm thick lead lining would take about 4 500 years. In any case the life of the lead lining was estimated to at least a thousand years.

In total a titanium canister with a lead lining was estimated to have a life of at least thousands of years, and probably tens of thousands of years."

The group of experts was unanimous in its judgement with the exception of one member, who delivered a statement of his own, saying that the life of the canisters can only be guaranteed for some hundred years.

6. COPPER CANISTER FOR SPENT FUEL

For spent unreprocessed nuclear fuel KBS has proposed to use a canister of pure metallic copper so-called Oxygen Free High Conductivity Copper. The design of the canister is shown of figure 7. The fuel in the canister is imbedded in lead in order to prevent deformation of the canister by external overpressure. The thickness of the copper was chosen to reduce the radiolysis of groundwater to a low level. The copper canister is used in combination with a buffer of highly compacted bentonite.

Before encapsulation the spent fuel assemblies are dismounted and the fuel rods are placed in special copper racks. Each rack can take 498 BWR-rods or 636 PWR-rods. The rack is then placed in a copper container. The empty space between the fuel rods is backfilled with lead in an oven at 380-400°C temperature. After cooling the copper canister is sealed with three consecutive lids The welding of lids is made by electron beam welding. Welding tests have been made with good result /20/. An ultrasonic test of the welds has been experimentally checked and does not involve any particular problems. The welds are also helium-leak-tested.

In the final repository, a canister is subject to mechanical stresses as a result of both the external overpressure caused by the hydrostatic pressure of the groundwater plus the swelling pressure of the buffer material and the internal overpressure caused by the formation of helium in the fuel.

The external pressure does not give rise to stresses which can lead to failure, not even if the swelling pressure should be unevenly distributed due to uneven water absorption in the bentonite. The lead around the fuel rods will protect the canister from being deformed by the external pressure. The internal pressure develops so slowly that critical deformation cannot occur within a period of one million years.

Any movements in the surrounding rock could also give rise to stresses on the canister. The elasticity of the buffer material and the ductility of the canister would, however, prevent failure of the canister in the event of the small rock displacements which are possible.

Thus, mechanical stresses cannot be expected to limit the service life of the canister to less than one million years.

As the copper is thermodynamically stable in pure water corrosion can only be sustained by some chemical substances which are dissolved in the groundwater. Investigations have shown that the only substances of importance are free oxygen and sulfides /13/.

Chemical analysis shows that the groundwater is practically free from oxygen at some hundred meters depth /14/. This is also evident from the presence of iron(II) (Fe^{2+}) in the rock minerals /2/. It has been conservatively assumed that the groundwater will contain 0.1 ppm of free oxygen. Another oxygen source is the air enclosed in the buffer material when the repository is sealed. A third source is the oxygen formed by radiolysis. Using upper limit values it has been calculated that these free oxygen sources can corrode about 4.5 kg of copper in 1 million years /13/.

By calculating the corrosion from sulfides it has been conservatively assumed that the groundwater contains 5 mg sulfides per liter. This is the highest value observed in any measurement and is too high in the chemical environment close to a repository. Sulfides could also be formed by microbiological reduction of sulfates. The sulfate-reducing bacteria require, however, organic material for their activity. It has been conservatively assumed that all organic material avaiable i.e. less than 12.5 mg per liter groundwater and less than 200 mg per kg buffer material will be suitable for such bacteria. With these assumptions the maximum corrosion attack from sulfides would be about 55 kg copper per canister and 1 million years.

Thus in total the copper corrosion would be at most 60 kg per canister after 1 million years. This is equivalent to 0.5 mm average corrosion depth on the 200 mm thick canister. If itis assumed that the oxidants coming from the tunnel are attacking only the upper 10% of the canister surface the average corrosion depth there would be about 2.4 mm in 1 million years.

Copper has a low tendency for pitting corrosion. Experimental observations show that the pitting factor decreases with increasing corrosion depth /13/. The largest observed pitting factor in a large study of copper corrosion in different soils was 25. This would be a very conservative value for the copper waste canister. Using this value the maximum corrosion depth would be 60 mm in 1 million years.

The group of specialists appointed by the Swedish Corrosion Institute have also evaluated the corrosion life of the copper canister. They concluded that it is realistic to expect a service life of hundreds of thousands of years for a copper canister with 200 mm wall thickness.

One of the specialists had, however, a deviating opinion and submitted a separate statement concluding that the life could only be guaranteed for thousands of years /15/.

The objections of the dissenting member are based on, among other things, the opinion that a future ice age could cause considerable fracturing of the rock, which would lead to a dramatic increase of the groundwater flow and thereby of the corrosion rate on the copper canister. This postulated effect of an ice age on the Swedish bedrock at a depth of 500 m does not agree with the geological interpretation of the pattern of fractures which can be observed today /2/. In the hypothetical case that a glaciation would result in extensive fracturing of the rock around the canisters, the buffer material, with its great potential swelling capacity, will seal new or widened fissures and the reported conclusion concerning the service life of the canister will not be affected.

7. ALUMINA CANISTER FOR SPENT FUEL

As an alternative to the copper canister KBS has supported development work at the ASEA company High Pressure Laboratory on a ceramic canister /2/. Alumina of the α-type - as a mineral called corundum or sapphire - has many properties which makes it very attractive as material for high level waste canisters.

Next to diamond, corundum and sapphire are among the hardest minerals occurring in nature, and deposits of these in the form of weathered materials in river beds and shingle on sea-shores exhibit a very high mechanical and chemical resistance over long periods of time, also geologically speaking.

The method used for producing the canister, hot isostatic pressing, is one of several high-pressure methods which can be accomplished with ASEA's QUINTUS presses.

A container and a lid are produced separately by pressing alumina powder at 100 MPa and 1 350^{o}C.

The alumina container is then examined by non-destructive testing methods. Ultrasonic examination and proof testing are the methods which can be used.

Ultrasonic examination can be applied to detect internal cracks as well as surface cracks exceeding approx. 1 mm size in the containers. This inspection can be carried out despite the presence of a surrounding steel jacket.

The proof testing is performed to ensure that the alumina container does not have any surface cracks exceeding a certain size. The maximum permissible crack depth is determined, with respect to the risk of delayed fracture, by the requirements on the canister life in the final repository. A fully reliable method of detecting such critical surface cracks is proof testing of the alumina material.

A proof testing method has been developed, where stresses in the alumina are generated by arranging a temperature difference between the inner and the outer wall of the container. Containers free from defects are not influenced by these stresses, whereas defective ones immediately fall to pieces. Equipment for 1/3-scale containers has been tested.

According to the fracture mechanism theory, a relationship can be established for approved containers between the load stress and the assured life in the final repository with respect to the risk of delayed fracture.

Before the encapsulation the spent fuel assemblies are dismounted - upper and lower tie plates are removed and the fuel rods are withdrawn from the spacer grids. The length of the fuel rods is reduced by a specially developed method. Todays equipment does not allow fabrication of larger canisters than about 3 m length whereas ordinary LWR-rods are close to 4 m in length. The length reduction is illustrated by figure 8. The rods are rolled to spiral rolls and the rolls are stacked in a steel container which is then enclosed in the alumina canister. The proposed canister is 3 m long and has 0.5 m outer diameter and 10 cm wall thickness. The weight would be about 2 metric ton. Each canister can take 144 BWR rods or 174 PWR rods.

Length reduction by means of spiralling the spent nuclear fuel rods has been tried out within ASEA-ATOM. Test bending has been done with both normal and embrittled, nonradiated fuel rod dummies as well as with fuel rods irradiated to 23 MWd/kgU at Oskarshamn Nuclear Power Station.

The following remarks can be made about the need for reducing the length of the fuel rods.

During the initial stage of the project it was considered unsuitable from the geological viewpoint to encapsulate full-length fuel rods in alumina canisters. It was surmised that rock movements might give rise to unacceptable stresses in such a long (approx. 5 m) alumina canister. Increased knowledge of earth movements and a suitable arrangement of the storage procedure have had the result that the need to reduce the length of the fuel rods has decreased in importance. Nevertheless, it has been considered preferable to continue the development work on an encapsulation process, which permits the containment of spent fuel rods in alumina canisters about 3 m long. This means that QUINTUS presses of the necessary size are available today. However, there is nothing in the process to prevent the production of alumina canisters of a size sufficient for the encapsulation of full-length fuel rods.

Hot isostatic pressing is also used to join together the container and cover of alumina. In this process the joint between the container and the cover disappears and a completely joint-free canister is obtained. Fig. 9 shows the basic principles of this process.

Joining together the cover and container in fact requires a temperature of at least 1 350°C at the joint. This high temperature is combined with an external pressure of about 70 MPa, which results in a pressure of about 100 MPa on the joint surface. At the same time, however, it is desirable to maintain a temperature below 900°C on the nuclear fuel. The specially developed furnace ensures that this temperature gradient in the canister can be achieved.

Those parts of the canister which are not heated to a temperature above about 1 000°C can withstand by a good margin the external pressure. The joint zone of the canister with the highest temperature is subject, on the other hand, to shrinkage deformation as a consequence of the stresses arising from the external pressure and thermal stresses. Certain residual stresses remain here also after the completion of the pressing and their magnitude must be limited to prevent a slow propagation of cracks.

Very comprehensive theoretical calculations have been made to:

- determine optimum pressing parameters for the sealing operation and from these,
- calculate the stress distributions occurring during both the heating and the cooling stages and also
- calculate the maximum residual stresses after the sealing operation.

It is primarily the nature of the cooling process which is of decisive importance to the quality of the canister. The canister temperature must decrease slowly after decompression to ensure that the built-in stresses can relax.

The sealing process has been demonstrated at ASEA's plant at Robertsfors in Sweden.

The alumina canisters are deposited in vertically drilled holes which are backfilled with clay. The detailed composition of this clay has not yet been specified but a mixture of quartz sand and bentonite would probably be acceptable.

In the final repository, the canister will be subjected to the action of the surrounding groundwater. However, this takes place at a very slow speed. Tests are currently under way to establish the durability of the hot-isostatically compacted aluminium oxide in the types of groundwater in question. These tests are being conducted at elevated temperature, 100 - 350°C, in order to obtain measurable effects. In the groundwater in question, however, deposition on the surface of the canister is more likely than erosion of the surface /17/.

Tests performed to date have shown that a canister of aluminium oxide with 100 mm thick walls can withstand the action of the groundwater for at least hundreds of thousands of years with an ample safety margin. The durability of the canister is only slightly affected by the surrounding geological environment.

Both theoretical and experimental studies concerning the strength and thermal properties of large ceramic bodies have also been carried out. The results show that the canisters can resist the forces to which they can be subjected in the final repository with adequate margin /16/.

The evaluation of the corrosion life of the alumina canister has not yet been completed by the Swedish Corrosion Institute and its reference group.

8. GLASS CERAMIC CANISTER

During the first months of the KBS project glass ceramic materials were considered as strong potential candidates for waste canisters. Preliminary studies were started on glass-ceramic code 9617 at Corning Glass Works in Corning, N.Y. This material was chosen because it was known from other applications to be fairly tolerant to different chemical environment. Further it seemed to be reasonably simple to develop a fabrication technique for large enough canisters. The approach would be to fabricate a container and a cover of the base material and then seal the final joint by a frit, which would be ceramed at lower temperature than the base material.

The preliminary studies were mainly concentrated on corrosion studies /18/. The code 9617 glass-ceramic is a composite of several phases -beta spodumene (Li_2O . Al_2O_3 . X SiO_2; X = 5-7; 90%) rutile (TiO_2; ~ 3%) spinel (Mg or Zn . Al_2O_4; ~ 3%) and residual glass (~ 5%). Because of this one would expect the composite material to exhibit different localized corrosion rates. This appears also to be the case. Scanning electron microscopy of the glass-ceramic surface erroded in water showed the glass phase to be removed leaving the crystalline phases relatively untouched. The preliminary data obtained indicated that the glass-ceramic would probably meet the requirements on a high level waste canister. It was, however, concluded that this could not be verified within the relatively short time schedule of the KBS-project. These types of materials should, however, be considered as an economically attractive alternative for long-time resistant waste canisters. Their development and verification would, however, require some years of work.

9. CONCLUDING REMARKS

The studies performed by KBS have shown that it is indeed possible to make engineered safety barriers for high level waste. These barriers would isolate the waste from contact with groundwater in a hard rock repository for a very long time period. Copper in combination with highly compacted bentonite would probably last for millions of years. Similar life-times seem probable also for alumina canisters.

The highly compacted bentonite is in itself a very efficient barrier. Calculations based on conservative assumptions show that it would probably take millions of years after canister penetration before the actinides in the spent fuel would be transported through this barrier /19/.

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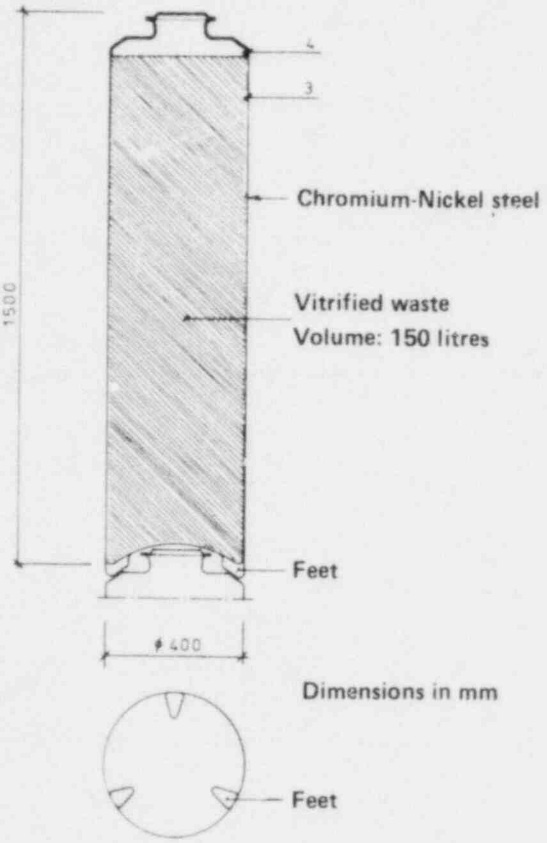


Figure 1. Waste cylinder. The vitrified waste is cast in a container made of chromium-nickel steel. The container is sealed with a welded-on lid. The feet enable the waste cylinders to be stacked on top of each other.

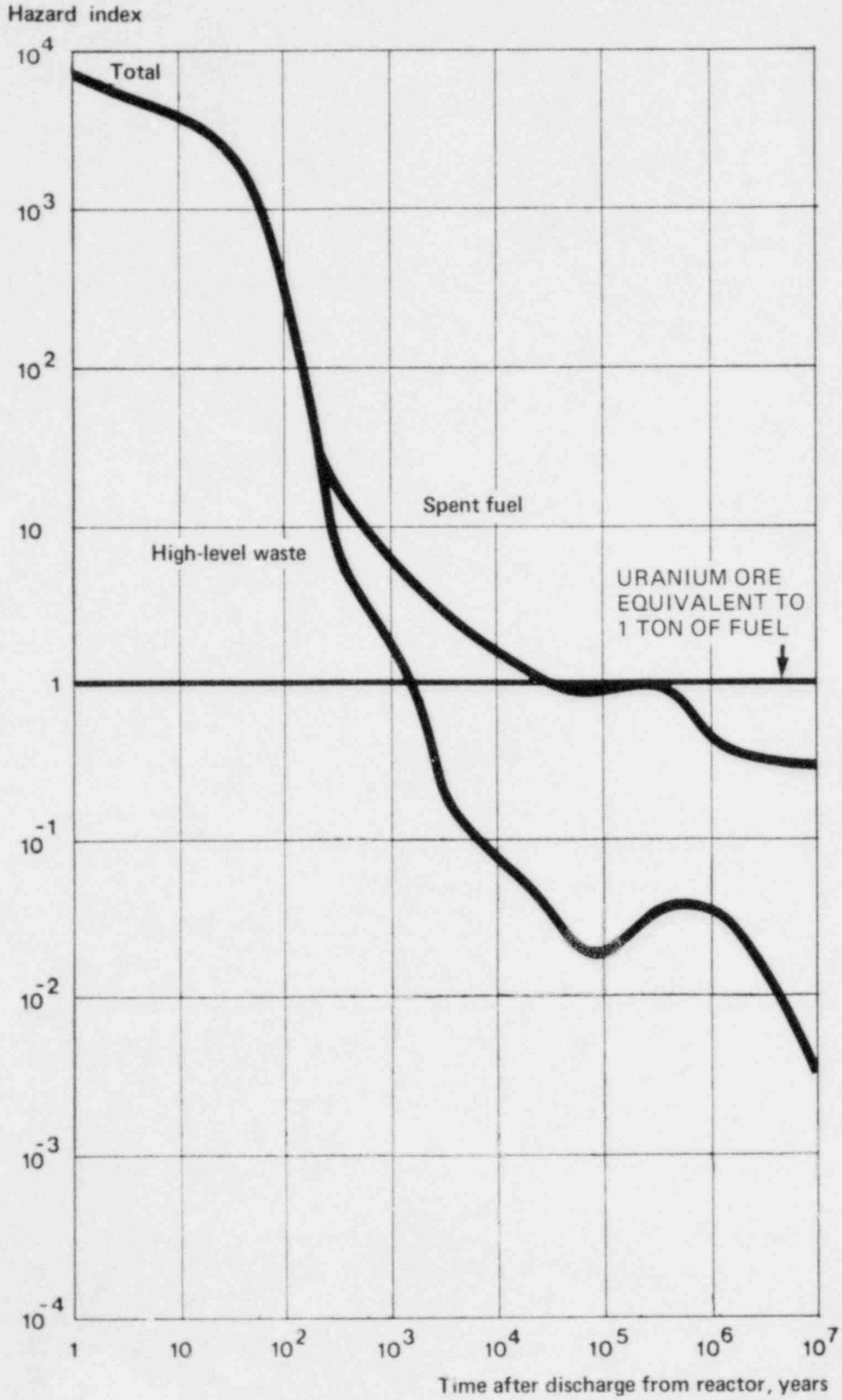


Figure 2. Potential hazard index for 1 ton of spent fuel and for high-level waste from 1 ton of spent fuel in relation to the quantity of uranium ore which is equivalent to 1 ton of fuel. Actual hazard is also dependent upon the exposure pathways of the elements to man.

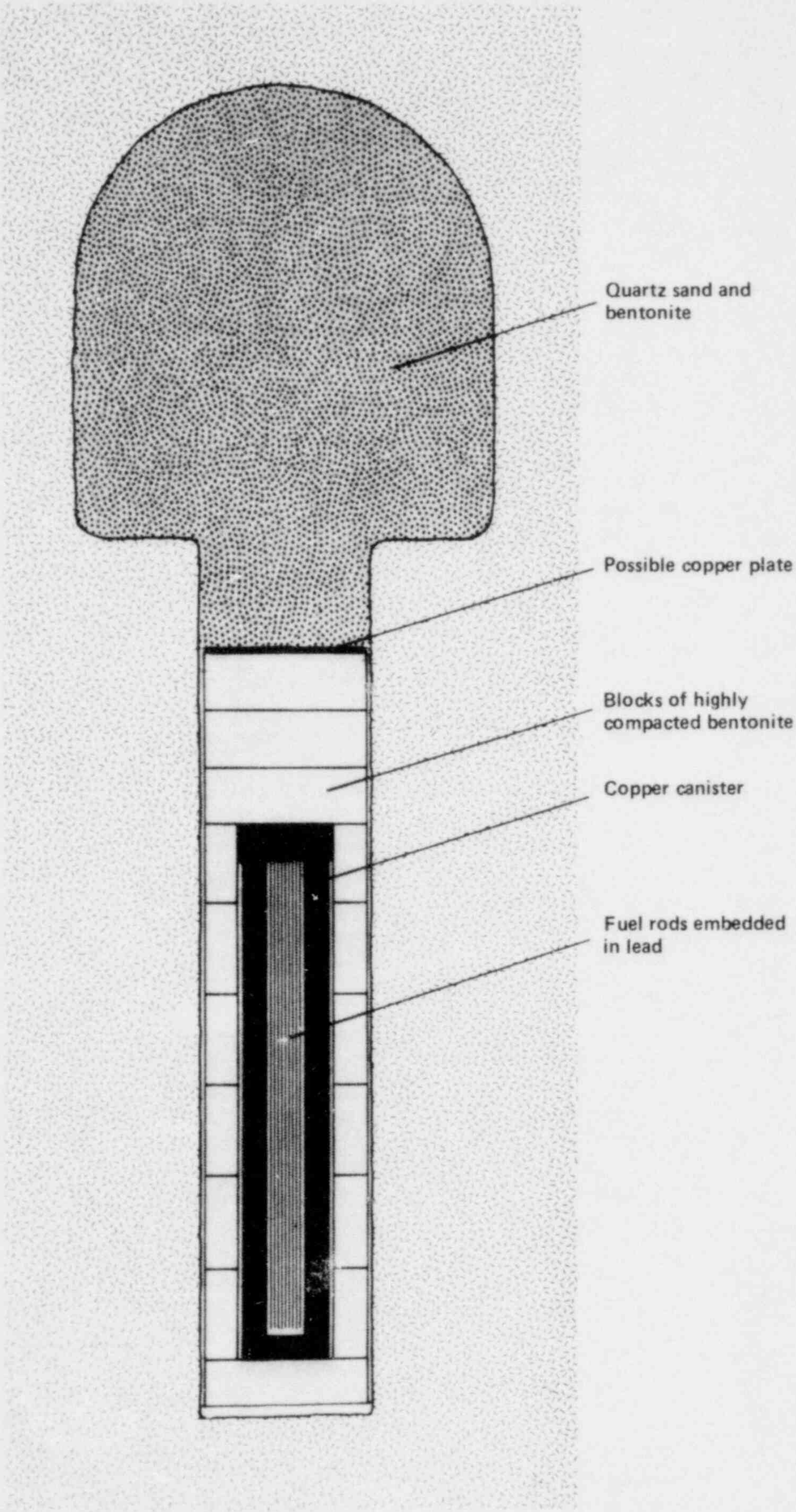
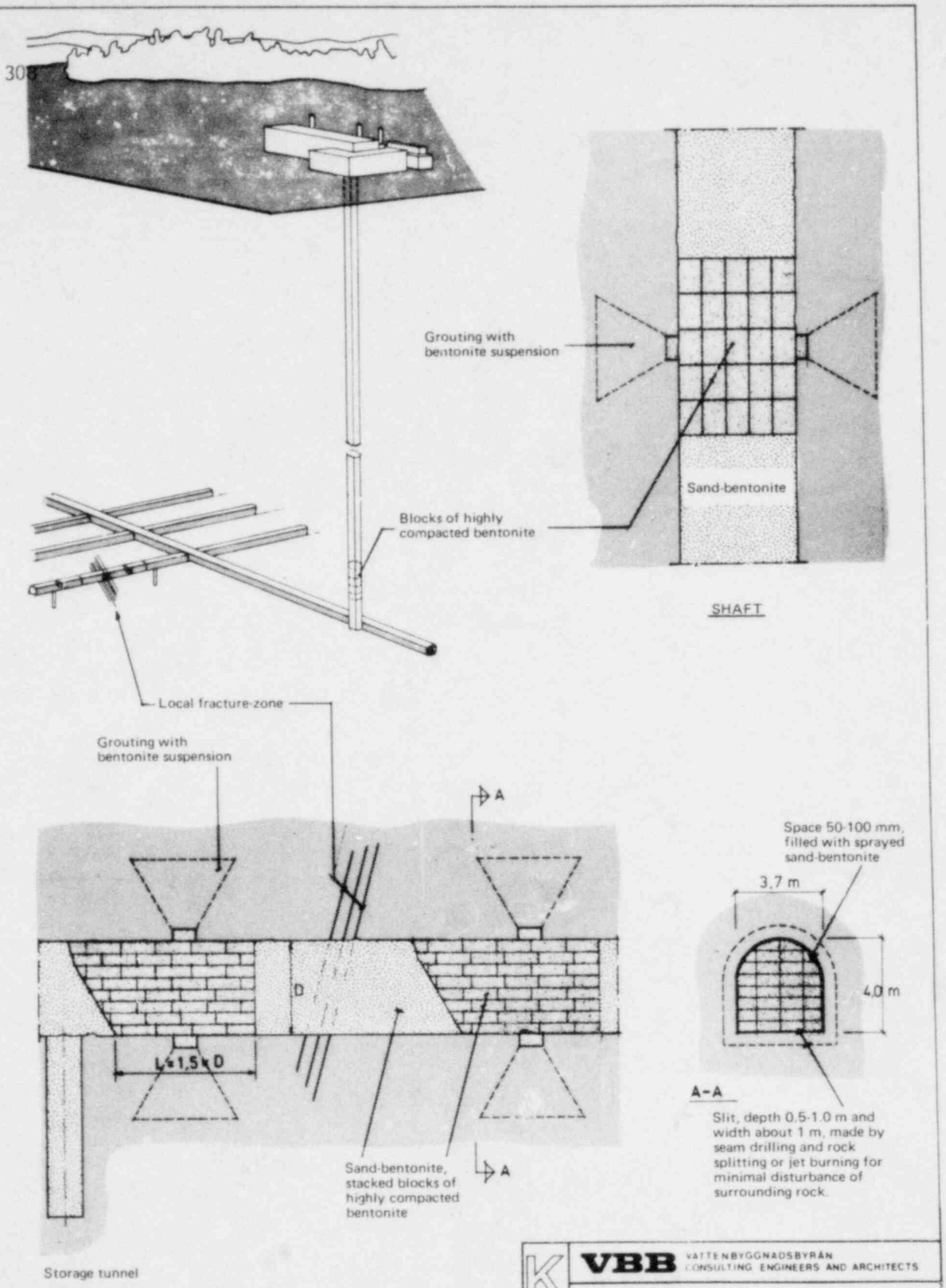


Figure 3. Section through tunnel and deposition hole with copper canister in final repository for spent fuel.



VBB VATTENBYGGNADSBYRÅN
CONSULTING ENGINEERS AND ARCHITECTS

KBS

FINAL REPOSITORY

Sealing of zone around shafts and tunnels

Figure 4

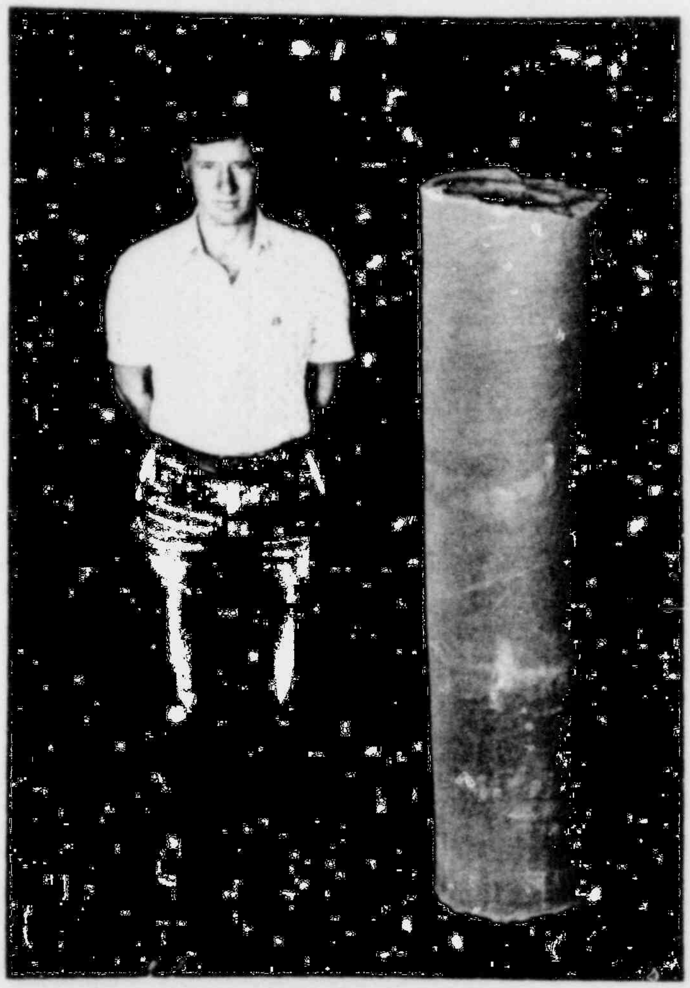


Figure 5. Block of highly compacted bentonite made by isostatic pressing.

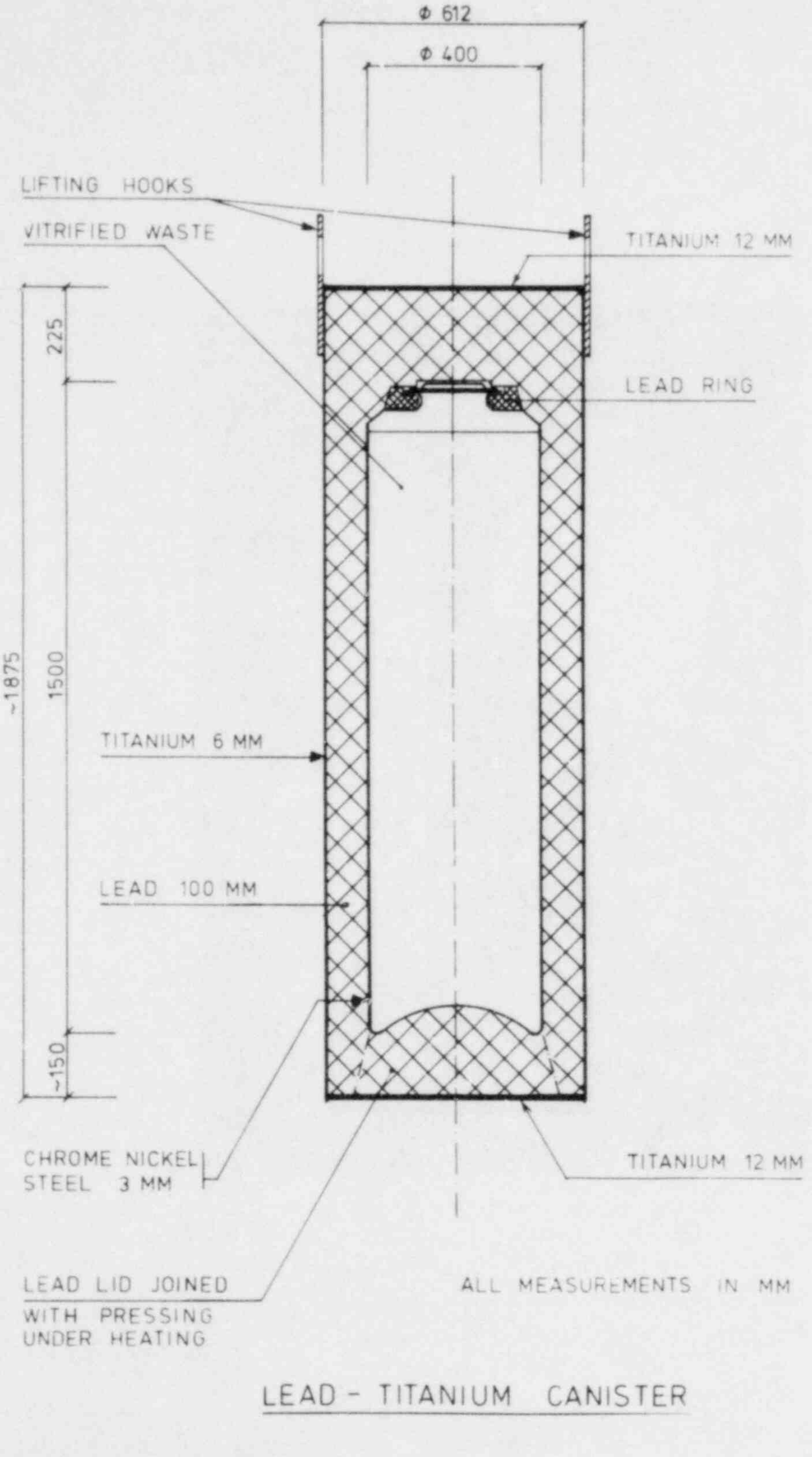


Figure 6. Lead-titanium canister. Waste cylinder with vitrified high-level waste enclosed in a canister of lead and titanium. Total weight approx. 3900 kg.

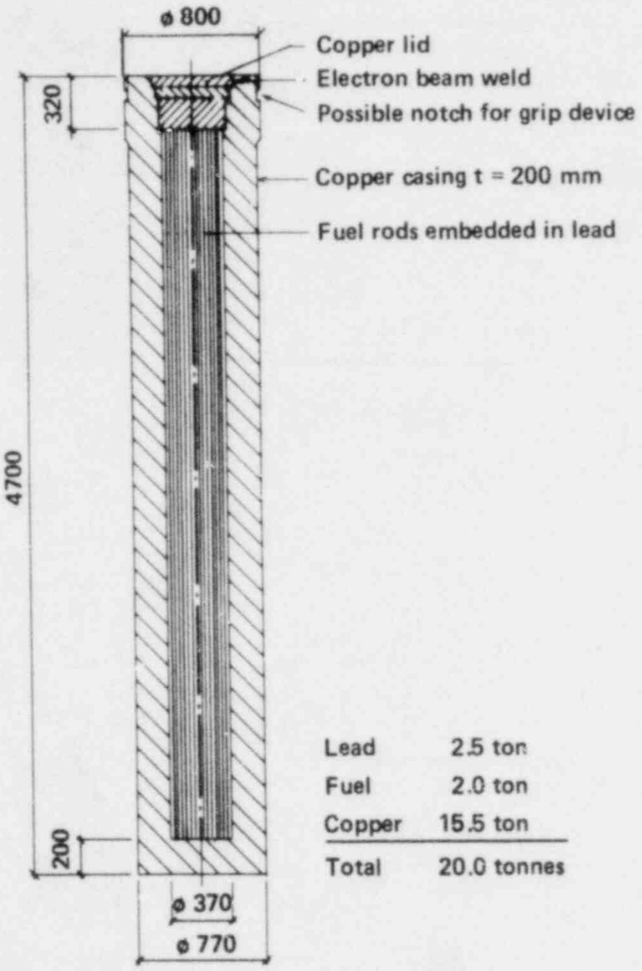


Figure 7. Section through copper canister with fuel rods embedded in lead.

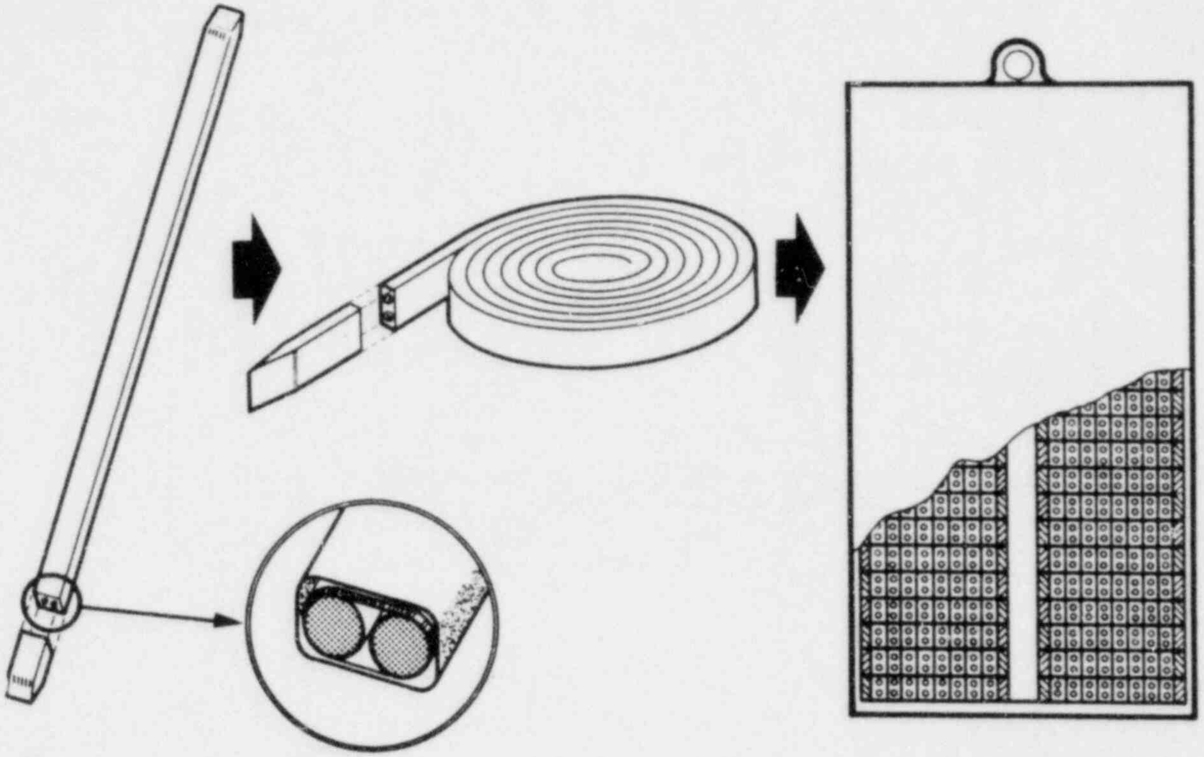


Figure 8. Two fuel rods are enclosed in a soft-steel cover and then rolled. The rolled packages are stacked in a stainless steel container.

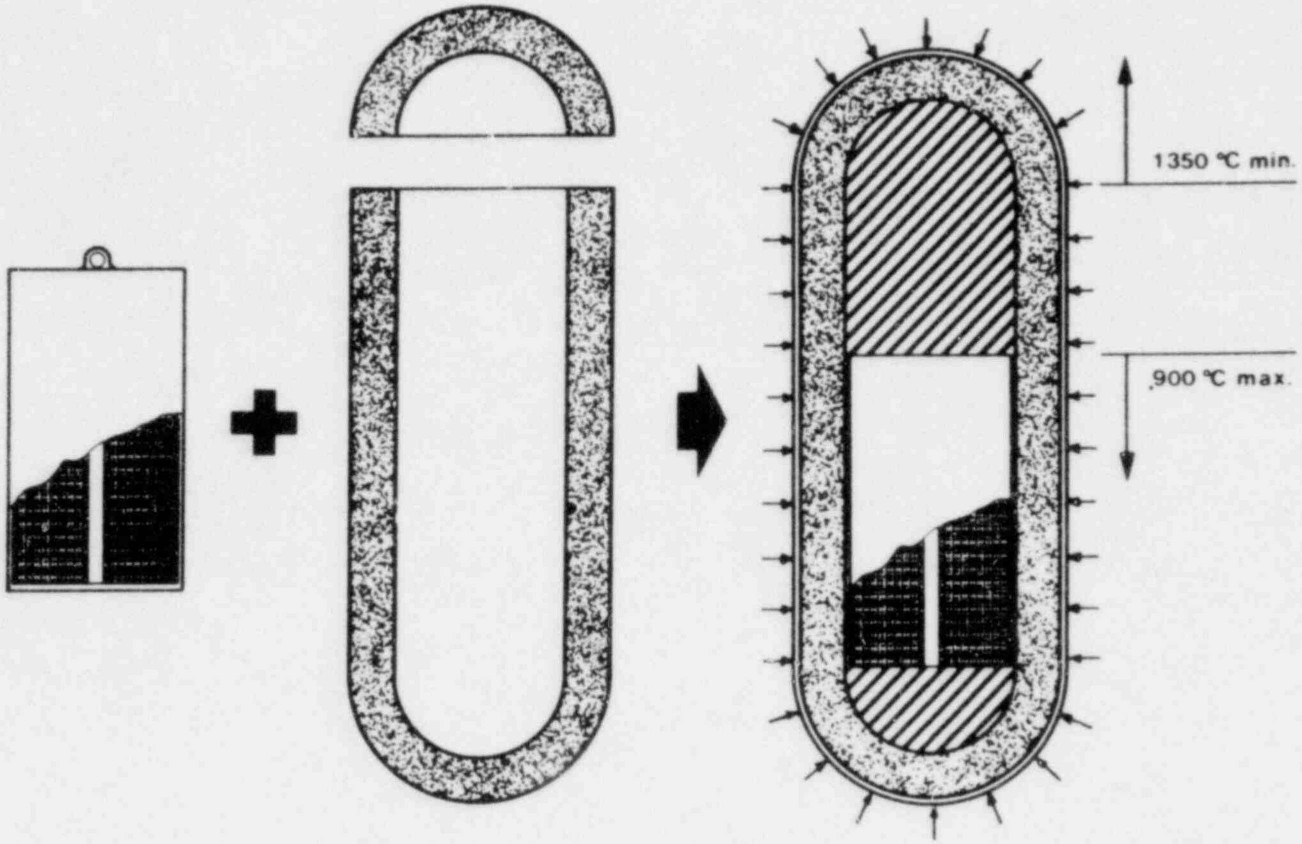


Figure 9. The stainless steel container with fuel rods is placed in the alumina container. The cover and the container are sealed by hot isostatic pressing to a jointfree canister.

Discussion Following

CERAMIC & PURE METAL CONTAINERS IN BUFFER MATERIAL

Presented by Per-Erick A. Ahlström

Stanley Logan - Los Alamos Technical Associates, Inc.
Question:
I wonder if you have considered mechanical breaching of the canisters by offset faulting which could, for example, shear a canister in one direction.

Ahlström
Response:
You mean from a big geological faulting? We have considered a possible type of faulting that could occur in the top of the stable bedrock that we have in Sweden and we have concluded that this would not be a big concern because to create faulting at this depth you would have an earthquake that would be very large compared to whatever has been observed in this part of the world.

Edward Gaffney - Pacifica Technology
Question:
Two questions about your bentonite overpack. One, what is the water content of it when you press it into the blocks? Two, what is the effect of the seams between blocks? Are they self-sealing, or is there a potential hydrologic path between the blocks?

Ahlström
Response:
First question, the water content when we press the bentonite blocks is about 10%. The second question, as I said, you fill powder in between. The blocks are pressed to a density of about 2300 kilograms per cubic meter. Then you fill powder between the rock and the blocks and between the canister and the blocks. This gives you a combined density of about 2100 kilograms per cubic meter. When the material takes water and becomes saturated it will swell very strongly. It has a swelling pressure of something like 5 megapascals, so every small crack and joint that is in between the blocks will be compressed and filled with the material. It will be a gel-type of material that will exist when it becomes water saturated.

M. Sombret - Centre de Marcoule, France
Question:
I am very sorry, Mr. Ahlström, you were not in a position to finish your paper in time, because I saw in the abstract of your paper that you mentioned glass-ceramic materials used as containers. So what I should like to know is how you can use this material--what I mean is,

to make glass ceramic materials you start with glass and then you perform one, two, or three thermal treatments. I should like to know if you intend to perform the thermal treatment after you have loaded the waste, or if it is a ready-made glass ceramic vessel?

Ahlström
Response:
We investigated various glass ceramics when we started the project. We found that the one that was most developed was a ceramic code-9617 made by Corning Glass Works in New York. The intention was to make a canister with the same idea as the ASEA Company was doing with the alumina canister. You make a container and the lid first. Then you have some frit that is ceramed at a lower temperature than the base material. They made preliminary studies on this type of material, mainly corrosion studies, and we concluded that we were not able to verify the corrosion rates within the time frame of the project, so only preliminary work was made within the KBS Project. It has been reported at the recent Boston meeting by the Corning people.

Bob Watt - Los Alamos, private citizen
Question:
You have rather low temperatures in your design numbers - 85 degrees, I believe. I am curious how you get this because the packing density in terms of canisters in space is comparable to that planned for, say, the WIPP.

Ahlström
Response:
We accomplished the low temperatures in two ways. We negotiated with the French that they lower the fission product content to 9% instead of their standard figures (13%). Then we proposed, as was described in the question this morning, to have an intermediate storage of the glass for 30 years after it arrives in Sweden so it would be about 40 year-old waste when it is put into the repository. The intermediate storage is very similar to the one in the Marcoule plant. In fact, it was designed by the same consultant that made the Marcoule plant.

THE EFFECT OF PRESSURE ON INTERFACE INTERACTIONS BETWEEN SOLIDS

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ABSTRACT

Fission product reactions and transport phenomena across solid-waste/rock interfaces are being studied in the laboratory under pressures equivalent to the rock overburden of a 2000 foot deep repository. This is important to understanding the dynamics of the repository since most reactions preferentially occur at interfaces, and these reactions are sensitive to pressure. A review of the theoretical aspects of the influence of pressure on interface reactions and the transport of material across a solid-solid interface is presented. Related systems that have pressure sensitive chemical reactions are described. The use of pressure response information to establish the kinetic mechanism controlling the transport of materials which are too slow for direct measurement is proposed as well as utilizing the beneficial aspects of pressure in the repository by designing canister to crush without being breeched.

Introduction

Understanding the potential release mechanisms for radionuclides from a repository requires that experiments be carried out to measure chemical solution rates and transport rates. Since, for any effective waste immobilization system, the transport rates are extremely slow, indirect experimental methods such as response to pressure may be used to deduce the pertinent mechanism and kinetic parameters for a given temperature in a reasonable period of time.

The effect of pressure itself will be one additional consideration in estimating the performance of a geologic repository. The leach rate of typical glasses has been established at one atmosphere. At higher pressures the rate mechanism could change and alter the leach rate or the glass may transform to a more stable high pressure form with new properties. These changes will be particularly pronounced at the interface areas where the surface will help to catalyze reactions. For these reasons, it is necessary to understand the effect of pressure to characterize the pathways for possible release of radionuclides.

The pressure experienced by the nuclear waste matrix in the repository will be due to the consolidation of the back fill and assumption of the over-burden pressure. If the repository is located 2000 feet below the surface, the over-burden pressure would amount to about 1933 lbs/in^2 (13.8 MPa or 0.139 kb) for a specific density of 2.3. A specific density of 2.7 has also been used in the literature.[1] The exact period of time for reconsolidation to occur is a function of the materials involved, the backfilling technique, the repository geometry and the ratio of the horizontal stress to vertical stress. The minimum time may be 150 years for salt and perhaps 500 years or longer for rock.[2] It appears that the rate of reconsolidation of the host rock cannot be estimated reliably at the present time.

A number of materials such as glass, ceramics and synthetic rock have been proposed for use in the waste/canister/rock system. However, there does not appear to be a clear set of criteria to evaluate these candidate materials, and each have some attractive characteristics to offer. The experimental response to pressure of these materials should help to identify potential nuclide loss mechanisms and evaluate numerical rates of release from the various encapsulating matrices. A discussion of all encapsulation media and potential canister materials is beyond the scope of this paper.

Theory

The waste repository can be affected in two ways by the application of pressure:

1. Chemical rate change, where the rate of formation of a compound that exists at low pressure may change, or a new compound may be formed that is more stable at elevated pressures;
2. Transport rate change, where the diffusion rate of the radionuclides changes.

The problem associated with products of enhanced rate of chemical reaction is that the waste may be converted at the interface to a new form that is more soluble than before. The change in diffusion rate would affect dissolution and migration rates due to a temperature or concentration gradient.

Looking first at the effect of pressure on diffusion, the two Fick's laws are used to define steady and non-steady state diffusion:

$$J = -D\frac{\delta c}{\delta x} \qquad \text{and} \qquad \frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2}$$

In these equations D, the diffusion coefficient, varies as a function of temperature by the Arhennius relationship. The diffusion coefficient also varies with pressure as shown by the analysis below:

$$D = a^2 \nu \exp(-\Delta G_v/RT) \exp(\Delta G_m/RT)$$

for interstitial diffusion, where:

- a is the lattice parameter of the crystal structure,
- ν is the crystal frequency and equal to the Debye frequency for pure metal,
- ΔG_v is the free energy change in an infinite crystal per mole of vacancies added, and
- ΔG_m is the free energy change in the region where atoms move from a normal position to an activated position.

The diffusion coefficient can be differentiated with respect to pressure to give:

$$\left[\frac{\delta \ln(D/a^2\nu)}{\delta P}\right] = -\frac{1}{RT}\left[\left(\frac{\delta \Delta G_v}{\delta P}\right) + \left(\frac{\delta \Delta G_m}{\delta P}\right)\right]$$

Using the thermodynamic relation:

$$(\delta \Delta G/\delta P)_T = \Delta V$$

we can write:

$$\left[\frac{\delta \ln(D/a^2\nu)}{\delta P}\right] = -\frac{1}{RT}\,(\Delta V_v + \Delta V_m) \equiv -\frac{\Delta V_a}{RT}$$

where ΔV_v is the partial molar volume of the vacancies,

ΔV_m is the partial molar volume of the activated atoms, and

ΔV_a is defined as the activation volume.

Since an increase in pressure will tend to reduce the volume of the crystal structure, the number of vacancies and, to a lesser extent, the number of activated atoms must decrease. This theory provides support for experimental evidence that D decreases with increasing pressure. Self diffusion data for metallic lead have shown that D decreases one order of magnitude for each increase in pressure of 980.6 MPa.

Diffusion at a boundary between two different phases (at the interface between waste form and canister or canister and rock) can be considered as analogous to a high-diffusivity path along grain boundaries. This enhanced diffusion will be lessened by increasing pressure because the boundary will tend to collapse. The interface will tend to become a Matano-like interface which can be analyzed as such to provide diffusion rates response.

Enhanced transport across a boundary also may be the result of decreased chemical activity in the second phase. Apparent uphill diffusion can occur in this way, and the equilibrium concentration may be higher in a second phase than in the first phase.

The rate of transport by diffusion across an interface will decrease with increasing pressure unless the relative solubility of the two phases is shifted adversely by pressure, i.e., greater solubility in canister and/or host rock.

The most significant effect of pressure on the repository may be the change it causes in chemical reaction rates and in the products formed.

The addition of pressure can produce an altogether new phase, possibly possessing quite different physical and chemical properties. The existence of new phases at elevated pressures arises primarily because some more compact form has greater thermodynamic stability. The Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

is used to relate the derivative of the transition pressure to the difference between the entropies and volumes of the two phases.

The accessibility of high pressure phases is usually limited by slow rates of conversion in the absence of suitable catalysts. However, the interface surface in nuclear waste barriers can behave as a catalyst for the reaction depending on the materials present. The exact susceptibility of solids to phase change under pressure will be influenced by the closeness of packing of the atoms in the low-pressure form. Crystals with particularly open structures and low densities will most likely rearrange. Those that are already dense, such as face centered cubic, cannot achieve much change other than by reducing the lattice parameter.

The energies of chemical bonds are on the order of 20-80 kcal per g-mole. If the material is not very compressible, then a pressure of 100 kb may only increase the energy by 1 or 2 kcal. New products produced by catalyzed reactions may be sensitive to volume change. The change of Gibbs free energy with pressure at constant temperature is given by the integral of VdP. If there is an overall volume change associated with a reaction, the equilibrium constant for the reaction may be considerably shifted by pressure. The application of pressure may also radically change the products of a reaction when new paths are favored while old paths are blocked.

Examples of the effects of pressure in altering reactions are found in natural silicate minerals. Because so many of them are built out of similar structural units, e.g., SiO_4 tetrahedra, many silicate minerals lie relatively close to each other on a Gibbs free energy scale, even though their chemical compositions may vary widely. The same melt or solution may crystallize along different paths, depending upon local pressure; and different paths can produce very dissimilar mineral assemblages. For example, the soda feldspar (albite), $NaAlSi_3O_8$, is stable at low pressure; but at pressures of 15-25 kb and temperatures between 600 and 1000° C Birch and Le Comte[3] found that albite changes to a mixture of silica and jadeite, $NaAlSi_2O_6$. A chemical separation can thus occur as a result of a shift in equilibrium under pressure.

Similarly, basalt has been found by Kennedy[4] and Boyd and England[5] to change into a mixture of garnet and jadeitic pyroxene at elevated pressures and moderate temperatures.

The general rule for structural change brought about by high pressure is that the high pressure crystal structures of a given compound tend to resemble the structures of the analogous compound made up of heavier elements in the Periodic Table. Even if diamond were not found in nature, one would suspect such a structure for carbon at high pressures on account of the existing structure of silicon and germanium.

When oxides are compressed, the larger oxygen atoms tend to shrink the most. By this means, the ratio of oxygen atoms to metal atoms is increased and the metal becomes increasingly capable of holding more oxygen atoms than before. Thus, the phases of oxides at high pressures are characterized by higher coordination numbers among their constituent atoms. An example is $Al_2O_3.SiO_2$ which is found in three distinct forms: low pressure sillimanite (containing AlO_6 and AlO_4); moderate pressure andalusite (containing AlO_6 and AlO_5); and the high pressure kyanite (containing only AlO_6).

The new material formed at the interface has different physical and chemical characteristics than the original media. It is not known whether some of the potential forms have greater or lesser resistance to hydrologic leaching. It would appear possible to either develop a pressure insensitive waste form or one that is easily transformed to a more desirable condition.

McCarthy, et al., have shown that the Battelle Northwest Laboratories' standard borosilicate glass is converted to the pyroxene mineral acmite ($NaFeSi_2O_6$) after two weeks under 30 MPa and 300° C[5]. The reaction products presumably are catalyzed at the metal interface under these conditions. Similarly, simulated calcine and shale reacted to produce crystals of pollucite.

A review of the effect of pressure on chemical kinetics is in order. The transition state theory assumes that there is a transition state between reactants and products. This can be written for a bimolecular reaction with reactants A and B as:

$$A + B \rightleftarrows AB^* \qquad \text{and} \qquad AB^* \rightarrow C + D$$

The activated complex, AB^*, is in equilibrium with reactants A and B, and the rate determining step is the transformation of AB^* to products.

A transition state, by its very nature, cannot be isolated for study. It can, however, be investigated indirectly using high pressure kinetics to provide information on its properties. Considerable work has been done in this area on organic reactions.

The rate of reaction is given by the number of transition configurations present (the concentration of AB^*) times a frequency of decomposition (assumed independent of composition or pressure). The pressure derivative of the rate constant yields the equation:

$$\left(\frac{\delta \ln k}{\delta P}\right) = -\frac{\Delta V^*}{RT}$$

where ΔV^*, the activation volume, is the difference of partial molal volumes, evaluated at the reaction condition:

$$\Delta V^* = \overline{V}_{AB^*} - \overline{V}_A - \overline{V}_B$$

The pressure derivative above is valid only if the rate constant, k, is expressed in pressure-independent concentration units, such as mole fraction or molality,or a correction term for compressibility must be included. In addition, there needs to be an expression for the functional behavior of $\ln[k(P)]$. A number of techniques have been applied, the simplest being a straight-line method which assumes that ΔV^* is pressure independent. This gives on integration:

$$\frac{\ln(k_P/k_1)}{P-1} = -\frac{\Delta V^*}{RT}$$

where k_P and k_1 are the rate constants at pressure P and 1 atm, respectively. Such methods are generally valid only for very limited pressure ranges.

The most common method for relating the rate constant to pressure is the use of the quadratic series:

$$\ln k = a + bP + cP^2$$

where a, b and c are constants. Other empirical forms have also been used.

The activation volume represents the second derivative of the experimental data, concentration as a function of time, at a given pressure. It is essential first that the experimental technique provides the most accurate data available. High pressure chemical kinetic experiments involve the determination of four variables: pressure, temperature, time and concentration. After the effect of pressure on the rate of a reaction has been measured experimentally and the results reduced to a value for the activation volume, the structure and properties of the transition state must be inferred from ΔV^*. Often the activation volume is compared to the volume change upon reaction, and this is used to ascertain the relative position of the transition state along the reaction coordinate. Alternately, ΔV^* may be compared with values found for reactions of known mechanism and comparisons so made. The absolute value of the partial molal volume of the transition state can be determined by separate determination of the partial molal volumes of the reactants. The results can then be compared with the volume of some model compound.

One of the most useful approaches is the division of ΔV^* into two parts, ΔV^*_1 and ΔV^*_2. The first term, ΔV^*_1, represents a structural contribution, or an intrinsic difference in molecular size between reactants and transition state due to changes in bonding. The second part, ΔV^*_2, is host matrix dependent (whereas ΔV_1 is not) and represents the change in volume of the matrix surrounding the reactants as they pass to the transition state. Most observed values of ΔV^*_2 are in the range of -50 to +20 cm^3/mole. Observations of an apparent activation volume greater than +20 cm^3/mole can be due to diffusion control of the reaction. In general, mass transfer limited reactions have very low values for the apparent activation energy.

A number of chemical reaction rates are found to increase with increasing pressure. It is the objective of this experimental study to examine the reactions that can occur in the waste/canister/rock system and predict their effect on waste isolation.

Experimental

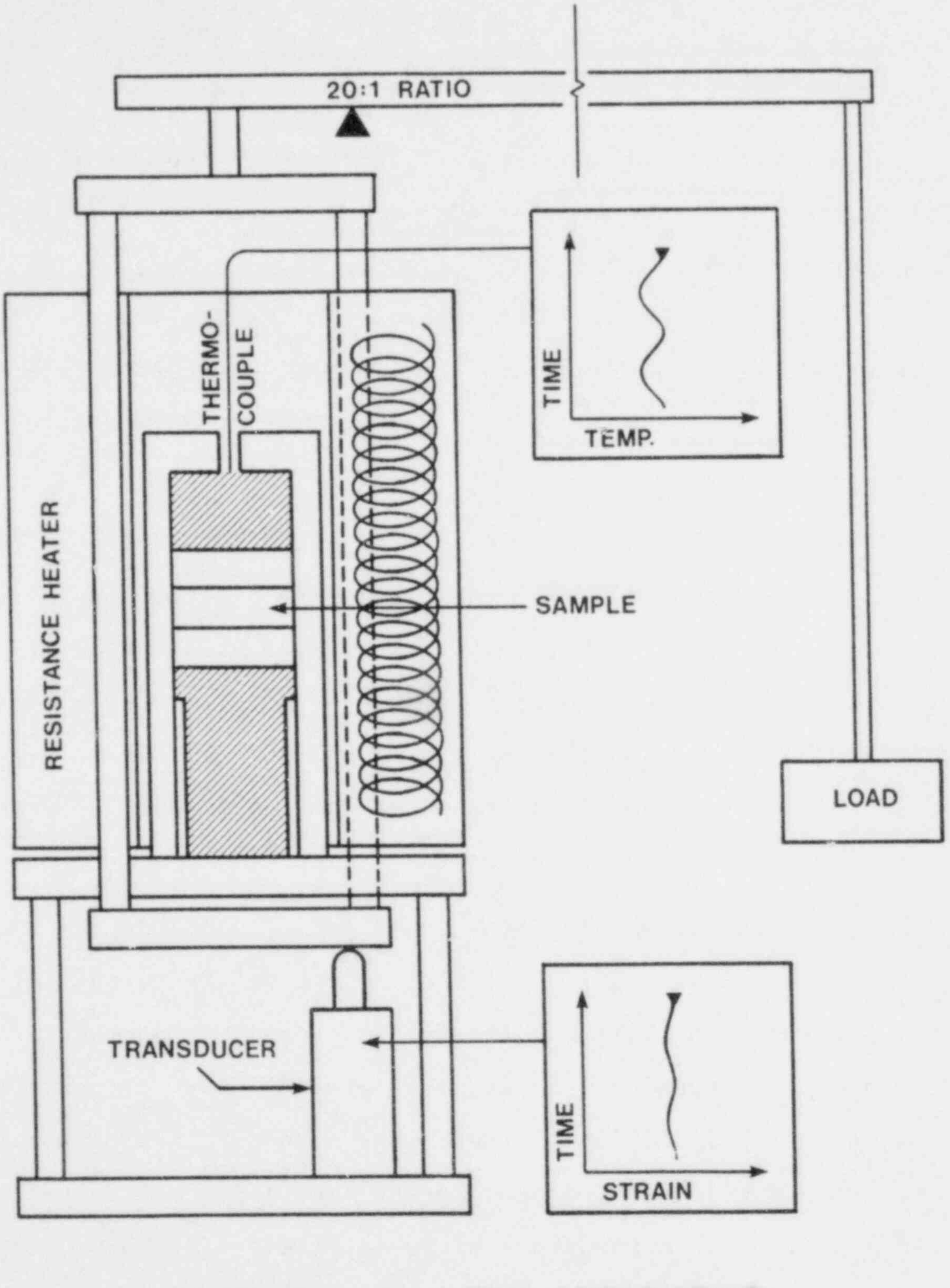
An experimental program is necessary to determine the direction and rate of potential interface reactions. The interfaces of concern are those imposed by design of the waste repository barriers, i.e., waste/ canister /rock interfaces, as well as internal interfaces due to cracking.

The experimental program should answer the two questions of what is likely to be produced at the interface and how fast will it be formed.

The experimental apparatus is designed to subject specimens of waste materials, canister metals and rock types to an uniaxial compression load in the range of 2000 psi at moderately elevated temperatures of 200-300° C for periods of several weeks. The specimens are then examined by electron microprobe to determine what concentration changes have occurred and what new materials have formed.

The samples are cylindrically shaped, 1" diameter by 3/8" to 1/2" thick pieces of glass, stainless steel (4140) and basaltic or granitic rock. A static load is applied with a modified Riehle Model CR-12 creep testing machine (S.N. R-84940) by means of hanging weights on a lever arm with a 20 to 1 mechanical advantage. The samples are maintained in compression by the creep machine with a cylinder and piston device.

Any change in axial dimension is recorded with a (Riehle-84940) transducer located between the bottom of the cylinder and the bottom of the piston. The output from the transducer is continuously recorded on the Riehle creep-time recorder. The sensitivity of the device is ~1×10^{-3} inches. The specimens are maintained at temperature by a 105V, 15 amp Marshall Resistance Furnace. The temperature is recorded on a micromax (Leeds & Northrup) time vs. temperature chart recorder using a Cromel-Alumel thermocouple which is calibrated with a Leeds & Northrup (8662) Potentiometer using



COMPRESSION LOAD APPARATUS

the boiling point of water as a standard. A temperature profile of the furnace is determined before each experiment. The temperature profile of the furnace is determined before each experiment. The temperature recorded in the test is obtained by direct contact of the thermocouple with the sample. The furnace thermostat is able to maintain sample temperature within ± 7° C. The samples are stacked in "sandwich" fashion in a 1-1/2 inch retaining collar in a metal-glass-metal-rock order and then placed between the top of the piston and the top of the cylinder. The furnace is then lowered into position and brought up to temperature, and the load is then slowly applied. At the conclusion of the experiment, samples are sectioned and analyzed for concentration changes of the fission product simulant and for formation of any new reaction products. Any new materials formed are characterized with respect to their physical and chemical properties.

Selection of Systems to Study

A number of systems have been proposed for use in containing HLLW in solid form. They all have as their objective the long term immobilization of all or a specific fraction of the fission products and neutron capture decay elements. The immobilization materials are in theory backed by a canister of metal or other material. The engineered barrier concept requires that the integrity of the canister remain intact for a number of years and that retainment be backed up by the immobilization material. In this case the canister must be designed not to crush under overburden pressure since reconsolidation will occur during the period in which the canister is required to remain intact.

High level liquid waste consists of soluble fission products and actinides in acid or neutralized solutions. A decomposition or calcine step is normally incorporated to convert the liquid to a solid. The solid calcine formed at this point has the disadvantage that it is a finely divided form and can easily dust. Moreover, it has a high surface to volume ratio and is readily subject to leaching action. Finally, it has poor thermal stability. As a result, the calcine is normally incorporated into a secondary medium such as glass, low melting metal or some other material.

To improve the properties of the calcine, the composition of the HLLW can be modified by the addition of materials such as nitrates of calcium and aluminum. The liquid mixture forms a powder called supercalcine that offers improved properties. The solubility of the supercalcine is five to six orders of magnitude lower than that of calcine, and the volatility can be reduced two to four orders of magnitude; however, it is still easily dispersed.

A different approach is to add slurries of materials such as clays and other aluminosilicates to the liquid waste to make a supersludge. It can be further treated to form a low-temperature ceramic or incorporated into a cement matrix. Perhaps the best studied system for incorporating wastes has been glass.

The earliest reference on the incorporation of radioactive wastes in glass matrices dates back to 1955. Multicomponent glass has the advantage of process simplicity and low-leachability structure. Because of many components available to make glass, the final characteristics can be closely controlled. One disadvantage of glass is that it tends to devitrify, thus increasing the surface area for leaching.

Ceramics are considered a potential waste form because they provide a high radionuclide loading in a thermodynamically stable crystalline phase. Their disadvantages lie in their more complicated process requirements and possible sensitivity to transmutation and stored energy effects.

Another material proposed for incorporating nuclear waste is a synthetic analogue of natural igneous rock called "Synrock"[8]. The host minerals selected for synrock were perovskite, hollandite and feldspar. The disadvantages appear to be low waste loading and very limited experience with the system.

Container materials proposed have been lead, copper, aluminum, titanium and steel, as well as non-metallic ceramics. It appears that the various canister materials have been proposed because of their expected chemical stability in a geologic media without the benefit of long term qualifying experiments. Moreover, the design of the containers appears to have been focused solely on sealing and transportation, neglecting consideration of whether they will withstand the overburden pressures. For some waste materials, it may be desirable to design the canister so that it will be readily crushed by the overburden without being breeched. This would hasten the conversion of the waste material to a more stable form.

The presence of water in the geologic repository must be considered. The water may be present in two forms: brine inclusions in salt, or as water of hydration in rock. Water can undergo radiolytic decomposition with the products entering into reactions with the waste/canister/rock system.

The discussion above identifies materials suggested for incorporation in a nuclear repository. Each should be studied to show their interfacial behavior at elevated temperatures and pressures. Standard reference materials, such as Battelle 76-68 glass, should be used in all experiments to make the results comparable under controlled conditions. That standard reference rocks have not been used, because of inherent difficulties of homogeneity, is a problem which must be addressed.

The absence of nuclear radiation in these experiments acts to limit the results. Radiolytic decomposition products and transmutation products are lacking, and radiation induced stored energy in crystal structures is absent. Ultimately it may be desirable to repeat a portion of the work using radioactive waste materials to determine these effects. It is common in experimental kinetic studies to hold as many variables as possible constant and to vary only one item at a time. This allows interpretation of the effect of each parameter in the system.

Application to the Waste Repository

The release of radionuclides from a repository can be considered as a flux of material across the interfacial boundaries of waste/canister/rock. This flux may be increased or decreased by changes occurring at these interfaces. As with all complex kinetic phenomena occurring in series, the slowest is the rate controlling step. It is desirable to identify the rate controlling phenomena so that potential failure, leading to an increase in release, can be characterized. At present, it is not possible to say whether alteration of the waste form is more disruptive to the mission of the repository than failure of the metal canister. Of course, breeching of the canister is necessary at some point to obtain a significant flux of materials to the host rock. Characterization of these reactions is necessary to assure adequate understanding of the repository dynamics.

Conclusions

Most reaction associated with the nuclear waste repository will occur preferentially at the waste/canister/rock interfacial boundaries because of surface energy, enhanced diffusion path and presence of foreign materials. Those occurring internally in the homogeneous bulk consist of zero and first order decomposition or conversion reactions.

Increasing the pressure produces new forms that are stable at higher pressures, and changes the rate of chemical and diffusional processes. Theoretical considerations show that the mass transport of the radioactive material by diffusion will most likely decrease, but that chemical reaction rates may increase with increasing pressure. Pressures arising from the repository overburden and the thermo-mechanical stresses may be sufficient to significantly alter the waste forms. The new reaction products formed at higher pressures may have completely different physical and chemical properties from the original system.

This experimental study is directed at resolving all or part of the following questions:

1. What reactions are occurring at the waste/canister/rock interfaces?
2. What are the characteristics of these products?
3. What are the kinetics associated with the rate of formation of these products?
4. What are diffusional transport kinetics across these interfaces?
5. What is the effect of pressure on the above?
6. How might these phenomena for a specific waste, canister or rock material affect the operation of the repository?

Acknowledgement

This research is being carried out in the Department of Materials Engineering at San Jose State University and is supported by a grant from the United States Nuclear Regulatory Commission. Funding for this program commenced August 24, 1978.

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Discussion Following

THE EFFECT OF PRESSURE ON INTERFACE INTERACTIONS BETWEEN SOLIDS

Presented by Robert Anderson

Robert Leachman - NRC
Question
It would appear to me that there are other things that need to be considered when you talk about the desirability of quickly achieving high pressure in a repository. One is the possibility of having super-heated water and so then increase corrosion rates. Do you not have to consider these other effects too, when you advocate high-pressure quickly in a repository?

Anderson
Response:
I would think so. One has to consider the radiation effects; one has to consider the total chemistry. It is a very complex problem. I feel that the considerations are there that we can use the pressure to help us. We can, perhaps in some media, prevent water inflow by quickly establishing pressures, and when we are worried about the effect of water, one way might be to establish pressures so that we have no driving force toward a low pressure regime. I have not talked about that, I am merely looking at the diffusion in the chemical characteristics.

Alexis Parks - Boulder, Colorado, private citizen
Question:
Another question related to the water. Is it possible to create, through sink holes or depressions on the surface above the repository, unexpected accumulations of water? Ultimately, if you did have pressure and the ground surface descends because of the plasticity of some media, such as salt, would that create a basin to serve as a reservoir for surface water?

Anderson
Response:
No. I would pass to my geology friends. There could be heave or there could be slump. My idealized drawing showed no intrusion, showed no defects at all occurring. I am not sure what amount of slump might occur. I am taxing my memory, but from what I have seen the repository heat loadings have been designed so there will be no surface slump and there will not be any heave. If you have slump or heave, you are talking about the physio-elastic properties of rock, and you want to make sure that you do not stress the rock or cause cracks. So I believe one of the design parameters will be to not allow large surface thrusts or downward slumps.

INCORPORATION OF SOLID HIGH LEVEL WASTES INTO METAL AND NON-METAL MATRICES

van Geel J., Eschrich H., Dobbels F., Favre P., and Sterner H.

EUROCHEMIC - MOL (Belgium)

INCORPORATION OF SOLID HIGH LEVEL WASTES INTO METAL AND NON-METAL MATRICES

van Geel J., Eschrich H., Dobbels F., Favre P., and Sterner H.

ABSTRACT

The main objective of incorporating solidified high level wastes of high specific activity into a matrix material is to obtain final waste forms with moderate inner temperatures, even at large waste loadings per meter length.

The temperature distribution in waste forms of vitreous beads embedded into a metal matrix (vitromets) during short- and long-term storage, are compared with those in vitreous blocks of equal heat generation per meter height.

It is found that for storage under water, inner temperatures below 100°C are assured in vitromets, produced from short cooled high level wastes, and containing high waste loadings per meter canister height.

The chemical and mechanical resistivity, as well as the thermal stability have been examined for various matrix materials whereby emphasis is given to lead- and aluminium alloys.

The corrosion of lead- and aluminium alloys in distilled water, brine solutions and dry salt has been examined at various temperatures.

The deformation behaviour of vitromets under axial compression is investigated at different temperatures and varying height-diameter ratios.

The maturity of the vitromet production is finally demonstrated by presenting process data from hot laboratory scale and cold semi-industrial scale production units.

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LIST OF FIGURES

LIST OF FIGURES
(continued)

INCORPORATION OF SOLID HIGH LEVEL WASTES INTO METAL AND NON-METAL MATRICES

1. INTRODUCTION

In many countries the established concept of managing solidified high level liquid wastes (HLW) includes interim storage for about 10 to 50 years in engineered facilities followed by disposal in stable geological formations.

As a result of the radioactive decay, solid waste products continuously change their chemical and physical properties which makes evaluation of the compatibility of these products with potential geological environments difficult. Any changes in the properties with time must be understood and shown not to lead to a premature deterioration of the required features initially present.

Today, experimental data are lacking on the short-term and long-term storage behaviour of high level waste forms of high specific activity, involving high temperatures within the product and high radiation doses which could enhance the rate of formation of some detrimental effects of these waste forms.

It is therefore expected that the first generation of HLW products will be produced assuring moderate inner temperatures which will probably tend to increase when more experience is gained.

Low inner temperatures can certainly be obtained in products of relatively small dimensions and low waste concentrations. These measures, however, result always in the production of an increased number of storage containers and/or unpractical height to diameter ratios.

In the search for alternative solid HLW forms which assure to a higher degree than glass monoliths the desirable long-term stability, several composite products were fabricated consisting of HLW particles incorporated in a metal or non-metal matrix.

Consequently the usual investigations on the chemical, thermal and mechanical stability as well as the interaction of the solidified HLW with its immediate environment had to be extended to the matrix material and the composite material.

Introduction (continued)

It is evident that matrix material of high corrosion resistance have primarily been studied. Among these are lead and lead-alloys which have shown since millennia high stability in natural environments.

The high heat conductivity of metals is, of course, particularly advantageous for HLW solids exhibiting a low thermal conductivity such as glasses and calcines.

2. CURRENT RESEARCH AND DEVELOPMENT WORK

The previous and current R and D work on the encapsulation of solidified HLW into metal matrices has recently been reviewed by Jardine and Steindler (1). In the following we therefore give only a brief summary of representative or new investigations in this field, especially those carried out at Eurochemic. In addition we describe some of our preliminary studies on the use of non-metal matrices for the conditioning of solid and solidified waste of high specific activity.

2.1 Calcine- and ceramic-metal matrix composites (ceramets)

Rhodes (2) and later Berreth et al. (3) developed processes for incorporating high level waste calcines in aluminium, iron, zinc and lead-tin to form composite products having thermal conductivities between 5 and 40 Wm^{-1} $^{o}C^{-1}$ depending on the metal used.

The high porosity and water-solubility of the calcines, and the "point to point" contact between the granules in the metal provide, however, pathways for water to penetrate and to dissolve the calcine. Furthermore, the high fraction of fines in most calcines also these produced in fluidized bed reactors cause non-uniform poor quality composites that are unsuitable for long-term storage.

To reduce the high penetrability of the calcines, studies were carried out to coat these type of particles, with pyrolytic carbon, nickel and molybdenum, chromium carbide and oxide, silicon, silica and alumina prior to their embedding (4). The remaining high intraparticle porosity of the granules still put a serious limitation to the concentration of the waste in the final composite material.

At Eurochemic, the MINERVA Process (5) was developed, among others, to convert the aluminium containing high level liquid waste to large size mineral-type phosphate granules of low solubility at temperatures no exceeding 550°C. These granules were then incorporated into lead alloys. Ceramets having leach rates below $1 \cdot 10^{-6}$ g · $day^{-1} \cdot cm^{-2}$ were obtained (5).

Figure 1 shows two examples of these ceramet products.

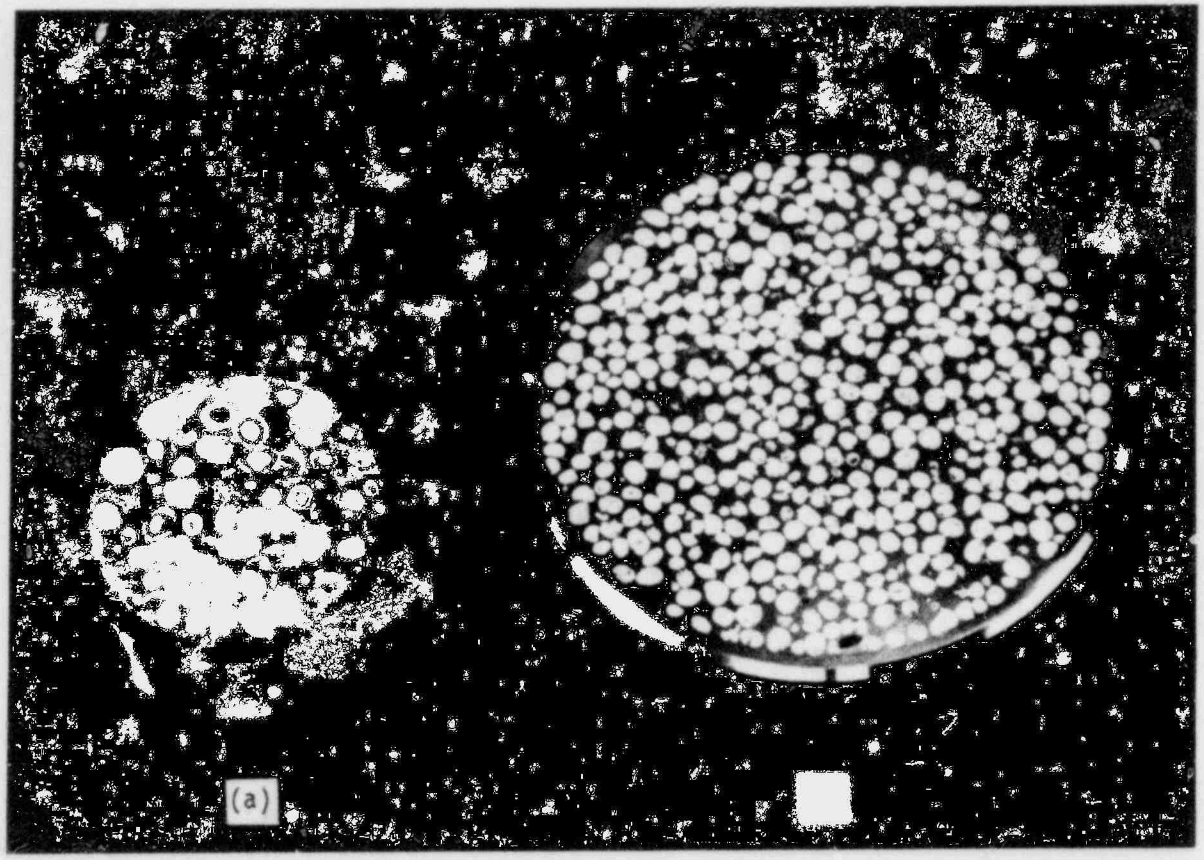


Fig. 1 - MINERAL TYPE PHOSPHATE GRANULES EMBEDDED IN (a) ALUMINIUM, AND (b) LEAD MATRIX

An interesting suggestion was made by McCarthy (6) who examined in cooperation with the Battelle Northwest Laboratories (7) cold and hot pressed discs of "supercalcines" of high density which would be suitable for incorporation into a metal matrix, and could yield composites with waste concentrations comparable to those in HLW glasses.

2.2 Glass-metal matrix composites (vitromets)

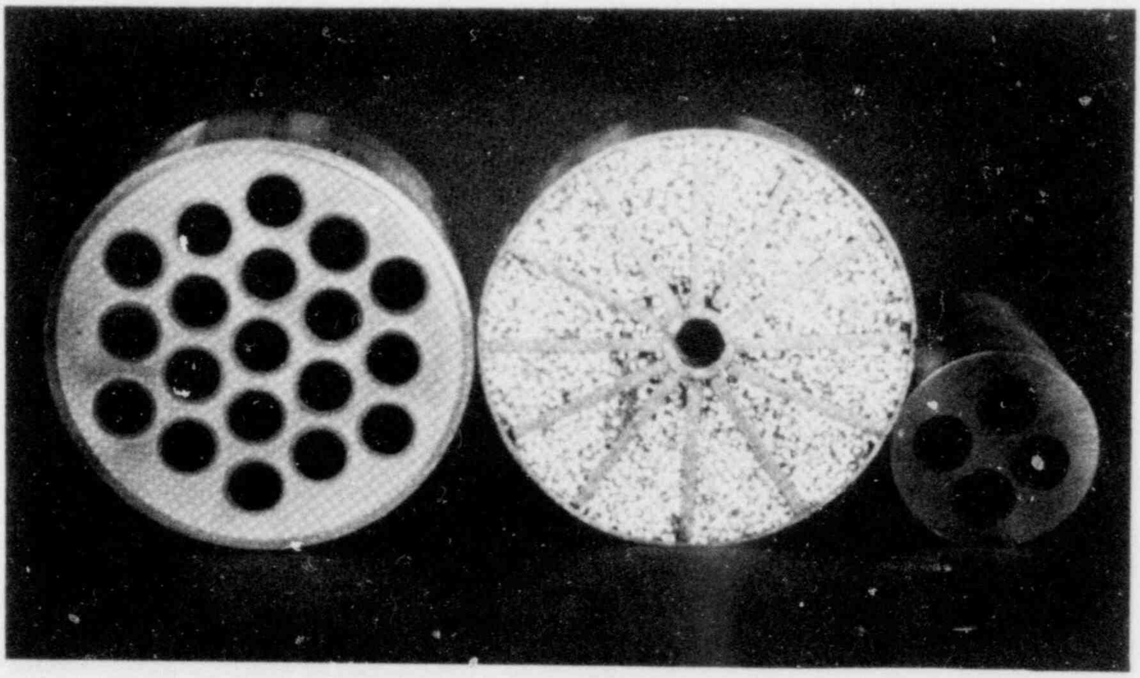
The design concept of the first types of vitromets was aimed at reducing the large temperature difference to be encountered between wall and centerline for canisters filled with vitreous high level waste.
This could be obtained by providing the canisters with metallic inserts of high thermal conductivity, such as shown in figures 2 a and b.

The homogeneity of these products could considerably be increased by transforming the glass melt first into small beads and then incorporating these beads into a molten alloy. Some examples of these type of vitromets are shown in figure 3. The techniques for beads production and incorporation into a molten metal have been tested at industrial scale at Mol and are described in paragraphs 5.1 and 3.1 respectively of this paper.

2.3 Cladding and scrout - metal matrix composites

A conditioning process for the hulls and structural components of spent fuel elements, based on mechanical compaction and encapsulation in a low melting filling alloy, is being developed by the Belgian Nuclear Research Center, S.C.K./C.E.N., under contract with the European Atomic Energy Community (8).

Compaction up to 75 % of theoretical density could be obtained at a compaction pressure of 150 MPa. The compacted briquettes have been embedded in Pb - 1.5 Sb alloy at atmospheric pressure and under vacuum. In the air casting tests the Pb-Sb alloy was heated to about 450 °C by an induction furnace. Rest porosities of 15 to 18 vol.-% were obtained and caused by air bubbles trapped in the irregularly deformed cladding material. Vacuum casting has lead to much better results. Rest porosities of 3.5 % were obtained which were shown to be completely isolated in the composite.



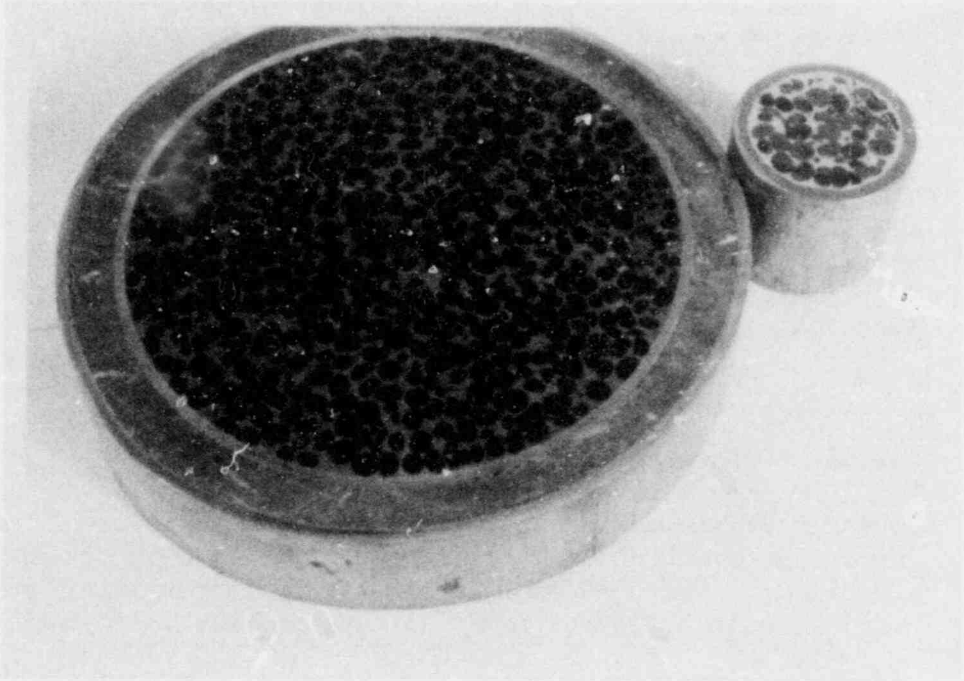
(a) (b) (c)

Fig. 2 - WASTE PRODUCTS CONTAINED IN CANISTERS PROVIDED WITH METALLIC INSERTS TO INCREASE THE THERMAL CONDUCTIVITY.

a) Canister of stainless steel filled with glass containing stainless steel tubes embedded in aluminium.

b) Canister of stainless steel provided with a stainless steel insert, filled with calcine granules embedded into glass.

c) Canister of stainless steel with bore holes, with filled glass.



(a) (b)

Fig. 3 - VITROMETS OF (a) BOROSILICATE GLASS BEADS - LEAD ALLOY AND (b) PHOSPHATE GLASS BEADS - ALUMINIUM ALLOY.

2.4 Non-metallic matrix material

2.4.1 Graphite, glass and thermosetting resins

Scoping studies were performed by Eurochemic on a laboratory scale to investigate if non-metallic material could be used to fill the intra-particle as well as the inter-particle voids of granular oxide calcines and phosphate ceramics. Some of the products obtained are shown in figure 4.

Graphite combines chemical stability with a relatively high thermal conductivity and, when properly mixed with a binder like phenolformaldehyde resin, can form a stable matrix after compression at 20 MPa and hardening at 180 °C.

Good wettability of the granules was observed by embedding the granules into pure thermosetting resins like those based on orthophthalic acid, styrene and glycol.

All further studies were ceased as those containing substantial amounts of organic substances were either believed not sufficiently radiation resistant and fire resistant to house waste of high specific activity.

2.4.2 Concrete

The use of cements to form concretes for incorporating solid or liquid wastes has received widespread attention in the management of radioactive wastes (9, 10). Concrete materials however, are generally porous and may break rather easily owing to atmospheric conditions. Proposed post treatments by impregnating the concrete matrices with a polymer material does not eliminate the internal porosity of the matrix, does not increase the mechanical strength and often leads to a product which is not fire resistant.

Eurochemic has developed a process for the purpose of embedding 16 tons of structural material, cut from the fuel elements (undissolved structural parts + parts of fuel pins), into a polymer concrete matrix. These residues contain highly activated material and relatively high amounts of core material.

The matrix material is a mixture of an inorganic aggregate (SiO_2, koalin), a polymer as a binder and chemical additives such as fire retardants $Al(OH)_3$ and water repellent chemicals (e.g. paraffins).

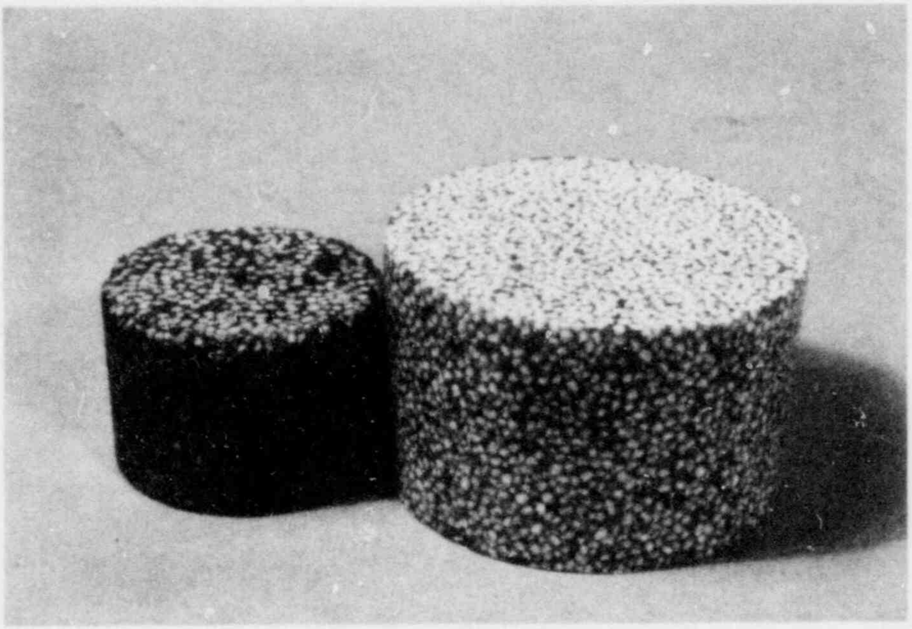


Fig. 4 - COMPOSITES OF (a) OXIDE GRANULES AND A GRAPHITE MATRIX, AND (b) PHOSPHATE GRANULES AND POLYESTER MATRIX.

Special effort was made to keep the weight fraction of the polymer low ($\leq$ 20 %) in order to yield a product with low content of organic material.

Many combinations of resins, fire retardants and aggregates were tested which finally resulted in matrix material composed of 50 wt-% SiO_2, 10 % kaolin, 20 % $Al(OH)_3$ and 20 % of a polyester based on orthophthalic acid, styrene and glycol.

The incorporation can be performed under water, thereby reducing air born contamination problems.

Water is however an inhibitor for most polymerisation reactions. The aggregate material was therefore pretreated with water repellent paraffins, prior to mixing the aggregate with the polymerisable compounds (11).

Demonstration tests at 1 : 1 scale with contaminated solids with a radiation dose of 100 R/h at contact have been performed. An inactive laboratory scale sample of the product is shown in figure 5.

The matrix material shows excellent flame and fire resistance (ASTM oxygene index 30), no porosity, high resistance to thermal shocks, a compression strength of 140 MPa, and no visual changement after an accumulated radiation dose of 10^{10} Rad.

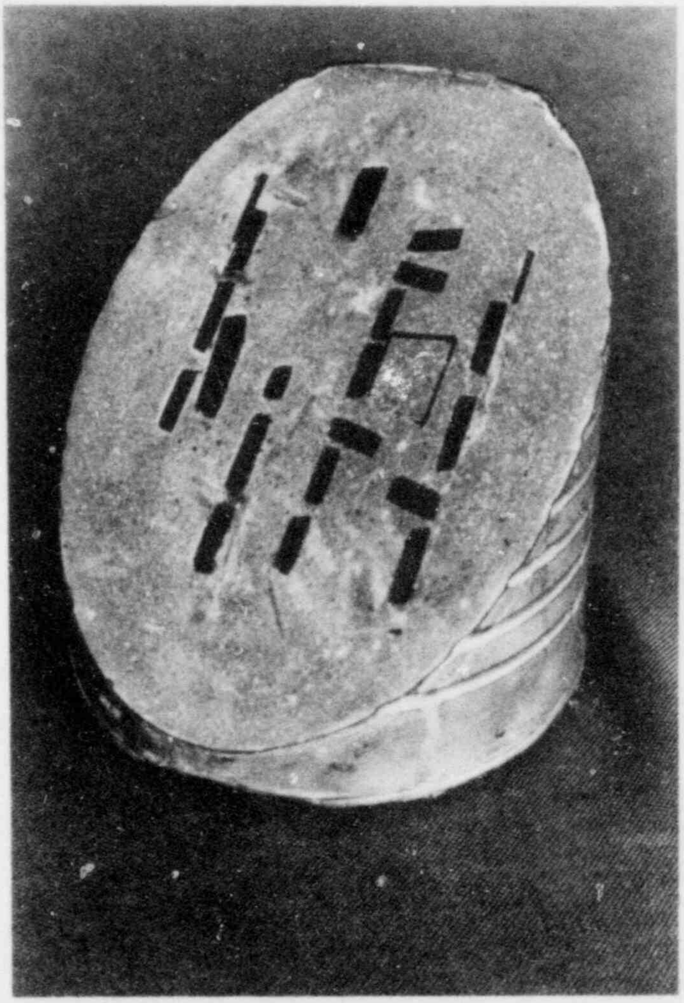


Fig. 5 - IRON PIECES INCORPORATED UNDER WATER IN A POLYMER-CONCRETE MATRIX.

3. INCORPORATION TECHNIQUES FOR METAL MATRICES

3.1 Vacuum casting

Vacuum casting is of particular interest for solids which have porosities of small size and difficult accessible by the filling matrix.

The casting technique shown in figure 6-a has been applied for embedding briquettes of compressed cladding material into a molten alloy (8).

Lamb (12) recently reported the experience with various vacuum techniques of which one was judged particularly promising. The canister is attached to the metal casting system by a tube at the bottom, the molten metal flows upwards through this tube when vacuum is pulled at the top of the canister.

The metal freezes in the tube, sealing the lower end of the canister. The canister content is now degassed and the pressure reduced to its desired value. The cooling water to the lower freeze valve is shut off to remelt the metal. The molten metal flows up through the canister due to the vacuum and penetrates the inter-particle voids.

3.2 Techniques developed at Eurochemic

The embedding procedure depends on the physico-chemical properties of both the matrix and the phase material to be encapsulated. For instance, incorporation of borosilicate glass beads in molten aluminium is relatively simple as the beads have a higher density than aluminium.
The beads can be poured directly into a canister which is prefilled with molten aluminium.

For composites in which the metal matrix has a higher density than the beads, a more complicated procedure has been applied. This procedure is illustrated in figure 6b.

The inner compartment of a double-walled stainless steel container is filled with the waste granules via an inlet tube which is closed directly after filling. The outer surface of the container is then heated by induction to a temperature of about 500 °C.

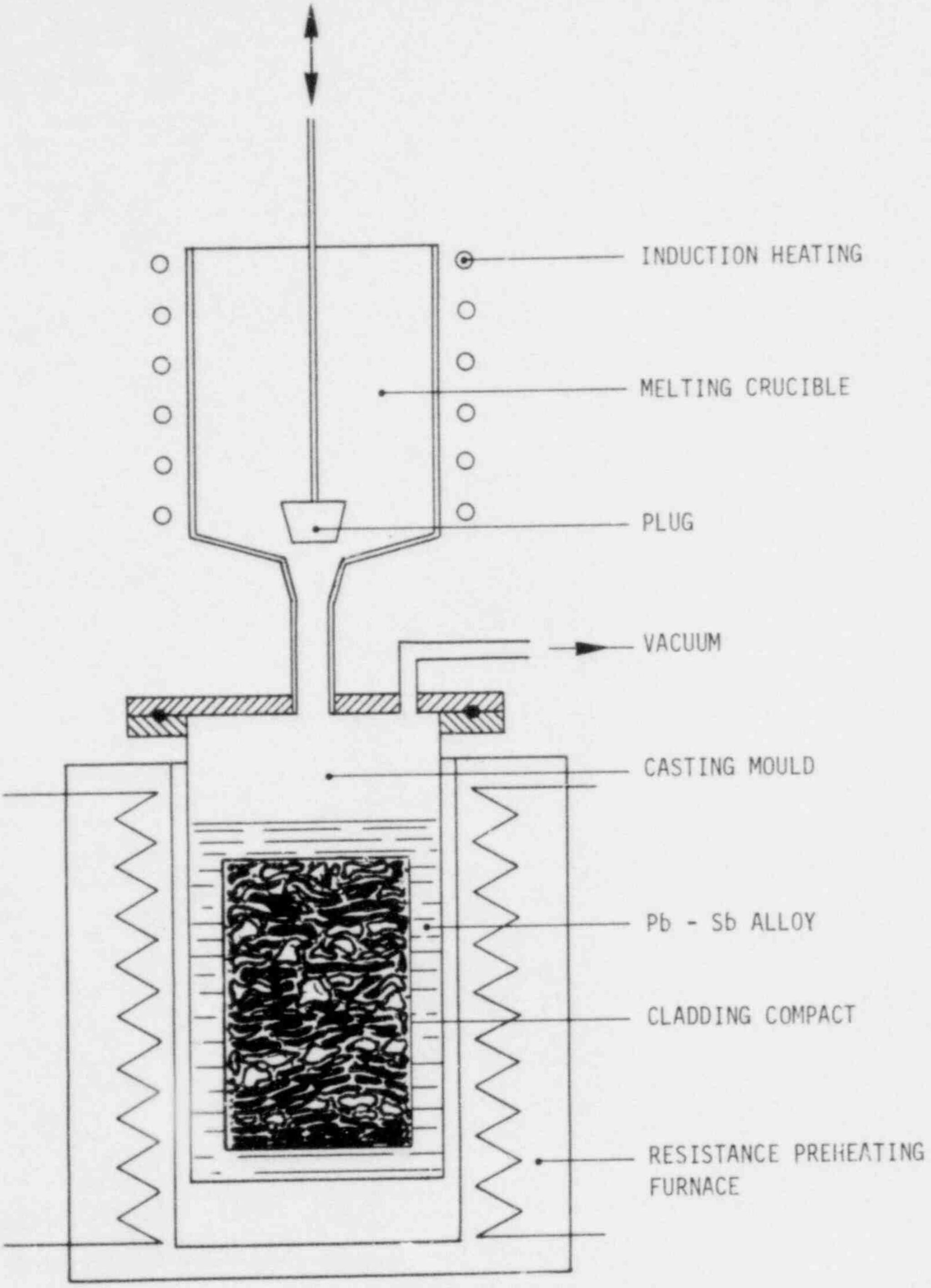


Fig. 6a - EMBEDDING OF COMPRESSED CLADDING MATERIAL IN MOLTEN LEAD (8)

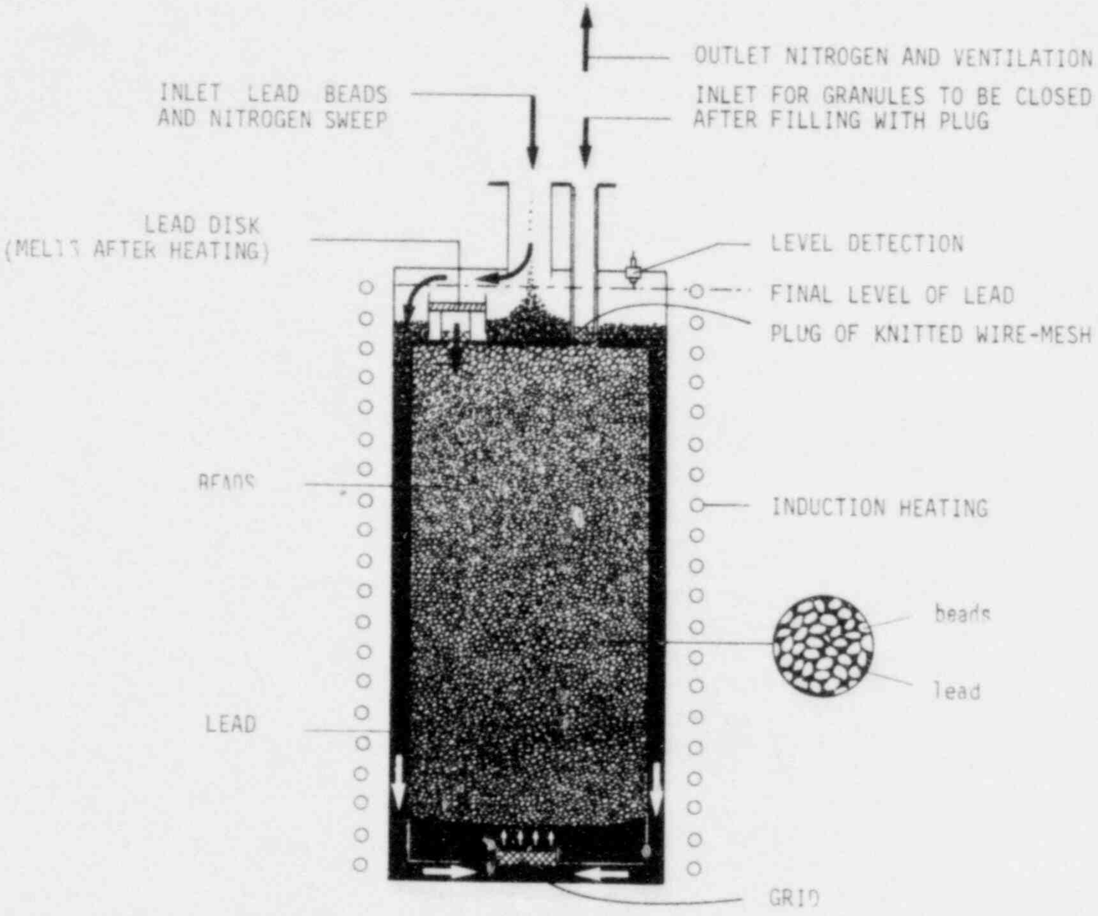


Fig. 6b - EMBEDDING OF GLASS BEADS INTO A LEAD MATRIX

Lead shot of 3 - 5 mm in diameter is then continuously fed between the inner and the outer wall of the container where it melts. The metal melt rises up via an opening at the bottom, provided with a grid, into the inner container filling-up the void space between the granules. Additional lead is added to completely surround the inner container by a layer of lead.

The container is zone-cooled from the bottom to the top eliminating the formation of cavities in the matrix during its solidification.

A series of products of different composition prepared in laboratory scale experiments have shown a homogeneous distribution of the granules within the metal matrix, which occupies about 30 % of the total volume. The bulk volume of the waste is not increased, as the matrix material only fills up the void space between the granules (13, 14).

4. PRODUCT CHARACTERISTICS

The assessment of the chemical and physical stability of solid HLW products which are incorporated into a metal or other matrix material, includes the study of the compatibility of the matrix material with the dispersed phase, the container material and with the environment in which the container will be stored.

The data reported here are limited to those obtained at Eurochemic and are related to lead and aluminium alloys as matrix material phosphate and borosilicate glass as dispersed phase, stainless steel as container material, and water, sodium chloride, and a rock salt deposit excavated from the ASSE II mine in the German Republic, as environmental media.

4.1 Chemical compatibility of metal matrix with storage media

Various lead and aluminium alloys have been exposed to chemicals present in potential intermediate and final storage media.

Periodical tests have been carried out in one liter flasks in which samples of pure alloys were contacted with bi-distilled water, and aqueous solutions saturated with a rock salt deposit excavated from the ASSE II salt mine. This salt, further called ASSE II salt, contains $\geq$ 99 wt.-% NaCl and traces of $MgCl_2$ and $CaSO_4$.

To study the influence of oxygen, nitrogen and CO_2 on the corrosion rate, part of the aqueous solutions was saturated with these gases. The alloys were also exposed to the dry ASSE II salt at temperatures up to 250 °C and for periods up to 172 days.

The results of the studies with lead alloys and executed at different temperatures are shown in Tables I and II. They are in good agreement with the data from AZIM (15) and GOUDA (16). Although the studies are still in progress, some general lines can be marked off :
Lead alloyed with antimony and tin, exposed up to 172 days at 110 °C to dry ASSE II salt, showed a corrosion rate of $\leq$ 0.001 mm yr^{-1}. An equal corrosion rate was measured when part of these alloys were contacted with a saturated solution of this salt at 50 °C (solution saturated with N_2 only).

TABLE 1 : COMPOSITION OF METAL ALLOYS USED IN OUR CORROSION STUDIES

Alloy identification	Corresponding material number according German standards	Maximum weight %									
		Aq	As	Bi	Cu	Fe	Sb	Sn	Zn	Pd	Total
Pb 99.99	23010	0.001	0.001	0.005	0.001	0.001	0.001	0.001	0.001	-	0.01
Pb 99.9 Cu	23021	0.0025	0.001	0.01	0.04-0.08	0.001	0.002	0.001	0.001	-	0.015*
Pb - Sb	23201	-	0.02-0.05	-	-	-	0.75-1.25	-	-	-	
Pb 98.5	23085	-	-	-	0.5	-	-	-	0.05	-	1.5
Pb - Sn 20	-	-	-	-	-	-	-	20	-	-	-
Pb - Sn 10	-	-	-	-	-	-	-	10	-	-	-
Pb - Cu - Sn - Pd	-	-	-	-	0.05	-	-	0.05	-	0.1	-

* Except copper and silver

TABLE 2 : CORROSION RATE* OF LEAD ALLOYS IN DRY ASSE SALT AND AQUEOUS SOLUTIONS SATURATED WITH THE ASSE SALT

Corrosion condition	Temp. (^oC)	Corrosion period (days)	Corrosion rate (mm yr^{-1})					
			Pb 99.99	Pb 99.9 Cu	Pb - Sb	Pb 98.5	Pb - Sn 20	Pb - Sn 10
Dry ASSE II salt Composition (wt.-%) Cl (60); Na (39); SO_4 (1.2): Ca (0.4); Fe ($6 \cdot 10^{-4}$); Mg (< 0.1)	110	161 - 176	0.0008	0.0004	0.0004	0.0007	0.0001	-
Immersion in saturated solution of ASSE salt								
a) Saturated with pure N_2 and under N_2 atmosphere	50	106	0.0004	-	-	0.0009	-	0.004
b) Saturated with air	50	92	-	-	-	0.016	-	0.013

*) Determined according DIN 50905

TABLE 3 : ELECTROMECHANICAL POTENTIALS AT ROOM TEMPERATURE OF VARIOUS METALS AND ALLOYS AS MEASURED IN AN AQUEOUS SOLUTION SATURATED WITH ASSE II SALT AND WITH AIR

ALLOYS (wt.-%)	E*	ALLOYS (wt.-%)	E*
Pt (99.9 %)	+ 470	Pb + Sb (12%) + Sn(4%)	- 367
Au (99 9 %)	+ 290	Pb + Sb (8.6 %)	- 373
Incoloy 825	+ 70	Pb + Hg (30 %)	- 374
Hastelloy C 4	+ 70	Pb (99.9 %)	- 376
Ag (99.9 %)	+ 68	Pb + Te (0.1 %)	- 377
S.S. 304 L passivated	- 52	Pb + Ca (0.1 %)	- 384
Monel 400	- 90	Pb + Ag (1 %)	- 390
Cu (99.7 %)	- 145	Wrought iron	- 396
Sb (99.0 %)	- 208	Al + Si (13 %)	- 624
Inconel 625	- 240	Al (99.5 %)	- 629
Sn (99.5 %)	- 350	Cd (99.9 %)	- 639
Pb + Sn (20 %)	- 354	Al + Mg (3 %)	- 647

*) Electrochemical potential towards normal hydrogen electrode

These low corrosion rates are most probably caused by the chloride ions, and also sulphate ions, which act as anodic inhibitors (15). X-ray diffraction patterns of the lead surface layer indeed showed the presence of $Pb_2Na_3Cl(SO_4)_3$ (ASTM 25-706) and $Pb_4O_3Cl_2$ (ASTM-6-405).
When however, this solution is saturated with air, the corrosion rate increases to 0.15 mm yr^{-1}. This is explained by the fact that oxygen participates in the cathodic processes underlying the corrosion of Pb in chloride solutions (17). Our results indicate that silver and copper as alloying elements are effective in decreasing the corrosion rate of lead in oxygen rich chloride containing waters.

Investigations are continued to simulate more precisely the storage conditions to be expected at large depths at elevated temperatures and at high pressures.

Pure aluminium seems to be equally corrosion resistant than lead in certain chloride containing media like the dry salt of ASSE II and the saturated aqueous solutions of this salt.

Also here chloride ions have a passivating effect by formation of an adherent and impervious layer.
X-ray diffraction patterns of the passivation layer on the aluminium alloy (type A-S 13) after a 2 years' contact with the ASSE II salt, showed the formation of delta- and eta alumina and the $Al_{11}(OH)_{30}Cl_3$ compound.

The stability and permeability of this passivation layer, by species controlling the anodic reaction, are under intensive investigation.

The galvanic effect of matrix material and canister material on the corrosion of both metals form also a considerable part of our corrosion studies. Table 3 shows the measured electrochemical potentials of metals and their alloys in aqueous solutions saturated with the ASSE II salt and with air. From this table bimetallic couples have been selected and recently been submitted to corrosion in the dry ASSE II salt at temperatures up to 200 °C and pressures up to 20 MPa.

4.2 Chemical compatibility of the matrix material with the canister material and vitreous beads

Microscopic investigation of the interface between lead or aluminium alloys and stainless steel (AISI 304) did not show any signs of interaction nor of liquid metal embrittlement of the canister material.
Corrosion attack and liquid metal embrittlement of liquid lead on ferrous alloys is however been reported in Literature (18) and primarily the result of the high solubility of nickel and chromium in molten lead.

The rate of interaction is extremely low, reason why Frye (17) found 304 stainless steel to be unattacked by lead during a 500 hours exposure at 400 °C.

As the embedding procedure described above involves liquid metal contact with canister material for about 7 hours, serious damage at the interface is not believed to occur.
Interaction of molten lead with phosphate glass beads has been investigated by electron probe analysis. Of the chemical elements present at the interphase, some minor penetration of lead into the glass phase was observed after prolonged heating to 72 hours. Tests are continued including aluminium alloys and borosilicate glasses.

Phosphate glass beads were immersed in commercially pure liquid lead at 400 °C for different time periods. After contact, the samples were cut perpendicular to the contact surface and the interphase was investigated qualitatively in an electron microprobe (resolution 1 - 3 µm). After 1 hour contact no interaction could be observed but after 72 hours, a slight enrichment of Na and Al in the glass phase near the interphase could be detected (~ 10 µm). The lead diffusion into the glass phase was 40 µm.

The tests have learned that no deterious effects will occur during the relatively short contact times at elevated temperature.

4.3 Thermal properties

The study of the thermal properties of the HLW containers is based on the heat generation data for borosilicate glass, presented in figure 7.
The thermal data for this reference glass are taken from Laude (19). This glass results from the vitrification of high level waste originating from the reprocessing of commercial LWR fuel, and contains 520 g/l of fission product oxydes. Simultaneously, the curves for HLW glass from the reprocessing of mixed oxyde fuel containing twice recycled Pu are presented (20).

The specific heat production of this latter glass was assumed to be equal to that of the reference glass at one year after discharge from the reactor.

The corresponding data for vitromets, containing 66 vol.-% of glass beads of 3 - 5 mm of equal composition and embedded in a Pb-2 % Sb matrix, are also presented.

Figure 8 shows the difference between centerline and wall temperatures for cylindrical vitromets, 60 cm in diameter as a function of time after reactor discharge of non recycled fuel.

A similar curve is drawn for massive borosilicate glass blocks of 50 cm in diameter, having an equal heat production per meter block height.

The relatively low temperature difference in vitromets can be explained by the thermal conductivity of the vitromet ($\geq$ 10 W m^{-1} $^{o}C^{-1}$), which is an order of magnitude higher than for the massive glass blocks (assumed λ = 1 W m^{-1} $^{o}C^{-1}$).

4.3.1 Intermediate storage

In figure 9a, the radius of vitromets and corresponding glass blocks at prefixed centerline temperatures and under natural air and water cooling, is plotted as a function of time after reactor discharge. The corresponding data of figure 9b shows the important decrease of container radius when waste from spent recycled fuel is considered.

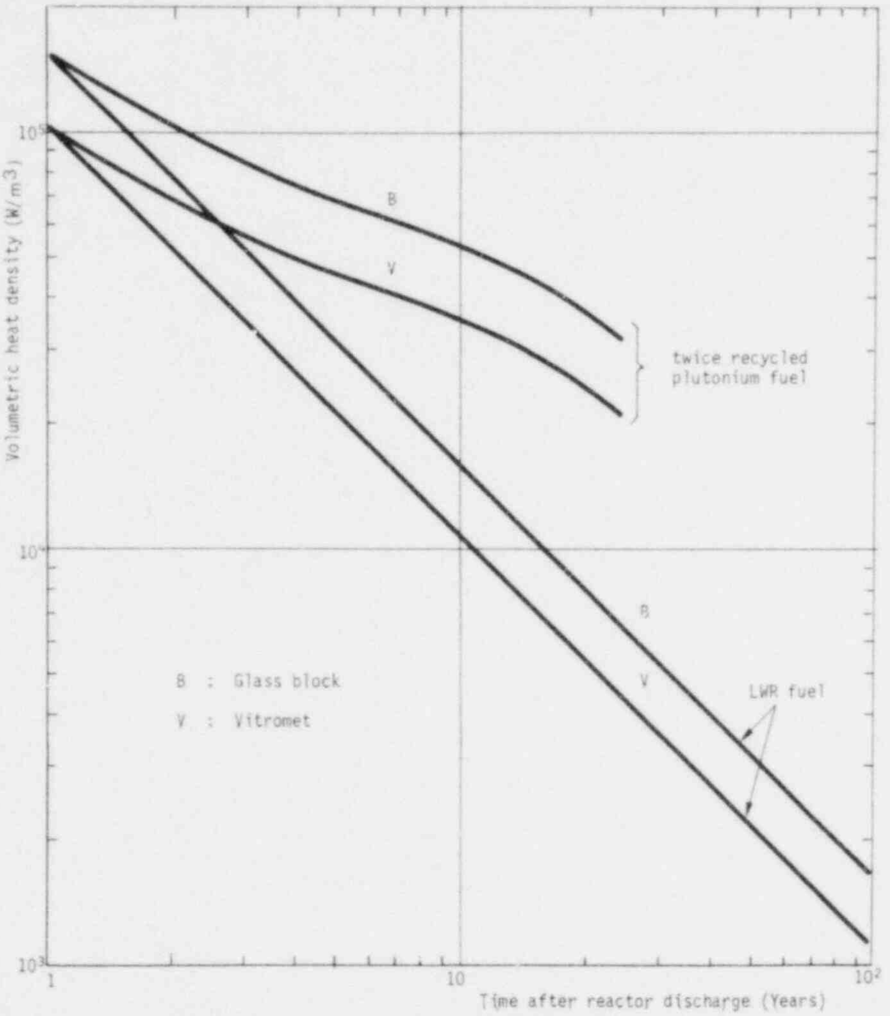


Fig. 7 - CALCULATED VOLUMETRIC HEAT DENSITY OF MONOLITHIC GLASS BLOCKS GENERATED FROM SPENT LWR FUEL (19) AND FROM TWICE RECYCLED PLUTONIUM FUEL (20), AS A FUNCTION OF TIME AFTER REACTOR DISCHARGE.

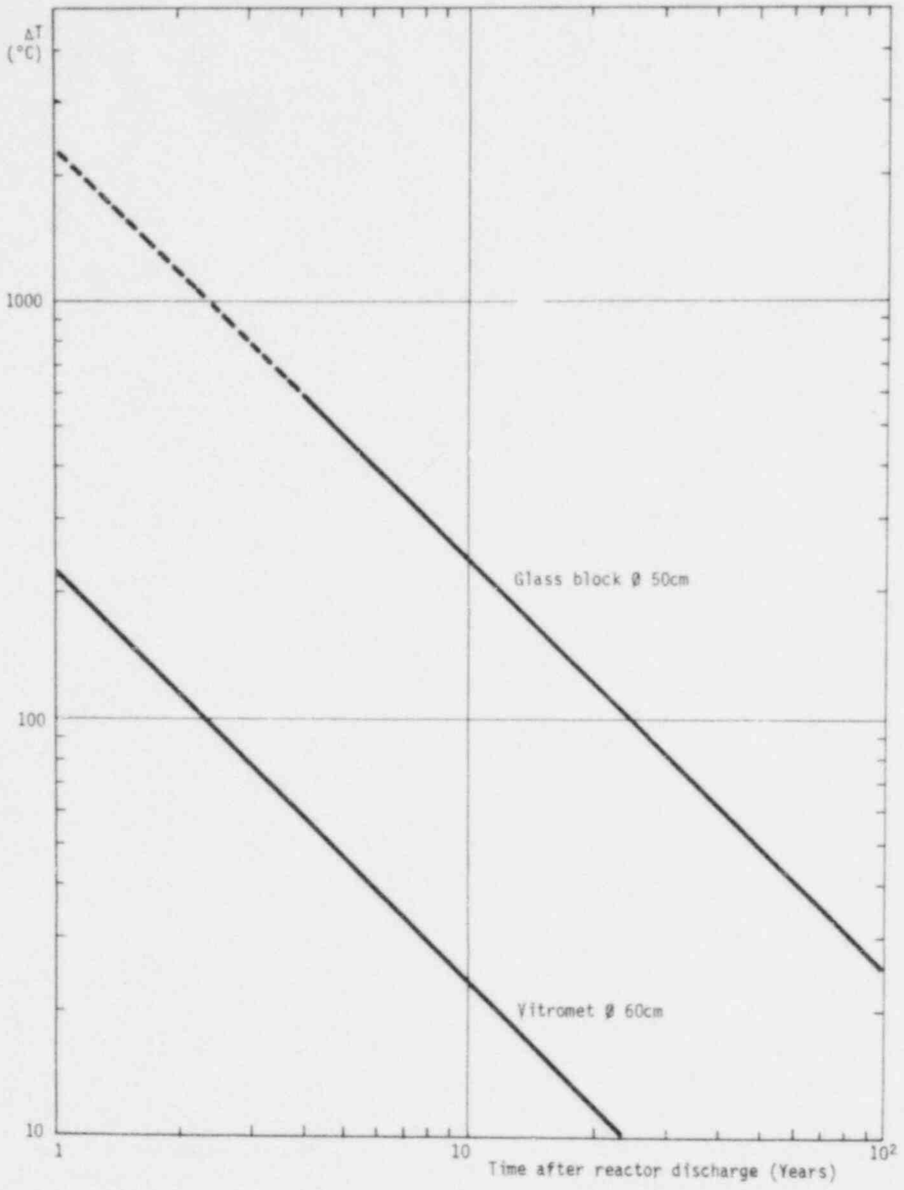


Fig. 8 - TEMPERATURE DIFFERENCE BETWEEN CENTERLINE AND WALL OF CYLINDRICAL GLASS BLOCKS AND VITROMETS OF EQUAL HEAT GENERATION PER METER LENGTH AS A FUNCTION OF TIME AFTER REACTOR DISCHARGE.

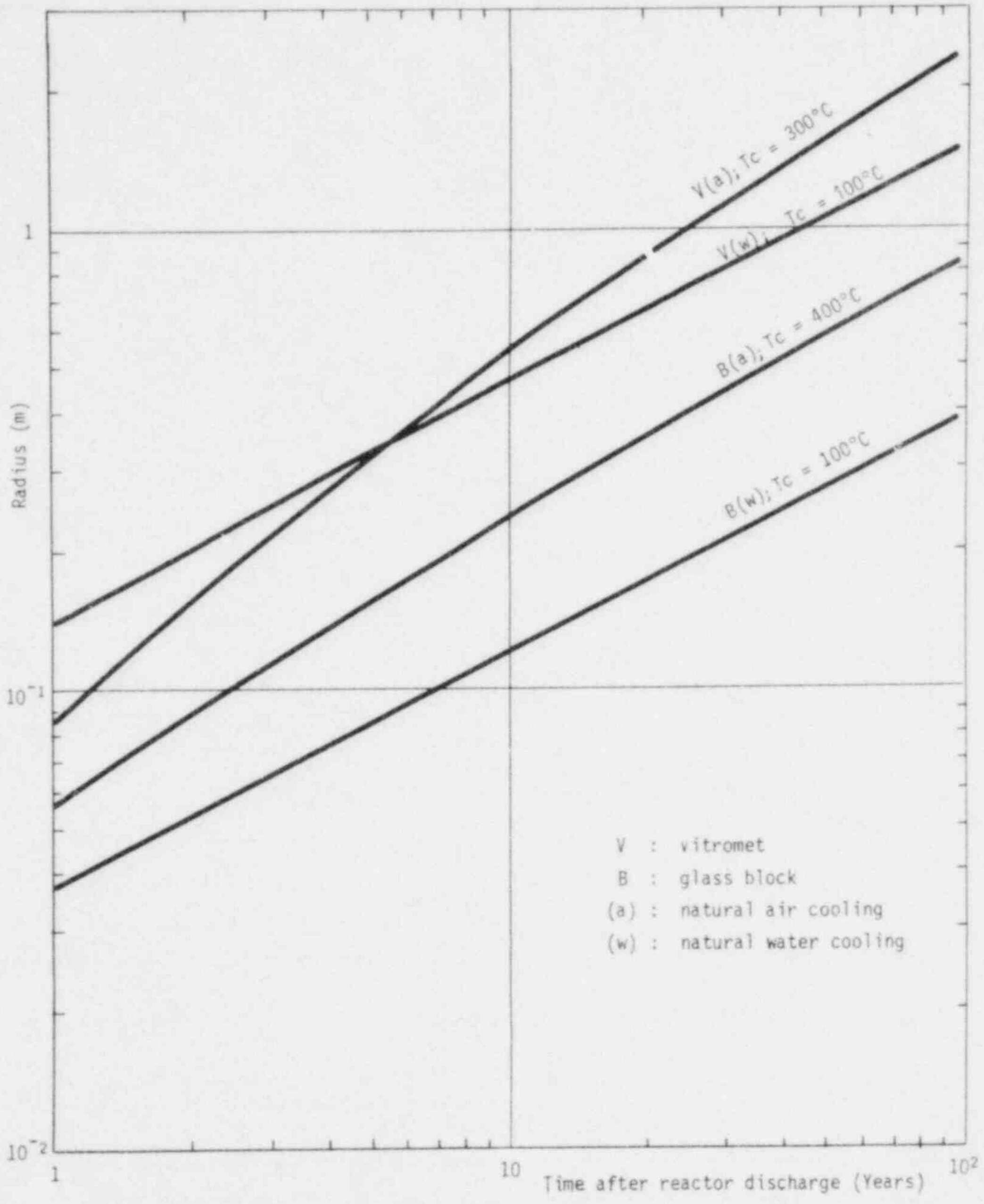


Fig. 9a - CALCULATED RADIUS OF GLASS BLOCKS, CONTAINING 520 kg/m^3 OF WASTE OXIDES, AND OF CORRESPONDING VITROMETS AT PREFIXED CENTERLINE TEMPERATURES, UNDER NATURAL AIR AND WATER COOLING CONDITIONS.

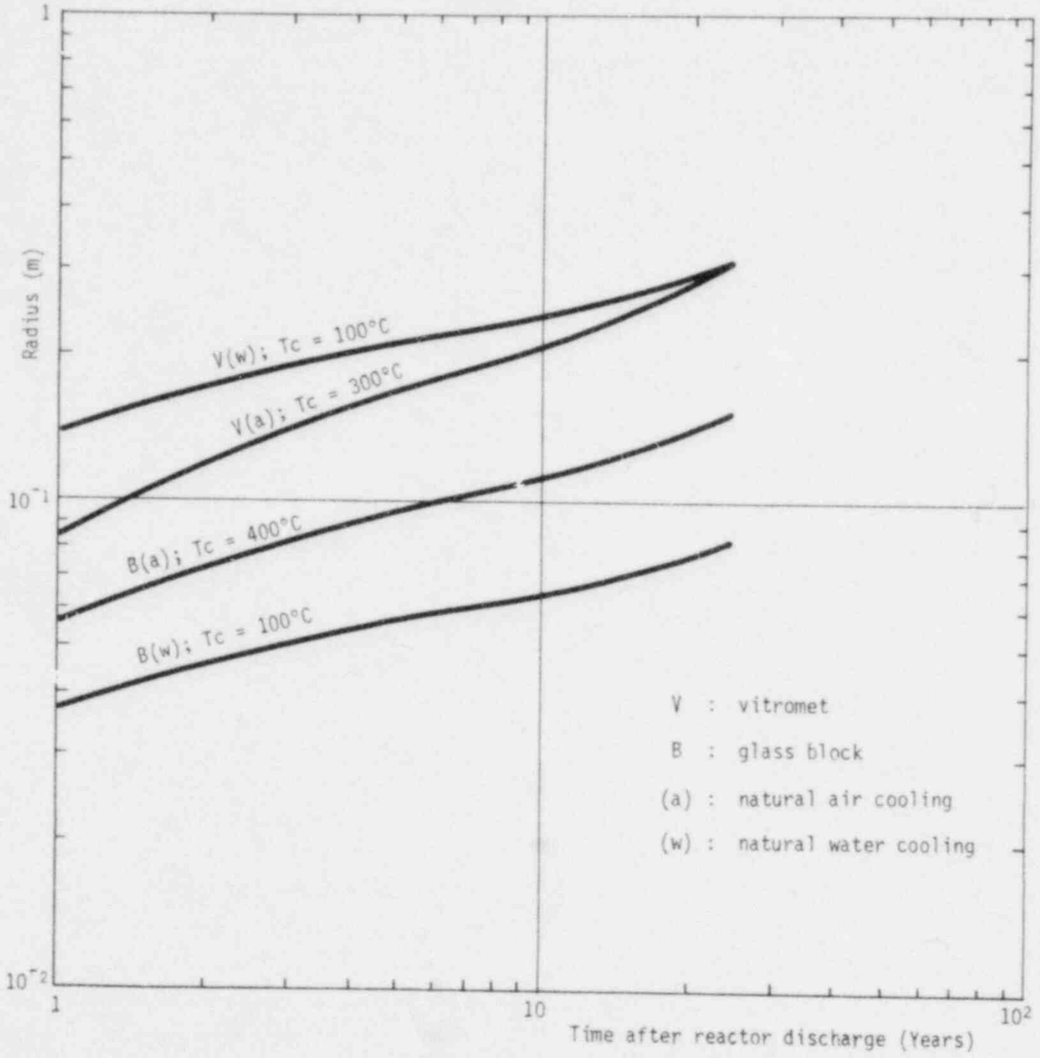


Fig. 9b - CALCULATED RADIUS OF GLASS BLOCKS GENERATED FROM TWICE RECYCLED PLUTONIUM FUEL (20) AND OF CORRESPONDING VITROMETS AT PREFIXED CENTERLINE TEMPERATURES UNDER NATURAL AIR AND WATER COOLING CONDITIONS.

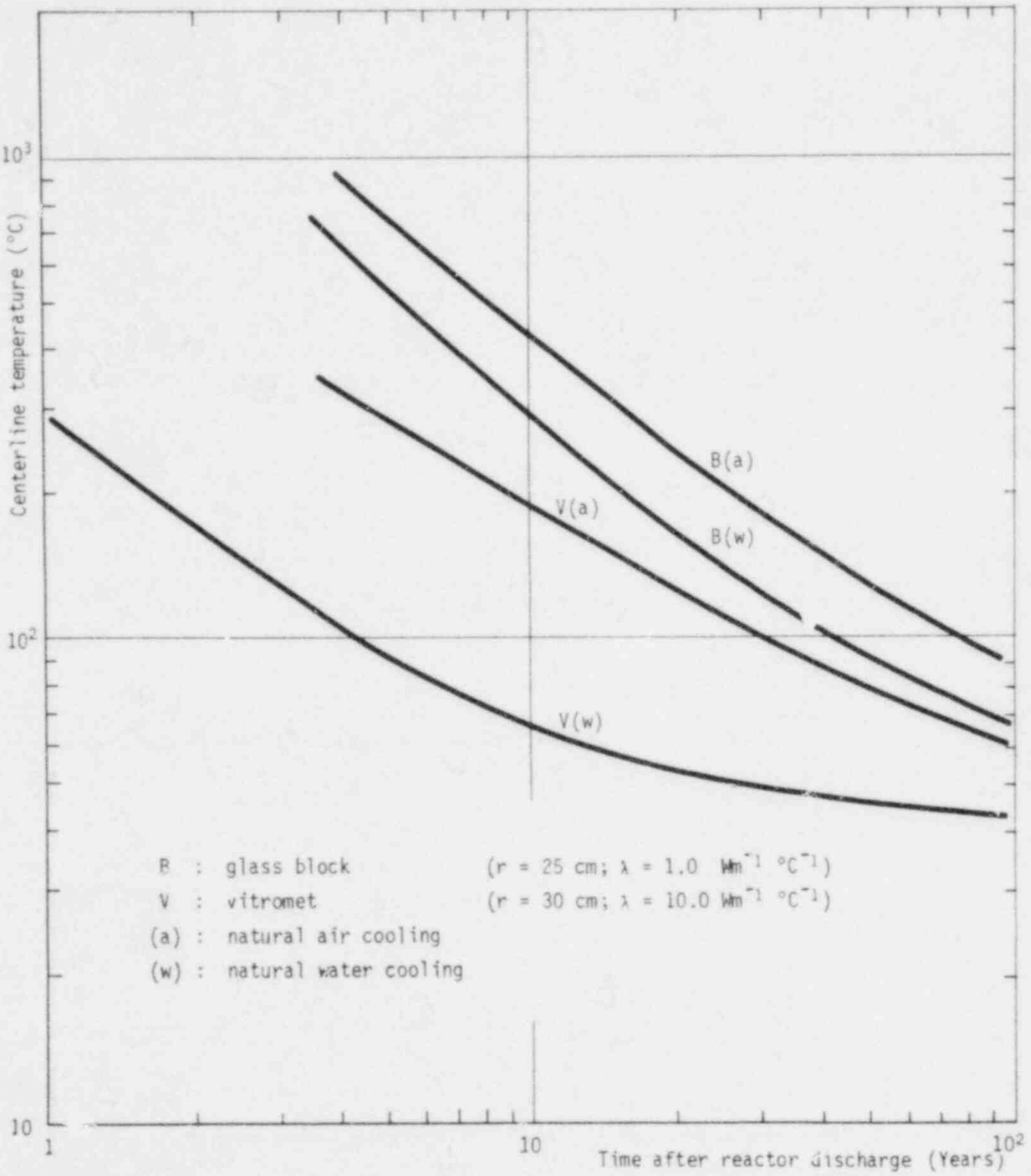


Fig. 10 - CALCULATED CENTERLINE TEMPERATURE OF GLASS BLOCKS CONTAINING 520 kg/m³ WASTE OXIDES AND OF CORRESPONDING VITROMETS UNDER NATURAL AIR AND WATER COOLING CONDITIONS.

The centerline temperatures of vitromets (Ø = 60 cm) and of glass blocks (Ø = 50 cm) of equal waste load per meter height, is plotted in figure 10 as a function of time after reactor discharge for storage under water or in free air. From these data, one can derive that the vitromets have centerline temperatures below 300 °C when stored in air, and below 100 °C during water storage, at an age of 4.5 years after reactor discharge.

4.3.2 Long term storage

Figure 11 shows calculated centerline temperatures in a vitromet and a corresponding glass block during its storage in an infinite salt formation of the ASSE II type.

The calculations assume a direct contact between the container and the salt deposit with a temperature dependent heat conductivity, as given by Kühn (21).

When storage takes place at least 14 years after reactor discharge, vitromets, 60 cm in diameter, have centerline temperatures below 100 °C.

For corresponding glass blocks, the calculated centerline temperatures amount to 260 °C under similar storage conditions.

Evidently, low centerline temperatures can be assured by applying small diameters or high waste dilutions. These measures however always imply an increased number of storage containers. This can be illustrated by calculating the number of canisters required for storing 335 liters of high level waste glass, resulting from the reprocessing of 5 tons LWR type fuel, irradiated to 33,000 mWd/ton and cooled for 4.5 years, and representing in total a heat source of 11.7 kW (19).

This glass must be stored in 9 containers of 18 cm in diameter and of 2 m height, assuming a maximum centerline temperature of 100 °C during water storage. This glass can be housed in one single vitromet, 60 cm in diameter and 2 m height, attaining the same maximum centerline temperature.

It is believed that the savings in the required number of canisters and in their cooling, handling, transport and storage offset by far the costs for the additional waste conditioning step, that is the incorporation in a metal matrix.

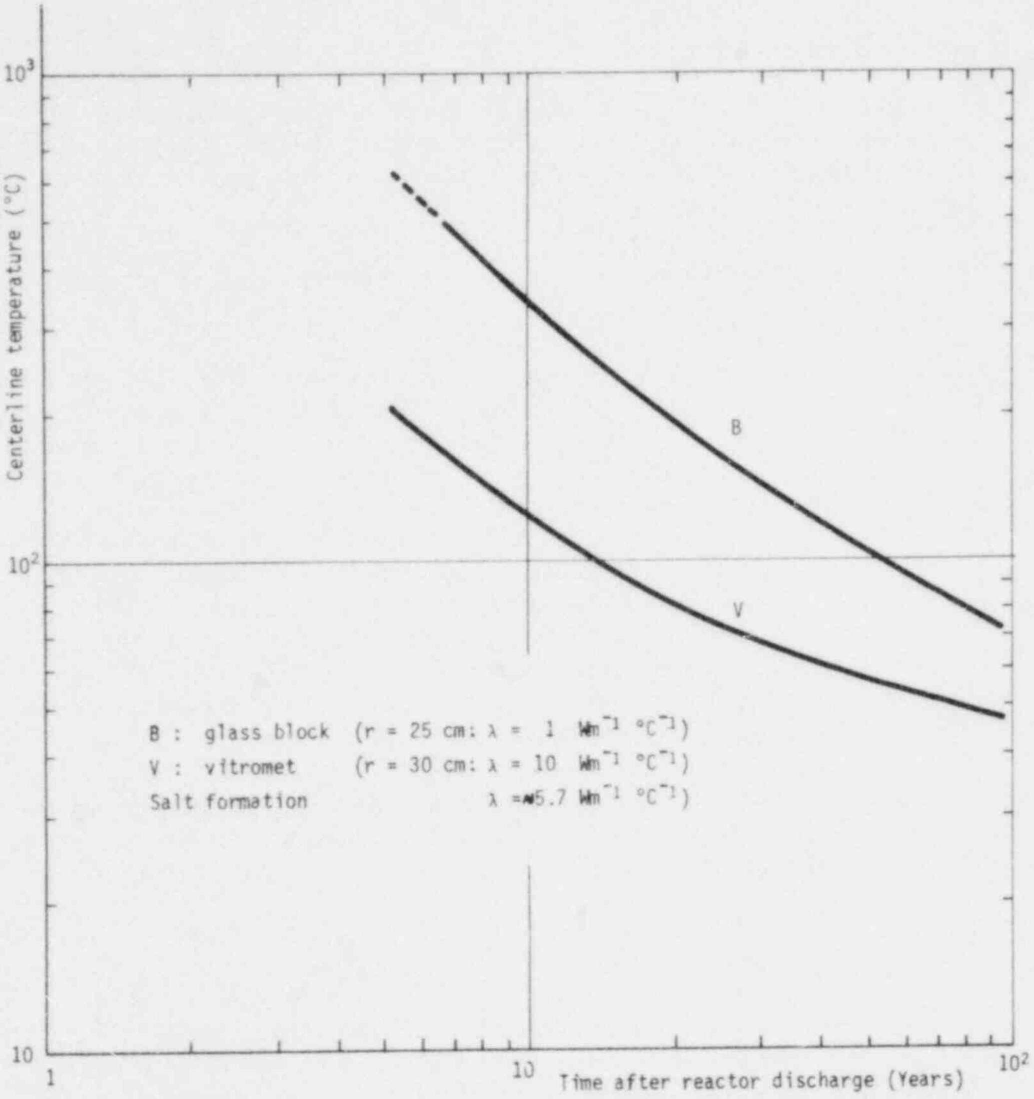
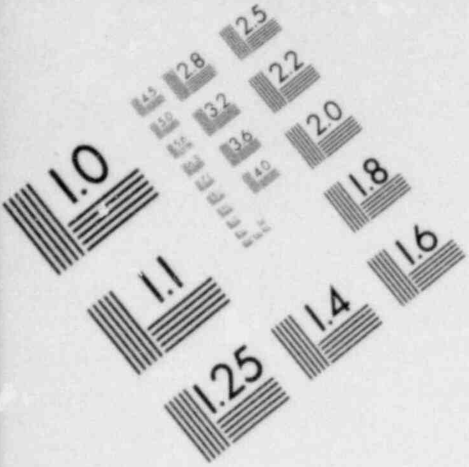


Fig. 11 - CALCULATED CENTERLINE TEMPERATURE OF GLASS BLOCKS CONTAINING 520 kg/m^3 WASTE OXIDES, AND OF CORRESPONDING VITROMETS WHEN STORED IN AN INFINITE SALT FORMATION OF THE ASSE TYPE.



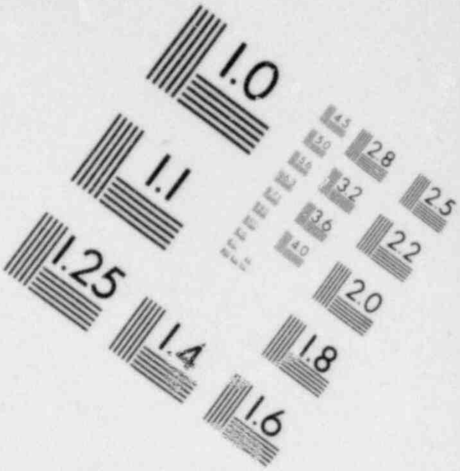
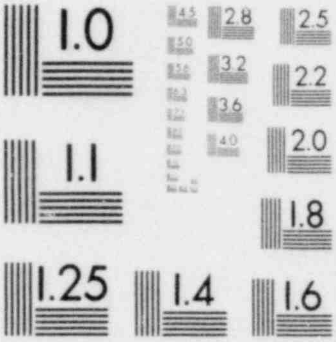
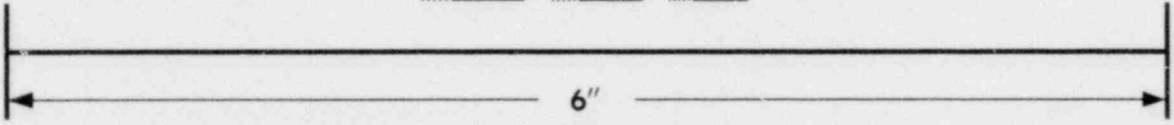
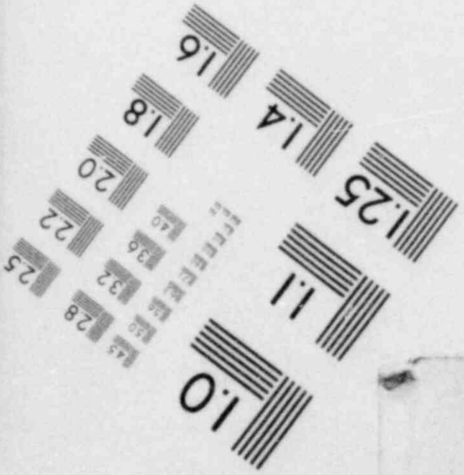


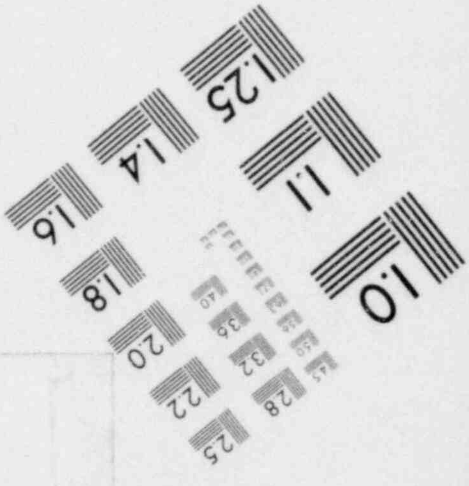
IMAGE EVALUATION
TEST TARGET (MT-3)

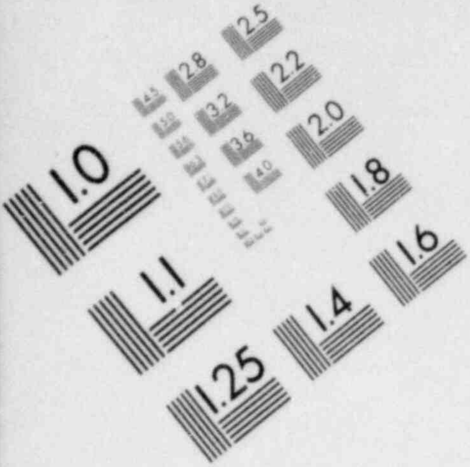




MICROCOPY RESOLUTION TEST CHART







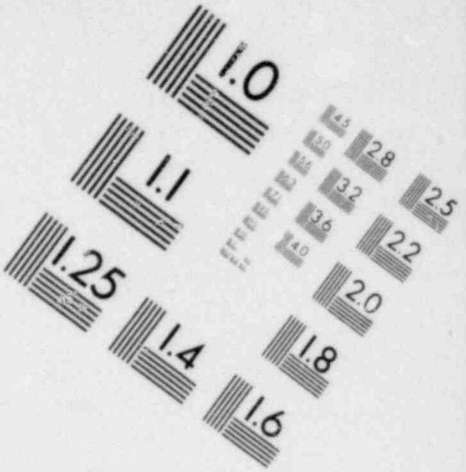
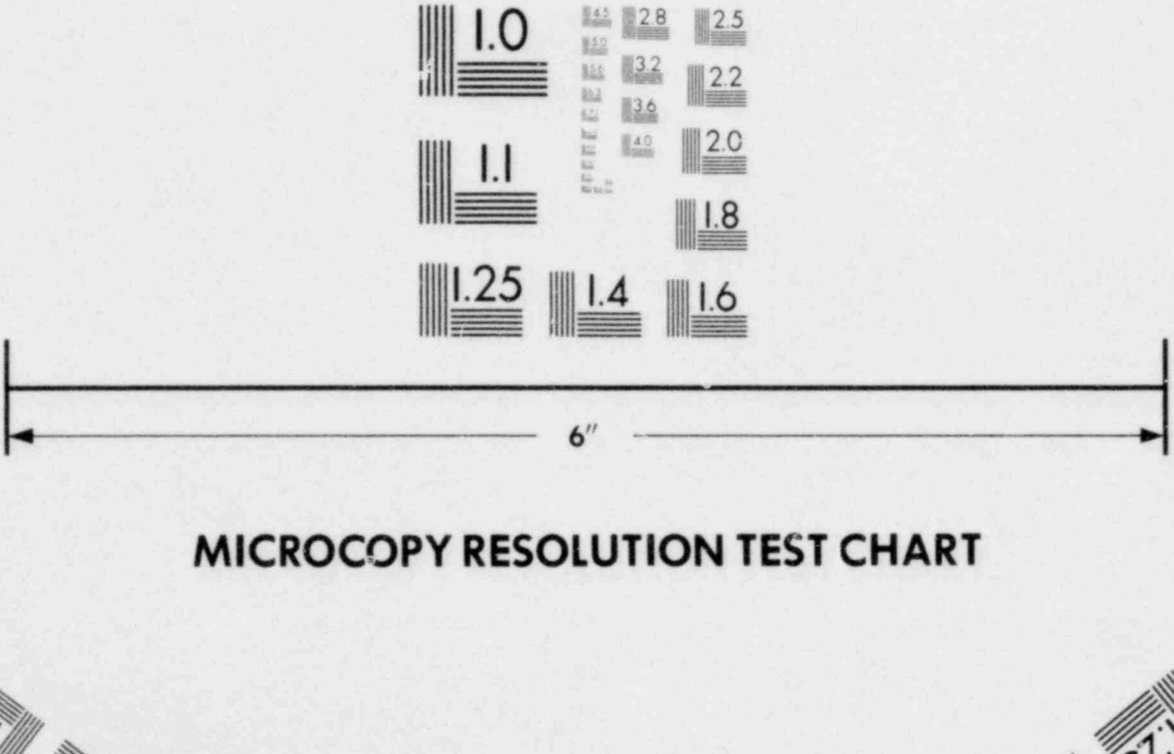
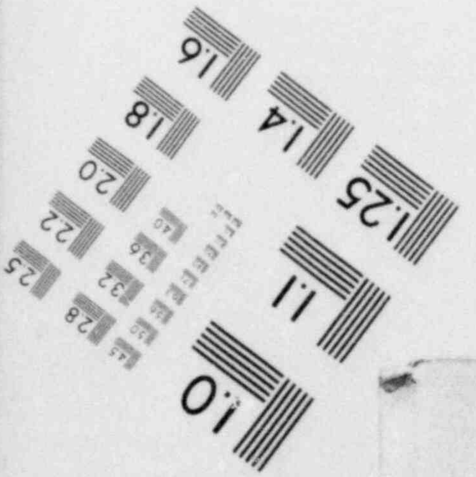
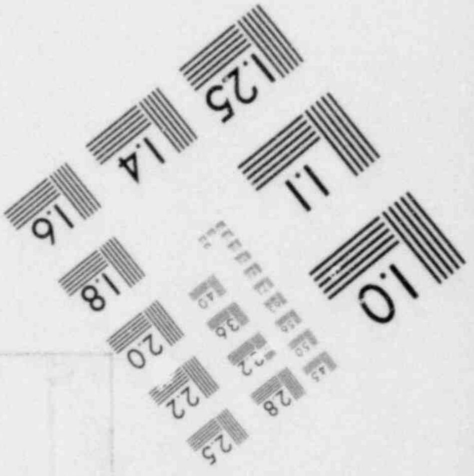


IMAGE EVALUATION
TEST TARGET (MT-3)



MICROCOPY RESOLUTION TEST CHART





4.4 Mechanical properties

Although the primary mechanism for the release of activity from solidified waste products will probably be by leaching, there is also the possibility of dispersion as a result of external forces acting on the container.

Mechanical impacts on the final containment can generally be divided into :

i) impacts over a short period of time, involving high energy transmission to the container (dropping, collision, etc..). The impact is generally concentrated on a small surface area of the containment;

ii) impacts over long periods of time involving a relatively large surface area (compressions, bending and torsion forces) which might be encountered in geological repositories (tectonic movements).

Both types of impact generally can result in deformation of the containment and increase of the leachable area.

The deformation of our vitromets was therefore investigated by compression of samples of different height to diameter ratio and at different temperatures.

Figure 12 shows the compression strength for vitromet blocks of different height-diameter ratio.

The vitromets were composed of phosphate glass and Pb-2 % Sb alloy.
Figure 13 shows the measured compression force at 1 % axial deformation and this at different temperatures. The compression had to be continued to 5 - 15 % (depending on the height to diameter ratio) before rupture occurred resulting in release of potentially respirable particles. This is shown in figure 14.

From figure 12 we may conclude that lead as matrix material can easily cope with the axial pressures caused by piling up vitromet containers up to say 10 m height.

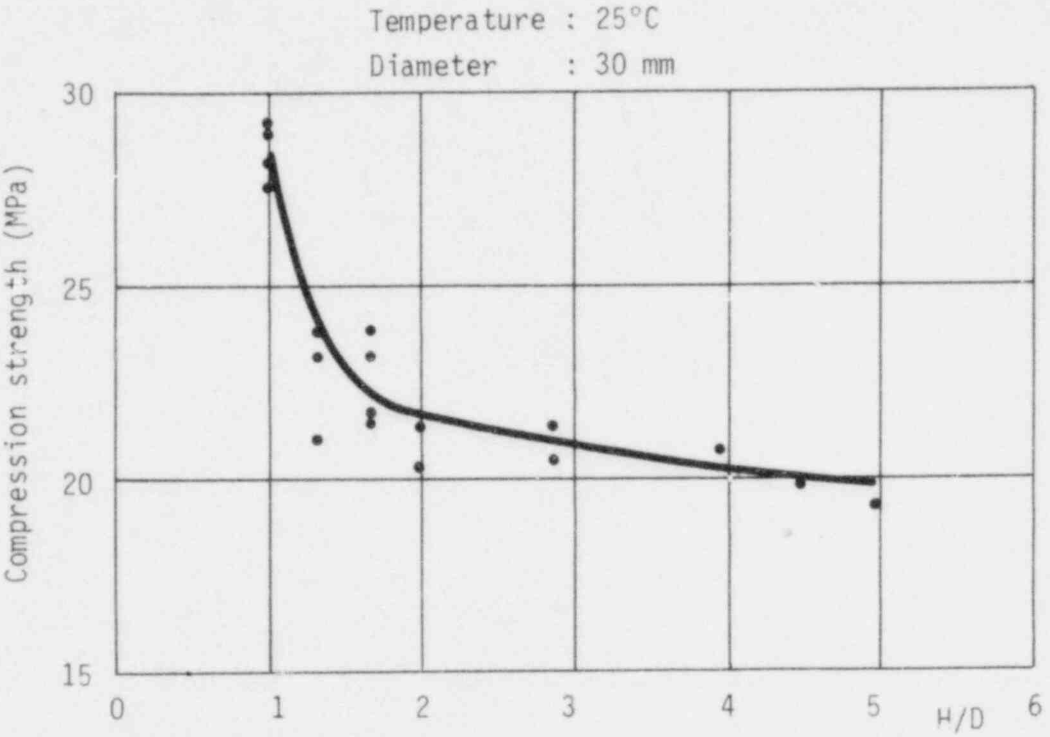


Fig. 12 - COMPRESSION STRENGTH OF VITROMETS, COMPOSED OF PHOSPHATE GLASS BEADS (3-5 mm) IN A Pb-Sb (2 wt%) ALLOY, OF DIFFERENT HEIGHT-DIAMETER RATIO (H/D)

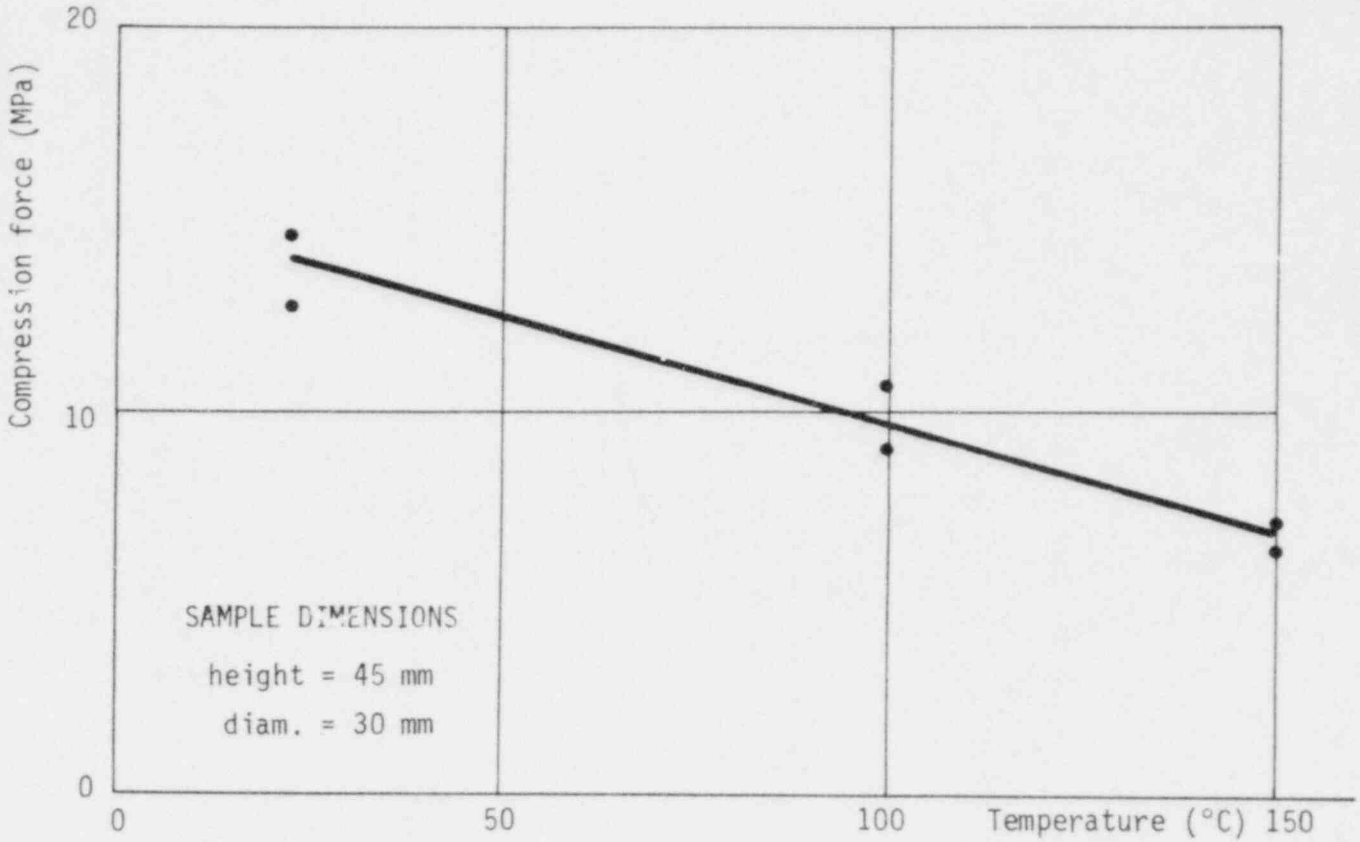


Fig. 13 - COMPRESSION FORCE AT 1 % AXIAL DEFORMATION AT DIFFERENT TEMPERATURES.

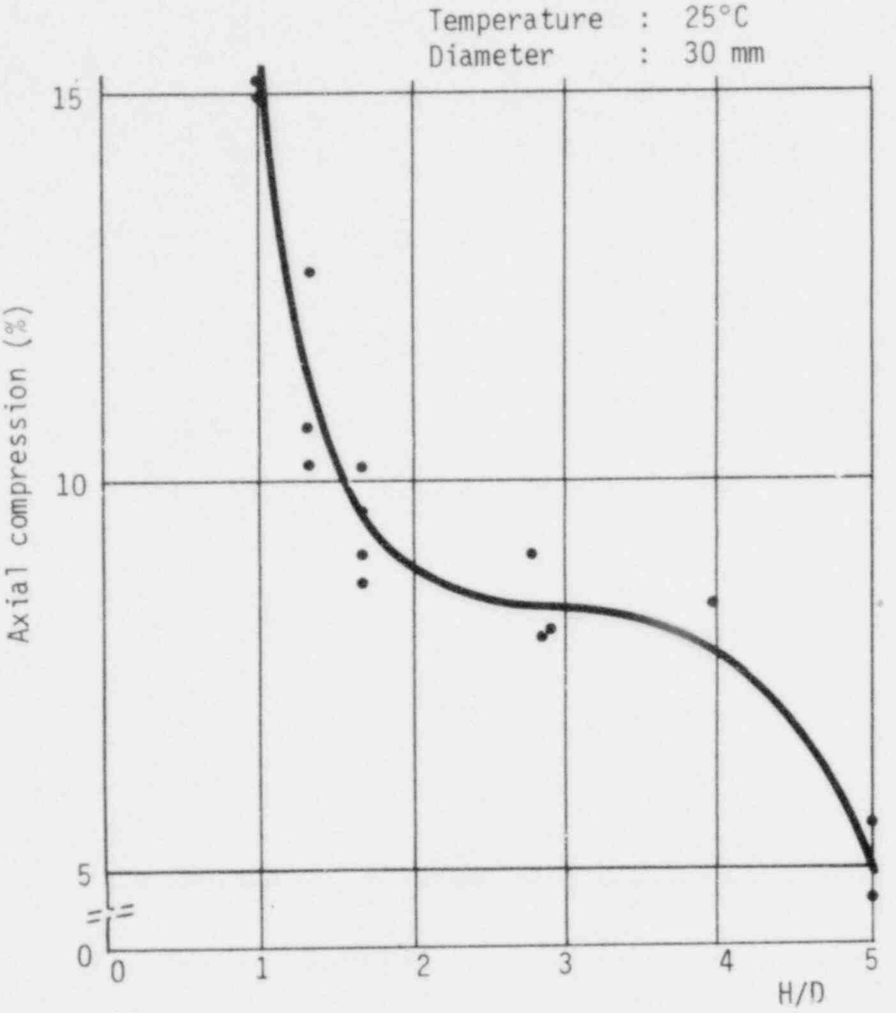


Fig. 14 - AXIAL COMPRESSION (%) AT FRACTURE AS FUNCTION OF THE HEIGHT DIAMETER (H/D) RATIO FOR VITROMETS COMPOSED OF PHOSPHATE GLASS BEADS (3-5mm) IN A Pb-Sb (2wt%) ALLOY.

Figure 14 shows that vitromet products can cope with high axial deformations before dispersion of glass beads or glass splinters occurs.

The long term creep behaviour of vitromets and particularly those containing lead or its alloys as matrix material, are actually under investigation at Eurochemic.

5. INDUSTRIAL APPLICATION OF VITROMET PRODUCTION

The embedding technology applied in the PAMELA process* (22) for solidification of liquid HLW has been demonstrated at 1 : 3 scale. The process comprises essentially :

- denitration and concentration of the liquid waste,
- vitrification and glass beads production, and finally
- incorporation of the glass beads into a metal matrix.

5.1 Vitrification and glass beads production

Vitrification of the liquid waste, without prior calcination step, is performed in a Joule heated ceramic melter (22). A glass stream leaves the melter, passes a heated vessel, the bottom of which has about 10 nozzles. The liquid glass drips from these nozzles. The droplets are caught on a rotating steel-disc, where they solidify to form glass beads. These beads are swept by pressed air into a container. The throughput of the installation tested was 6 kg phosphate beads per hour, which corresponds to a reprocessing capacity of 2 tons of LWR fuel per day.

During bead production continuous sampling was easy. In case of off-standard glass quality, the beads can easily be recycled to the melter by a pneumatic transport system.

5.2 Incorporation of glass beads in a metal matrix

Figure 15 shows the pilot installation used for producing vitromet products of 22 cm in diameter and 1 meter in height.

The embedding technique applied here was that described in § 3.2 and shown in figure 6b.
A full scale container is presented in figure 16.

Heating occurs by induction of medium frequency (10 kHz).

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* developed by GELSENBERG AG (Federal Republic of Germany) in cooperation with the EUROCHEMIC COMPANY (Belgium) and with the support of the German Ministry of Research and Technology.

The course of the temperature at various spots within the canister was measured. This showed that the entire embedding operation lasts less than 7 hours.

During the embedding procedure a fairly homogeneous temperature distribution over the entire canister was obtained.

Steel canisters, provided with stress gauges, turned out not to be stressed. This was expected as the thermal expansion coefficient of the lead alloy is larger than that of stainless steel.

5.3 Hot cell experience

A lab-scale PAMELA plant was constructed and installed in two hot cells at Jülich from 1973 to 1974. Thirteen hot runs took place whereby in total, about 200 l Purex type waste solution (origin : Eurochemic). About 15 kg of phosphate glass beads with a specific activity of 1 - 4 Ci/g have been produced.

Incorporation of this glass was performed by Eurochemic in a hot cell unit at Mol. So far, two vitromet blocks with a total activity of 7000 Ci have been produced. Details are shown in table 4. It was found that contamination of the outside canister and of the hot cell was negligibly low.

5.4 Full scale demonstration plant

It was recently decided to construct a demonstration facility for the solidification of 65 m^3 of high-level Purex-type waste, (~ 400 Ci/l) presently stored at Eurochemic and resulting from earlier operation of the reprocessing plant.

The demonstration facility should be in active operation in 1985 and will be constructed in the framework of a joint venture of DWK (Deutsche Gesellschaft für Wiederaufarbeitung von Kernbrennstoffen mbH) and the Ministry of Research and Technology of the Federal Republic of Germany.

TABLE 4 : ACTIVE GLASS BEADS AND VITROMET PRODUCTION

Period	Amount of glass beads (3 - 5 mm) kg	Total β-activity kCi	Block dimensions of vitromet	
			Diameter cm	Height cm
Dec.'74 - Dec.'76	15.7	38	-	-
August '75	1	2.5	8	10
September '75	2	4.5	14	10

Fig. 15 - CANISTER ENTERING INDUCTION FURNACE PRIOR TO METAL EMBEDDING.

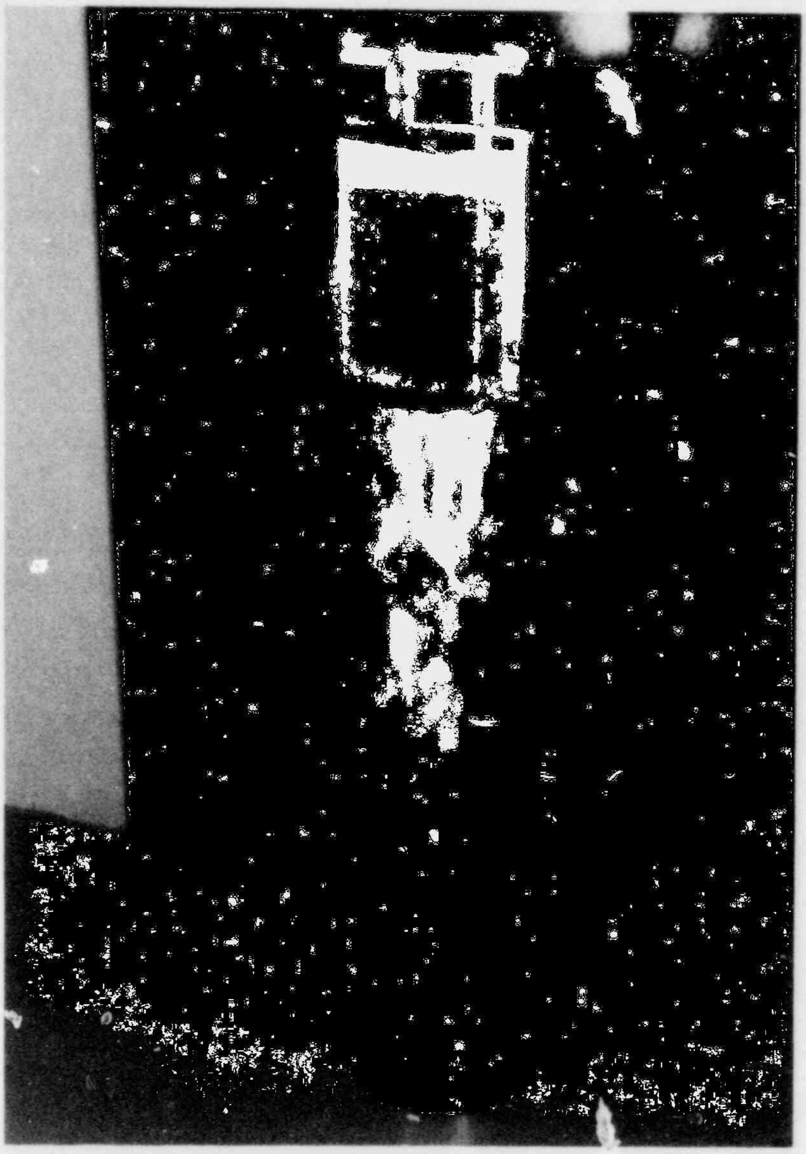

Fig. 16 - A TYPICAL VITROMET PRODUCT COMPOSED OF PHOSPHATE GLASS BEADS AND A Pb-Sb ALLOY MATRIX.

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Discussion Following

INCORPORATION OF SOLID HIGH LEVEL WASTES INTO METAL AND NON-METAL MATRICES

Presented by J. van Geel

Larry Hench - University of Florida
Question:
Since you are able to get sampling during the production, how much variability have you seen in your glass bead production?

van Geel
Response:
No data are available today, apart from a noticed variability of 10% in our glass bead dimensions.

PNL-SA-7369

STESSES AND CRACKING
IN HIGH-LEVEL WASTE GLASS

S.C. Slate
L.R. Bunnell
W.A. Ross
F.A. Simonen
J.H. Westsik, Jr.

December 1978

Presented at the Nuclear Regulatory Commission
Conference in Denver, Colorado
December 19, 1978

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Pacific Northwest Laboratory
Richland, Washington 99352

ABSTRACT

The purpose of this paper is to discuss the causes and consequences of cracking of high-level waste (HLW) glass in large canisters. Under normal operating conditions a certain amount of cracking is expected. The major causes of cracking are thermal and residual stresses in the glass. Cracking can also be caused by severe impacts, although this is expected to occur rarely. In this paper we present data on the cracking of simulated HLW glass in full-scale canisters filled by the in-can melting and the continuous melting vitrification processes. We discuss how cracking occurs and how it affects the performance of the glass. Comments on how alternative waste forms compare to glass are made where information is available. We conclude that the amount of cracking in HLW glass can be controlled within acceptable limits.

SUMMARY

One of the most important aspects in determining the safety of a waste management system is quantifying the ability of a waste form to contain radioactive elements. Part of the extensive worldwide effort to characterize this ability is concerned with mechanical durability. The purpose of this paper is to discuss the area of mechanical durability--specifically cracking--as it relates to cast waste glass in steel storage canisters. Cast waste glass was selected because of its advanced state of development: full-scale demonstrations, including radioactive tests, have been conducted for a number of years in several countries.

In this paper we discuss the major causes of cracking, which are thermal and residual stresses and impacts. The conditions found in actual canisters are so widely varied that theoretical predictions of cracking are impractical, although they are useful in understanding observations. We conclude that the best way to understand cracking is to evaluate a series of full-scale glass canisters that have experienced a range of conditions. We include data from full-scale canisters of glass filled by the in-can melting and continuous melting processes that are currently under development at the Pacific Northwest Laboratory.

It is important to study cracking so that its effect on the safety of a waste management system can be evaluated. For most situations, the amount of cracking should have no significant effect on the safety of surface operations. Also, recent work on glass behavior in disposal environments does not indicate that cracking causes any adverse effects.

We conclude that waste glass will crack when it is cast in large canisters. Under normal conditions, the surface area caused by cracking is less than 1 cm^2/g. Most of the surface area is not available for environmental interactions because the pieces are tightly packed. This area is also associated with a small amount of glass; 50% of the surface area results from about 1 wt% of the glass. Severe impact accidents

will increase the surface area by factor of 4 to 10. Respirable particles will also be produced in an impact accident, but they will constitute 0.1 wt% of the glass. The increase in surface area and number of particles will not directly increase release levels, because the canister and the facility or shipping cask will contain the glass. We recommend several areas of additional work to support studies on the effect of cracking on the waste management system. These areas include continued evaluation of full-scale canisters and leach testing of large blocks of cracked glass.

CONTENTS

FIGURES

INTRODUCTION

Many groups around the world are developing the technology to manage high-level radioactive wastes. The goal of this management effort is to isolate the wastes from man's environment. To achieve this goal, a system of three major barriers is being developed. The first barrier is a durable solid waste form. Glass is currently accepted as the reference waste solid because of its advanced state of development. Other solid forms have been proposed as alternatives to glass, but they are, as yet, not completely developed and have not been tested on a full-scale. The second level of containment is an engineered barrier. The storage canister is an important part of this barrier, especially during surface operations. During disposal, the engineered barrier may include overpacks and very-near field geology modifications. The third barrier is a stable geologic formation.

An important aspect in evaluating the safety of a waste management system is determining the ability of the waste form to contain the radioactive elements. Many countries have been extensively characterizing glass waste forms to demonstrate their durability under a wide range of conditions. One important aspect of this work is mechanical durability. The purpose of this report is to discuss the mechanical durability of cast waste glass inside steel storage canisters.

Mechanical durability is the ability of a material to resist mechanical failure--which is, in the case of glass, cracking. Cracking in glass is caused primarily by thermal and residual stresses and impacts. Cracking affects the ability of the glass to contain the radioactive waste elements by increasing glass surface area and the number of small particles. The amount of exposed surface area must be considered when evaluating the effect of leaching on a canister of glass. The exposed surface area depends on the canister's condition and the packing tightness of the glass, and is not just the total of the glass area. If a canister fails by an impact accident, the primary release will be small particles. It is important to be able to quantify the number of particles and their size in order to evaluate the effect of the accident.

We selected cast glass for our study because the technology for its production has progressed far enough to allow full-scale tests in significant numbers. Glass has been at the stage of full-scale demonstration for a number of years. Radioactive demonstrations have been made by the United States at the Pacific Northwest Laboratory (PNL) and by France at the AVM plant. Non-radioactive process development is currently being conducted in several countries.

Although glass is emphasized in this report, we have included information on alternative waste forms where it was available. Most of this information is based on theoretical studies or lab-scale tests.

PRODUCTION OF GLASS IN LARGE CANISTERS

The goal in developing the technology for large scale solidification is to reliably produce an acceptable waste form in the simplest, safest manner possible. Several processes for producing large canisters of glass have been developed with this goal in mind. The expected ease of producing radioactive waste glass was one reason why glass was selected for early development. This expectation has been realized by the production of radioactive glass in the United States, France and England.

Two basic vitrification processes have been developed. The first is a batch melting process, where liquid or calcined waste is mixed with glass-forming frit and melted in the storage canister. This is the technique used in the in-can melting process, which is being developed at PNL in the United States. It is also used in the HARVEST process, which is being developed in England. The second vitrification technique is a continuous melting process, in which liquid or calcined waste is mixed with glass frit and continuously melted in a glass melter. The molten glass is then poured into the canister. Continuous melting is being developed in several countries. The most fully developed processes are the joule-heated ceramic melter at PNL and the metallic melter at the French AVM plant. The batch and continuous processes each produce high-quality waste glass; however, there are some differences that may affect the mechanical behavior of the glass. We have selected the PNL in-can melting (ICM) and continuous melting (CM) processes as being representative of the two types.

IN-CAN MELTING

The ICM process uses the storage canister as the melting crucible for the glass.(1,2) Figure 1 shows the ICM furnace connected to a spray calciner. The spray calciner is an integral part of both the ICM and CM processes. The calciner converts liquid wastes to a fine powder of waste oxides by spray drying.(3) During the ICM process a stainless steel

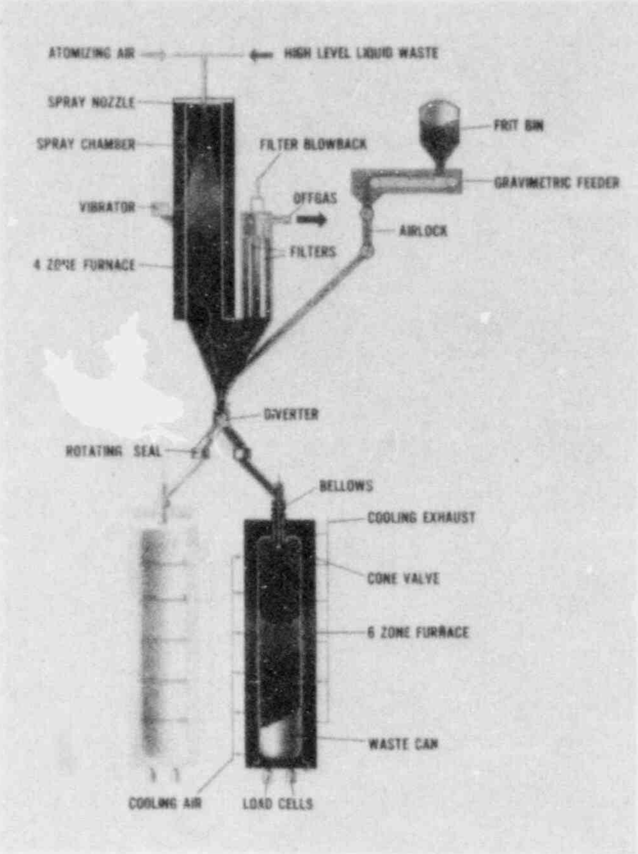


FIGURE 1. Schematic of the In-Can Melter Furnace Connected to the Spray Calciner

canister is placed on the bottom of the furnace and is covered by an insulated top. The canister is then connected to the calciner through a hole in the furnace top and is preheated to 1050°C before feeding is started. As the waste oxides fall into the canister, they are mixed with glass-forming additives. At 1050°C this mixture melts, "fixing" the waste in the glass. When the canister is filled and feeding has stopped, it is held for two hours at 1050°C so that the frit can completely react with the waste and so that bubbles can escape. The canister is cooled to 700°C while it is still in the furnace, then it is removed. The canister is then cooled until it reaches its steady-state temperature for storage.

The ICM process has been under development at PNL for about eight years. Twenty full-scale canisters of non-radioactive glass have been produced. These canisters, like those shown in Figure 2, have ranged from 12 in. to 28 in. in diameter. In 1970 two nearly full-scale canisters were filled with radioactive waste in the Waste Solidification Engineering Prototype (WSEP) program. Two more radioactive canisters will be produced in 1979.

CONTINUOUS MELTING

A schematic drawing of a CM melter is shown in Figure 3. To date, most CM tests have been made using calcined waste.(4) However, liquid waste can also be fed directly to the melter.(5) The waste and glass formers are fed onto the surface of a pool of glass that is contained in a ceramic-lined cavity. Energy for vitrification is supplied by joule heating. At high temperatures glass becomes an electrical conductor. Electricity is passed through the glass between immersed electrodes, generating heat evenly throughout it. Waste glass is continuously drained from the bottom of the melter and poured into a storage canister. During filling, the canister is contained in an enclosure that maintains its canister temperature near 600°C and monitors the filling process. When it is full, the canister is removed and cooled.

The ceramic melter has been under development for about four years at PNL, with two full-scale melters currently in operation. About forty canisters, like these shown in Figure 4, ranging from 12 in. to 36 in. in diameter have been filled and evaluated. The majority of canisters produced are 24 in. in diameter, which is the reference size for defense waste solidification.

STORAGE CANISTER

The basic PNL design for a waste canister is a single-wall pipe with a flat bottom. The top will be flat, or may be slightly domed for large-diameter canisters. The top has an opening that is carefully designed to

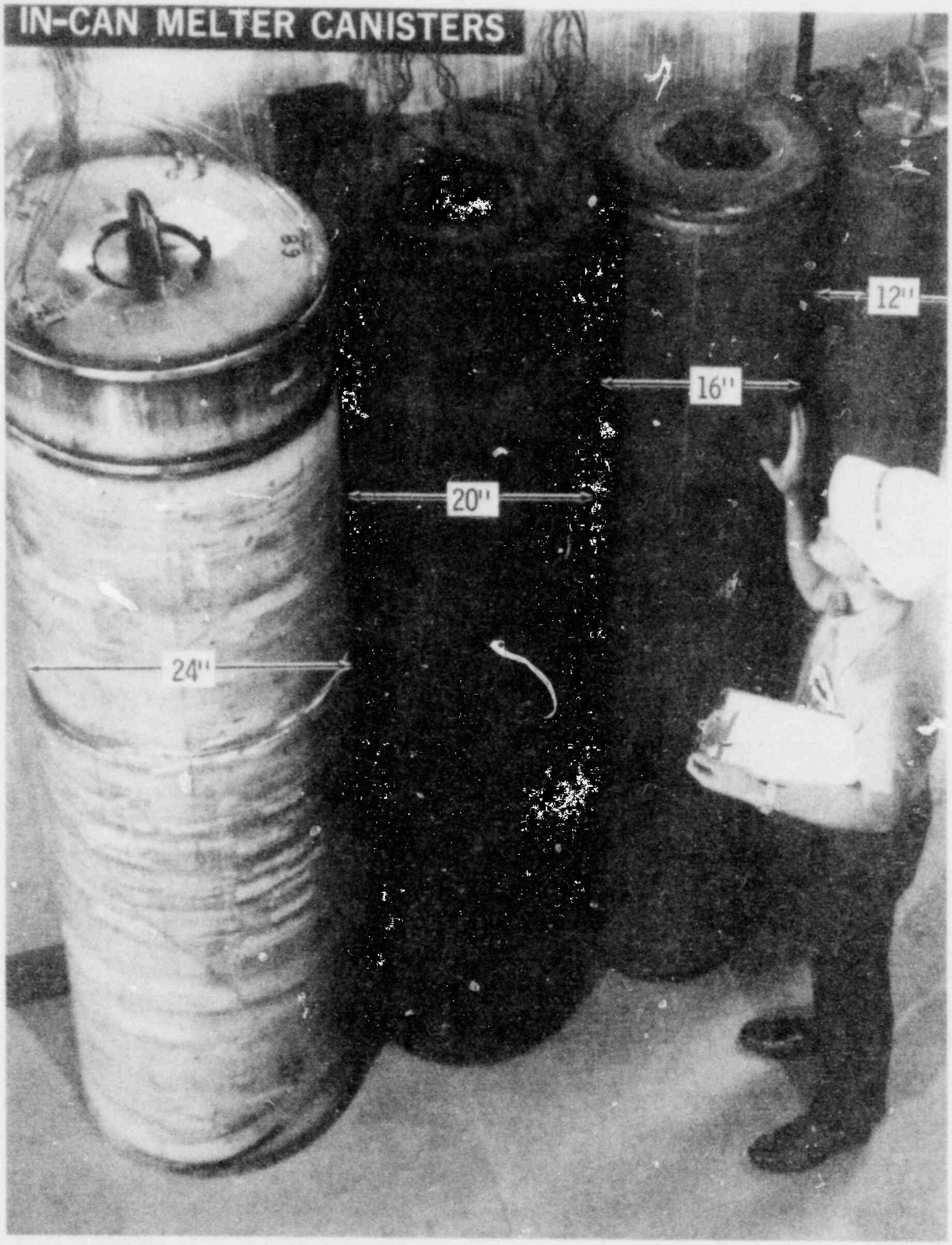


FIGURE 2. Full-Scale In-Can Melting Canisters

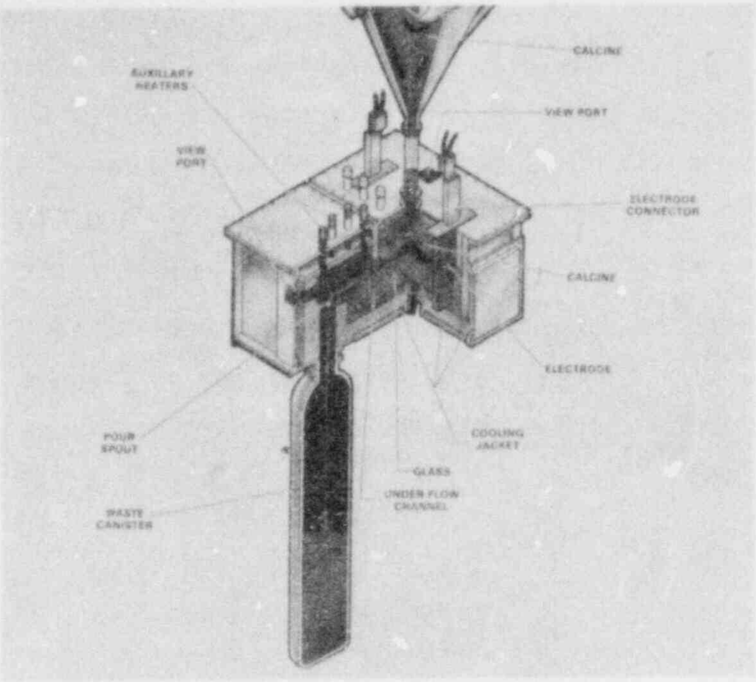


FIGURE 3. Schematic of the Joule-Heated Ceramic Melter for the Continuous Melting Process

FIGURE 4. Full-Scale Continuous Melting Canisters

couple to the solidification equipment and to be easily sealed. The diameter of the canister will range from 12 in. to 36 in., and its length will be about 10 ft. The canister material will be a stainless or carbon steel. Figure 5 shows the current PNL reference design for an ICM canister for heat-generating wastes. Note that this canister has internal fins. These are necessary to achieve the high melting rates needed for large-scale production and for improved heat transfer through the glass.

The presence of the canister is a very important factor when evaluating the performance of the glass in any particular circumstance. The relationship of the storage canister to the waste glass has been reviewed by Slate and Ross.(6)

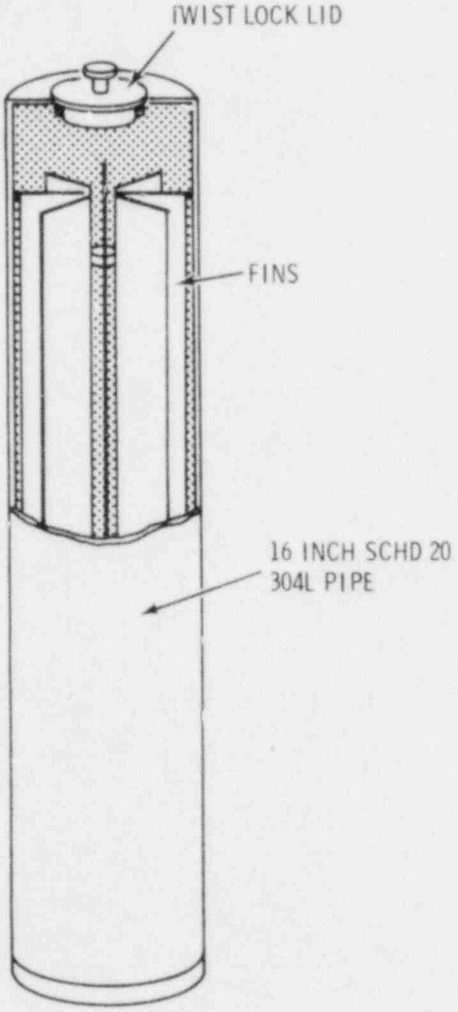


FIGURE 5. Reference In-Can Melting Canister Design

CONSEQUENCES OF CRACKED GLASS

Liquid HLW is solidified so that it will be in a form that will minimize any chance of radioactivity release. For glass there are three potential mechanisms for the release of radioactive materials; 1) chemical attack by water (leaching), 2) dispersal of very fine particles, and 3) volatilization of certain radioisotopes. The amount of cracked glass in a canister affects leaching and the dispersal of particles.

In this section we will briefly discuss the effect of cracking in the three areas of waste management: the solidification facility (which includes interim storage), transportation, and disposal.

THE SOLIDIFICATION FACILITY

A solidification facility for high-level waste will be designed to safely contain all radioactive materials inside, so that if radioactive materials are released from the glass they will be contained within the facility and not released to the environment. While in the facility, the storage canister is the primary means of preventing a release from the glass. It is also designed to prevent damage to the glass during normal operations.

The two major mechanisms for a release are an impact or leaching. A release from an impact is very unlikely because current canister designs can survive a fall of 9 m onto an unyielding surface. If a failure did occur, the small amount released in the form of particles would be contained by the hot cell. If a water pool is used for interim storage a small number of canisters may be expected to crack from stress corrosion. A small amount of radioactive material would then be released to the pool by leaching. However, pool contamination is expected to occur, especially if spent fuel is stored in it. Any contamination can be easily removed by standard purification equipment. In either an impact or pool release, it would be very unlikely that even occupational exposure would measurably increase.

TRANSPORTATION

The waste must be transported from the solidification facility to the disposal site. The risk of a release during transportation should be small because the transportation casks are designed to provide complete containment of all radioactivity for all but the nearly incredible accidents. However, studies have shown that the greatest potential for a release is during transportation. This makes it very important that the HLW is contained in a durable solid.

If a severe accident does breach the cask, the primary release mechanisms are volatilization and dispersal of respirable particles. Volatilization is only important at temperatures where glass is molten, so the amount of cracking has no effect. The volatile behavior of glass has been previously studied and reported.(7) The quantity of respirable particles that could be dispersed is small and is discussed in the section on impacts.

Releases from nuclear facilities and transportation casks have been well studied. We can conclude that such releases are extremely unlikely.

DISPOSAL

It is currently hypothesized that the geologic medium used for final disposal will provide complete containment of all radioactive materials for as long as they are toxic. Many groups are currently evaluating this hypothesis by studying the mechanisms by which a release could occur. The most important release mechanism is leaching and subsequent transport of radioactive material along a water pathway. The influence of cracking on disposal is related to leaching. With increased surface area that results from cracking, there is a potential for leaching of radioactive material more rapidly.

The glass surface area in an average canister is estimated to be 10 to 20 times the area of a canister of uncracked glass. However, this area is on pieces of glass that are tightly packed--something like a three dimensional jigsaw puzzle. Many surfaces between pieces are also under a compressive stress caused by the canister. Thus, initially, most of the glass is not directly exposed to leaching. The water has long diffusion paths along the cracks between the glass. After a long period it is expected that the canister will no longer protect the glass and that more surface area will be exposed. Thus, release rates may increase with time. However, most of this exposed surface area is on small particles near the can wall; particles that are 1 wt% of the total glass have over 50 wt% of the exposed surface area. Radioactive materials will be leached primarily from these particles, while 99 wt% of the glass will remain intact for much longer periods.

Once the exposed surface area is quantified, the interaction of the glass with the materials in the repository must be understood before releases can be estimated. A salt repository should not have any flowing water present, so no significant leaching reaction with the glass is predicted. However, after the mine is sealed a saturated brine may form around the glass. When the glass becomes exposed after the expected eventual degradation of engineered barriers, leaching will occur. However, some studies on leaching have indicated that the quantity of leached material does not increase directly proportional to surface area.(8,14)

The consequences of increased glass surface area during disposal are not known. More information is needed on repository conditions and on leaching in large blocks of cracked glass. However, tests indicate that cracking should not aversely affect the safety of a repository. The glass can be further protected by additional barriers, such as overpacks. These barriers will prevent water contact with the glass during the decay period of a majority of the fission products. After the decay period of about 500 years, the repository temperatures and resultant leach rates are much lower.

CAUSES OF GLASS CRACKING

Glass cracks when internal stress levels exceed its bulk strength. The bulk strength of glass is determined by the size and distribution of defects within the glass. The effect of the defects in waste glass can be seen by comparing the strength of defect-free glass fibers (with tensile strengths of 10^4 MPa) with the strength of waste glass (which averages 38 MPa).

Early studies on brittle materials have attempted to predict how defects affect strength. Griffith used fracture mechanics concepts to relate the effect of discrete crack-like defects to the reduction of the theoretical strength of glass and other brittle materials.(9) Weibull extended Griffith's concepts to consider the effects of distributions of variously sized defects throughout a brittle material.(10) Although the concepts from these studies are important in understanding cracking behavior, they cannot accurately predict cracking in waste glass. This is because there is a great variety of defects in waste glass that generally cannot be quantified. It is necessary to rely upon measured bulk strength in analyzing glass/canister systems.

It is still important to study internal defects to see what the effects of the different types defects are and to discover ways of eliminating them. The defects create localized stresses and act as crack initiation sites. Some defects have very little affect on strength, while others may cause microcracking that can significantly affect strength.

INTERNAL DEFECTS

Most of the internal defects found in waste glass occur during processing. Defects may also result from thermal or radiation damage over long periods; their effects, however, are expected to be minor.

Structural defects consist of closed porosity (internal bubbles that are not connected by cracks), voids, and crystals of non-vitrified materials. There is a minor increase in surface area due to the presence of these defects, but this is negligible when compared to the surface area from cracking. Porosity in ICM canisters results from gases released by the chemical decomposition of anions in the waste. The residual bubbles are generally 100 μm in diameter and are less than 1% of the volume for the bulk of the glass.(11) A design change that involves placing the canister in the furnace will allow higher temperatures to be maintained in the top of the canister so more bubbles will have a chance to escape, thereby reducing the size and amount of porosity.

Bubbles in CM canisters are caused by gas release during vitrification and by air entrainment during pouring. Visually, the porosity appears to be the same as that in ICM canisters for most glass compositions. Pouring can also cause strings and voids. Strings are very fine filaments of glass caused by extremely slow pouring rates; they solidify rapidly and can form voids. In addition, voids, like those in shown Figure 6, form where the glass has solidified before completely filling the

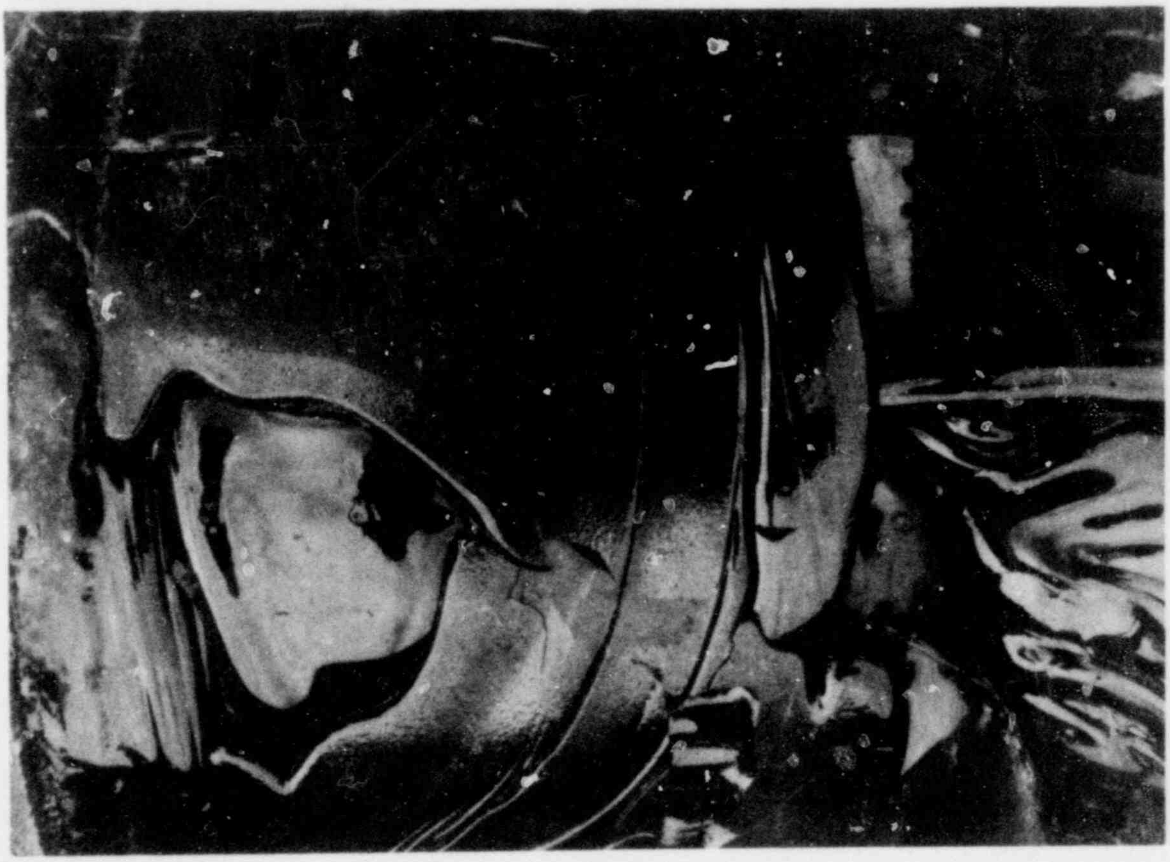
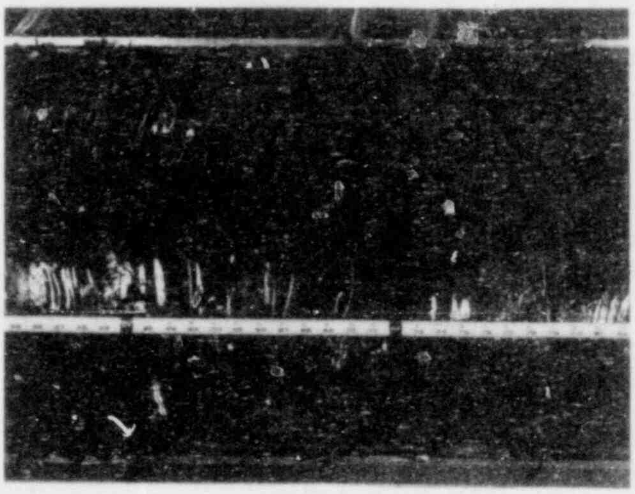


FIGURE 6. Casting Voids in a Non-Insulated CM Canister

Insulated



Non-Insulated

FIGURE 7. Qualitative Comparison of Glass in an Insulated and a Non-Insulated Canister

canister. These defects occur when the glass does not remain hot enough during filling. It is possible to reduce or prevent pouring defects by keeping the canister at a higher temperature with insulation and supplemental heating. Figure 7 compares an insulated and a non-insulated canister. We are confident that proper temperature control of the canister will reduce the amount of porosity and will nearly eliminate strings and voids.

Crystalline inclusions are insoluble waste components present in both ceramic and metallic phases. The concentration of phases is determined by both glass composition and processing temperature. Glass samples from early full-scale tests have shown insoluble waste components in the glass, but there has been no evidence of significant cracking. Metal nodules (2 to 4 mm in diameter), shown in Figure 8, are found in ICM canisters. They do not appear to cause cracking since they have higher thermal expansion coefficients than the glass.

Defects may also occur during high-temperature storage (>550°C) and from radiation effects. Laboratory tests on devitrification--the major form of thermal damage--have shown that small crystal phases have little effect on strength or impact behavior. However, larger crystals can affect strength because they produce some microcracking. Radiation damage

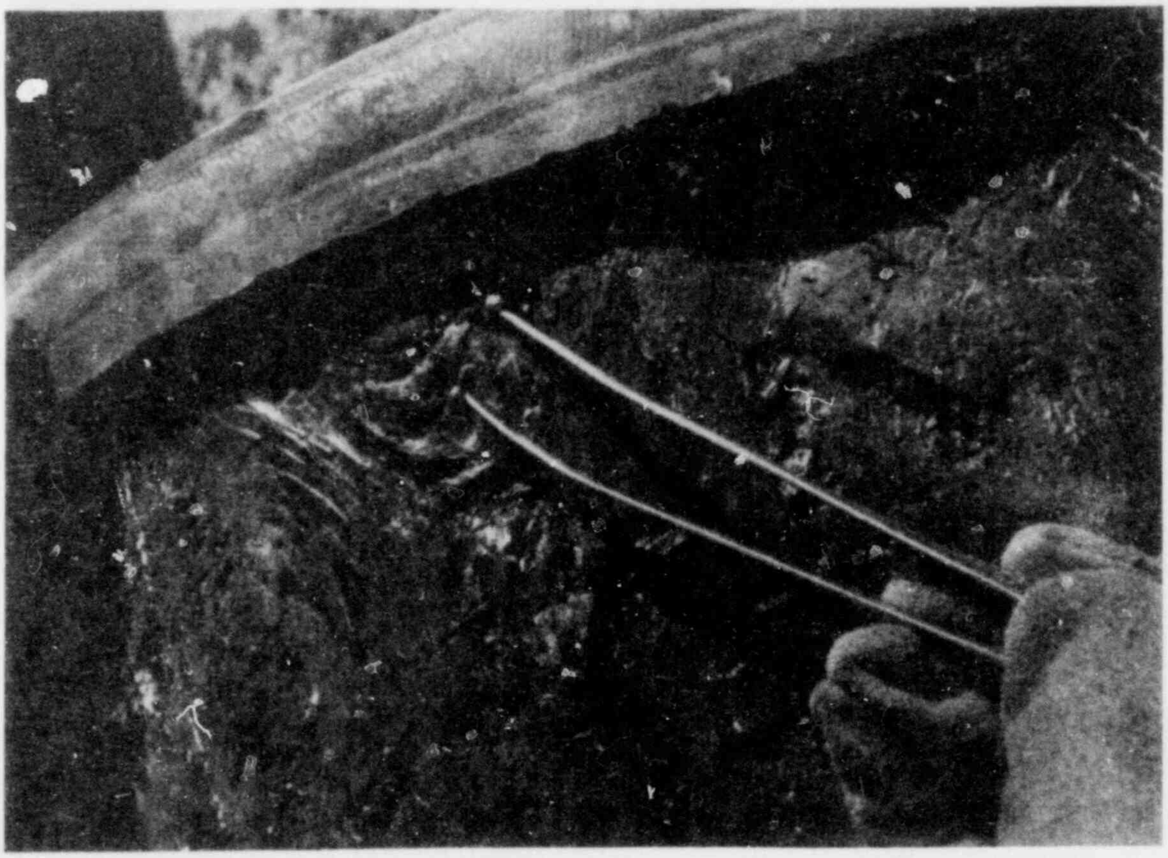


FIGURE 8. Metal Nodules in an ICM Canister

in glass is produced by alpha radiation. Tests show that damaged glass will expand or contract up to 1% of its volume. The waste glass button shown in Figure 9 has received an equivalent radiation dose greater than that anticipated during storage of commercial waste for one-half million years. Buttons like this one have remained solid and vitreous, and exhibit impact behavior similar to that of unirradiated glass.

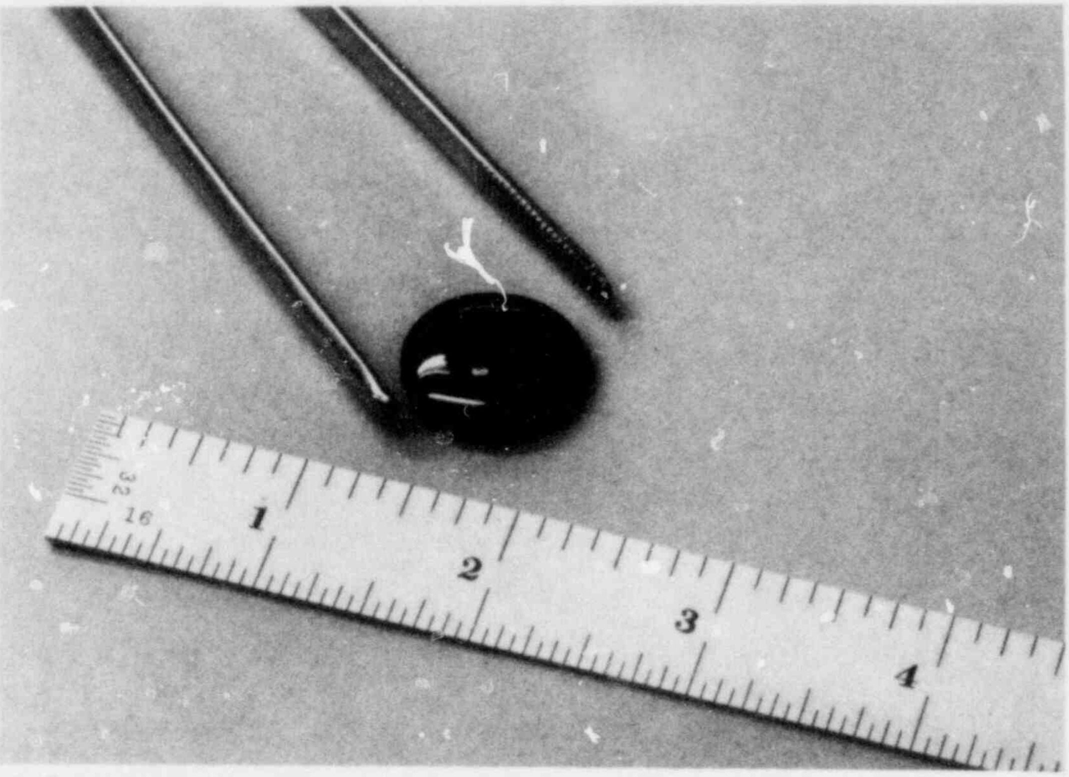


FIGURE 9. HLW Glass Aged to Radiation Dose Equivalent 500,000 yr

Most alternative waste forms also have structural defects. Some initial studies of ceramic materials have shown effects similar to those seen in glass. Processing defects in small-grained materials cause less microcracking than in large-grained polyphase materials.$^{(12)}$ Thermal damage is not as likely as in glass, but radiation damage does occur in crystalline waste forms. The crystals expand when irradiated. Some have small density charges (1 to 2%) like glass. Others have large expansions (up to 14%) which will modify the structure. If these changes are nonuniform, large stresses will occur, causing cracking.

THERMAL AND RESIDUAL STRESSES

Thermal and residual stresses will occur in glass as a result of anticipated normal processing and handling. The stresses are caused by strain differentials that arise from temperature gradients through the glass. Temperature gradients occur during filling, cooldown after filling, and any time the canister changes temperature when shifted from one environment to another. Gradients also occur if the glass is self-heating.

The gradients that occur in large canisters of glass vary significantly from one canister to the next, and are largely unknown. As a result, we conclude that it is impractical to accurately predict cracking. The best way to understand cracking is to measure it in as many full-scale canisters as possible. The data from these measurements is correlated with the thermal treatments the canisters experience. The reproducibility of results among similarly-processed canisters is also evaluated.

There are three important areas that are considered in evaluating cracking from thermal and residual stresses. These areas are:

- Determine at what time in the processing cycle the different types of cracking occur so that appropriate processing changes can be made.
- Measure the surface area of the glass pieces.
- Model different thermal cycles to try to predict cracking. This is important to help interpret quantitative results and to predict the effect of self-heating on cracking.

Types of Cracking

There are distinct types of cracking that occur during canister filling, cooldown, and storage. The types of cracking are also influenced by the location of the glass in the canister.

The main causes of cracking during filling of CM canisters are temperature gradients from uneven filling and thermal shock from the wall.

Uneven filling causes irregular temperature gradients in the main body of the glass, so the resulting cracks are hard to evaluate. The gradients are small, so little cracking is expected.

The cracking near the walls of the canister is usually quite regular. At the start of pouring, glass will contact the cold canister walls, where thermal shock causes severe localized cracking. Concentric layers layers 2 to 4mm thick occur to a depth of 2 cm. Figure 10 shows a piece of the top layer. This effect is less apparent in the top of the canister where the wall is much hotter when the glass contacts it. This suggests that preheating the canister to the glass transition temperature would substantially reduce localized cracking. If the glass never contacts the wall, as with the voids in Figure 6, no cracking occurs and the glass retains a shiny finish.

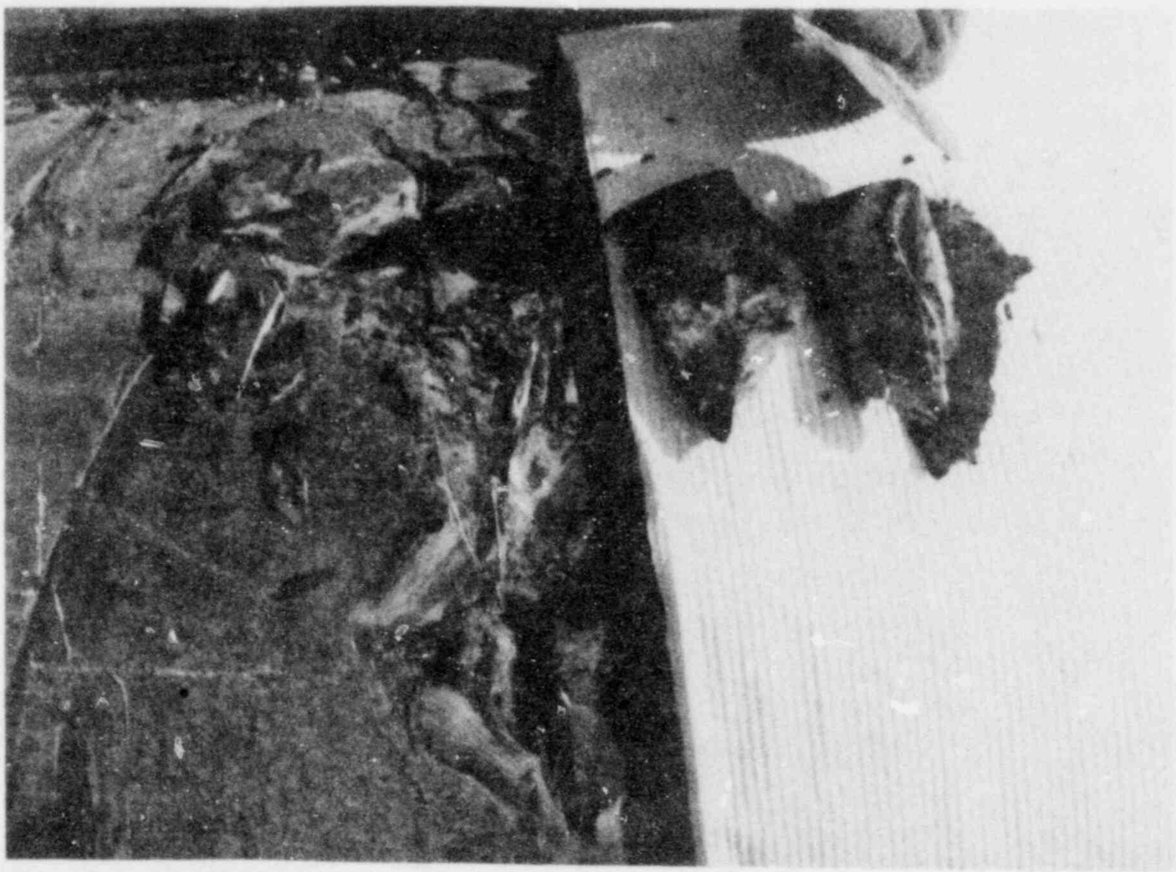


FIGURE 10. Thin Layer of Cracked Glass Near the Canister Wall

Cooldown from the filling temperature causes most of the cracking found in glass. Cracking occurs because permanent strains are set up in the glass when there is a temperature gradient across the glass as it solidifies. After this gradient disappears, strains build in the glass. If there is no gradient when the glass solidifies (as in annealing) no permanent strains occur. The amount of cracking depends on the temperature at which cooling begins and upon the rate of cooling.

The initial cooling temperature profile of a typical CM canister is shown in Figure 11 at 0 hr. The gradient near the wall has little effect on the glass that is already broken by thermal shock. New cracking occurs in the glass under the surface layer at approximately 5- to 10-cm

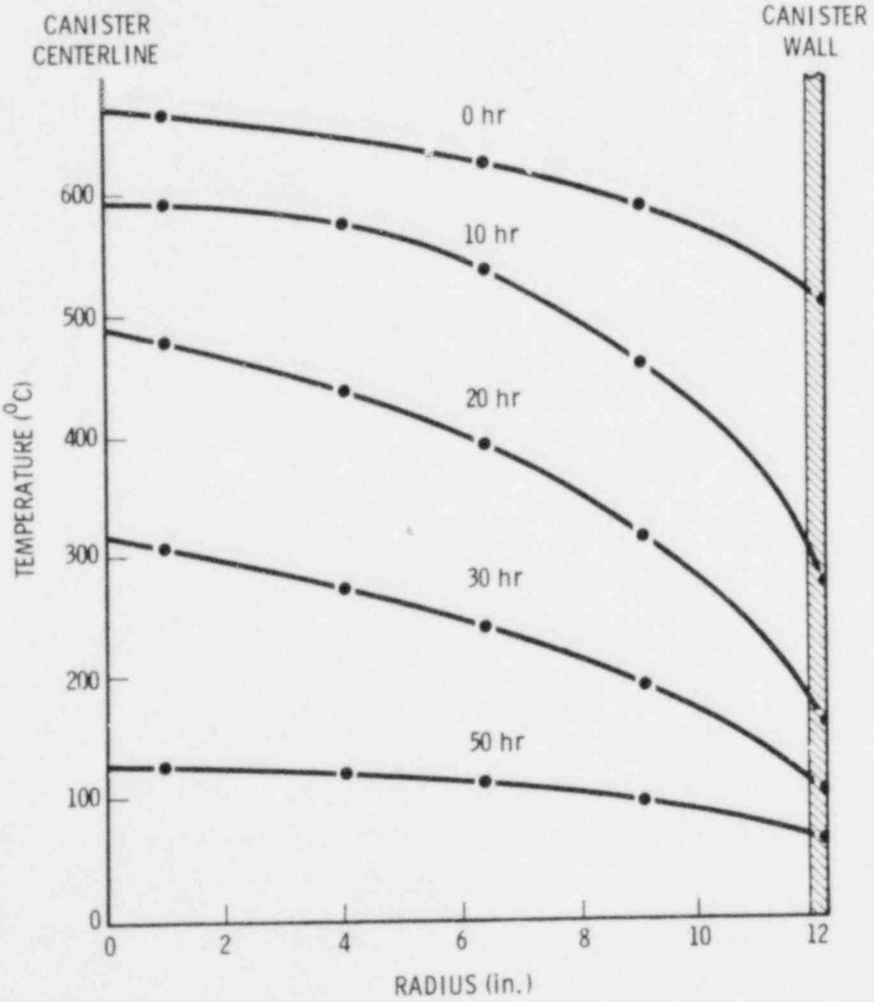


FIGURE 11. Temperature Gradient vs. Time in a 24 in. CM Canister

intervals, with the larger pieces near the center. If the glass cools uniformly from about the transition temperature, cracks like those shown in Figure 12 may occur. In this case, a layer of glass cools and contracts around a hotter central core, causing the nearly symmetric fractures. In CM canisters, cooldown causes cracking at large intervals that results in a small increase in surface area.

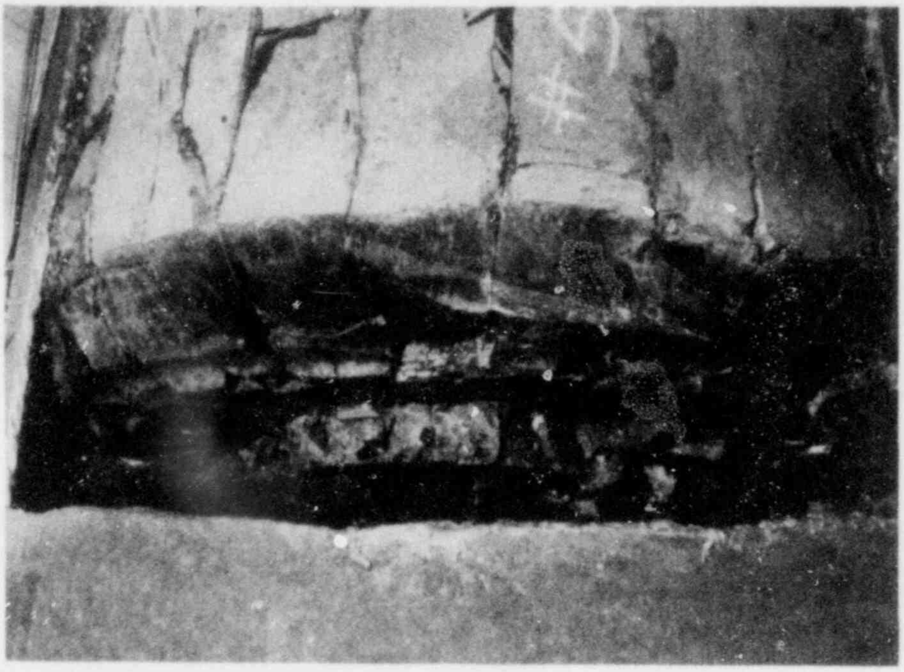


FIGURE 12. Equally Spaced Cracks from Cooling in a CM Canister

Cooldown of ICM canisters significantly differs from CM canister cooldown in several ways. The major difference is the fact that the glass reacts with and bonds to the ICM canister walls. While cooling, the canister shrinks more than the glass does so it moves axially with respect to the glass and causes compressive stresses at the glass/canister interface. This effect, coupled with high temperature gradients near the wall, causes severe localized cracking. Glass fragments like those in Figure 13a exist to a depth of about 2 cm. Below that, the glass is broken into large chunks, shown in Figure 13b. Some of this cracking is caused by removing the canister wall.

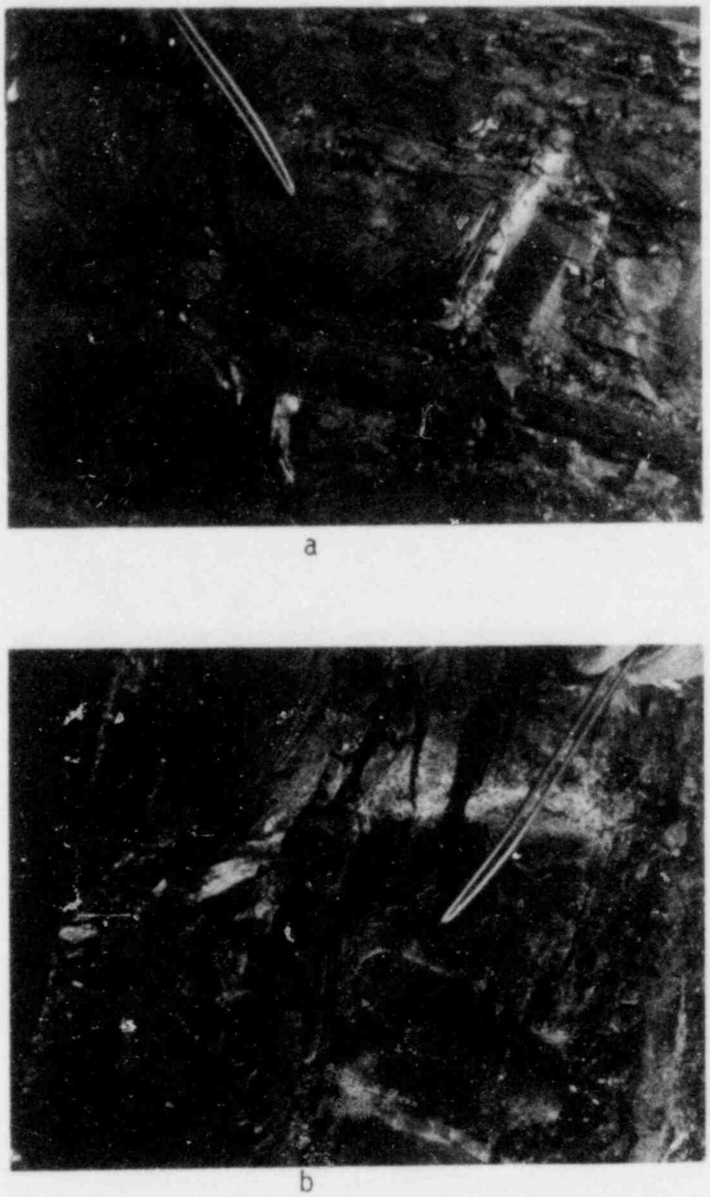


FIGURE 13: Cracked Glass in an ICM Canister
a) Severely Broken Glass on the Surface
b) Solid Glass under the Surface Layer

Another difference is the presence of the internal fins. The fins cause cracking because they shrink away from the glass during cooling as a result of their higher expansion coefficient. The glass also sticks to the fins, which aggravates the effect. Figure 14 shows cracks in a cross

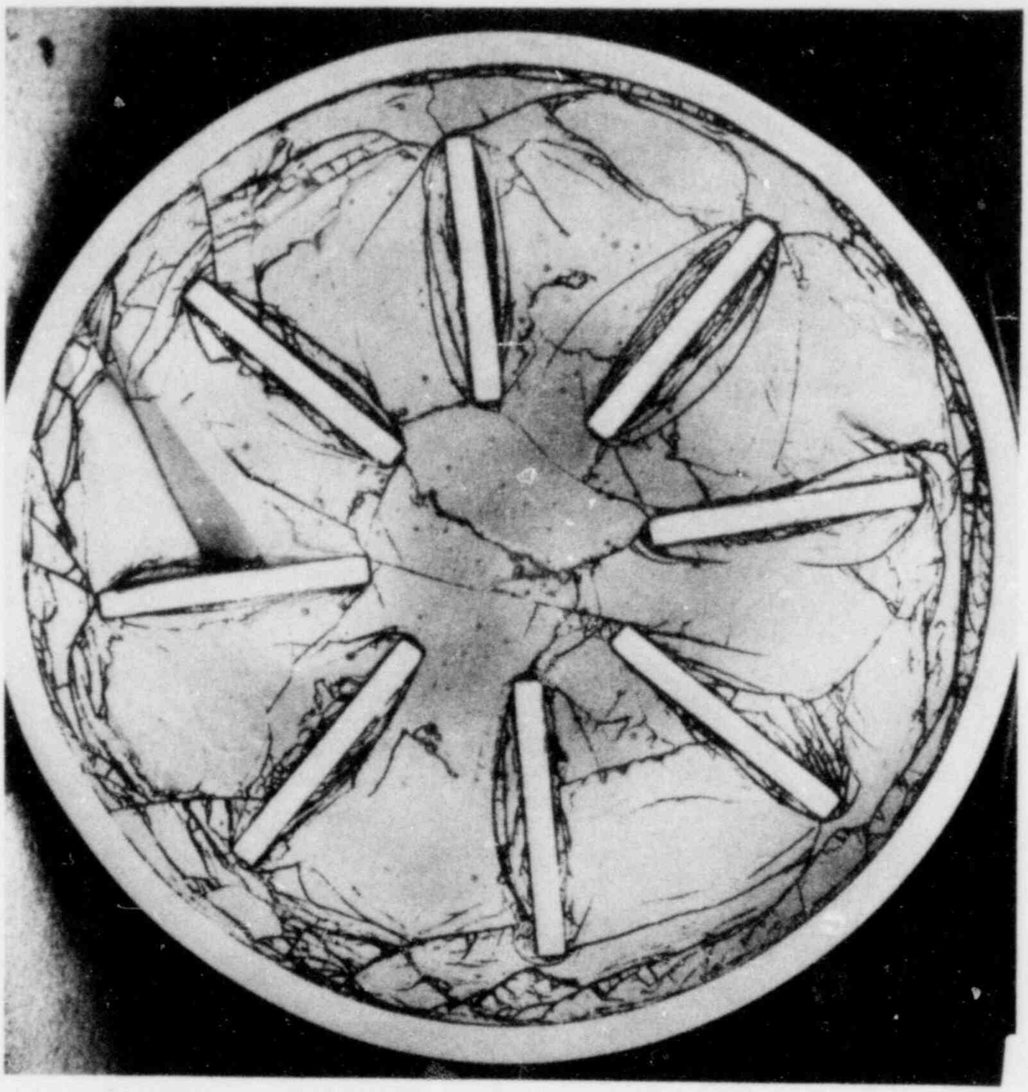


FIGURE 14. Glass Cracking Pattern in a Cross-Sectioned 8-in. Canister as Revealed by Dye Penetrant

section of an 8-in. ICM canister. The cracking patterns are symmetric around the fins. This can be reduced when the expansion coefficient of the fins is matched with that of the glass.

After the canister has cooled, it is sealed, decontaminated, and placed in storage. The handling operations involve moving the canister between environments of different temperatures. The temperature changes may cause some minor additional cracking. Further cracking will occur in self-heating glass when the temperature gradient through the glass decreases because of the decay of the heat-producing elements. This has the same general effect as cooldown although the cracking is modified. Modeling indicates that cracking in high-heat glass should not be significantly greater than in low-heat glass.

Because of the apparent severity of cracking under expected cooling conditions, annealing has been considered as a possible remedy. In the case of waste glass, annealing would limit fracturing and the resulting surface area increase. Cooling could proceed at any practical rate until the glass reaches its annealing point, which would be approximately 500° to 550°C for a typical waste glass. Further allowable cooling rates to prevent fracture are on the order of 1°C/hr. This would imply that nearly 3 wk would be required to cool a 24-in.-diameter canister. To date, crack-free annealing has only been achieved in heated 6-in. CM canisters. The glass/canister bond in most ICM cnaisters causes cracking even when annealed. For example, the canister in Figure 14 was cooled slowly yet cracking is present at the glass/metal interfaces. Even if the glass is properly annealed, the subsequent handling steps may cause cracking.

Under normal conditions, severe localized cracking occurs on the surface of the glass with fractures of the inside material spaced 5 to 10 cm. We identified CM canister preheating as being the best method of significantly reducing cracking. The same factors discussed here apply to other ceramic materials that would have cracking behavior similar to that of glass.

Surface Area

Glass surface areas and particle sizes have been measured in canisters from 6 in. to 36 in. in diameter. Figure 15 shows that the results of a series of tests using 6-in.-diameter by 5-ft.-long CM canisters. There was a 12-fold surface area increase from air cooling. This is equivalent to 0.95 cm^2/g, which is similar to values found in a recent series of tests using large (16-, 24-, and 36-in. diameter by 10-ft-long) CM canisters.

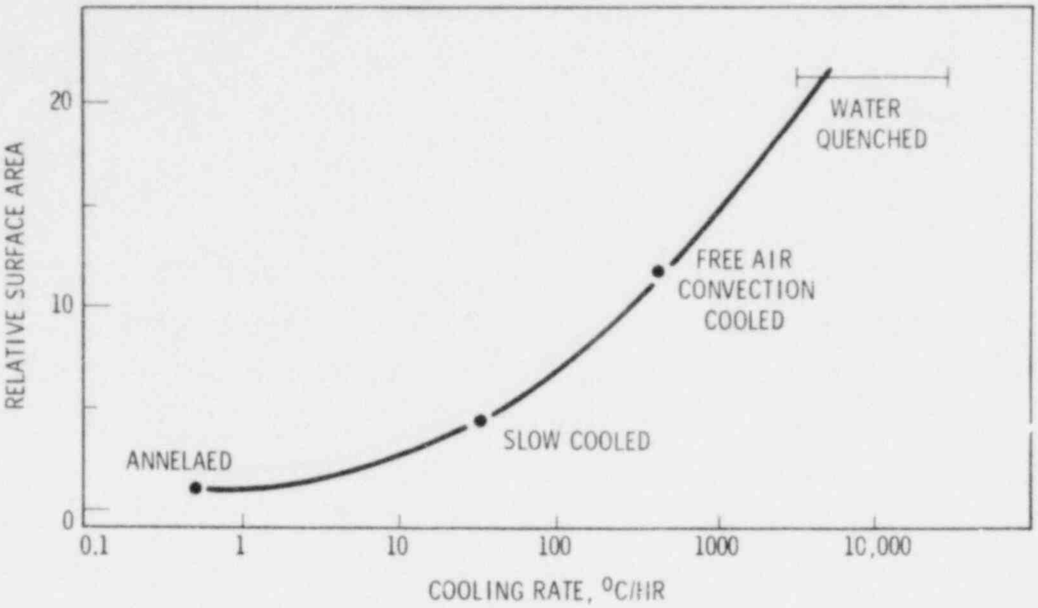


FIGURE 15. Effect of Cooling Rate on the Generation of Increased Surface Area in 6-in.-Diameter Glass Castings

For each of these canisters, a full-length 120° section of wall was removed, the glass was removed, and a sieve analysis was made. Figure 16 shows an opened 24-in. canister. The layering and voids in the figure are due to premature solidification of the glass, because the canister was not insulated. In all cases the glass was not bonded to the canister wall. Concentric layers of glass and small particles were near the surface, with the pieces increasing to 6 in. in diameter near the center. Force was required to remove the glass pieces, which caused additional generation of fines, so the reported data should be considered conservative. Figure 17 shows a log-log plot of the sizing data from the outer inch of glass in a non-insulated 24-in.-diameter canister. The results and the wide scatter in the data were similar for the different canisters tested. Sedimentation size analysis showed the fraction of dispersible, or sub-10 μm, particles to be 2.7×10^{-3} wt%.

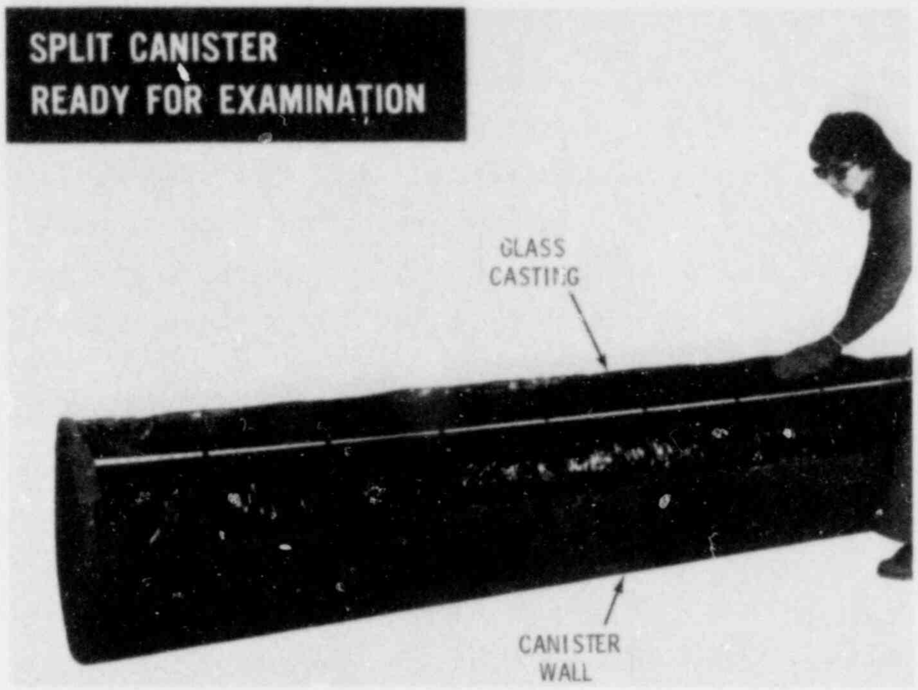


FIGURE 16. Opened 24-in.-Diameter CM Canister

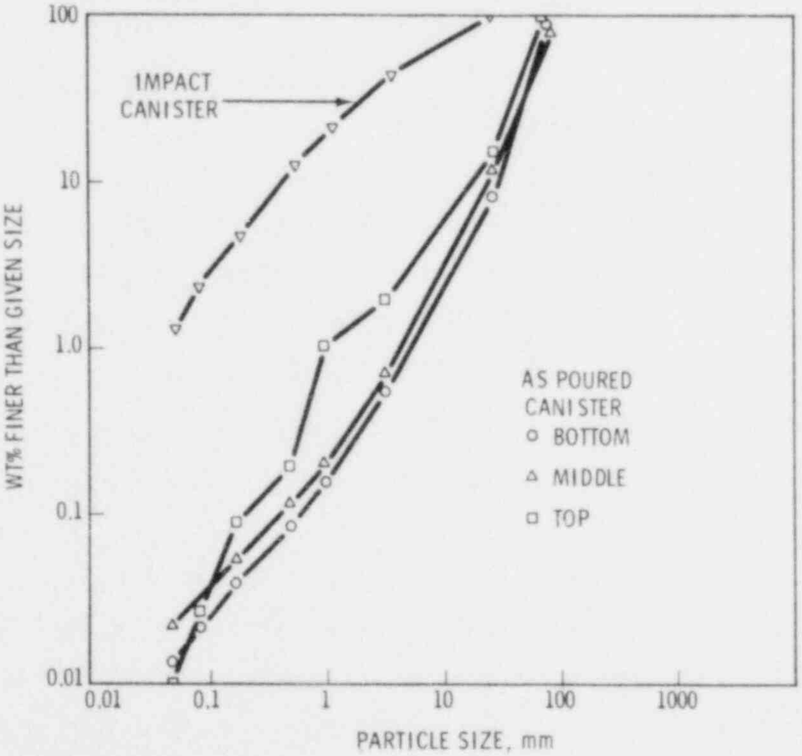


FIGURE 17. Particle Size Data on a 24-in.-Diameter CM Canister

The glass particles were assumed spherical, so the sizing data could be used to compute surface area per gram of glass for the different canisters tested. The calculated area was 0.63 cm^2/g for the 16-in. canister, 0.91 cm^2/g for the outer portion of the 24-in. canister, and 0.56 cm^2/g for the 36-in. canister. These canisters were not insulated during filling. The ratio of the total surface area in the canister to that of an uncracked glass monolith was 13 for the 16-in. canister, 27 for the 24-in. canister and 34 for the 36 in. canister. The increase of the ratio results from the relative constancy of the surface area per gram values and the lower surface/volume ratio in large canister diameters. These ratios do not indicate that large diameters are undesireable because the surface area is constant on a weight basis. Larger diameter canisters may in fact be better because there are fewer small particles near the surface on a total glass basis.

Fracture Modeling

We have developed heat transfer and stress models to analyze the process of glass solidification and cooling. The objective of the analyses was to relate stress levels and cracking to processing variables (i.e., cooling rates, thermal treatments, canister size, etc.). The analyses estimate internal stress levels which cannot be measured in the opaque waste glass by available experimental techniques. They also indicate the extent to which experimental observations of cracking in nonradioactive glass can be applied to the radioactive situation.

Finite element codes have been adapted for the prediction of residual and thermal stresses. Thermal and mechanical interaction between the canister and glass are simulated using a unified analysis approach for the glass and canister stresses. Predicted stresses exceed the yield strengths of canister materials and thus elastic-plastic behavior is treated. Glass behavior is treated as purely elastic below the softening temperature range. The instant freezing concept of Bartenev(13) is employed to simulate the transition temperature range in glass.

Figures 18 and 19 show predicted stress levels in the glass for various cooling conditions. Also, differences between nonheating glass and a high heat content glass of 100 watts/liter are shown. In all cases, filling was by the ICM process and glass properties were based on data given in Appendix A.

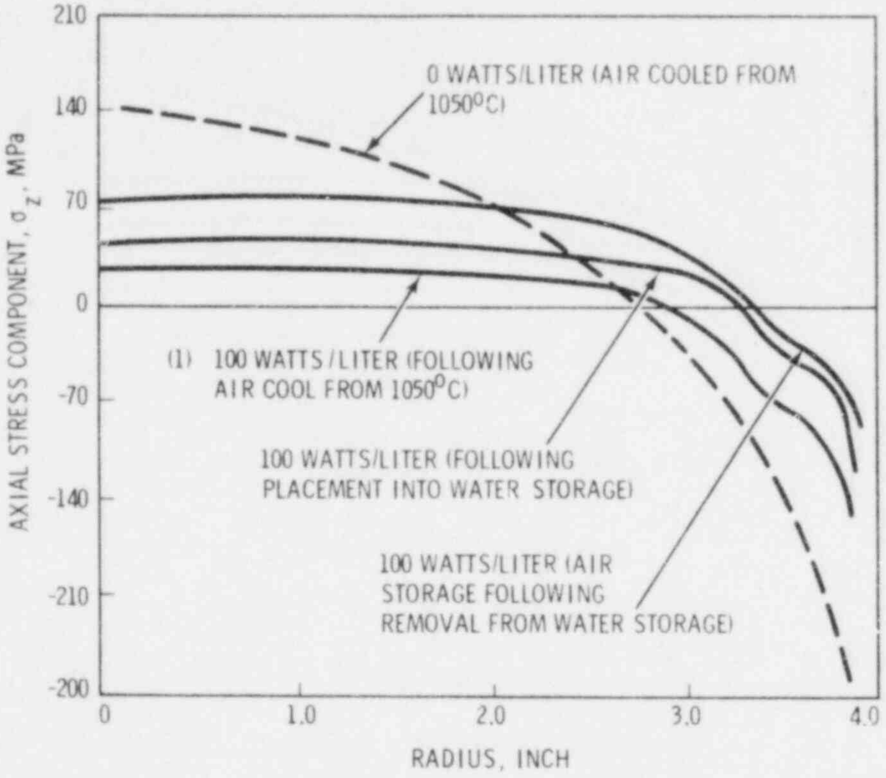


FIGURE 18. Effect of Heat Content on Glass Stress

Figure 18 shows a clear trend of lower residual and thermal stresses for the self-heating radioactive glass (curve 1) than for the nonradioactive glass. Thermal cycling (placement in water storage) increases glass tensile stresses in response to a reduction of tensile residual stress in the canister wall due to rapid cooling of the hot canister. As shown in Figure 19, glass stress increases as the heat generation rate in the glass decreases in response to radioactive decay.

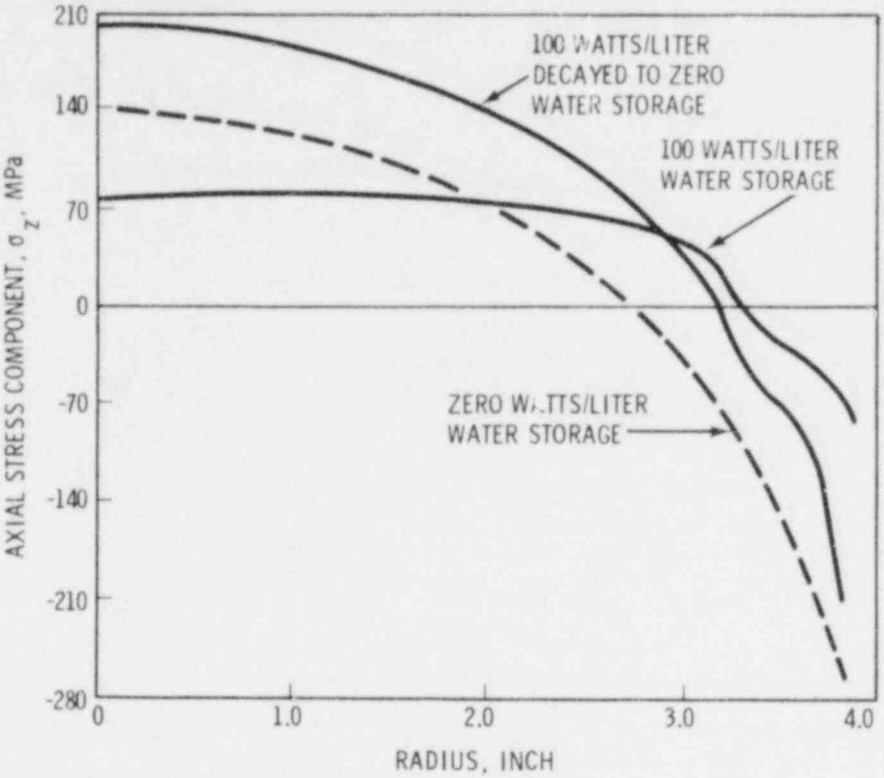


FIGURE 19. Change in Glass Stress as Heat Decreases During Storage Period

The analyses suggest that radioactive glass with high heat rates will be less extensively cracked initially, but may over long time periods continue to crack due to a decaying heating rate. The cracking would be similar to that from process cooling.

The calculations have clearly predicted stresses greater than observed glass tensile strengths. Figure 20 shows the result of a simulation of the cracking in a canister with internal fins. A nonheating glass was used and the stresses were caused by the thermal expansion mismatch between the glass and the stainless steel fins and canister. Figure 14 (page 22) shows that the cracking adjacent to the 304L fins in the sectioned canister is similar to the analysis of Figure 20. The additional modes of cracking are thought to be a result of cooling rates of the experimental canister, which are more rapid than the very slow rate considered in the analysis.

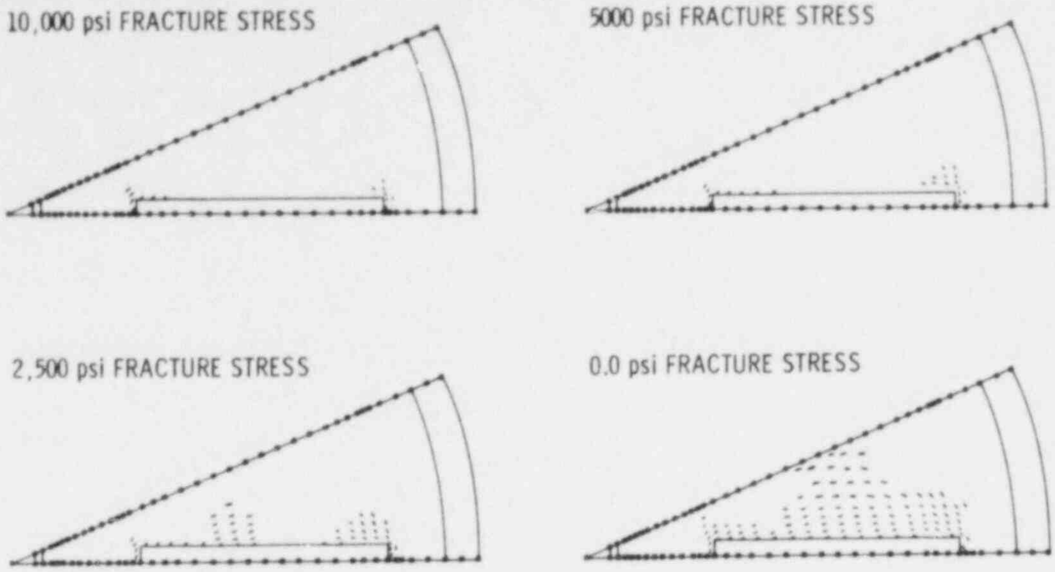


FIGURE 20. Predicted Cracking Patterns in an 8-in.-Diameter Canister With 8 Fins

Energy balance methods have been used to estimate glass surface areas resulting from cracking. In these calculations it is assumed that the elastic strain energy associated with stresses in the glass is transformed to surface energy associated with the newly-formed glass surfaces. However, the calculated elastic strain energy under typical conditions has been found to exceed by as much as two orders of magnitude the surface energy associated with measured surface areas. Evidently, the excess strain energy either is dissipated as heat and sound, remains as residual stresses in the fragments, or is transformed to kinetic energy. If one were to predict surface area increases solely on the basis of gross energy balances, the results would suggest erroneously that the cooling of a canister will crack the glass into particles as small as 40 μm. It is probable that initial cracking at low stress levels during cooling releases strain energy and relieves stress. The subsequent thermal and residual stress in the fragments may be below the material strength and the cracking process will be arrested. Laboratory tests have been made on the amount of energy needed to form new surfaces. The cracking process is apparently very complex, because only 1% of the available energy is used in creating new surface area.(14)

Because of the complex nature of cracking an energy balance may be the only technique available to actually predict the surface area in a canister. However, further research is needed before this technique can be used with accuracy.

IMPACT STRESSES

Cracks in the glass can also result from stresses created by external mechanical loadings. Under normal storage and handling such stresses will not be significant. Our focus has been on stresses and cracking from severe impacts that have a low probability of occurring.

We have conducted experimental impact tests using both full-scale and subscale canisters filled with glass. Two series of impact tests (1975 and 1977) have been conducted. The main objective of the 1975 series was to evaluate the extent of glass fracturing as a result of impact.(15) In the more recent 1977 series, the focus was on canister integrity. Both test series showed the capability of canisters to sustain the impact of a 9-m drop (13 m/s) onto an unyielding surface without breach of containment. The 9-m drop corresponds to federal requirements for the transportation of nuclear materials(16) and is considered to be a severe impact with a very low probability of occurrence.

The main objectives of the 1975 tests were to estimate the quantity of respirable glass fines (<10 μm) produced and the increase in glass surface area. The specimens were annealed nonradioactive waste glass in cylindrical 304L stainless steel canisters. Six 1/2 scale CM canisters (6-in.-diameter) like the one in Figure 21 were impacted at room temperature and at velocities up to 13 m/s. Twenty-two smaller specimens (2-in.-diameter) were tested at room temperature, and at a elevated temperature (425°C) at velocities up to 35 m/s. The tests included specimens that were essentially glassy and specimens which had been partially devitrified by thermal treatment.

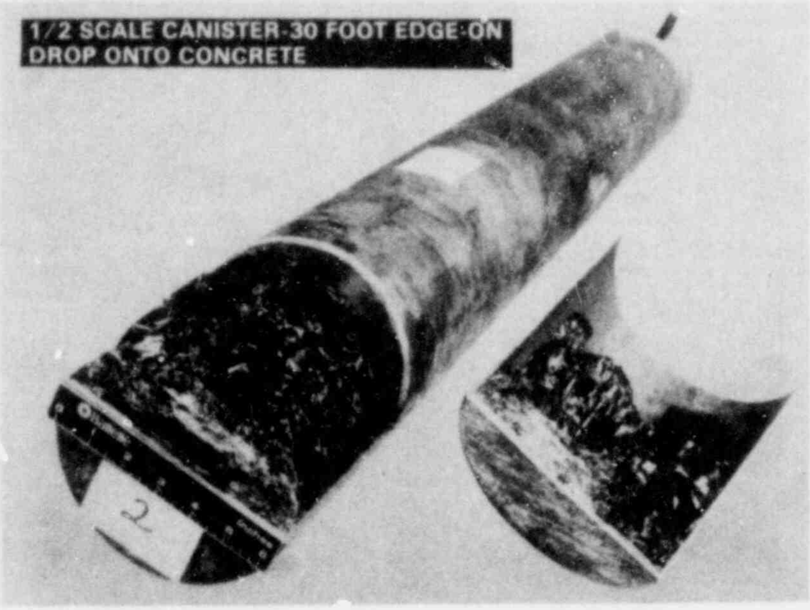


FIGURE 21. Half-Scale Canister After Impact

Figure 22 shows estimates of sub-10 μm size fines for impact velocities of up to 35 m/s. Optimistic and pessimistic bounds are shown corresponding to data scatter limits. The velocities represent impact onto an essentially unyielding target. For impact onto soil or impact in a protective package, glass breakup predicted by the figure would correspond to much lower equivalent velocities. It should be noted that the fines produced in the tests were confined within the barrier provided by the canister and did not become airborne.

Figure 23 shows estimates of fractional increases in surface area. Geometric area increases are strongly affected by velocity, ranging from a few percent for controls to factors of 10 to 100 at 35 m/s. Tests at elevated temperatures consistently led to higher surface areas from more particles greater than 100 μm; the quantity of particles less than 100 μm was not markedly affected by test temperature. The change in quantities of larger particles could be due to the presence of the canister. As discussed in Appendix B, the canister tends to shrink around the glass and produce compressive stress in the glass. Heating tends to reduce these compressive stresses, which may make the glass more prone to fracture.

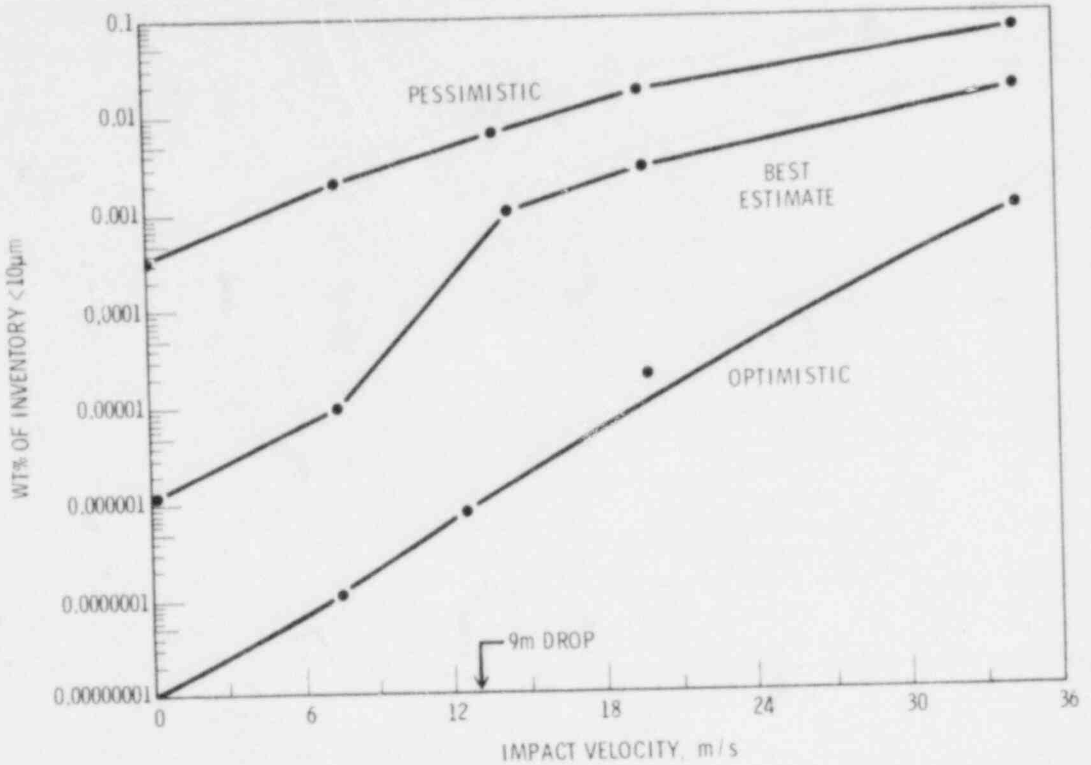


FIGURE 22. Prediction Curves for Sub-10 μm Fines Generation

Analyses of respirable fines and glass surface area have been performed for one of the full-scale canisters impacted in the 1977 test series. This was a non-insulated canister filled by the CM process. It was 24 in. in diameter, weighed 2000 kg, and was dropped from 7.5 m. Sizing for glass fines from the most heavily damaged portion of the canister is shown in Figure 17 for comparison with data from canisters that had not been impacted. Only the bottom 0.5 m of the glass in this canister appeared severely damaged by the impact; the glass above this point appeared to be in the original condition. The calculated surface area of the most severely damaged region was 21.3 cm^2/g, which compares to 0.91 cm^2/g for as-fabricated glass. A sedimentation size analysis of a glass sample from this canister indicated that the respirable fraction was increased to 0.13 wt% from 2.7×10^{-3} wt% by the impact. The canister was not breached under the above conditions, so there was no release.

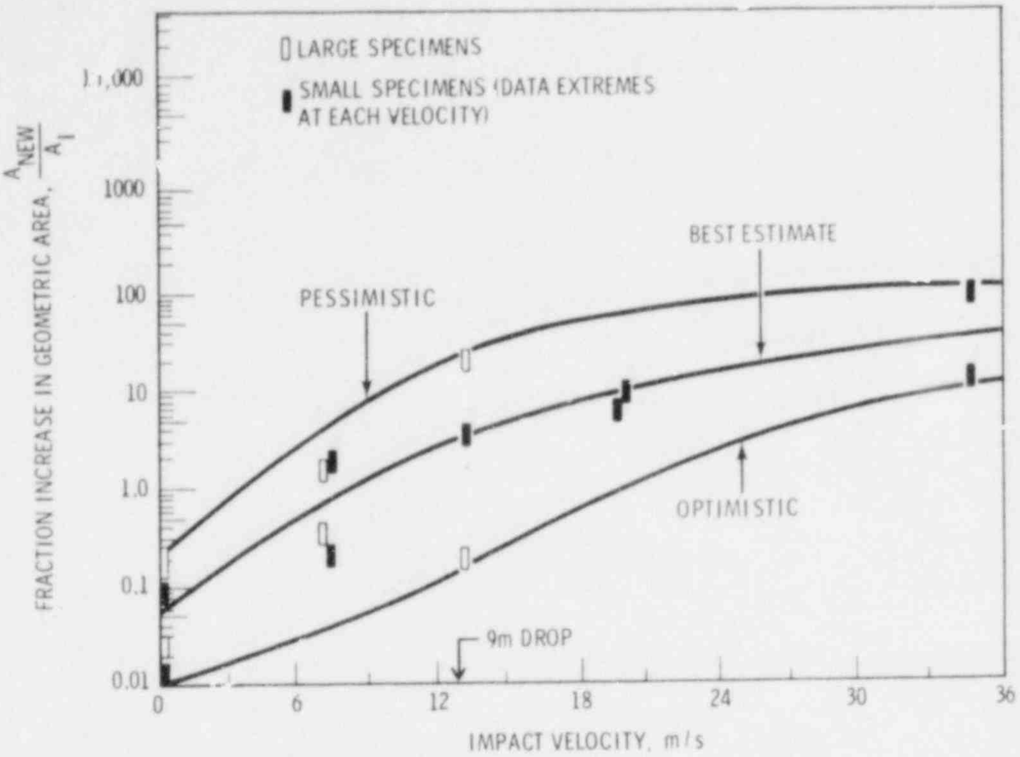


FIGURE 23. Fractional Increase in Geometric Surface Area

Full-scale impact tests are very important in evaluating glass breakup because it is impossible to create the actual cracked state found in a canister in a laboratory test. However, laboratory studies are helpful in comparing glasses of different compositions and are necessary in comparing radioactive glass with nonradioactive glass. In our lab tests a punch-and-die apparatus was used to impact 3-gram glass samples at energies between 30 and 215 Joules. Figure 24 compares data using this procedure on particle generation for several glasses.(14) The data indicates that glasses of widely varying composition have similar impact behavior. Other laboratory work is currently being conducted using both simulated and radioactive waste glasses.

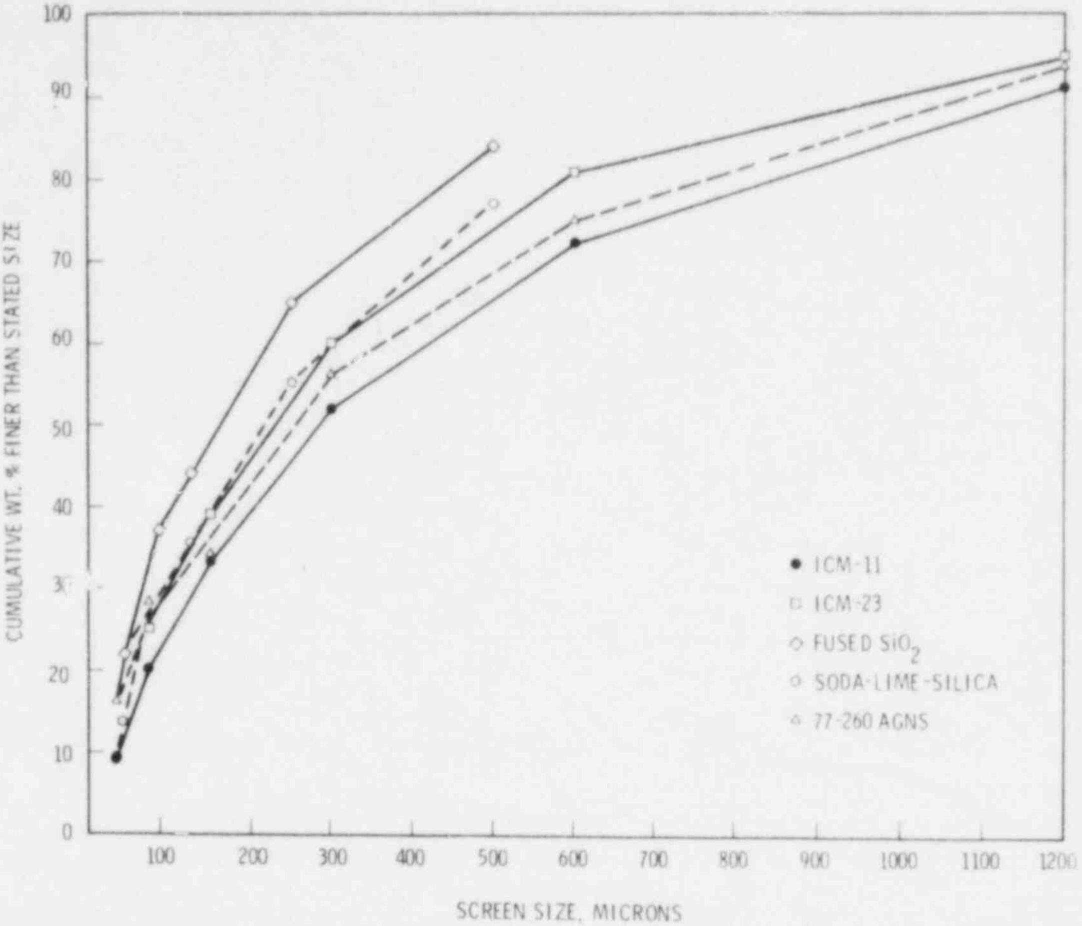


FIGURE 24. Particle Sizes Produced in Various Glasses by 215 J Impact

CONCLUSIONS AND RECOMMENDATIONS

Glass is the most highly developed of the many waste forms that have been proposed for the waste management system. It has been shown to be a durable and stable form that provides the necessary containment of radioactive elements. Large castings of waste glass have been produced using actual radioactive waste in the United States and France. Full-scale, non-radioactive solidification systems are currently being developed and tested in several countries.

Cracking occurs in waste glass that is produced in large canisters. This cracking increases surface area and produces respirable-size particles. The importance of the cracking depends upon the effect it has on the safety of the overall waste management system. We conclude that cracking does not have a significant impact on safety in the solidification facility or during transportation. Current work on glass behavior in a disposal site does not indicate any serious problems. Advanced overpack designs can prevent waste/geology interactions for long periods (up to 1000 yr) if reduced releases are necessary.

This review of glass cracking has led to several interesting conclusions, which are summarized below:

- Under normal conditions an almost constant amount of cracking is found in different size canisters. In canisters ranging from 6 in. to 36 in. in diameter the surface area is between 0.5 and 1.0 cm^2/g.
- Severe impacts will cause extensive cracking, but only in a localized region. For a standard 9-m drop, the surface area in the canister will increase by a factor of 4 to 10, depending on the size of the canister and the original state of the glass.
- Most of the surface area in a canister is on the very small particles. Particles that are 1 wt% of all the glass in the canister have 50% of the surface area.

- Thermal and residual stresses are the major cause of cracking in glass waste.
- Analytical models of cracking are useful in interpreting observations and in estimating self-heating effects. Quantitative predictions of cracking are currently not possible.
- Devitrification or radiation damage generally do not cause cracking.
- Typical waste glasses have impact properties similar to commercially produced glass.

In preparing this paper we have identified several areas needing more study. These studies have begun at PNL and elsewhere. We recommend that evaluations of cracking in full-scale canisters be continued. Efforts should be made to relate different processing conditions to the amount of cracking. The existing analytical models for predicting cracking should be refined . Leach testing should be expanded to include large blocks of glass and other waste forms that are cracked.

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16. Code of Federal Regulation, Title 10, Part 71, Appendix B - Hypothetical Accident Conditions.

APPENDIX A

PROPERTIES OF SIMULATED HLW GLASS

Extensive work has been done worldwide to quantify the physical properties of waste glass. Most of the data on borosilicate glass is summarized in the two Annual Reports on HLW glass prepared by the Pacific Northwest Laboratory for the U.S. Department of Energy(1,2). We are reproducing here some data on the properties pertinent to understanding cracking in glass. Most of these properties are, to a good approximation, independent of composition. The properties continue to be measured on new glass compositions as they are developed to be sure there are no major differences caused by compositional variation.

Thermal Expansion Measurements

The thermal expansion parameters of a large number of glass samples from both full-scale canisters and laboratory tests were determined using a push-rod dilatometer. All heating was done in air, at 4°C/min. A typical plot is shown in Figure A-1, which illustrates some of the characteristic parameters of a sample. These parameters are:

- the thermal expansion coefficient, determined from the slope of the linear portion of the curve--generally RT-400°C
- T_g, the glass transition temperature--the point at which the thermal expansion rises sharply, corresponding to a change to the supercooled liquid state
- T_s, the dilatometric softening point--the temperature at which the push-rod sinks into the sample.

The thermal expansion coefficient remains close to 9×10^{-6} /°C for most glasses. The values for T_g and T_s varied between samples, but usually were near 520° and 550°C, respectively.

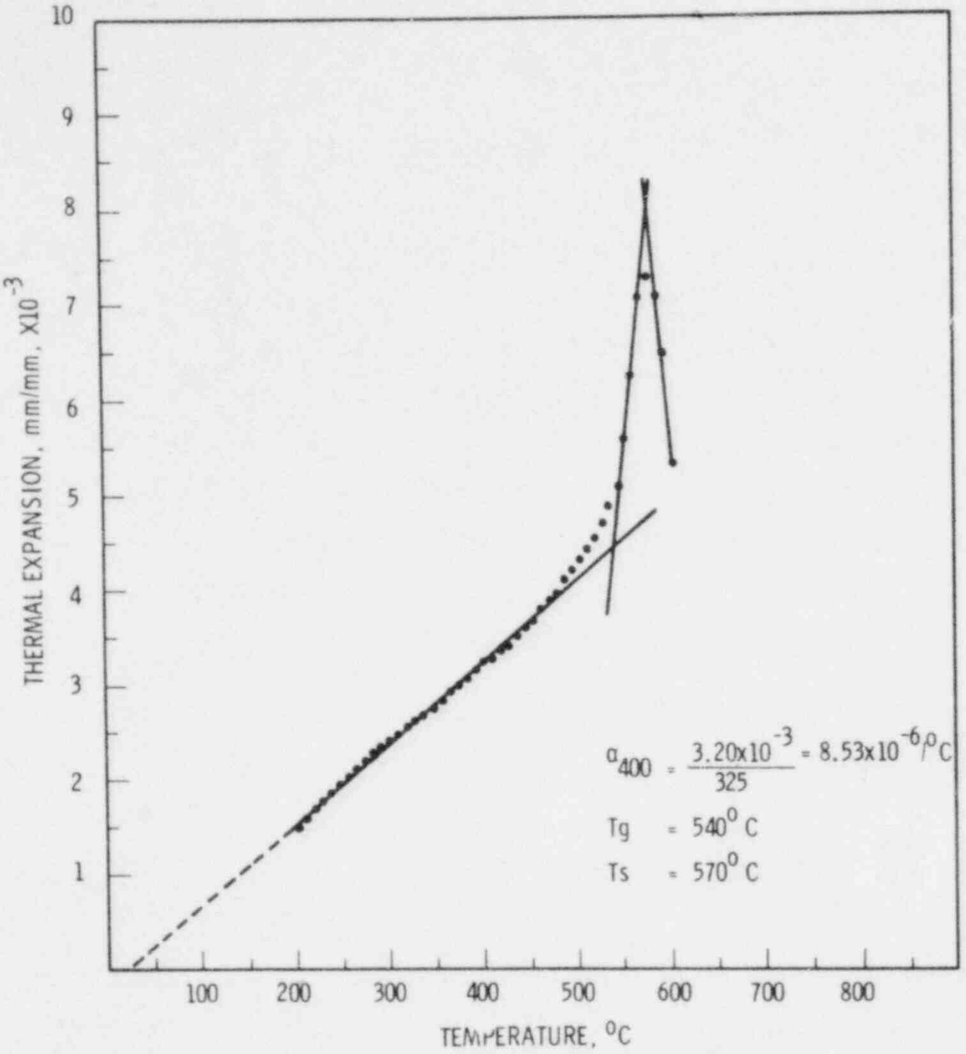

FIGURE A-1. Thermal Expansion Curve for Typical Waste Glass

Young's Modulus

Young's Modulus has been measured as a function of temperature on one glass. Figure A-2 shows that the values remain nearly constant over the range of 25^0-450^{0}C. The curve drops off above 450^{0}C because the glass is approaching its dilatometric softening point. Above this point Young's Modulus has no meaning, because the glass cannot support a strain.

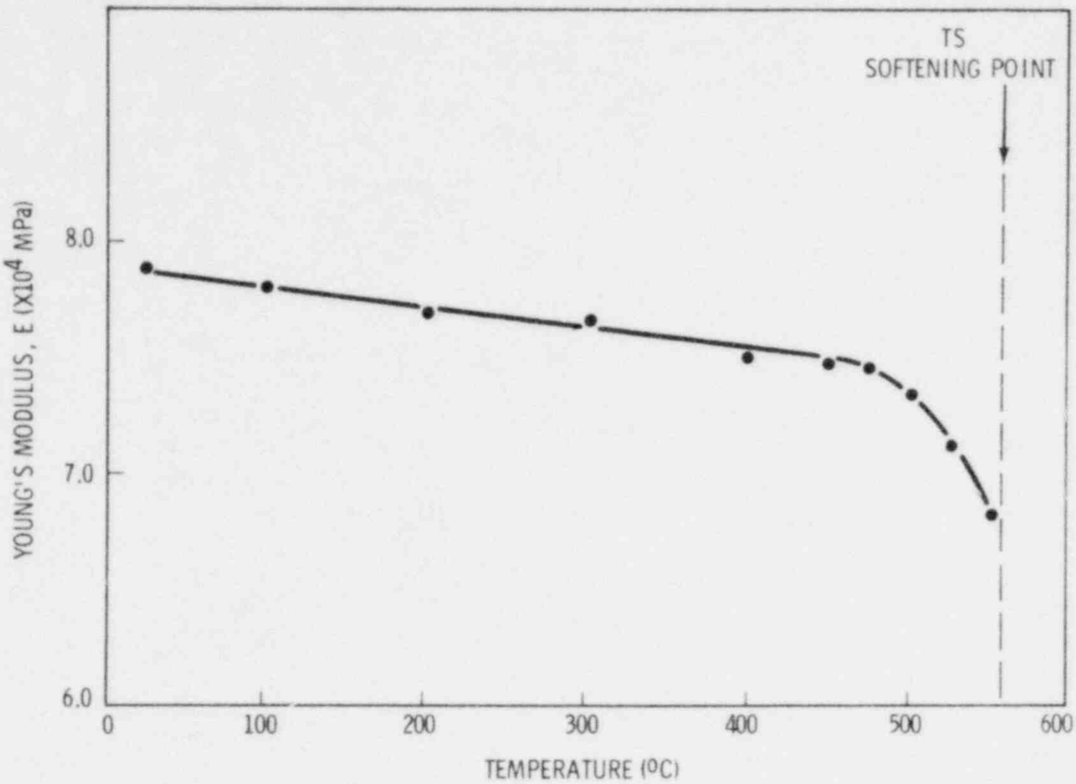

FIGURE A-2. Young's Modulus

Tensile Strength

The average strength of a waste glass has been measured to be 38 MPa with a standard deviation of 7 MPa. This value was obtained by using the Brazilian Test on 29 samples. The loading speed was 0.05 cm/min.

Density

Values of density from room temperature to 1300°C have been measured for several glasses. Figure A-3 shows values for four glasses. The dashed "s" shaped curve is hypothetical although Tool has found this type of curve for another silicate glass.(3) The higher values for the 72-68 glass are due to a high ZnO content, which is no longer typical in waste glasses.

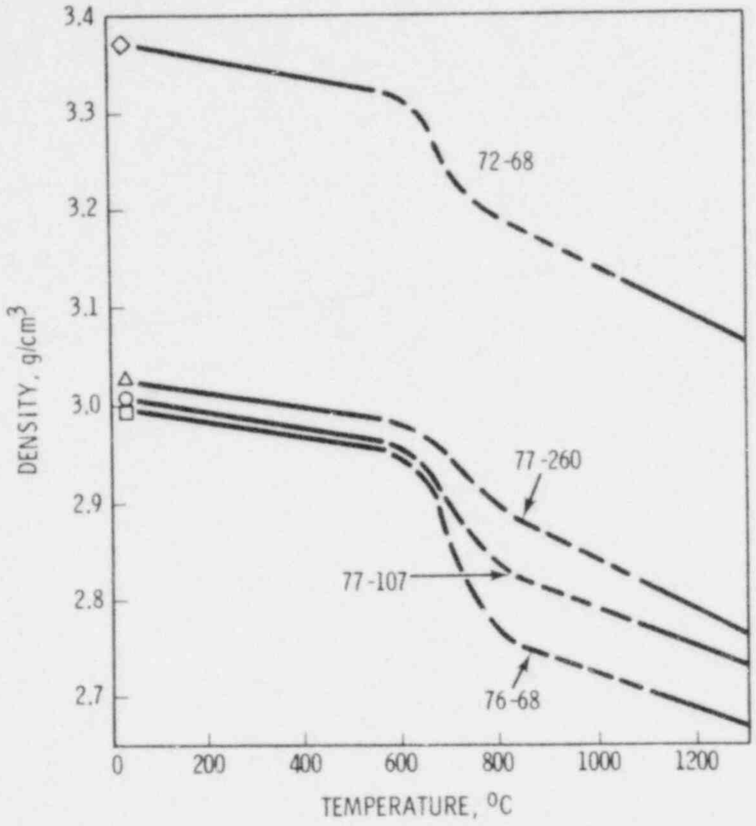

FIGURE A-3. Density of Several Waste Glasses

Specific Heat

The specific heat as a function of temperature is shown in Figure A-4. The peak sketched in at the glass transition temperature results from the energy requirement for the glass to change from a super cooled liquid to a liquid.

Thermal Conductivity

Data on thermal conductivity of waste glasses is limited. The data presented in Figure A-5 is from one glass composition. Some preliminary experiments indicate that the conductivity does not change much with respect to composition or the amount of devitrification. Tests are being developed to measure the effective conductivity of glass at temperatures above 500°C and to measure the effect of cracking.

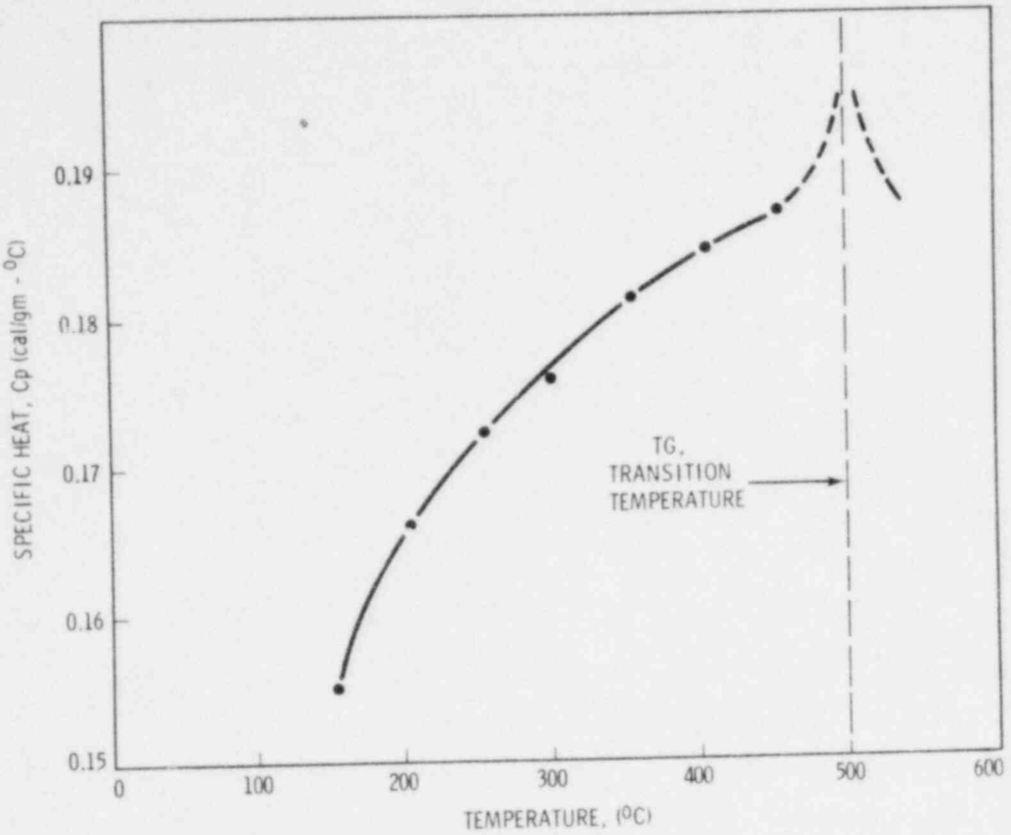

FIGURE A-4. Specific Heat

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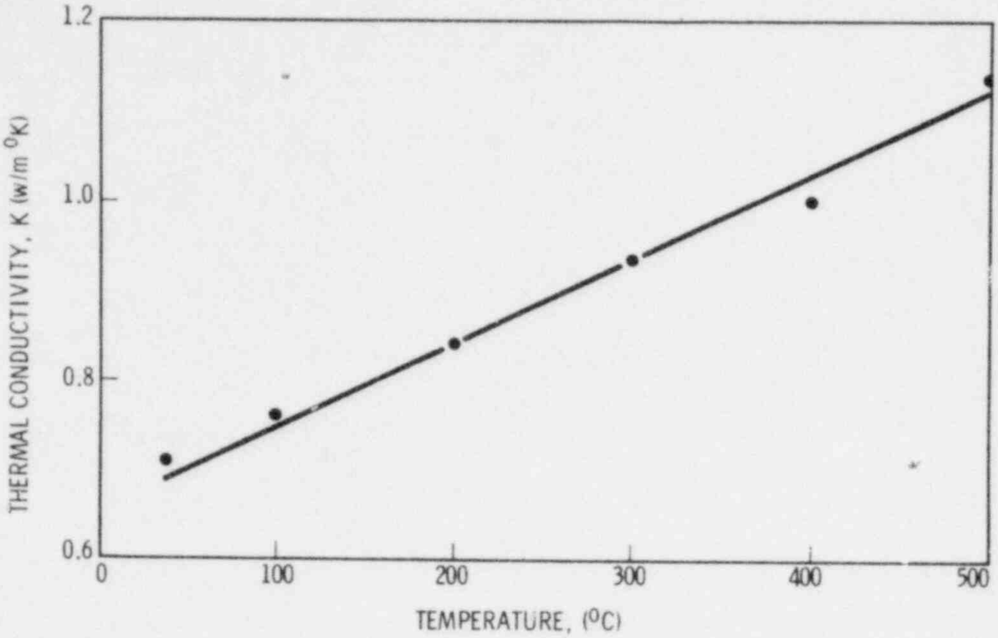

FIGURE A-5. Thermal Conductivity

APPENDIX B

RESIDUAL STRESSES IN CANISTERS

When considering heat transfer rates and stress states in canisters of glass, it is necessary to treat the canister and glass as a single system. It is, therefore, appropriate in this paper to briefly discuss stresses and possible cracking of canisters.

The basic cause of residual stresses in canisters is that the typical canister materials, such as 304L stainless steel, have thermal expansion coefficients which are about twice that of glass. Upon cooling after filling, the canister tends to contract tightly about the solidified glass, and tensile residual stresses are created in the wall of the canister.

Residual stresses have been measured in canisters filled by the ICM process. Electrical resistance strain gauges were attached to the canister wall, and that portion of the wall was cut free of the canister. The change in strain as a result of cutting is a measure of the residual stress in the canister wall. Such measurements have consistently shown tensile stresses at levels nearly equal to the yield strength of the canister material.

Recently at PNL, high temperature strain gauges have been used to monitor strains in a canister during filling by the CM process. These measurements have also shown a final state of tensile residual stress in the canister wall. The initial data, however, indicate somewhat lower levels of canister residual stress for the CM canisters when compared to ICM canisters.

Tensile residual stress in the canister wall has implications for glass cracking, as well as for possible canister cracking. Tensile residual stresses in the wall cause compressive stresses in the glass which will to some degree reduce the extent of cracking in the glass. The experimentally observed increase in glass cracking in heated canisters under impact conditions is thought to be due to a reduction in the compressive prestress provided by the canister.(1)

In evaluating canister integrity, tensile residual stresses are a detrimental factor in some cases. Canister materials of interest are tough and ductile enough that residual stresses will not have any bearing on brittle fracture. Also, the number of stress cycles experienced by a canister are few so that the detrimental effects of tensile residual stresses on fatigue life are not of concern. The major concern is the potential for canister failure by stress corrosion cracking for those canisters that are stored for interim periods in water basins. However, canister cracking under such conditions is considered unlikely provided water chemistry is suitably controlled and metallurgical sensitization of canister materials during processing is avoided.(2)

Computer model studies have yielded predictions of canister residual stresses. Figure B-1 shows predicted trends for glasses with internal heat generation rates ranging from zero to 100 w/l. For all cases, the initial air cooling of a canister of molten glass from 1050°C resulted in tensile residual stress in the wall of the canister. However, the presence of heat generation tended to reduce the level of this tensile stress. The consequences of subsequent water cooling on canister stress levels are also shown in Figure B-1. Immersion of the high-temperature canisters (50 and 100 w/l curves) results in a quenching action. Thermal stresses and plastic deformation of the canister wall during the quench result in a decrease in the canister tensile residual stress. For the assumed conditions of the analyses, compressive canister stresses are predicted. However, examination of experimental canisters shows fractures in the glass at or near the glass-canister interface, and the presence of such fractures would preclude development of compressive stresses in the canister wall.

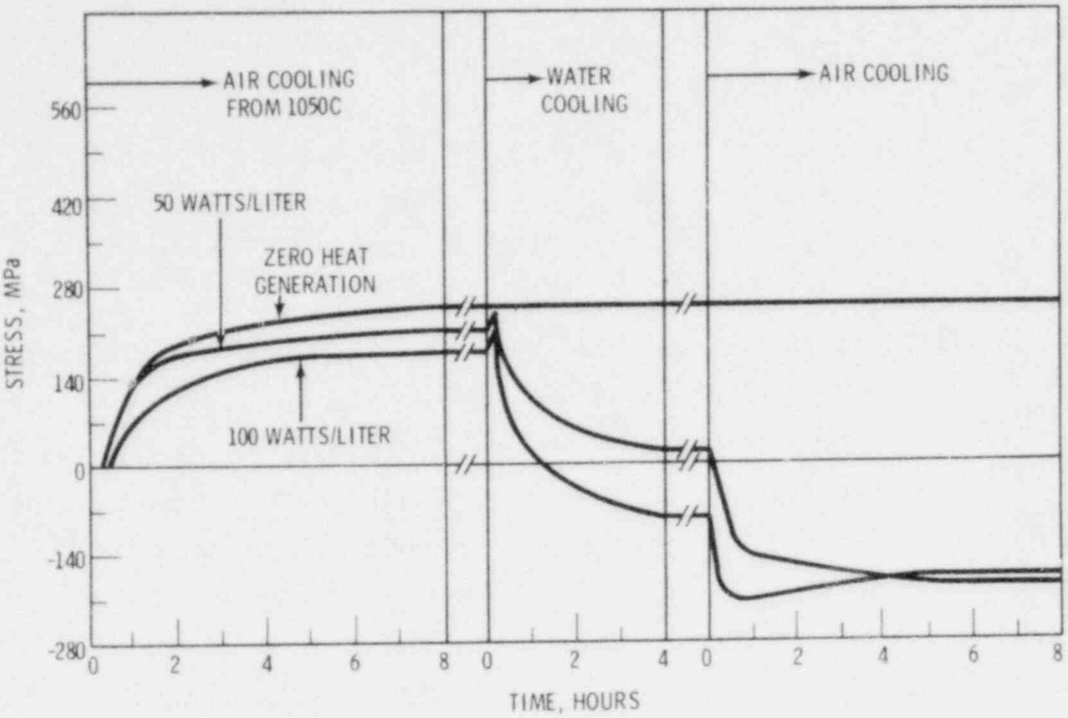

FIGURE B-1. Effect of Heat Generation

A number of techniques for altering the state of tensile residual stress in the canister wall have been proposed, and some of these have been studied at PNL. Thermal treatments have been tried. For example, canisters have been quenched in water after heating to an elevated temperature and they have been subcooled from room temperature by immersion into a low temperature bath. Reductions of measured tensile stresses have been observed, but the stresses have not been entirely eliminated. The benefit obtained from the limited trials at PNL have in general fallen short of expectations.

Other stress reduction schemes involve modification of the canister construction. One proposed approach has been to select a canister material that has a thermal expansion coefficient that more closely matches that for glass. Special alloys with lower expansion coefficients are available, although factors of costs, availability, mechanical properties, corrosion and welding characteristics, etc., may preclude their use for canister application.

In another proposed stress reduction scheme, a conventional canister is used with an internal liner of a low-strength crushable material. The concept is to allow the compliant liner to deform and thereby relieve stresses in the canister wall. Candidate liners of expanded metal have been investigated at PNL, but have been subject to excessive attack by molten glass. Other problems with liners also arise since a liner will most likely act as a thermal barrier. Melting of glass in the ICM process will be seriously impaired if a liner is used. Also, cooling of heat generating glasses during storage will be made difficult by the presence of a thermal barrier. The use of a liner may be more attractive for the CM process and with low-heat wastes where the problem of having a thermal barrier is not severe. Nevertheless, the impact on cooling rate after filling must be evaluated.

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Discussion Following

STRESSES AND CRACKING IN HIGH-LEVEL WASTE GLASS

Presented by Steven Slate

Pedro Macedo - Catholic University
Comment:
One thing that you said was radiation damage did not cause cracking. That is true. Although the heat caused by radiation will give you a significant additional stress because there will be a temperature gradient across the sample as cast, or even after cooling, which will only disappear several years later. So that will increase your cracking situation. That is something that you cannot anneal out unless you re-melt the glasses at some later date.

Slate
Response:
We expect cracking to be similar in appearance to the slide I showed that pictured large cracking at regular intervals. Our fracture models are able to predict cracking from self-heating.

Macedo
Question:
What strength modulus of rupture do you put in your glass?

Slate
Response:
The strength we are talking about is 37 MPa (5000 pounds per square inch) ultimate strength or fracture strength.

Macedo
Comment:
That is relatively high if you assume that there will be water and there will be stress corrosion which will probably bring it down to maybe something like 2000 or 1000 pounds per square inch.

Slate
Response:
We have ongoing work that will be evaluating the stress-corrosion type of phenomena that reduces the strength of glass.

Etienne Roth - CEN, Departement de Recherche et Analyse, Saclay, France
Question:
My question is in the same line as the previous one. When you look at radiation damage, do you look at intermediate doses or do you always look at the maximum dose? Because some damages might, though it may not be very probable, be annealed by radiation itself, so some effect might appear at intermittent values of radiation doses.

Slate
Response:
We have looked at glass samples that have received a variety of doses from less than 5,000 years all the way to 500,000 years.

Jeff Stokes - IRT Corporation
Question:
Have you formulated any ideas as to what constitutes an acceptable increase in surface area from the point of view of the long-term integrity of the stored waste?

Slate
Response:
If you are asking for a criterion on glass surface area in a canister, I do not know if I am prepared to provide one. We feel that a glass surface area of approximately ten times what you would have in a canister that was not cracked would be probably acceptable. One square centimeter per gram in a 12-inch diameter canister is about a factor of 10 increase.

Most of these data are on canisters that have not been filled in an entirely prototypic manner. Some of them have been filled without any temperature control. The canister wall was relatively cold when the glass contacted it, so thermal shock was greater than would be anticipated under actual conditions. Another factor, which I did not mention, is our sampling technique. When you look at cracked glass containers like this, the pieces are packed together tightly. It is like a 3-dimensional jigsaw puzzle. In fact, the pieces are under compression because of the canister. To pry the pieces out we use a big screwdriver. This in itself generates a lot of particles, especially very small ones. I am going to claim that the data I have presented is very conservative. I feel comfortable saying that.

David Berick - Environmental Policy Institute
Question:
Could you discuss briefly your experience with homogeneity in the cross section of the glasses in both of your glass-forming processes--especially the in-can melting process? Is there separation chemically or isotopically in your glass formation?

Slate
Response:
There is a difference between the bottom of a canister and the top. I would feel more comfortable if, after the meeting, you would talk to, for example, Wayne Ross. He has studied the compositional difference in the glass between the bottom and the top of the canister. I have primarily addressed my attention to the type of cracking that you would find in a canister.

Berick
Question:
Have you found any additional effect on cracking due to this compositional difference in the glass formation?

Slate
Response:
We have seen differences in cracking between the bottom and the top in, for example, continuous melting canisters. However, this is primarily due to the difference in the temperature. When the glass hits the bottom everything is cold, by the time the glass gets to the top, the canister is much warmer and things even out. Now as far as internal defects which are influenced by segregation, I think that the slide I showed was from an ICM canister. You will have to talk to Wayne Ross, I think, to really get a good feel for the effect of the differences in composition.

Wayne Ross - Battelle Pacific Northwest Laboratory
Response:
The in-can melting system operates at a temperature such that there are residual crystallites in the glass, as was pointed out in one micrograph. These are primarily materials such as ruthenium, palladium, rhodium, and occasionally some of the rare earths, particularly cesium. In some cases, these materials will settle to the bottom of the canister. In those cases, you do have a higher concentration of crystalline material at the bottom, but these materials are still uncracked and are much tougher. It is much more difficult to get them out of the canister than is a material that is pure glass.

Berick
Question:
Again getting back to the cracking question. Have you noticed differences in cracking in the glass because of this inconsistency in the composition?

Ross
Response:
No, there is not a major difference.

Lawrence Hench - University of Florida
Comment:
I would like to comment on the phenomena you were describing. It is perhaps tempting to take a bulk leach rate and multiply it by an effective increase in surface area and use that for the effective leach rate of a cracked sample. It turns out that should not be done. The reason is that, through a series of studies that we have done on the leaching of mixed powder systems, it turns out that when you have a mixed size distribution of powders, the fines tend to concentrate around larger particles and set up heterogeneous corrosion cell effects on the surface, greatly accelerating the leaching rate at those contact points and often in scanning-electron-microscope micrographs you can actually see little holes burrowed down in the bigger particles caused by the heterogeneous

cell attack of little particles. In terms of the type of curves that I was describing this morning, that phenomena tends to throw the kinetics into an effective, total dissolution mode and often results in missing the diffusion modes. The net effect is one of going very quickly in the linear time regime and speeding everything up. So there is a multiplier effect of the particle size distribution that is greater than just the effective surface area increased by the fraction. For the record, it is important not to make just that simple multiplication in calculating leaching rate.

Ross
Comment:
Obviously, it is not a straight forward phenomena allowing surface area to be multiplied by leaching rate. It is sometimes interesting for general comparison, but in reality it does not always hold. One of the things we have found in powder tests is much lower leach rates than in samples where we have used polished surfaces. Again, here we have a granular material, but it does leach at lower rates, possibly because of the solution that is set up and the back reactions that are possible within the powders. It is a very difficult situation to understand. How samples will leach along a crack is still much of a question that we have not answered yet, but we are planning research in that area.

Slate
Response:
That is one point that is brought out in the paper. The fact that you say there is so much surface area in the canister--that does not mean that it is exposed to reactions. It is like I mentioned before--all the parts are pressed tightly together so when you say a gross surface area in the canister, that does not mean all that surface area is available for reaction.

Roy V. Harrington - Ferro Corporation
Question:
Why are you not considering annealing as a means of reducing cracking?

Slate:
Response:
We have considered annealing. We have even tried it. The 6-inch diameter impact canister I showed was annealed, so we could rule out all external effects in evaluating how much cracking occurs from an impact. The problem you get into is that for large canisters, especially 24-inch canisters which are being considered for defense-waste solidification, the cooling times are very long--say, three weeks to cool one 24-inch canister. When you are talking about three canisters per day, you may have an inventory of 60 canisters, all in different furnaces, all cooling at different temperatures.

It becomes a very complex problem and you have to weigh that complexity against the possibilities of release during the canister life. That is why I said the factor of 10 increase in surface area may be allowable. It does not really appear that this surface area affects releases too much. To predict releases you have to look at the amount of exposed surface area and the fact that most of the surface area is on small particles.

Bob Watt - Los Alamos, private citizen
Question:
In view of the effect pointed out by Dr. Hench, do you intend to make some full-scale tests of waste canisters with or without cracks, characterize the surface area some way, and then measure a leach rate at elevated temperatures?

Slate
Response:
A leach test with a full canister is currently being planned at PNL.

Weathering of Natural Glasses*

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ABSTRACT

The weathering of naturally occurring forms of glass provides clues which can help us understand the variables that control the long-term stability of man-made glasses. In this regard, the study of obsidian and tektite glass are particularly relevant to the vitreous forms proposed for high-level waste disposal. For these natural glasses the leaching rate is quite slow, and their weathering is mainly caused by surface hydration. The hydration process leads to the loss of alkali metals and the formation of a surface layer that has a density different from that of the bulk material. As this layer grows thicker, the strain at the interface with the material in the interior causes cracking and exfoliation of the hydrated coating. The resulting surface topography becomes rougher, which because of the increased surface area accelerates the weathering process. Thus, exfoliation, composition changes, and cracking are linked to the hydration process and are governed by its rate. Two of the variables that are directly correlated with an increased hydration rate are alkali metal and intrinsic H_2O content in the bulk material, while Ca and Fe contents tend to have an inverse correlation.

Weathering of Natural Glasses

It has been known for almost twenty years that a fresh surface of the volcanic glass obsidian develops a hydrated surface layer that grows thicker with time (1). Archaeologists and geologists have used the thickness of this layer as a technique for dating the obsidian implements of primitive societies and the occurrences of volcanic flows (2,3). The hydrated material (perlite) has about 3.5% H_2O by weight, as compared with about a tenth of that in the bulk material. Thus, the surface layer tries to increase in volume, but this is prevented by its attachment to the underlying material. The resulting strain at the interface can be seen in thin sections by viewing the sample between cross polarizers; the interface appears as a thin, bright band (1). The stress at the boundary has another consequence; when the hydrated layer has increased to a thickness of about twenty microns, the stress is sufficient in natural samples to cause a separation of the layer. This can appear as extensive cracking or exfoliation of the surface.

The hydration of obsidian and similar artificial glasses is well described by the ion-diffusion model of Doremus (4). In this model, the alkali metal ions move to the surface as hydronium $(H_3O)^+$ ions move into the material. For soda-lime glass this process has been confirmed by the data of Lanford and co-workers at Yale (5). Such a diffusion process has the behavior given by the equation below:

$$\text{Thickness} = \sqrt{K \times \text{time}}, \quad \text{where} \qquad \text{(I)}$$

$$K = A \exp\left[-\begin{pmatrix}\text{activation}\\ \text{temp., } ^{\circ}\text{K}\end{pmatrix}/(\text{temp., } ^{\circ}\text{K})\right].$$

For obsidian the activation temperature is typically 10^4 °K and $A \sim 3$ to 20×10^{15} $[(\mu m)^2/1000 \text{ yrs}]$. This behavior has been demonstrated for obsidian for extended periods by Friedman and Long (3). In contrast, Lanford's determination of the time dependence for soda-lime glass shows that the ultimate thickness of the hydrated layer is limited because of the competition of the hydration and leaching rates (5). (Soda-lime glass hydrates at about the same rate as obsidian but is leached at ten times the rate of obsidian.)

Table 1 indicates how the hydration layer thickness depends on the time and the temperature. In the presence of exfoliation the predicted behavior is strongly modified because after a 20 μm layer grows as $\sqrt{\text{time}}$, the layer flakes off and the process starts over. Thus, at high temperatures the loss of surface proceeds at a rate that is nearly proportional at the time. (It should be noted that the hydration process does not require the presence of liquid water; even in desert regions there is sufficient humidity to give rates close to those quoted here.)

As an example of another naturally occurring material, I have considered tektite glass (6). Its composition is similar to that of obsidian (see Table 2) with a somewhat smaller concentration of the alkali metals. Preliminary measurements by Lanford indicate that the hydration rate for tektites is somewhat lower than typical obsidians (private communication).

There is a small amount of information on leaching rates for obsidian and tektites. For tektite glass the rate (at 25°C) is 2×10^{-9} g/cm^2·d; for obsidian the value is 2×10^{-8} g/cm^2·d. (For comparison, the corresponding rate is 2×10^{-7} g/cm^2·d for soda-lime glass.) One should, of course, keep in mind that these rates are strongly dependent on the temperature.

In general, we see that high silica glass which has a low alkali metal content has superior properties for both leaching and hydration. It also seems likely that the addition of Ca and Fe retards both processes (7). None of this is new; it has been known to glassmakers for hundreds of years. In waste disposal we have tended to use only one property of glass — that it will hold in solution a wide variety of elements in high concentrations. It should be obvious that in over-taxing this flexibility we should not expect a highly durable glass to automatically result.

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(6) J. A. O'Keefe, Tektites, University of Chicago Press, Chicago, 1963.

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Table 1

Calculated hydration layer thickness using $A = 10^{16}$ [$(\mu m)^2$/1000 yrs] and an activation temperature of 10^4 °K.

Temp. (°K)	Time for a 20 μm layer (yrs)	Layer Thickness in 1000 years (μm)	
		from eqn. (I)	considering exfoliation with no increase in surface area
250	10^7	0.2	0.2
300	10^4	6	6
350	10^2	65	200
400	3	380	6700
450	0.2	1500	10^5
500	0.02	4600	10^6

Table 2

Comparison of the chemical compositions of several forms of glass

Oxide	Typical Obsidian	Average Tektite	Soda-Lime Glass	Zinc Borosilicate 72-68	Interim 76-183
SiO_2	75.85	73.87	72.03	27.3	35.5
Al_2O_3	12.81	12.69	1.40	—	1.0
Fe_2O_3	0.85	0.47	0.06	—	—
FeO	0.57	4.16	—	—	—
MgO	0.16	2.18	2.39	5.9 + SrO + BaO	2.0
CaO	0.48	2.23	7.86		
Na_2O	3.74	1.38	15.87	8.1	10.0
K_2O	4.20	2.28	0.14		
TiO_2	0.25	0.75			6.0
P_2O_5	0.03	~ 0.04	—	—	—
MnO	0.05	0.10			
B_2O_3				11.1	9.5
ZnO				21.3	—
CuO				—	—
Waste				26.3 (PW-4b)	33.0 (PW-7a)

Discussion Following

WEATHERING OF NATURAL GLASSES

Presented by Thomas Tombrello

Bob Watt - Los Alamos, private citizen
Question:
What is the composition of the obsidian shown on the slide?

Tombrello
Response:
It is 75 percent silicon dioxide, on the order of 6 to 8 percent akla-line metal oxides, small amounts--10 to 12 percent--aluminum oxide, hydrogen at a few tenths of a percent, and calcium at about a percent. Also, a few percent of a lot of things, and variable. There really is no such thing as a standard of obsidian. It is a natural product.

Pedro Macedo - Catholic University of America
Comment:
We do make glass with the composition of tektites at Catholic University. We can incorporate about 15 to 20 weight percent nuclear waste. The way we do it is by starting with a porous silica material into which we incorporate the nuclear waste by simple aqueous chemistry techniques and then after drying, collapse to a monolithic non-porous glass structure whose leaching rates are approximately 0.5×10^{-9} grams per square centimeter per day.

Tombrello
Response:
Very good. That is within the range of a natural tektite, certainly.

Macedo
Comment:
We have looked at exfoliation. Exfoliation comes basically when there is a change in volume due to hydration that is big enough to cause the stress to pop the surface off. That has to do with the amount of alkali present. The difference between the obsidian that you did and the tektite is that you decreased the amount of alkali, so you decreased the swelling and it just can stand there.

Tombrello
Response:
That is certainly true for tektites. If you have managed to make them, have you made them with as low a hydrogen content, for example, and does that affect the properties?

Macedo
Comment:
I really thought that was going to be the case. We did this leach study as a function of water content and the water content dropped down.

I think our lowest was roughly 20 ppm's and our highest was 2000 ppm's. No change in leach rate.

David Martin - Iowa State University
Question:
My question is related to the one that Dr, Macedo just asked. Why does exfoliation occur at 20 microns rather than 5 microns or 100 microns? The stress state for a thin layer is the same regardless of the thickness of the layers. Is that not the case?

Tombrello
Response:
It is not clear that it is a uniform sort of thing that always occurs at the same place. My guess is it tends to occur because of non-uniformities, and that if you look at a real sample things will tend to flake off at different thicknesses. But one seldom finds thicknesses that are greater than about 20 microns in natural samples, so I use that as a standard number.

Bob Watt - Los Alamos, private citizen
Question:
Relative to hydrogen not affecting reaction rate of tektites, I am curious whether the strain field, namely the compressive state from the center to the outside of the tektite, has been measured and is known not to have an effect.

Tombrello
Response:
I do not think it has been measured. There has not been a lot of work on tektites with this in mind. Most people were trying to find the source of tektites. They were trying to catalog them. There has not been much on etching or on the induced strain, except from the point of view of trying to understand the aerodynamics of them. One idea was that the etching, the fluted patterns, for example, on the outside, reflected etching of strained regions in them. One was not sure whether the fluting was due to just aerodynamic ablation of material, or whether it occurred afterward on exposure to ground water. The latter is what geologists think, but I do not think it is by any means conclusive.

Bob Watt
Question:
We have seen glass marbles formed by dropping molten glass on steel plates (previous paper by van Geel). I wonder whether their strain might have a similar characteristic to that of the tektites and, if so, whether people have looked at that corrosion rate.

Tombrello
Response:
I do not think so. Not geologists, anyway.

Robert Williams - EPRI
Question:
First, I would like to acknowledge that EPRI has also been quite interested in the porous glass matrix technology insofar as it may offer superior leachability. Secondly, I would like to ask you to acknowledge that to the extent that waste management is a problem, that it is a systems engineering problem in its broadest sense. Would you not concede that other parameters in the waste disposal system might accommodate some of the increase in leachability that you allude to in your concern about super-high leach-resistant glasses?

Tombrello
Response:
I am afraid I have looked at this, as someone said, as a typical university professor. Picking out a single problem and looking at that, not at the whole system. However, I think one might well try to isolate a few of the separate problems. One clearly has to look at the whole system, but at the same time, one has to look at the microstructure of what is going on as a number of papers this morning showed.

The Genie's Bottle

Banquet Address by

Senator Harrison H. Schmitt

New Mexico

December 19, 1978

Nuclear Regulatory Commission

Conference on High Level
Radioactive Solid Waste Forms

THE PROBLEM OF NUCLEAR WASTES

A solution to the problem of nuclear wastes, a solution which is environmentally sound, technically possible, economically feasible and politically acceptable, will be found only if we all use a little common sense.

Let me try to restate the basic elements of the problem:

Nuclear wastes exist in a variety of forms, a variety of potential benefits, and a variety of potential hazards. They will not just go away. More will be created every day for many years to come no matter what we may do about nuclear energy in general.

Even if we stop all nuclear power and nuclear weapon production this instant, the tailings, the low level processing debris, the defense wastes, and the fuel rods would all still exist. Even if we could stuff the nuclear genie back into its bottle, we would have to get rid of the bottle!

Stuffing the genie back into the bottle solves very little and takes away a great deal. It would take away one option we have for removing a <u>nationally</u> dangerous dependency on foreign supplies of petroleum. It would take away one option we have for eliminating an <u>environmentally</u> dangerous dependency on coal and oil.

Until fusion energy, solar energy and new portable fuels such as hydrogen are available as technical and economic alternatives to fossil and fission fuels, uranium, thorium, natural gas and conservation through efficiency are the most acceptable national and environmental means of surviving as a nation. For the next few decades, coal can be and must be utilized, but at environmental costs we all must work to minimize through technology and appropriate substitutes.

But I repeat, uranium, thorium, natural gas and conservation through efficiency are our best environmental friends for many decades to come.

Large quantities of natural gas and uranium are potentially available in and near North America and need only common sense in tax, regulatory and foreign policies to make production of these fuels a reality.

Efficiency is a matter of technology and investment both of which are traditionally American resources.

Finally, in this context, let me emphasize the importance of greatly reducing our dependence on foreign oil in our fight against inflation. The recent increase in oil prices by OPEC and the continual decline in domestic production serve to underline the economic foolishness of the Administration's persistent discouragement of the production of low cost domestic energy.

Management of Nuclear Wastes

The major unknown in an environmentally and economically sound energy policy for the next several decades is the management of nuclear wastes. If we wish to solve them, problems of natural gas and uranium supply have obvious solutions as do problems of plant siting and construction. In the same way, increased conservation through efficiency in general are matters of R&D, investment and national will.

However, there are not yet any obviously acceptable means for long-term management of nuclear wastes.

In the short-term we can continue to provide interim above-ground storage until the right long-term answers are found.

In the long-term there are two general options for the management of these materials. We can reprocess them to extract their useful components and minimize the actual waste or we can try to permanently isolate them in their entirety from the human environment.

Deep geologic disposal of all nuclear waste was first recommended by a National Academy of Sciences panel in 1957. Salt was given as the preferred medium. On the other hand, whole new technologies and understandings of our earth have evolved during the 21 years since this recommendation was made. Thus, our waste management policy is now held captive by recommendations that are more than two decades old.

As a geologist, I personally believe that we will be able to demonstrate that it is technically feasible to safely dispose of wastes in a variety of deep geologic formations. Whether those formations include salt or not will not be clear until the Sandia Laboratory's experiment near Carlsbad, New Mexico, has borne results.

A growing number of geologists feel, however, that there are inherent physical advantages to geologic media other than salt and at least equivalent attention should be put into experiments related to those media. In particular, crystalline rocks, such as granites, and vitric tuffs have some theoretical advantages over salt which should not be ignored.

I am encouraged by the interagency review group's recommendations to this effect.

Nuclear Wastes as a Resource

The nuclear waste management option I consider most exciting, however, is the potential of beneficial utilization of such materials or specific isotopes contained in them. The problem then becomes the more desirable one of "resource" management, rather than "waste" management.

At my request as its ranking Republican member, the Senate Subcommittee on Science, Technology, and Space held four days of hearings on the management of nuclear wastes and the scientific and technological base for their disposal and utilization. The hearings focused on nuclear waste management alternatives, the composition of the waste forms, transportation of the wastes, away-from-reactor storage, reprocessing, and beneficial utilization.

After hearing a good deal of testimony on the subject and talking with a number of people who are already involved, I believe that the utilization of the individual components of nuclear wastes has the potential to supplement significant quantities of our national resource import requirements, provide resources for some new beneficial technologies, as well as making the ultimate management of actual wastes a more manageable problem.

A number of other important conclusions can be drawn from these waste management hearings:

1. Contrary to Administration policy, public utilities do not now consider spent fuel rods as wastes that should be permanently buried. Several witnesses expressed the concern that the energy and other resources that are contained in spent fuel will not be considered worthless by future generations. Some witnesses stated perceptively that simply burying these wastes in the ground now would create a valuable ore deposit to be mined in the future.

2. Reprocessing and tailoring the waste form to fit a particular geologic medium hold the promise of providing a secure barrier to waste mitigation. Crystalline and ceramic hosts for various waste components appear more promising than glass in this regard.

3. Current policy uncertainties about reprocessing and past neglect of many waste management alternatives suggest that interim above ground storage should be utilized until our policy and technology become fully developed.

4. More attention needs to be paid to the transportaton aspects of waste management and the possible conflicts between the jurisditions of the Nuclear Regulatory Commission, the Department of Transportation and states and cities.

5. Photochemical partitioning combined with beneficial utilization is a potential waste management option which should be further developed. Techniques for photo-chemical separation, being examined by the

> Los Alamos Scientific Laboratory and others would contribute significantly to reducing the thermal and radiation output of any actual wastes that remain after reprocessing.

This partitioning technology is particularly worthy of further development.

Perhaps the most obvious resources that could be recovered from nuclear wastes are uranium and plutonium. Unless we can make use of these resources, our dependence on fission energy in the future must be viewed as limited.

Using our present forecasts for uranium requirements and uranium reserves, it has been projected by a recent National Academy study that we will not be able to meet known requirements for the uranium needed by existing and planned reactor systems. It is estimated that shortages of uranium production will be 10% to 20% of the requirements of the 250 conventional nuclear reactors forecasted by the 1990-2000 time period. If we were to recover waste fuel resources for future use in light water reactors uranium requirements could be reduced by 22% and enrichments by 14%.

Some other uses of the resources in waste include the use of cesium^{137} in the treatment of sewage sludge to eliminate pathogens and as a non-carcinogenic means of food preservation; the use of strontium^{90} in power generators in remote locations; the use of krypton^{85} in self-luminous light sources; and the recovery of catalytic metals which could supplement our uncertain sources of foreign supply.

Such partitioning also appears to be applicable to the enhanced recovery of uranium from ores as well as lower cost enrichment procsses. These results would have the beneficial side effects of expanding our uranium resource base, reducing the quantity of undesirable mill tailings and reducing the energy requirements for nuclear fuel production.

In light of the new techniques and possibility for beneficial utilization of nuclear wastes, it is important that in the short-term we look for storage options that allow retrieval of these wastes so that they can, in fact, be turned into resources.

Nuclear Politics

We must also be aware of some political facts of life.

Some citizens in many states, not the least of which is New Mexico, are questioning the advisability of permanent disposal of nuclear wastes within their borders. These citizens, if they are a majority, have the right through appropriate legislative means to withhold their approval for such disposal. We must be prepared to offer them a better alternative to disposal if nuclear energy is to attract the investment of human and economic resources most feel it must.

In addition, the leaders of the other citizens of the world are committed to move forward with nuclear energy and waste reprocessing with or without the United States. Thus, the genie's bottle is broken; it is not just without a cork.

The Administration's hope that our sacrifice of various nuclear options such as reprocessing and breeder reactors will significantly affect nuclear proliferation or the availability of nuclear weapons in the world is wishful thinking at its best and extraordinarily dangerous at its worst.

The commercial and military nuclear race we began is still on. The rules of the race are changing rapidly. If we want to insert our views of nuclear morality and common sense into these new rules we better be the dominant competitor in the contest.

Conclusion

In conclusion, it is safe to say that the genie's bottle is here to stay. We have only begun to explore the waste management alternatives for either disposal or use of this bottle. It is time to bring discussions of all reasonable options to the public and with the public we must realistically assess the potential and risks of each such option.

We must think of not only what must be done for managing nuclear wastes in the next 10 years, but look at the next 20 years, and even 50 years, to assess what future needs will be and what research and development must be done today to make the most attractive options available to meet these needs.

Most of all we must create flexible options. We can never know all that our children will know or need.

PLENARY SESSION III

SPENT FUEL, CRYSTALLINE, AND OTHER FORMS

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CEMENT BASED NUCLEAR WASTE SOLIDIFICATION FORMS

by

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CEMENT BASED NUCLEAR WASTE SOLIDIFICATION FORMS

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Abstract

Cements are major candidates for solidification of low-level, intermediate-level and defense high-level wastes for a combination of reasons including ease of processing, necessity of only low temperature for processing, inexpensive materials required, and the resulting properties of the solidified form. Modified cement processing may be considered as an option for generating waste forms permitting higher thermal loading. Previous and current work on the physical, mechanical and thermal properties; stability; and solubility of the waste forms relevant to their immobilization of RW species is discussed. Optimally processed cement-waste mixtures may constitute a durable low temperature ceramic waste form.

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Introduction

Cementitious composites and concrete (1) are widely used construction materials, and have been extensively utilized in the nuclear industry for reactor structures and shielding. Because of their generally favorable properties, relative ease of the technical processes involved and low cost they have been extensively used in low level nuclear waste solidification.

Two major types of hydraulic cement are used for these purposes: "portland" and "high alumina" cements. Both types of cement can be used as matrices for incorporating primary waste containment forms, which may serve to replace the usual "aggregate" of concrete. When mixed with water, these cements hydrate, causing hardening to form a dense "cement paste," which compares in strength and hardness to many types of natural rock.

The most valuable engineering properties of normal cement pastes, cement composites and concrete are their workability, durability (against atmospheric weathering, chemical attack), watertightness, and dimensional stability (to shrinkage and/or expansion after setting).

The relevant properties of concrete that should be examined when considering its usefulness as a material for incorporating radioactive waste are its ease of forming a monolithic mass, resistance to leaching, thermal stability and conductivity, and radiation stability. Strength development is frequently correlated with other properties; it appears generally to be adequate and may be enhanced by special processing (2). Many of the basic properties of cement paste and concrete --e.g., density, durability, strength, and shrinkage--depend strongly on the porosity of the cement paste matrix, which in turn depends on the amount of water used in processing, which will be discussed later. Volume stability is probably not critical, but in the event that it leads to the formation of microcracks, a decrease in strength and an increase in leachability may occur.

Cement Solidification Processes

A. Summary of Experience

There has been no past experience with commercial high-level waste solidification in a cement or concrete waste form. However, various solidification alternatives have been considered (3,4). Among the alternatives are three that use cement and concrete: 1) conversion to cement and residual salt, 2) shale fracturing, and 3) shale cement. In all three cases the wastes would be stored at the NFS site, West Valley, New York, a federal repository, or both.

1. Conversion to concrete. In this process, the sludge and supernate would first be separated by centrifuge. The sludge would be exposed to a series of drying and washing steps before being finally incorporated as the aggregate into a cement and placed in steel containers. Liquid discharged from the centrifuge would be treated by ion exchange to remove Cs. The Cs-bearing, ion-exchange zeolite would be periodically combined with the dried sludge and incorporated into a cement matrix.

Nine of the 23 alternative plans discussed in a recently published report (5) on the alternatives for long-term management of dense HLW at the Savannah River Plant consider the use of concrete for waste solidification. (The average chemical composition of fresh HLW from the Savannah River Plant is shown in Table 1.) In all nine cases, the cement, Cs-zeolite, and dried sludge will be combined in a concrete mixer with water, and poured into carbon steel containers 2 ft (0.6 m) in diameter by 10 ft (3 m) high. The welded, inspected, and decontaminated canisters will be deposited at onsite or offsite disposal localities. Each canister would consist of 200 gal (760 liter) of concrete containing 36.4 kCi (0.182 KCi/gal) of ^{90}Sr-^{137}Cs with a heat output of 209 watts. The conceptual waste solidification process is shown in Figure 1.

2. Shale fracturing. In this technique, a grout consisting of liquid sludge, or dried sludge waste forms mixed with a blend of cement and other additives is pumped down a well and injected into a shale formation. The shale is first fractured by pressure from a small volume of water, and the grout is then injected into the initial fracture. As the crack propagates, it is filled with grout. Injection continues until the batch of waste-grout is depleted. The grout sets a few hours

TABLE 1. Average Chemical Composition of Fresh SRP High-Level Wastes.

Constituent	Molar concentration
$NaNO_3$	3.3
$NaNO_2$	<0.2
$NaAl(OH)_4$	0.5
NaOH	1.0
Na_2CO_3	0.1
Na_2SO_4	0.3
$Fe(OH)_3$	0.07
MnO_2	0.02
$Hg(OH)_2$	0.002
Other Solids	0.13[a]

[a] Assuming an average molecular weight of 60. Source: U.S. ERDA (5).

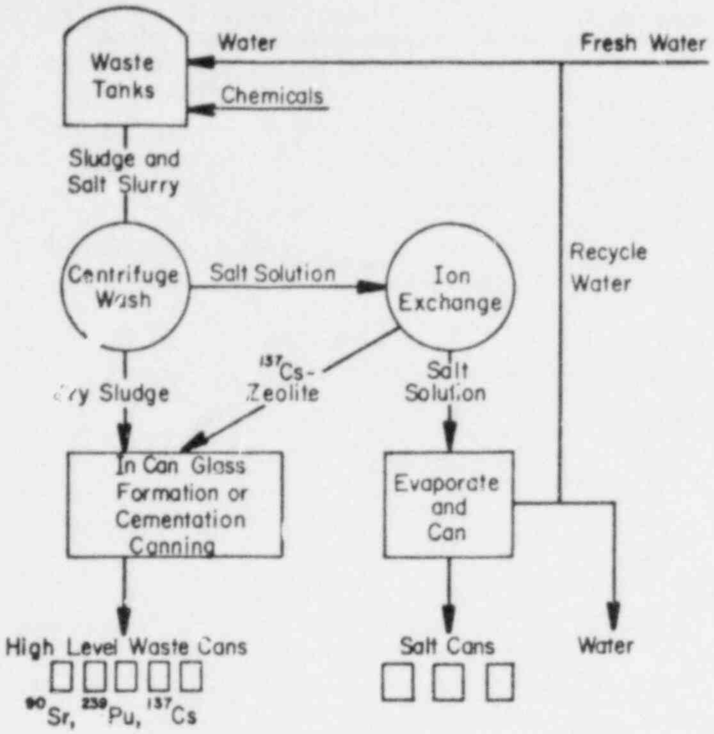

FIG. 1. Conceptual Waste Solidification Process. Source: U.S. ERDA (5).

after injection, permanently fixing the radioactive waste in a rock-like sheet of cement composite within the shale formation. Subsequent injections ideally form sheets parallel to and a few feet above the first.

The shale fracturing technique is illustrated in Figure 2. This process has been successfully used at Oak Ridge National Laboratory for permanent disposal of locally-generated intermediate-level waste (ILW) solutions.

3. Shale cement process. This concept involves a process carried out at ambient temperature, and entails combining the liquid wastes with an appropriate mixture of cement and solid mineral additives, including a Cs sorbent such as Conasauga shale, to form a grout. The grout is then pumped into drums where it solidifies, and the drums are stored in a retrievable manner. At present, the shale cement option is only a laboratory tested process.

Each of the above alternatives has its advantages and disadvantages, but they constitute two major process possibilities plus a number of sub-options. Additional discussion of the cement concepts and alternatives is given in a recent NAS/NAE report (6).

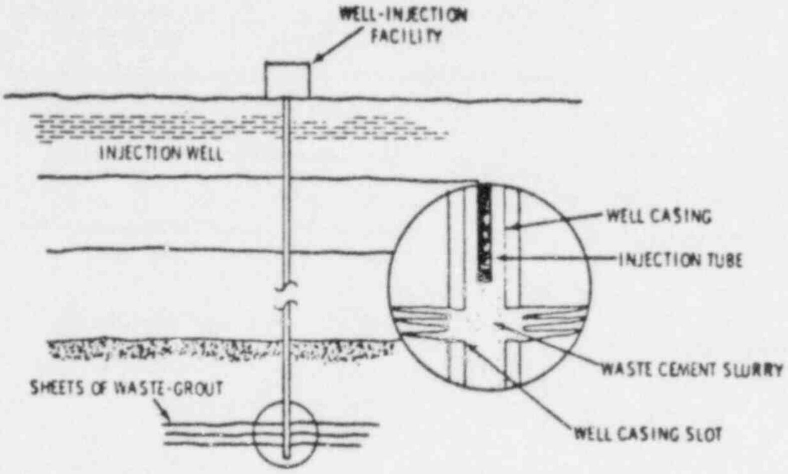

FIG. 2. Shale Fracturing and Grout Concept. Source: U.S. NRC (4).

B. Reactor Wastes and Defense Wastes

The majority of low- and intermediate-level wastes upon which R&D has been conducted for potential cement solidification processes, are various reactor wastes and defense wastes. Miscellaneous liquid and sludge low-level wastes from LWR and BWR waste treatments have been considered in a number of places (7,8) for solidification in cement. As mentioned before, Oak Ridge National Laboratory (ORNL) has used cement solidification processing extensively, having blended over one million gallons (3.8 million liters) of intermediate-level waste solution with cement and clays and injected the waste mixture into cracks produced in shale formations (9,10). The ILW is composed of a mixture of all the liquid wastes produced in hot-cell, pilot plant, and reactor operations. The beta-gamma activity after concentration of the solution is generally ≤ 2 Ci/gal (0.5 Ci/liter) with ^{137}Cs being the major radionuclide; alpha activity is ~ 1 mCi/gal (0.25m Ci/liter (11). Aqueous sodium nitrate waste based on neutralized Allied-General Nuclear Services (AGNS) acid fuel reprocessing waste has been investigated at Brookhaven National Laboratory (BNL) for incorporation in concrete (8a, b). AGNS neutralized waste is 2.5 $\underline{M}$ $NaNO_3$ with $\sim 1\times10^{-4}$ $\underline{M}$ cesium and strontium.

Defense high-level radioactive wastes are stored in underground tanks as alkaline liquids with precipitated sludge layers at Savannah River (12) and Hanford (14,15). After the radioactivity decay heat has diminished to an acceptable level, water is evaporated from the liquid waste to form salt cake to reduce volume and mobility. The radioactive liquid waste at Idaho Chemical Processing Plant is presently being converted to a granular calcine, then stored in underground, stainless steel bins in reinforced concrete vaults (13).

Studies on incorporation of simulated SRP waste in concrete have been conducted by Savannah River Laboratory (16) and by Brookhaven National Laboratory (8). These sludges are hydrous oxides of the base metals formed by caustic precipitation from metal nitrate solutions. Each sludge also contained ∿400 ppm strontium.

Following initial studies with simulated SRP waste sludges, SRL incorporated actual radioactive sludges in concrete on a lab-scale basis (17,18). The sludges were removed from three tanks at SRP. The major radionuclide activity in the sludges is contributed by ^{90}Sr which ranges from 16 to 75 mCi/g. Gross alpha activity ranges from ∿0.1 to 0.3 mCi/g.

Incorporation of simulated Hanford wastes in concrete has also been investigated (14,15). Simulated dried Redox and Purex sludges were used in the investigations.

Simulated Idaho Chemical Processing Plant (ICPP) calcine has been incorporated in concrete by Idaho National Engineering Laboratory (INEL)(19,20) and BNL (8a, b).

C. Properties of Cement-Waste Mixes

1. Mixing characteristics. In order to achieve the most favorable properties in the final product, it is desirable as in all concrete formulations to mix the cement with the least water possible, consistent with the requirements of the mixing and placing methods. Workers at SRL treated mixes by the following formula, where the total amount of water required for cement/sludge mixtures can be expressed as:

$$w = w_c + w_s\,[1 + a(s/c)]$$

where w_c = water required by cement,
w_s = water required by sludge,
s/c = weight ratio of sludge to cement,
a = interaction coefficient for each cement-sludge pair.

This equation can also be expressed as:

$$w/c = (w_c/c) + (w_s/s)(s/c) + a(w_s/s)(s/c)^2$$

where w/c = weight ratio of water to cement,
w_c/c water required per gram of cement,
w_s/s = water required per gram of sludge.

An illustration is given in Table 2, which lists parameters calculated for combinations of six types of cement and three simulated SRP waste sludges. The interaction term, a, suggests that some reaction is occurring between cement and sludge when water is added.

TABLE 2. Parameters Calculated for Various Cement-Sludge Combinations.

		SRP Simulated Sludge		
Cement Type	W_s/s	I	II	III
	W_c/c	0.449	0.341	0.229
		Interaction Coefficient, a		
I	0.323	1.49	0.22	1.44
II	0.278	1.07	0.82	0.90
III	0.303	1.21	0.43	1.18
V	0.286	0.45	0.16	1.05
I-P	0.323	0.59	0.46	0.53
HAC	0.257	0.22	0.00	0.60

It was shown that the relative hydrophilic nature of the SRP sludges can be ordered:

sludge I > sludge II > sludge III.

2. Setting time. The addition of waste to cement/water mixtures has been shown to decrease set times (21,17). A "set" is reached when sufficient hydration has taken place to give a mix friable rigidity. The set time of neat portland type II cement (w/c = 0.26) has been measured at ∿188 minutes; addition of certain sludges were found by SRP workers to reduce the set time to as little as 8 minutes. While the behavior is complex, retarders added in small quantity may be used to increase that set time to a week. Set time may be increased by using additional water, but this is generally undesirable. Recent work in this laboratory (22,23) has been carried out to investigate the mechanism of action of water reducing and retarding admixtures.

3. Heat liberation. The setting mechanism of all classes of hydraulic cements is caused by hydration reactions which are exothermic, of greater magnitude in calcium aluminate cements than in portland cements. The magnitude of this effect on the initial cement can be determined; and it will in general be supplemented by effects of exothermic reactions of wetting of dry sludges. In contrast, certain waste solutions tend to retard the setting of cement. Further, there may be a dilution effect lowering the heat effect of hydration, reducing the maximum temperature generated in the early stage. Other factors affect the maximum temperature generated, including the percentage water used in mixing, and the final density of the consolidated composite.

4. Mechanical Properties. Compressive strength and tensile strength of hardened cement pastes are normally a function of water/cement ratio (2,17) composition, as well as curing time, conditions, and temperature. The composition must exhibit sufficient strength to withstand handling, transportation, and possible accident situations without major damage. But also, other favored properties are generally associated with high strength. Addition of a waste form by many has been shown to decrease the strength of the hardened composite, though this is not always the case. Investigators using a simulated sludge containing 50 mole % iron oxide, 50% aluminum oxide (hydrous) reported the following data for compressive strengths (17), as shown in Figure 3.

5. Leachability. One of the important properties of any waste form is its leachability with respect to the RW species contained: i.e., the lower the leachability (17,24,25) the less the potential risk. One of the most simple expressions used for leachability is the expression as L, in g $cm^{-2}d^{-1}$:

$$L = \frac{1}{FA}\frac{\Delta m}{\Delta t}$$

where F = weight fraction of species in the leach specimen,
A = surface area of the leach specimen,
Δm = mass of species leached during time t,
Δt = time interval between changes of leachant.

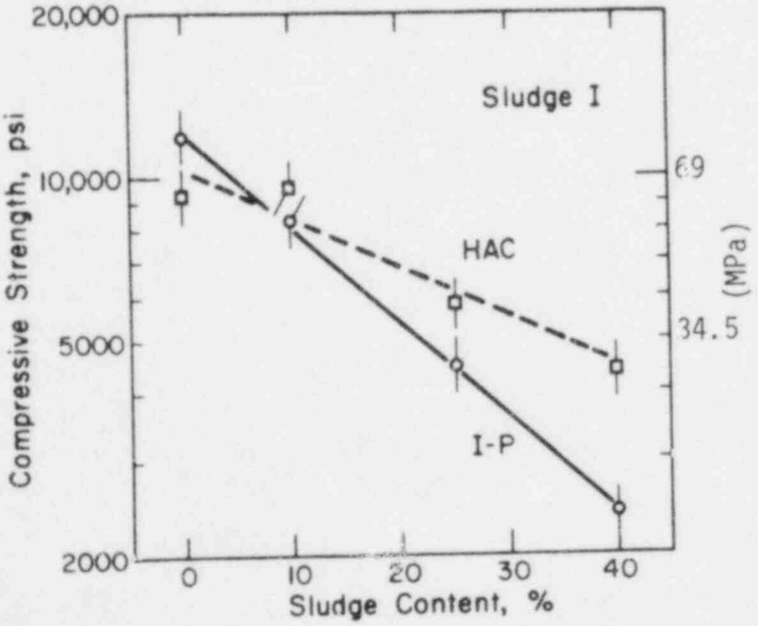

FIG. 3. Compressive Strength of Concrete-Sludge Specimens. HAC = High alumina cement; I-P = portland-pozzolanic cement.

TABLE 3. Chemical Composition of Washed, Dried SRP Waste Sludges.

Element[a]	Wt % (mol %)[b] in sludges from SRP tanks Tank 5
Fe	27.5 (39.6)
Mn	10.8 (15.9)
Al	1.5 (4.6)
U	15.4 (5.2)
Na	6.1 (21.6)
Ca	0.6 (1.3)
Hg	0.1 (-)
Ni	5.0 (7.1)

[a] Major elements only.

[b] Calculated from sum of elements without O, N, or C.

Cesium, strontium, and alpha emitters are the species of grestest concern in radioactive waste solidification and have received the largest attention concerning their leachability (17,18,26). Other species in cement/waste composites that have been leach tested are sodium nitrate (17) and iodine (27).

Illustrations of the usual form in which leach data are presented are given in the following figures, in which leachabilities are presented first of cement-waste mixes [actual sludge 5, SRL (17)], the composition of which is given in Table 3. The order of comparison of the leachabilities of the three types of RW species is always about the same, although they may be affected somewhat by additives (Figure 4). Figure 5 shows also the total cumulative fraction leached as a function of time, which is expressed for Sr from sludge III (composition given in Table 2) in the data of Figure 5 (16,17). Often, less than 0.01% ^{90}Sr and 0.001% alpha emitters were leached from small specimens in six weeks.

The leachability of Cs was decreased by initially adsorbing it in a zeolite, and then incorporating it into the cement-simulated sludge mixes, as shown in Figure 6. This illustrates that it is possible to decrease the leachability by more than two orders of magnitude when a type I-P cement is used to incorporate the Cs-zeolite and sludge (Figure 6).

Typical compositions of waste sludges which are under investigation for disposal by hydrofracturing techniques at ORNL are given in Table 4 (28), while proportions including cements, clays, etc. which were commonly used are shown in Table 5. While varying in compositional detail from

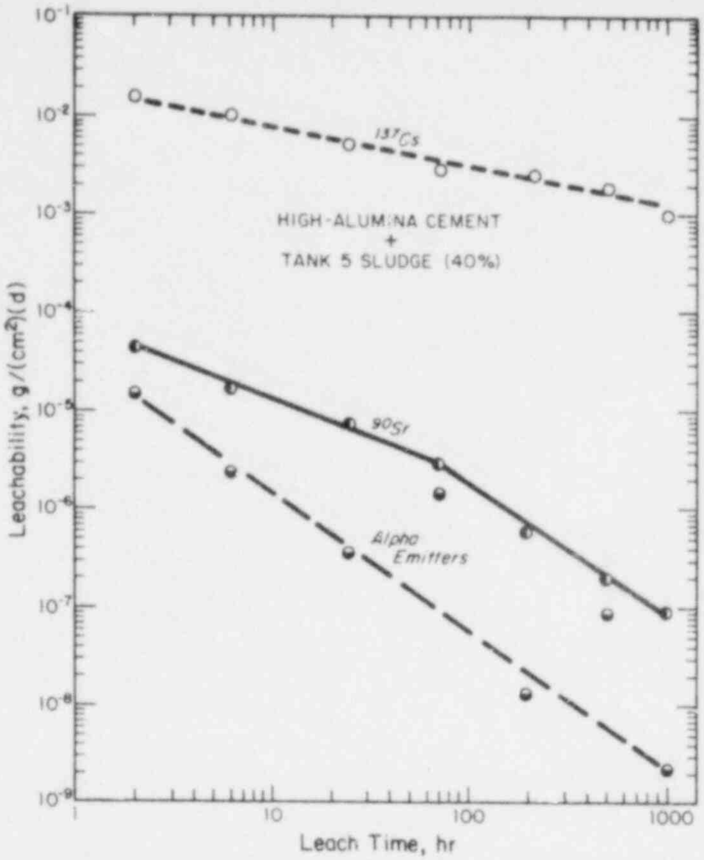

FIG. 4. Typical Leachabilities of Radioactive Concrete Waste Forms.

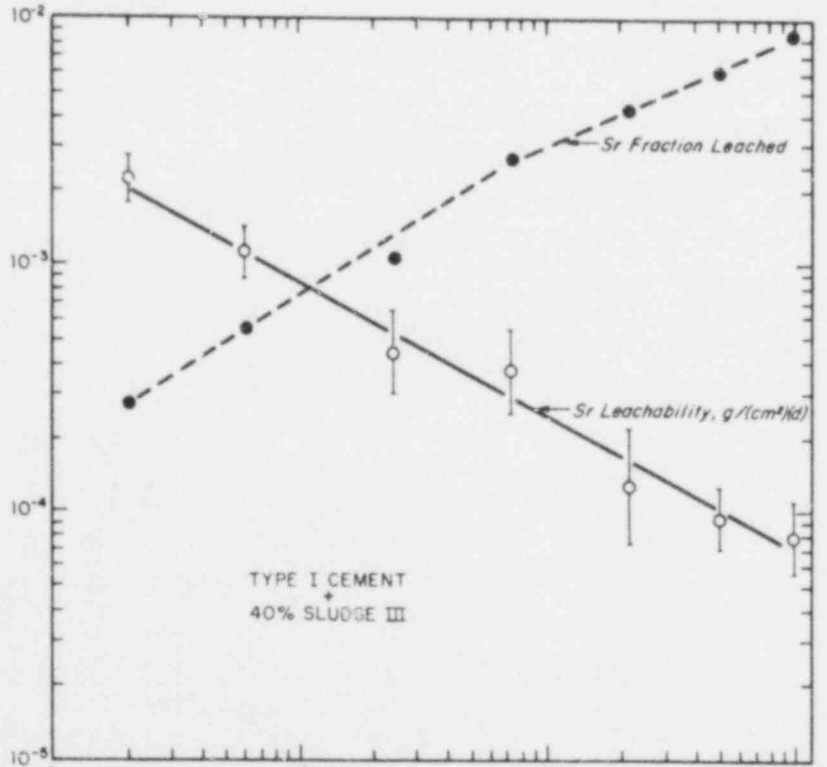

FIG. 5. Typical Leach Test Results.

the SRL sludges and also in the nature of the additives used, the Cs leachabilities were shown similarly to be improved by use of selected additives.

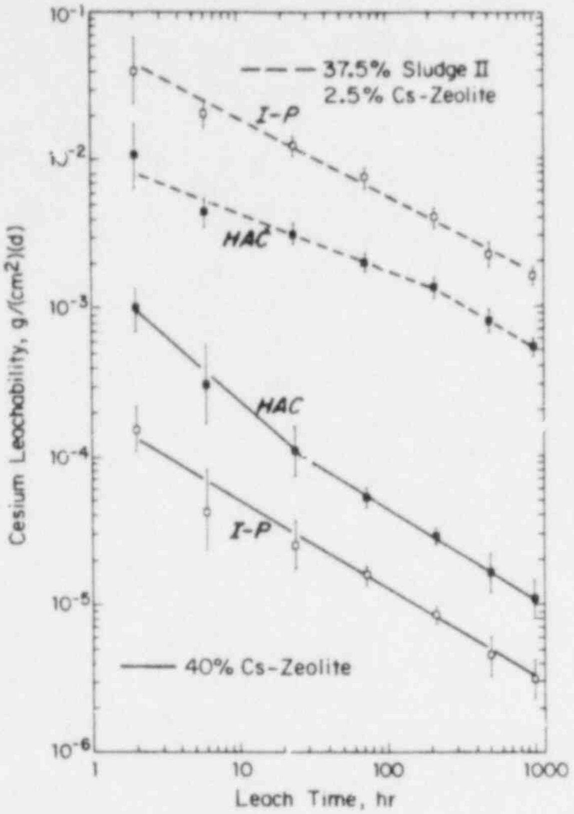

FIG. 6. Cesium Leachability of Concrete Waste Forms Containing Cs-Zeolite.

TABLE 4. Composition of ORNL Waste Sludge.

Cation*	wt %
Iron	10-50
Aluminum	0-7
Lead	0-1
Chromium	0-1
Calcium	0-1.5

*Present as hydrated oxides and insoluble compounds combined with 0-30 wt % water-soluble material.

TABLE 5. Composition of Hydrofracture Sludge Grout.

Component	Content in grout (wt %)
Cement	27.2
Fly ash	12.6
Indian Red Clay (or Conasauga Shale)	2.1
Simulated sludge	8.8
Water	49.0

Data presented by ORNL researchers (10) for Cs leachability from the hydrofracture grout compositions showed the possibility of decreasing the leachability by 2-3 orders of magnitude by use of the proper sorption additives (11) as shown in Figure 7. Most data were measured on samples initially cured for 28 days.

The leachability data of various radionuclides are also presented in a different manner, fitted to a diffusion equation (29). A theoretical expression was developed which correlated the cumulative fraction of a species that had left the waste solid in time t:

$$\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right) = 2\left(\frac{D_e}{\pi}\right)^{1/2}\left(t\right)^{1/2},$$

where $\frac{\Sigma a_n}{A_o}$ = total fraction removed,
V = volume of the specimen (cm^3),
S = surface area exposed to leachant (cm^2),
D_e = modified effective diffusivity (cm^2/s),
t = time(s).

For example, data obtained for cesium leached from a hydrofracture grout specimen were fitted to the above equation to give a D_e of 1.2×10^{-9} cm^2/sec. Studies on simulated as well as actual hydrofracture grout showed that the effective diffusivity of strontium was in the order of 10^{-10} cm^2/sec. An example illustrates the significance of an effective diffusivity of 1×10^{-10} cm^2/sec; with a 200-liter drum filled with this concrete and all surfaces exposed to running distilled water for one year. Using recent data on fixation of Iodine-129 in such grouts (27) it would mean that only about 0.7% of the total initial iodine would be removed from the concrete during this period.

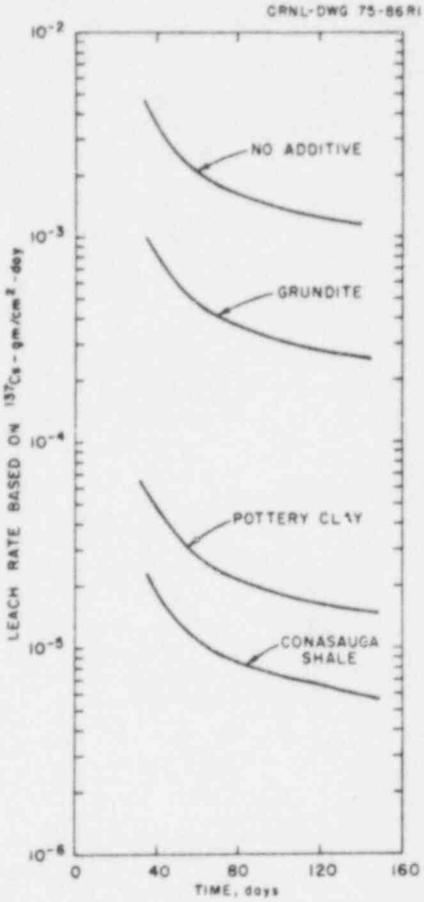

FIG. 7. Leach Rates of ^{137}Cs from Grouts with Various Mix Additives.

One of the important aspects of the studies is a comparison of the leach rate with that obtained by other forms. Results of the hydrofracture grout studies associated with the disposal of intermediate-level radioactive liquid waste showed that grouts can provide leach rates comparable to those obtained for waste incorporated into borosilicate glass. Figure 8 compares the predicted amounts of cesium leached from a grout containing Conasauga shale (28) (to fix the cesium) with those for a borosilicate glass. At short times a slightly smaller fraction of cesium is leached from the glass product than from the grout, whereas at long times a smaller fraction is leached from the grout product than from the glass.

Results of BNL research (8b) on low-heat generating high-level waste using a cement-vermiculite or cement-zeolite process, presented Cs and Sr release data, as well as those of $NaNO_3$ leaching. For the latter composites, type II portland cements proved to be somewhat superior to high-alumina cements. Polymer impregnation further improved the properties by 1-2 orders of magnitude (30).

An earlier report (7) describes international work on cement solidification of low- and intermediate-level waste, including in the UK, in the USSR, Czechoslovakia, Italy (31), France and Germany. Limited tests on the leachability and other properties of waste-cement products have been performed in Japan (32-34), related partly to possible sea disposal.

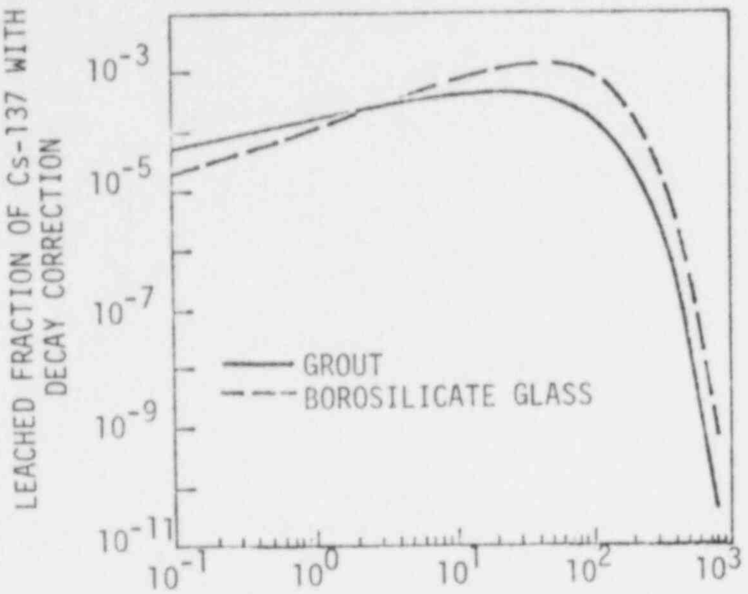

FIG. 8. Comparison of Calculated Amounts of ^{137}Cs Leached from a Borosilicate Glass and a Cementitious Grout.

Recent work from Germany (35) has used bentonite-containing cement grouts for reducing Cs leachability, while Sr leaching was improved by making a dense block.

6. Thermal Properties. Thermal stability of cement forms has been discussed in detail by others (17,8). There is considerable variation in thermal stability of cement composites, depending upon composition, microstructures, heating rate and other factors.

Thermal conductivity of typical cement pastes may range around 0.6 $Wm^{-1}K^{-1}$ (contrasted with glasses of 0.9 - 1.3 $Wm^{-1}K^{-1}$)(36,37). This limits the heat transfer, and requires lower thermal loading of the cementitious materials. An option is to increase the conductivity by densification of the solid. Research on special high density cements (a true low temperature ceramic) is described in the next section.

7. Special Low Temperature Ceramic/Cement Waste Form. Work at The Pennsylvania State University with cement pastes processed at elevated temperatures and pressures resulted in synthesis of materials with ununusually high strength (up to 10 times that of normal cements), high density, and very low porosity. Such materials, having already been processed at relatively high temperatures, appeared to have special potential for radioactive waste isolation and disposal (38).

TABLE 6. Atomic Concentrations of Cations in Calcined Simulated HLW.*

Atom	PW-6 (at.%)	PW-4b (at.)
Fe	16.9	14.3
Na	60.5	--
RE	6.4	27.8
Mo	3.5	15.4
Zr	3.2	13.9
Cr	1.4	1.5
Ni	1.6	4.8
Cs	1.6	7.1
U	1.9	2.6
Sr	0.8	3.6
Ba	0.8	3.6
K	0.3	1.3
Co	0.3	1.3
Te	0.4	1.6
P	0.2	0.6
Ag	0.1	0.3
Cd	0.1	0.3
	100.0	100.0

*Supplied by John Mendel, Battelle-Pacific Northwest Laboratories; calcined at 773K (500°C); XRD shows major $NaNO_3$ in PW-6.

Very modest temperatures [from the standpoint of ease in processing--in the range from 373 to 573K (100 to 300°C)] were used for the cement hot pressing. The products have very low permeability, very low porosities ($\sim$3%) compared with normally hardened pastes (20 to 40%), and superior volume stability and thermal stability. Two different simulated waste compositions (calcines) studied are given in Table 6: PW-6 and PW-4b analyses [after firing at 773K (500°C) for one hour]. For some experiments, a sample of PW-6 that had been heated to 973K (700°C) for 7 hours to remove much of the nitrate was used (38).

The cements used included Portland cements (ASTM Types I, III, and V) and non-Portland hydraulic cements (white, calcium aluminate, regulated-set, and expansive). Compositions and properties of these different cements and other details are given in Refs. (39,40).

Small cylindrical specimens were prepared by hot pressing of cement and

TABLE 7. Tensile Strength (Splitting) of PW-4c Specimens Mixed with Different Ratios of Cement, and Hot Pressed at 423K (150°C), 345 MPa (50,000 psi), for 0.5 hours.*

Sample Composition		Splitting Strength		w/c Ratio[a]	w/s Ratio[b]
% Cement*	% PW-4C[†]	MPa	(psi)		
100	0	34.0	4850[c]	---	0.10
90	10	35.5	5147	0.100	0.11
80	20	28.0	4080	0.02	0.10
70	30	26.4	3820	0.071	0.10
60	40	15.2	2206	0.062	0.10
50	50	13.5	1955	0.059	0.10

*High-alumina cement.

[†] Similar to PW-4b.

[a] Water/cement ratio.

[b] Water/solid ratio.

[c] Calculated from the compressive strength. (Tensile splitting strength is $\sim$0.10 compressive strength.)

waste in two configurations: one mixed with the waste, and a second in which the waste was segregated in the core, either as loose powder or as a pellet. Typical tensile strengths (ca 0.1 x compressive strength) are given in Table 7, where they are seen to be 5-10 times those of normal cements. They were shown to be generally thermally stable (to fracturing).

Various accelerated leach tests (38) were performed, and the high density forms shown to have considerable improvement over normal cements, for they were even relatively acid-resistant. PW-6, which contained substantial $NaNO_3$, was in some cases successfully encapsulated.

Work is continuing to study the potential of alternate "low-temperature ceramic" processing at normal to slightly elevated T,p ambient, at lower pressures but at elevated temperatures, with the goal of attaining properties similar to those reported herein, and under various intermediate conditions.

Recent work has begun to address the preparation of low temperature ceramic waste forms incorporating supercalcine waste, one example of which is given in Table 8.

TABLE 8. Compositions of Supercalcine 77.25.

Oxide	wt %	Oxide	wt %
RE_2O_3	19.6	U_3O_8	11.0
ZrO_2	4.2	Fe_2O_3	2.6
MoO_3	4.5	Cr_2O_3	0.3
SrO	0.9	NiO	0.1
BaO	1.3		
Cs_2O	2.5	CaO	1.0
Rb_2O	0.3	Al_2O_3	16.25
CdO	0.1	SiO_2	22.45
Ag_2O	0.1		
Na_2O	5.9		
P_2O_5	6.9		

Twenty percent of the simulated waste was blended with different cements, a type III and a high-alumina cement, and comparisons were made between the effects of normal treatment and hot pressing [at 250°C (523K) and 50,000 psi (345 MPa)] preparations. Strengths of the hot pressed samples were very high, as expected, although the others were adequate. Accelerated hydrothermal "leaching" tests were performed at 200 and 300°C (473 and 573K). In deionized water the alpha-emitter simulators were almost undetected, Sr was found to be relatively low, but somewhat variable, dependent upon experimental parameters, and Cs was larger, as expected. Other elements such as Mo and Cr varied in somewhat unusual manners. Experiments are also in progress using high p/T brines as leachant, which in most instances are more corrosive, but there are exceptions. The preliminary results are thus very encouraging-especially in deionized water, and, in some respects, in the brines as well. Other less rigorous processing conditions may be potentially useful as well (42).

8. ORNL Studies. Researchers at ORNL (28) are conducting preliminary scoping experiments to determine the effects of high temperature and pressure on fresh hydrofracture-type grouts containing a simulated waste material composed of hydrated oxides of iron, aluminum, and lead. Durable, homogeneous specimens were prepared with either type I or type III Portland cement by subjecting the wet mixes to 1600 psi and 250°C for 24 hours (see Table 9). Qualitatively, the resulting specimens appeared to be quite stable. No apparent deterioration was observed after heating at 200°C in air for several weeks or after being submerged in a brine solution at 217°C and 300 psi for 72 hours, and further durability tests are now in progress. Continued studies are in progress.

9. Other Relevant Investigations. Radiolysis. It is well known (43) that water is subject to radiolytic decomposition; and that under certain

TABLE 9. High-temperature, High-pressure Grout Formation.

Component	Content in grout (wt %)
Cement	44
Fly ash	10
Clay	10
Simulated waste	16
Water	20

conditions also the gaseous decomposition products undergo recombination. Gases produced by in situ radiolysis of water within concrete in sealed, solidified nuclear wastes during long-term storage could conceivably breach containment. Therefore, candidate waste forms (matrices containing simulated nuclear wastes) were irradiated with ^{60}Co-gamma and ^{244}Cm-alpha radiation. For cement waste forms exposed to gamma radiolysis, an equilibrium hydrogen pressure of 6 to 7 psi was reached that was dependent on dose rate.

It was calculated (44) that alpha radiolysis, which will predominate after about 300 years, may cause a final hydrogen pressure of as high as 1,600 psi after approximately 10^5 years. Oxygen pressure may reach 300 psi. However, for the first several hundred years, the results suggest that radiolytic pressurization in sealed containers of concrete plus SRP wastes will be low. Furthermore, these high pressures may never be reached in the presence of elevated temperatures and a gamma radiation field. The effects are compositionally dependent, and also vary with dose rate; therefore relatively long period tests utilizing relevant composition ranges at relatively low dose rates are needed in order to determine the best procedures for designing specific cement-waste forms.

Experience in the USSR. Cementation techniques have been utilized for a long time in the Soviet Union (45) for disposing of low-level nuclear wastes. Liquid wastes are mixed with portland cement to produce a monolith. Because of the expense of transport, however, a preferred disposal method has been to introduce liquid wastes into deep geological strata collectors, which include favorable geologic structures, and mineralogies including clays, feldspars and other mineral species which are adequate sorbents of the radionuclides. Monitoring of local temperature build up, and through wells at distance are used to control the amount of waste acceptableand prevent transport to the biosphere (46).

Discussion

A summary statement from the recent NAS/NAE Report by the Panel on Waste

Solidification (6) (pp. 133-137) provides an evaluation of the status of the R&D on the cement/concrete waste forms. A brief excerpt stresses the vital point:

> "The results of laboratory work described above, especially those from Oak Ridge, INEL, SRP, Brookhaven, and Pennsylvania State University all suggest that a cement-based composite for incorporating HLSW is a workable, simple, and tested option."

There are apparent advantages and disadvantages, and some remaining uncertainties that must be answered before the possibilities and limits of applicability of a cement or low temperature ceramic waste form can be established. Table 10, below, adapted from the Panel's report (6) summarizes some of the apparent advantages and disadvantages, of which the balance is strongly weighted toward the former. The table also presents some of the areas within which more fundamental information is needed.

Conclusions

Within the cement or low temperature ceramic waste form there are a number of sub-options which can be developed. The form selected must be tailored for the specific waste composition, and also for its potential final storage site. Table 11, also adapted from the Panel's report (6), provides a matrix of some (but by no means all) of the process options, process parameters, and certain of the important property parameters. Future R&D should be directed to development of composites which will enable maximizing the waste loading while improving the composite properties to minimize the potential for leaching of the contained waste. The development involved in such optimization will also have a pay-off in the field of low-level waste management.

TABLE 10. Advantages and Disadvantages of Cement Waste Form.

Cement Waste Form Advantages:

1. Employs lowest solidification processing temperatures
2. Simple remote-control processing is possible
3. Can be pressure-injected into geological formations
4. Mixtures can be embedded into metal or concrete containers
5. Cost is low

Disadvantages:

High strength requires temperatures below 350-500°C
(Under some conditions) leachability is higher
Question of radiolysis is not yet settled: needs more work

TABLE 11. Process-Property Matrix.[a]

Parameters	Grouting	Cast Concrete	Pelletization
<u>Process Parameters</u>			
Complexity	Mixing-Transport/ Injection	Mixing-Transport-Curing: Possibly Polymer Impregnate	Mixing-Pelletization-Transport: May Impregnate or Transport in Metal Containers
Maximum Temperature	Ambient	Ambient or Steam Curing (or Pressing)	Ambient
Ease of Remote Operation	High	High	Medium
<u>Property Parameters</u>			
Leachability[b,c]	Medium	Potentially Low; Low*	Potentially Low
Thermal Conductivity	Low	Low	Low
Thermal Stability	Very good up to approximately 300°C; Complete loss of strength between 500-900°C		
Dispersibility	Medium to Low	Low	Low

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[a] Comparisons are relative to glass.

[b] Depends on density of cement product.

[c] Some difference between portland and high-alumina cements.

*Low temperature ceramic form.

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Discussion Following

CEMENT BASED NUCLEAR WASTE SOLIDIFICATION FORMS

Presented by Della Roy

Robert Leachman - NRC
Question:
I should like to get a clarification of one thing. I understand that there is considerable experience for disposal of intermediate-level waste at ORNL. The number I vaguely recall is that they have injected something like 0.6 megacuries, which is a rather large amount of activity, approaching 1 percent of the total inventory of radioactivity in waste materials. I also have a rather vague recollection that the specific activity is not too dissimilar from the defense waste. My question is: if these numbers are right, does this constitute somewhat relevant experience for disposal of defense waste by the grout method?

Della Roy
Response:
Yes. I think the latter statement is true. I think that the level is approximately right. I have quoted the figures in the written report, but will not try to find them right now. A very large amount of activity has been injected there. There has been very careful monitoring in wells to see that there has not been transport of the nuclides. Control specimens have also been made in the laboratory, and samples have been prepared at the same time as preparing the grout, so there is adequate control work carried out. Activity is certainly in the range of the aged defense waste or, if commercial waste were stored for a while, the thermal loading might be somewhat similar.

Ray Blanco - Oak Ridge National Laboratories
Comment:
I do not think you can compare the intermediate-level waste disposed at ORNL, or low-level waste I should say, with the DOE waste. The alpha content of the ORNL waste is less than 10 nanocuries per gram. Thus, it is not comparable with DOE waste. As you said, it contains around 1 curie of cesium per gallon. You did not quite describe the operations at ORNL correctly. All of the liquid wastes at ORNL are concentrated by precipitation with alkali, the supernate evaporated, and the concentrate disposed of by hydrofracture.

Della Roy
Response:
I was quoting directly from a report that may not have contained complete information. I appreciate your clarification.

Blanco
Comment:
Only very small amounts of higher level waste are produced. They are not handled directly. They are mixed with all of the other wastes. I think that may be a little confusing.

Della Roy
Response:
And the distinction that the transuranics are very low is important.

Leachman
Question:
I should like to ask another question. In the National Academy of Sciences' report they speak of supergrout just as you did. What is the range of experience with supergrout? Is this a limited laboratory-tested concept or does it have testing equal to the other concepts?

Della Roy
Response:
As a broad concept, to some extent you could consider any of the grouts that have incorporated special additives other than just the waste form and the cement to be a form of supergrout if they have some component that is added especially to tie up the waste. There are other approaches including other processing steps that may be taken. Densification that would minimize porosity, leachability, or simply physical transport is another way of generating the same characteristics.

Leachman
Question:
Do I understand, then, that the ORNL experience, where they put various clays in, is one aspect of what you are terming supergrout? Do I also understand that there could be other things that are, as of yet, untested in the field?

Della Roy
Response:
Yes, I think it is true that there are other possibilities untested in the field. I think that the ORNL work is certainly the best example of the demonstrated technology, while the other is, so far, just laboratory demonstrated.

Blanco
Comment:
Dr. Roy has summarized this work very well, but I would like to add a couple of items. Two of the problems that people have mentioned with concrete are the radiolysis of the free water, which was mentioned by the speaker, and the release of the free water with a rise in temperature. We are trying to do something about these problems by removing the free water by heating the concrete at about 250°C for about 15 to 18 hours. We can remove the free water. This will decrease the amount of radiolysis and prevent the release of water vapor with an increase in temperature. We are also finding that these concretes, that have additives to hold the radionuclides, have good catalytic properties in recombining hydrogen and oxygen. We are not ready to publish the results yet, but we are startled by the very fast rate of recombination. So we are very hopeful that these two items that have hampered the use of concrete for higher levels of waste can be overcome.

Della Roy
Response:
I am delighted to hear you say that. I was aware that the work was going on. I have heard of those results orally, but I did not want to commit anything in writing that was just verbal communication. I am delighted that you could give us that information firsthand.

Robert Pohl - Cornell University
Question:
Can you comment on the use of cement for stabilizing uranium mill tailings? Any work that you have done or that you are aware of, in particular with regard to long-term stability?

Della Roy
Response:
I think there is potential for such stabilization. Some of our preliminary work with leaching studies--some of the formulations--were very good for uranium. Some were not quite as good. We have not, as yet, finally analyzed all the information. Obviously, you do not want to have uranium in the highly oxidized state. I think, if you can keep it in the reduced state, that would be obviously more desirable. I think it has potential.

I. Eugene Reep - Rockwell, Hanford Operations
Comment:
With reference to your advantages of lower cost, I would caution that we should perhaps go back to the so-called defense waste documents prepared both at Savannah River, Hanford and Idaho. The ones at Hanford and Savannah River included alternatives for the solidification of high-level waste as a concrete or cement form. Where we would have to package the high-level waste for subsequent transportation, handling and placement in a geologic repository, we find that the added waste volumes increase costs in numbers of containers and so forth to the point that these costs more than offset any potentially lower processing costs. However, the risk may be slightly lower, I do not recall. Where the real advantage to concrete comes in, we feel--and we have done some preliminary studies here--is where we handled the waste as a bulk--let us say either in a vault that may be near the surface or let us say underground in a repository that could hold it in a bulk form like pumping it into a tunnel. But if we have to package the waste, it actually turns out to be more expensive.

Della Roy
Response:
Yes, I should have reproduced material from the alternative documents, but I could not get 23 alternatives on one slide.

Bob Watt - Los Alamos, private citizen
Question:
I am curious what might be the activity per gram of grout or some similar number. I did not see it in your notes.

Della Roy
Response:
I have it here. It varies with the waste. I think I had better give you that privately. It will take a little while to find it, but I do have it.

Watt
Question:
There will be a correlated question, for which I guess you would also not have the answer, namely, the thickness of the grout layer and the hazards of somebody putting a well through that particular formation containing grout.

Della Roy
Response:
I think those potential hazards have been considered in the environmental impact statement that is written at ORNL. I do not have a copy of it with me.

Watt
Comment:
But that was for intermediate level.

Della Roy
Response:
Yes.

Watt
Question:
I am wondering whether you have done that for your high-level proposal.

Della Roy
Response:
That has not been done in similar detail for the others, as far as I am aware.

Chauncy Kepford - Environmental Coalition on Nuclear Power
Question:
You mentioned the stabilization of iodine in your grouts and concrete. Could you perhaps suggest how long the iodine might be retained in the matrix. What will be the chemical form?

Della Roy
Response:
The most stable form has been making insoluble barium iodate and incorporating that in the cement. Long-term leaching studies of this form have been made. The indications are that it would have a very slow leach rate and, if not incorporated to very high levels, would be very suitable for sea disposal. Again, I would refer you to the ORNL work on this.

M. Claude Sombret - French Atomic Energy Commission
Question:
If you would allow, I have two questions. The first is a technical one. The other pertains maybe more to philosophy. The first one, Dr. Roy, did you perform your compressive test on the real waste, and if yes, did you measure the variation of the value versus time?

Della Roy
Response:
No. First, all the work we did was on simulated waste but the Savannah River Laboratory work used real waste. I believe that ORNL also used some real waste.

Sombret
Question:
The other question: I am not very well aware of the regulation about the licensing in the U.S., but I wonder if such a product containing 20 percent of water could be acceptable from that standpoint?

Della Roy
Response:
As we indicated, and as Raymond Blanco from ORNL indicated, we want to decrease the amount of molecular water. Most of what is there should be tied up as hydroxyl, which will be quite different.

Sombret
Comment:
You have to fear some radiolysis and evolving of hydrogen. This is exactly the same problem that German people have to face with the incorporation of degrading materials into cements and concrete.

CALCINE PRODUCTION AND MANAGEMENT

by

B. R. Dickey
G. W. Hogg
J. R. Berreth

ABSTRACT

The process technology related to calcination of power reactor wastes is summarized. The primary calcination processes developed are spray calcination, fluidized-bed calcination, and rotary kiln calcination. Calcines from the spray calciner and rotary kiln are fed directly to a glassification process. The fluidized-bed product can either be fed to a waste form conversion process or stored. The major process steps for calcination are feed preparation, calcination and product handling, and off-gas cleanup. Feed systems for the three processes are basically similar. Gravity flow and pump pressurized systems have been used successfully. The major problems are fatigue failure of feed valve bellows, plugging by undissolved solids, and calibration of flowmeters. Process heat input is by electrical resistance heating for the spray and rotary kiln calciners and in-bed combustion or in-bed heat exchange for the fluidized-bed system. Low-melting solids which can cause scaling or solids agglomeration in any of the processes is a major calcination problem; however, feed blending, process operating conditions, and equipment design have successfully controlled solids agglomeration. Primary off-gas cleanup devices for particulates are cyclones, sintered metal filters, venturi scrubbers, and HEPA filters. Scrubbers, condensers, and solid adsorbents are used successfully for volatile ruthenium removal. The years of pilot-plant and plant-scale calcination testing and operation of the three systems have shown that reactor wastes can be calcined safely and practically.

SUMMARY

Calcination processes generally considered to be the most developed are spray calcination, fluidized-bed calcination, and rotary kiln calcination. Calcine produced from these processes can be fed to candidate waste form conversion processes. The major process steps in any calcination process are feed preparation, calcination and product handling, and off-gas cleanup.

The spray calciner and rotary kiln calciner are designed primarily for direct coupling to glassification processes; a fluidized-bed process may be directly coupled to various waste form processes or the calcine can be stored in canisters.

Spray calcination consists of atomizing the liquid wastes into the top of a cylindrical calcining chamber. Process heat is supplied by a multi-zoned electrical resistance heater mounted external to the calciner. Droplets of a nominal 70-μm diameter are required for effective spray drying. The dried and calcined solids leave the bottom of the spray chamber where they either fall into the product removal line or are entrained in the off-gas. Solids in the off-gas are removed by stainless steel sintered metal filters located in the filter chamber. The filters are blown back based on pressure drop across the filters, and the solids are discharged at the bottom of the spray chamber. Additional particulate removal to obtain the required DFs is provided by a venturi scrubber and HEPA filters. Volatile ruthenium, if present in significant quantities, is removed by solid adsorbents. Iodine and NO_x removal would also be considered in a plant-scale calcining facility.

The rotary kiln calciner is a rotating barrel positioned at a slight angle to the horizontal to facilitate the flow of solids through the kiln. Process heat is provided by a multi-zone furnace. Evaporation and drying occurs in the upper portion of the kiln and calcination in the lower portion. Average residence time of solids in the kiln is 30 seconds; solids fall by gravity from the lower end of the kiln into a glass process. Off-gas exhausted from the upper end of the kiln first passes through a wet scrubber for particulate removal. Volatile ruthenium is removed by solid adsorption.

Fluidized-bed calcination occurs by spraying the liquid wastes directly into a fluidized bed of particles at a temperature of 400-500°C. The bed is fluidized by forcing air up through a distributor plate located at the bottom of the bed. Process heat can be supplied by an in-bed heat exchanger or by in-bed combustion of a hydrocarbon fuel. The product consists of both bed particles (0.2-0.7 mm) and fines particles (< 0.2 mm). Solids are discharged continuously or intermittently and may be stored as calcine or fed to other waste form conversion processes. Most of the particulate entrained in the calciner off-gas is removed by a cyclone and venturi scrubber; HEPA filters are normally the final particulate removal device prior to release of the off-gas to the atmosphere. As with the spray and rotary kiln calciners, volatile ruthenium is removed by solid adsorbents. The amount of volatile ruthenium requiring removal is minimized by the reducing atmosphere created by in-bed combustion and the uniform bed temperature of ~500°C.

Basic feed system requirements in any calcination process include capability for feed blending, maintaining undissolved solids in solution, accurate metering and flow control, and resistance to corrosion and erosion. Gravity and pump pressurized feed systems have been used successfully. In the gravity system, feed is transferred by airlift to a constant head feed tank connected to the calciner. Feed then flows by gravity through flow meters, control valves, and to the calciner. A pump-pressurized feed system has been used in the spray calcination process. A slip stream is taken from a pressurized feed circulation loop and fed through small diameter tubing to the atomizing nozzle at the top of the calciner. Major problems experienced with the various feed systems are fatigue failure of metal bellows valves, feed plugging from undissolved solids, and calibration maintenance on flow meters. Operating experience based on operation of various pilot plants and the plant-scale Waste Calcining Facility (WCF) in Idaho has not revealed problems of sufficient magnitude to jeopardize operability of any of the calcination processes.

The primary purpose of waste calcination is to convert the liquid waste to a mixture of oxides. Primary requirements of any calciner are process heat input at rates consistent with the desired capacity, feed introduction compatible with the process, solids generation of the desired form, product removal, and the ability to accept reasonable variations in feed composition. Process heat input by electrical resistance heating and in-bed combustion (fluidized-bed calciner only) have proven reliable. Pneumatic atomizing nozzles, commercially available or modified, are satisfactory for the spray and fluidized-bed calciners. Droplets generated by an internal mix nozzle supplied by Spraying System Company are of the required size (40-70-μm diameter) for drying and calcination in the spray calciner. A standard flat-faced 1/2-J nozzle by Spraying Systems Company has proven adequate for feed introduction, particle size control, and generation of "seed" particles in a fluidized bed. All of the calciners have adequate unit capacity to be compatible with fuel reprocessing waste production rates or calcine feed rates required for the various waste form conversion processes. Low-melting point solids can cause scaling and/or solids agglomeration in any of the calcination processes. Feed blending, process operating conditions, and equipment design have proven adequate for controlling solids agglomeration.

Off-gas cleanup is concerned primarily with particulate removal, volatile fission product removal, and cooling and condensing as required. The off-gas temperature from the calciners is approximately 500°C and must be cooled to the range of 150-200°C. Decontamination factors for particulate and volatile ruthenium in the respective ranges of 10^5 - 10^8 and 10^4 - 10^7 are required. Primary cleanup devices used or proposed for plant-scale systems include cyclones, sintered metal filters, venturi scrubbers, and HEPA filters for particulate removal and scrubbers, condensers, and solid adsorbents for volatile ruthenium removal. With the exception of the sintered metal and HEPA filters, the particulate removal devices are based on many years of industrial experience. Sintered metal filters are reliable and practical for the relatively small off-gas flows from the spray and rotary kiln calciners; use of sintered metal filters for a large volume off-gas system such as the fluidized bed is questionable. Use of HEPA filters for particulate removal in all the off-gas systems is for final cleanup prior to stack release; the primary particulate cleanup devices are the cyclone, sintered metal filters, and wet scrubbers. Control of volatile ruthenium to ALARA limits is dependent primarily on minimizing the formation during calcination and removal of the volatile ruthenium leaving in the calciner off-gas. Various solid adsorbents such as silica gel, ferric oxide, and hydrous zirconium oxide are effective in removing volatile ruthenium. Plate-out of volatile fission products, particularly ruthenium, must be controlled to prevent major operating problems.

Materials of construction, though often neglected, is one of the most important areas that must be addressed if process reliability is to be obtained. Based on pilot-plant and plant-scale experience to date, Nitronic-50 and possibly 304L, are candidates for the feed system, 347 SS for the calciner vessel, and Nitronic-50 for the off-gas cleanup system.

A quarter of a century of laboratory, pilot-plant, and engineering-scale waste solidification experience has shown that high-level power reactor wastes can be calcined safely and practically. Plant-scale operation of the WCF since 1963 on defense wastes, and the current hot operation of the rotary kiln at Marcoule in France, have not revealed problems that would seriously compromise calciner reliability.

The technology currently is available for calcining high-level or a blend of high- and intermediate-level power reactor wastes using a spray, rotary kiln, or fluidized-bed calciner. Calcine can be stabilized (volatiles removal) or the calciner can be directly coupled to candidate waste form conversion processes. Near-term emphasis should be on process refinements and fundamental understanding of the process behavior of existing processes and large-scale radioactive demonstrations to obtain plant-scale data on steady-state process behavior, equipment reliability, materials of construction, and the many safety-related questions.

CALCINE PRODUCTION AND MANAGEMENT

I. INTRODUCTION

The purpose of this paper is to summarize the state of technology for calcining high-level liquid wastes from the reprocessing of light water reactor fuels. Primary emphasis will be on calcination process technology and calcine management. Major process steps required of any calcination process are feed preparation, calcination and product handling, and off-gas cleanup. Significant concerns in calcine management are calcine storage (interim or long-term) calcine stabilization (removal of volatiles), interface with calcine conversion processes, and calcine properties.

Many calcination processes have been studied since the early 1950s; however, the three processes generally considered to be the most developed are spray calcination, fluidized-bed calcination, and rotary kiln calcination. Some process variations of these three processes will be discussed, but the state of technology of feed systems, calcination, and off-gas cleanup as proposed or applied using these processes will be the main emphasis. Areas not addressed are remote maintenance and decontamination, safety analysis, other less developed calcination processes, and the economics of calcination.

Calcination of high-level liquid wastes can be justified using one or more of the following bases:

- Calcine requires less surveillance than liquid wastes.
- Volume reduction of 7-8 fold.
- Starting material for other waste forms.

Long-term storage of liquid high-level wastes in tanks requires dedicated monitoring to ensure availability of cooling for decay heat removal, off-gas cleanup, and the integrity of the storage system. While liquid storage is considered practical and safe for some years, solidification to calcine or other waste forms is felt to be required for high-level waste management.

A volume reduction of 7-8 fold occurs on calcination of high-level liquid wastes. Thus, there is an economic advantage resulting from the volume reduction. An economic disadvantage is the capital and operating costs of the solidification process and the more sophisticated system required for heat removal from solidified high-level wastes.

All of the calcination processes discussed herein can be connected to various waste form conversion processes. The spray calcination and rotary kiln processes are normally considered directly coupled to either an in-can melter or a joule-heated ceramic melter for producing glass. However, glass can be produced by direct feeding to an in-can melter or joule-heated ceramic melter. Calcine produced by fluidized-bed calcination can be stored in canisters or coupled to other waste form conversion processes. Glass does not require calcination as an intermediate step; sintered ceramics, metal matrices, or pellets would normally require calcine as a starting material.

The process description for the calcination processes is given in Section II. Calcination technology is discussed in Section III: process requirements, operating or proposed systems, major problems, operating experience, and a technology assessment are given. Requirements, operating experience, and problems are also discussed for materials of construction. Major considerations in calcine management are discussed in Section IV.

II. CANDIDATE CALCINATION PROCESSES

Major process steps are common to all solidification processes; these include feed preparation or blending, calcination, and off-gas cleanup. A schematic diagram of a generic calcination process is shown in Figure 1. The primary purpose of a calcination process is to convert the high-level liquid wastes or a blend of high- and intermediate-level liquid wastes into oxides which can be stored or converted into other waste forms. The spray calciner, fluidized-bed calciner, and the rotary-kiln calciner are the three processes receiving the most attention for near-term application. Both the spray calciner and rotary kiln are designed primarily for direct coupling to a glassification unit. The fluidized-bed calciner in operation at the Idaho Chemical Processing Plant (ICPP) produces a calcine that is stored in underground bins.[1] Processing of the higher heat generating power reactor wastes in a fluidized bed would require calcine storage in canisters or coupling of the fluidized bed to a waste form conversion process. Basic process descriptions for the spray, rotary kiln, and fluidized bed calciners are given below.

1. Spray Calciner

Liquid wastes are normally pumped to the spray calciner at a pressure in the range of 1 to 2 atmospheres.[2] A basic requirement of the process is the generation of fine droplets which can be evaporated and calcined in the short residence time in the 500°C calciner chamber. A simplified schematic diagram of the spray calcination process is shown in Figure 2. Waste is pneumatically atomized using an internal mix nozzle at the top of the calciner chamber; spray droplets of a nominal 70-μm-diameter are evaporated, dried, and calcined as they fall through the spray chamber. Process heat is provided by electric resistance heaters mounted on the wall of the calciner; heat is transferred to the droplets by both convection and radiation. Spray calcine typically contains less than 0.5 wt% moisture.

Some scale buildup on the interior walls of the spray chamber can occur as a result of too high a feed rate or the presence of low melting point compounds in the feed (e.g., sodium nitrate). A vibrator can be mounted on the vertical wall of the calciner to minimize solids deposition and maintain heat transfer rates.

Approximately 50% of the calcine passes from the product removal line at the bottom of the spray chamber; the remainder is entrained in the calciner off-gas. The off-gas consists of water vapor, oxides of nitrogen, atomizing air, some volatile ruthenium, and spray calcine. The primary particulate

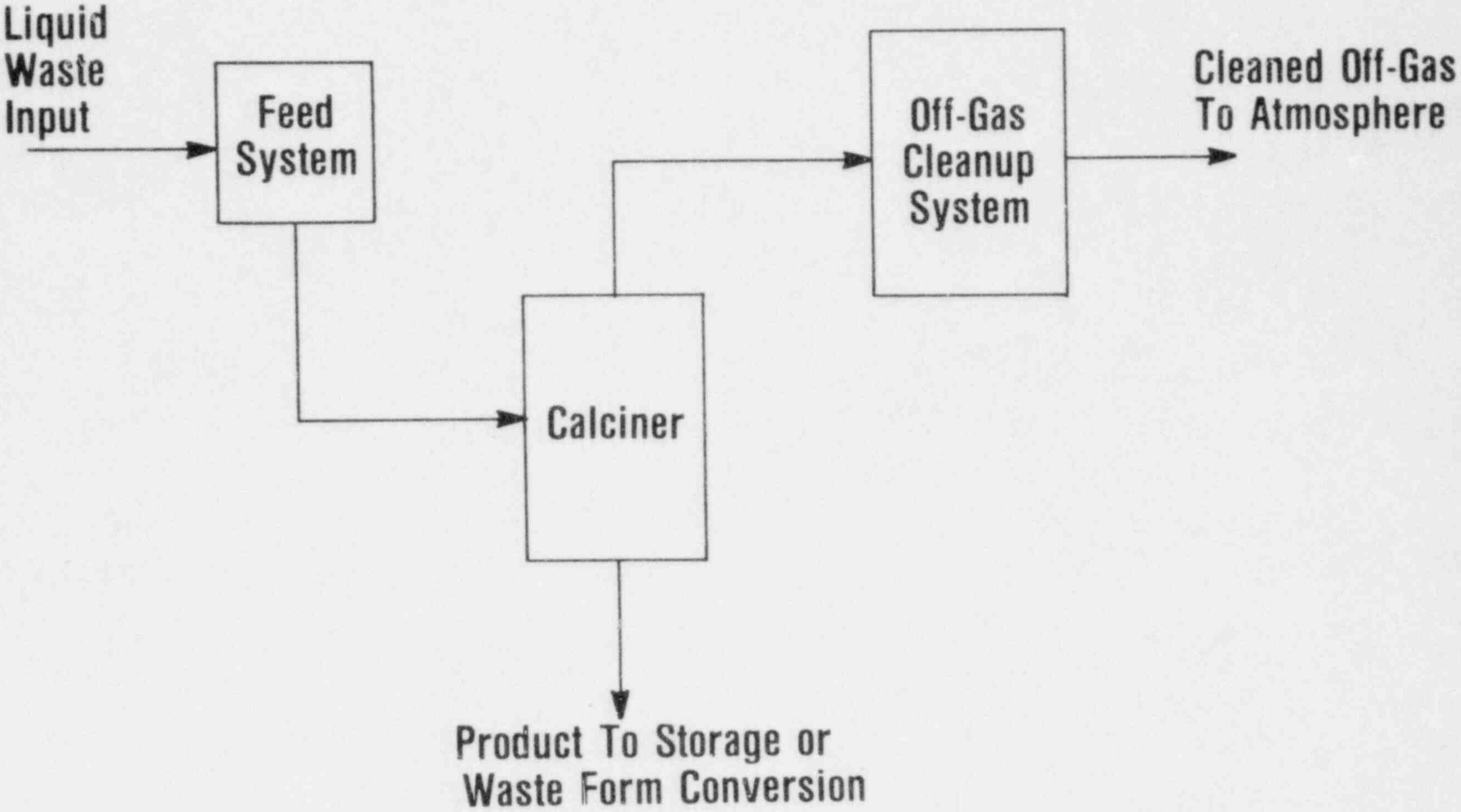

Figure 1. Generic Spray Calcination Process

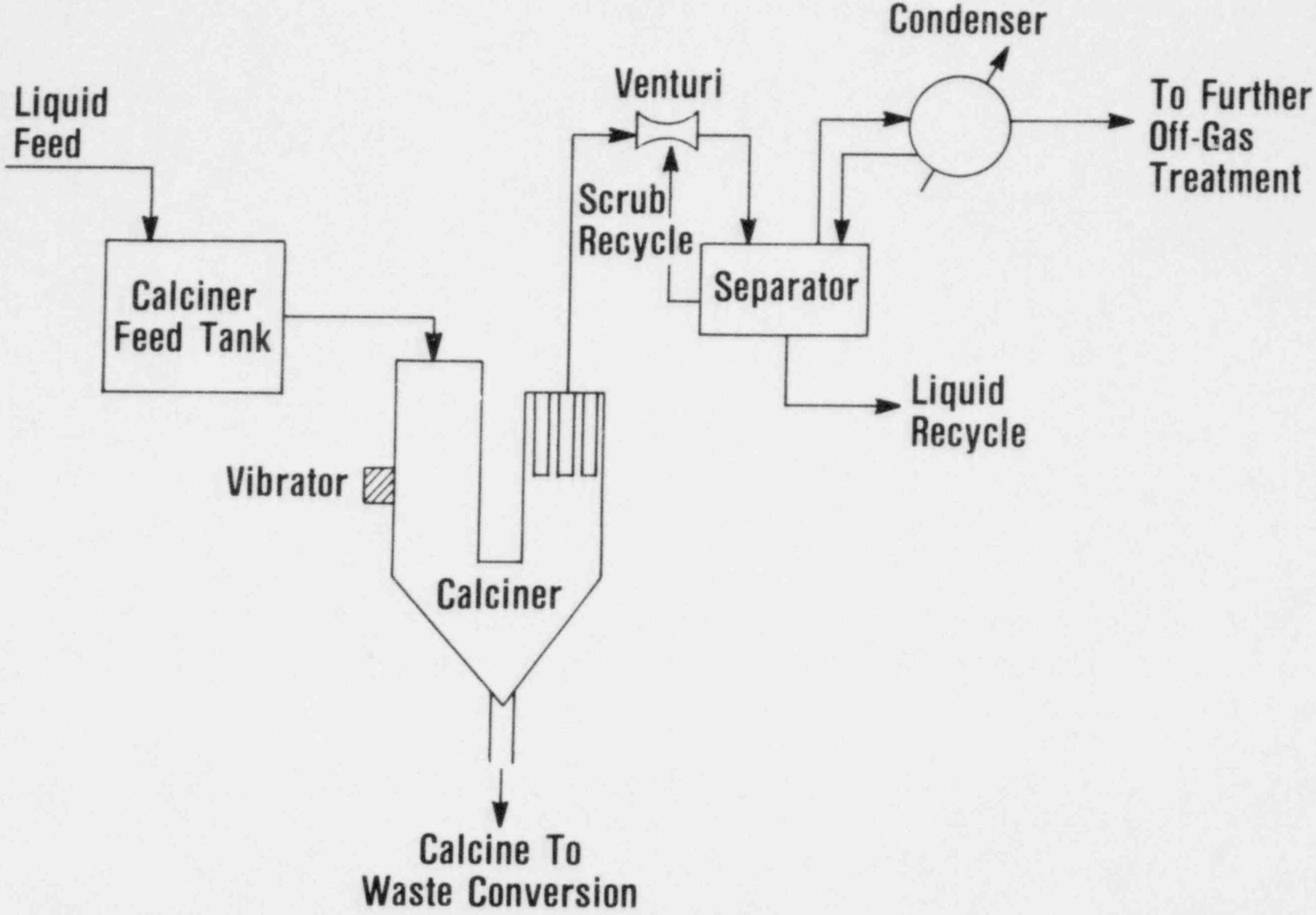

Figure 2. Spray Calcination of High-Level Wastes

removal device is a series of sintered metal filters. Approximately 0.1 wt% of the particulates in the off-gas pass through these porous stainless steel filters. The entrained particulates collect on the filters which are periodically pulsed with air to remove the solids. Solids from the blowback pulse in the filter chamber are discharged with the calcine falling directly from the calcination chamber.

Further off-gas treatment steps are required to remove additional particulates and volatile ruthenium. A reference system is based on a venturi scrubber-separator followed by a condenser. Volatile ruthenium, if present in sufficient quantities, can be removed by a number of solid adsorbents. The removal of NO_x and possibly iodine would be considered in a production-scale plant.

Storage of the spray calcine has not been seriously considered. Calcine falling from spray chamber or from the filter chamber is directly coupled to an in-can or joule-heated ceramic melter.

2. Rotary Kiln

The rotary-kiln calciner is a rotating barrel positioned at a slight angle to facilitate the flow of the calcined solids.[3] Liquid waste is fed by gravity to the upper end of the kiln. The rotating barrel of the kiln is approximately 3.6-m long and 27-cm in diameter. Seals at each end of the kiln are sufficiently tight to result in a slight negative pressure inside the kiln with respect to the surroundings. The basic calcination process using a rotary kiln is shown in Figure 3.

Average residence time for conversion of HLLW to calcine is 30 seconds; the relatively short solids holdup time minimizes the generation of volatile ruthenium. Process heat is provided by a zoned electrical resistance furnace surrounding the kiln. Evaporation and drying primarily occur in the upper portion of the kiln at a nominal temperature of 600°C. As the dried waste flows down the 3-degree incline, further drying and calcination occur at temperatures as high as 900°C. Calcine holdup in the kiln is normally 3 kg. The product, containing little moisture and residual nitrate, flows by gravity from the lower end fitting into the melting furnace.

Off-gas is exhausted at the upper end of the kiln countercurrent to the liquid feed. Entrained dust is removed by a wet scrubber and recycled to the calciner feed. Less than 0.1 wt% of the calcine entering the scrubber passes to the off-gas treatment system. Off-gas from the scrubber passes to a partial condenser; condensate is recycled to the feed system. Volatile ruthenium is removed from the condenser off-gas by adsorption.

3. Fluidized-Bed Calcination[4]

Liquid wastes are solidified by spraying the wastes into a fluidized bed of hot granular solids at a temperature of ~500°C. A reference fluidized-bed calcination process is shown in Figure 4. The bed (particle diameters from 0.2 to 0.7 mm) is fluidized by forcing air upward through a distributor

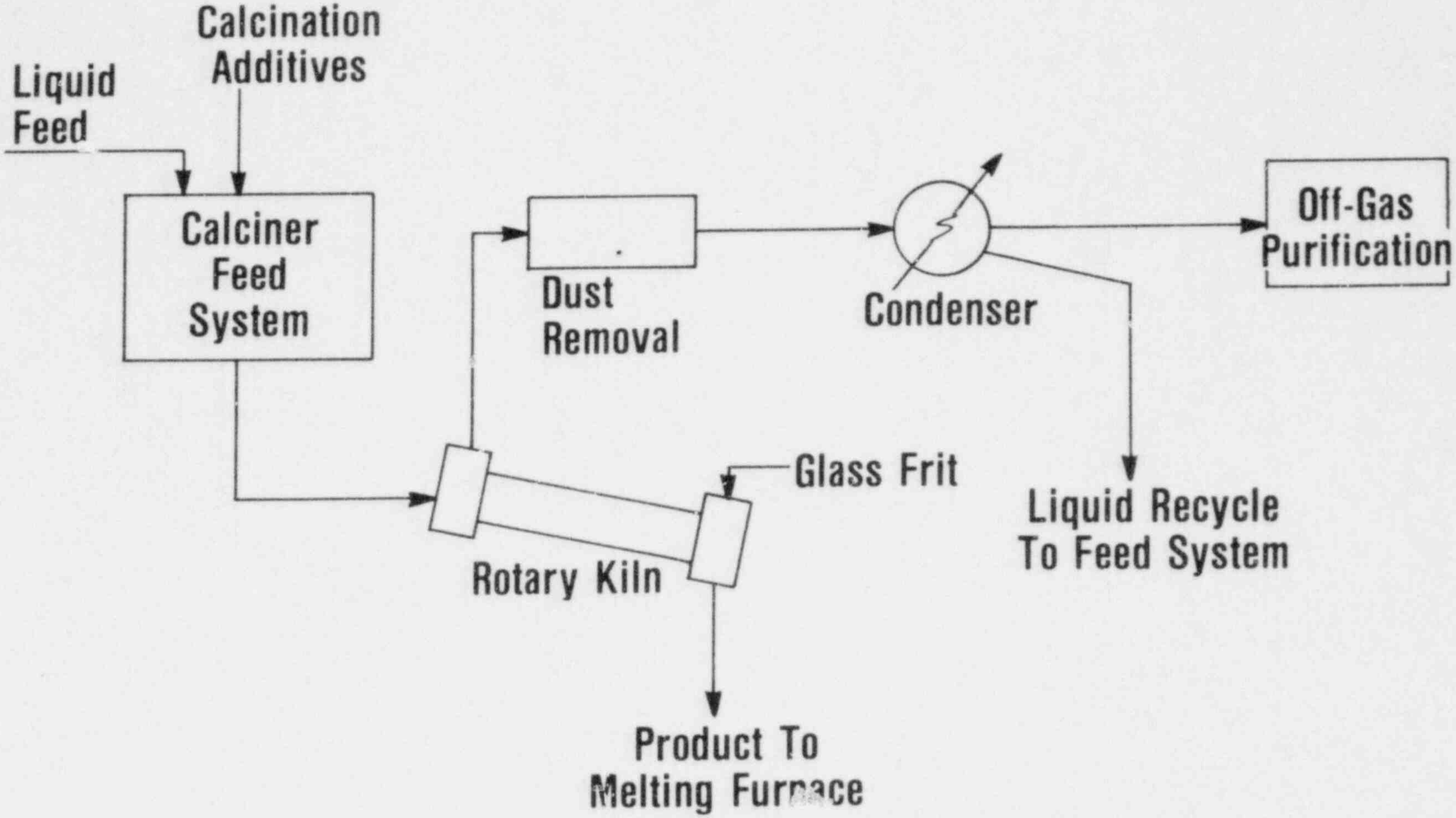

Figure 3. Calcination of High-Level Wastes by Rotary Kiln

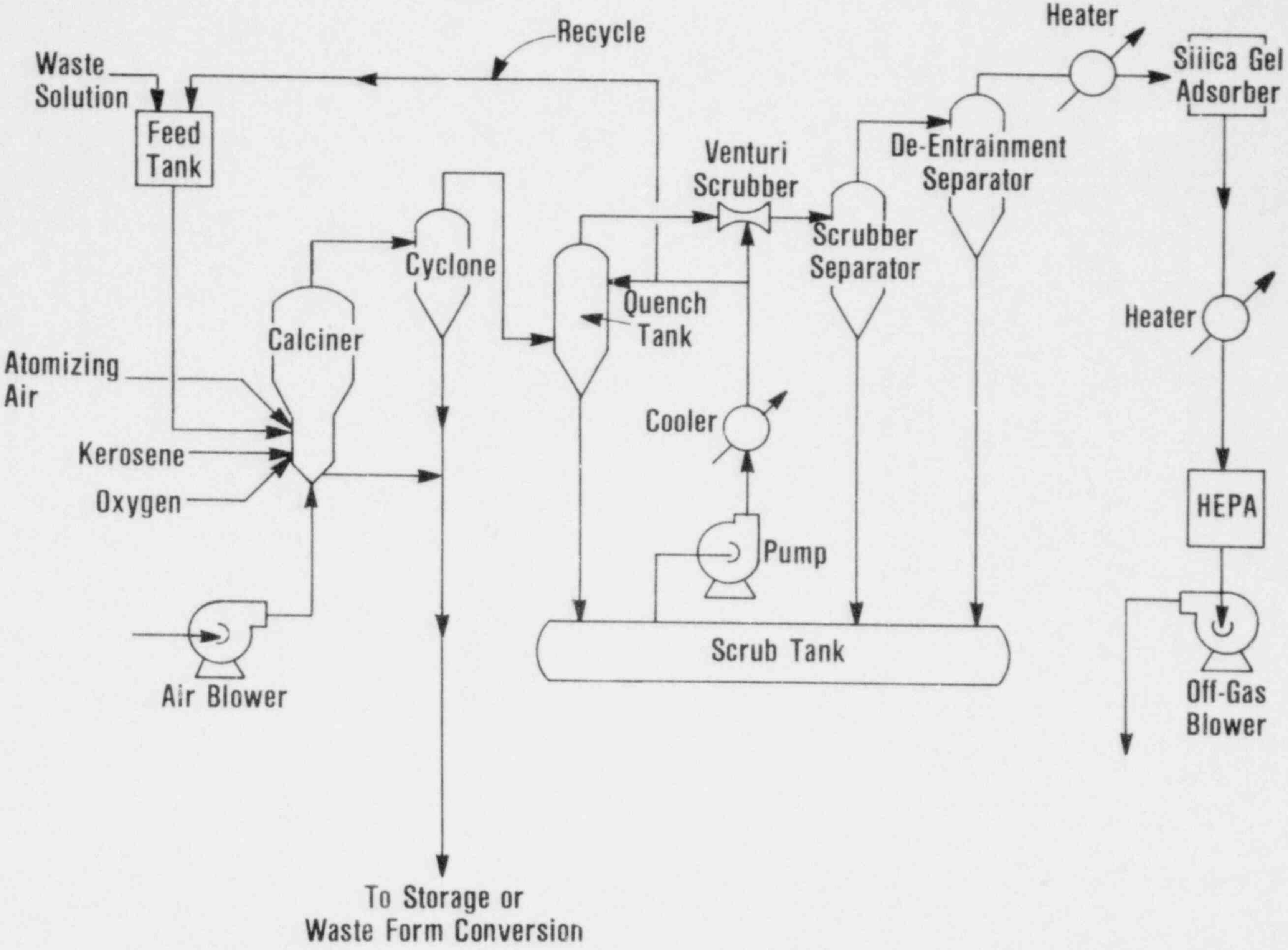

Figure 4. Fluidized-Bed Calcination of High-Level Wastes

plate at the bottom of the bed. The fluidizing air causes a rapid mixing of the solids and results in a bed of particles of uniform composition and temperature. Liquid wastes sprayed into the bed in the form of droplets are evaporated on particle surfaces or spray-dried before coming in contact with the bed particles.

Process heat is normally supplied by an in-bed heat exchanger or by in-bed combustion of hydrocarbon fuel. Fuel and oxygen are introduced directly into the bed where combustion occurs. The bed temperature must be maintained at a minimum of 500°C for high combustion efficiency.

Calcine generated in the fluidized bed consists of both bed particles (0.2 - 0.7 mm) and fines particles (< 0.2 mm). Except during startup, the fluidized bed is made up of dissolved and undissolved solids present in the feed. Solids from the bed are discharged continuously or intermittently through one or more product takeoff ports near the bottom of the bed.

Off-gas from the fluidized-bed calciner contains particulate, water vapor, atomizing and fluidizing air, oxides of nitrogen, some volatile ruthenium, and combustion gases (if in-bed combustion is used to supply process heat). The primary off-gas cleanup devices for particulate are the cyclone and venturi scrubber; HEPA filters are provided to supply the DF required prior to release of the off-gas to the atmosphere. Though some volatile ruthenium may be removed by the venturi scrubber, removal by solid adsorbents is the most practical method.

III. EVALUATION OF CALCINATION TECHNOLOGY

1. Calciner Feed System

Considerations important to selecting the calciner feed system include process requirements, anticipated major problems, methods for controlling flowrate, feed metering techniques, operating experience, and the status of the technology.

1.1 Process Requirements

The feed system must be capable of mixing additives with the wastes and concentrating the wastes as required. Undissolved solids must remain suspended, and the calciner feed must be accurately metered.

To operate reliably, the feed system must be resistant to radiation, must not result in plugging by suspended solids, and must be resistant to erosion and corrosion.

1.2 Typical Feed Systems

Simplified diagrams of feed systems (not including evaporation systems) proposed for fluidized bed and spray calciners are shown in Figure 5. Details of the rotary kiln feed system were not available, but the basic principles for fluidized bed and spray calciners would also apply to the rotary kiln calciner.

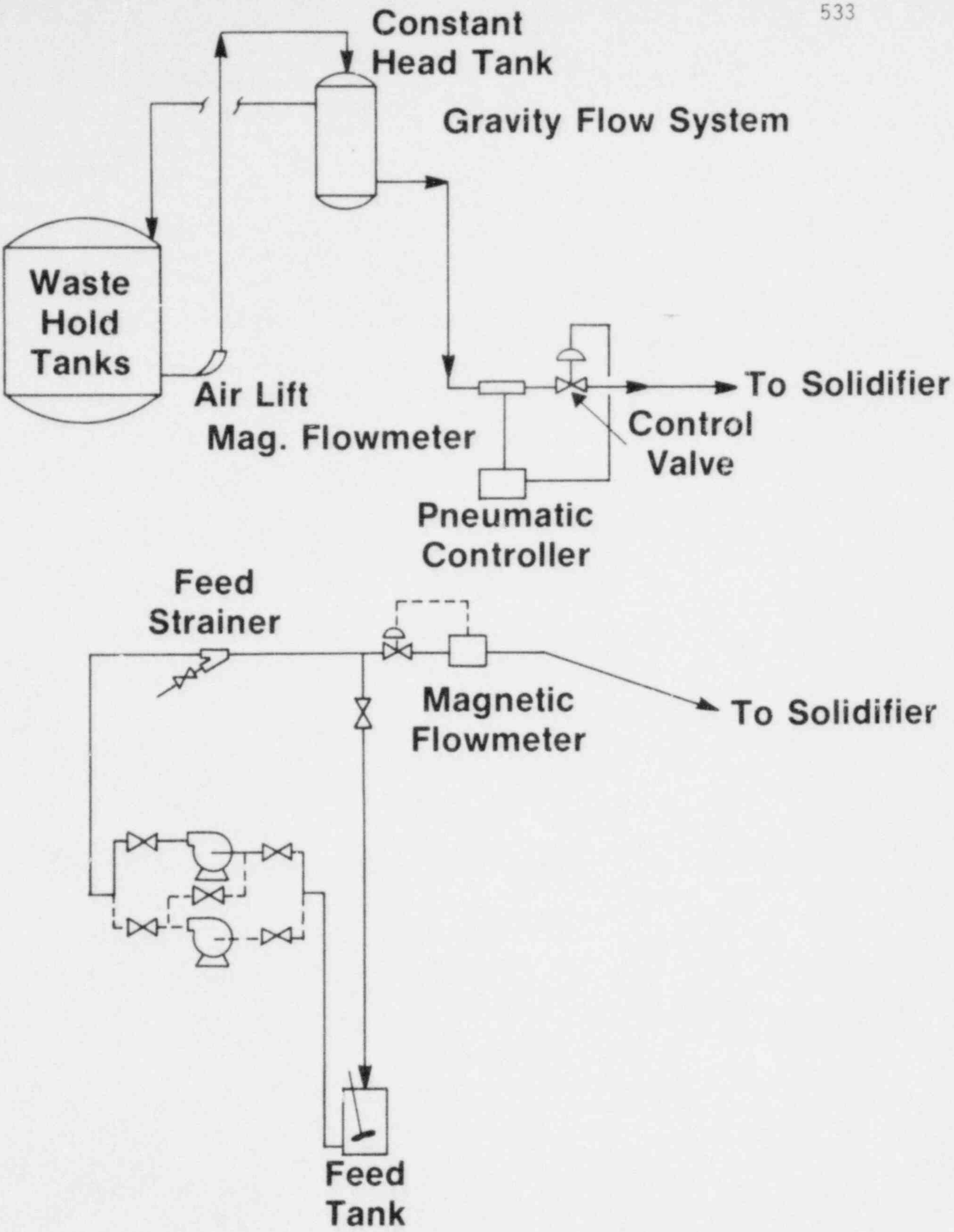

Figure 5. Typical Calciner Feed Systems

1.2.1 Candidate Feed System for Fluidized-Bed Calciner. Feed to the fluidized-bed calciner consists of HLLW and ILLW blended and complexed with necessary additives (e.g., scrubbing solution recycle, powdered iron) concentrated for calcination.

Evaporator Feed System. An airlift from each large plant waste tank is used to transfer the waste through an underground line to an empty waste blend tank. High-level waste is mixed with intermediate-level waste. Recycle solution from the scrubbing surge tank in the off-gas cleanup system is pumped into the blend tank and mixed with waste feed at the specified ratio. Powdered iron and other additives are blended as required and the feed solution mixed by air sparging. Some cooling is required during the addition of powdered iron.

Feed is transferred from a blend tank to the evaporator feed tank where a constant head is maintained by an overflow. Excess feed overflows back to the appropriate blend tank. The evaporator consists of a column and heat exchanger. Evaporator feed flows into the column and circulates through the shell-and-tube steam heated heat exchanger. The liquid is heated to boiling and is forced into the column where flash vaporization occurs. The column would operate on a semi-continuous basis with feed and scrub recycle metered into the evaporator system until the desired concentration is obtained.

Calciner Feed System. The calciner feed system is capable of receiving concentrated waste from the evaporator system and metering the feed through atomizing feed nozzles to the fluid bed in the calciner vessel.

Concentrated feed is transferred by air lifts from the evaporator to one of the two waste hold tanks and to the calciner feed tank by another airlift. A constant head is maintained in the calciner feed tank by an overflow line. Excess feed overflows back to the appropriate hold tank. The feed is pumped or will flow by gravity through a flowmeter, a control valve, and finally through a feed nozzle into the fluidized bed. Continuous operation is maintained by filling one waste hold tank while the other waste hold tank is being emptied.

Two waste hold tanks are provided to supply the feed tank. Each tank is equipped with a cooling coil or jacket to remove any heat generated by steam jets or fission product decay heat. Steam is supplied to the cell jacket for heating the vessel contents. Each vessel has an air-stream sparger near the bottom and a decontamination ring near the top.

A flowmeter and a control valve in each feed line controls the flow to each nozzle. The flowmeters are an electromagnetic (EM) type consisting basically of an unobstructed pipe section, lined with a Kynar insulator. The end surfaces of the electrodes are flush with the inner surface of the insulating liner and contact the fluid to be metered. A known problem with an EM-type flowmeter is that electrical fields from adjacent electric motors affect the calibration. This problem must be considered in designing the system.

1.2.2 Feed System for Spray Calciner[5]. The feed system proposed for spray calcination has been used successfully during the Waste Solidification Engineering Prototype (WCEP) and present Waste Fixation Program (WFP) at Hanford. Waste is jetted batchwise from waste hold tanks to the feed tank. An electric motor-driven propeller agitates the feed tank. Airlifts are used to transfer dilute suspensions; vertical cantilevered shaft pumps used at Savannah River Laboratory (SRL) have shown more promise for concentrated radioactive slurries. A pressurized feed recirculation loop is used from which a slip stream is fed to the calciner. The slip stream flows through a small diameter tubing which includes a control valve, flowmeter, and atomizing nozzle. A single feed tank can be used if the liquid waste volume is sized for a canister. A strainer is used in the WFP feed system to remove solids that tend to plug the EM flowmeter and atomizing nozzles.

1.3 Major Problems

a) Fatigue failure of metal bellows valves used for primary containment of feed solution and feed system plugging sometimes occurs when processing feed containing undissolved solids in fluidized-bed calciners.

b) EM flowmeters tend to plug and cannot be calibrated to provide good quantitative values for feeding individual spray nozzles.

c) Storage of spray calciner waste slurries is complicated by undissolved solids resulting in heterogeneous melt formations and deposition of solids in waste tanks causing plugging, hot spots, and accelerated corrosion.

d) Accurate liquid sampling is essentially impossible with air sparging of slurries containing large amounts of suspended solids.

2. Calciner

The basic function of the calciner is to convert high-level liquid wastes into a mixture of oxides. Evaporation, denitration, and calcination are the primary processes occurring in the calciner.

2.1 Process Requirements

Primary process requirements for calcination are process heat input, feed introduction compatible with the specific process, control of solids generation for compatibility with the specific process, continuous or intermittent removal of solids from the calciner, and the ability to accept feed compositions over a reasonable range.

Other considerations such as the unit throughput capacity, inventory of calcine in the calciner, the residence time of the solidified waste in the calciner are important from the standpoint of process economics, safety, and product characteristics. Key equipment design features of the various calciners are shown in Figure 6.

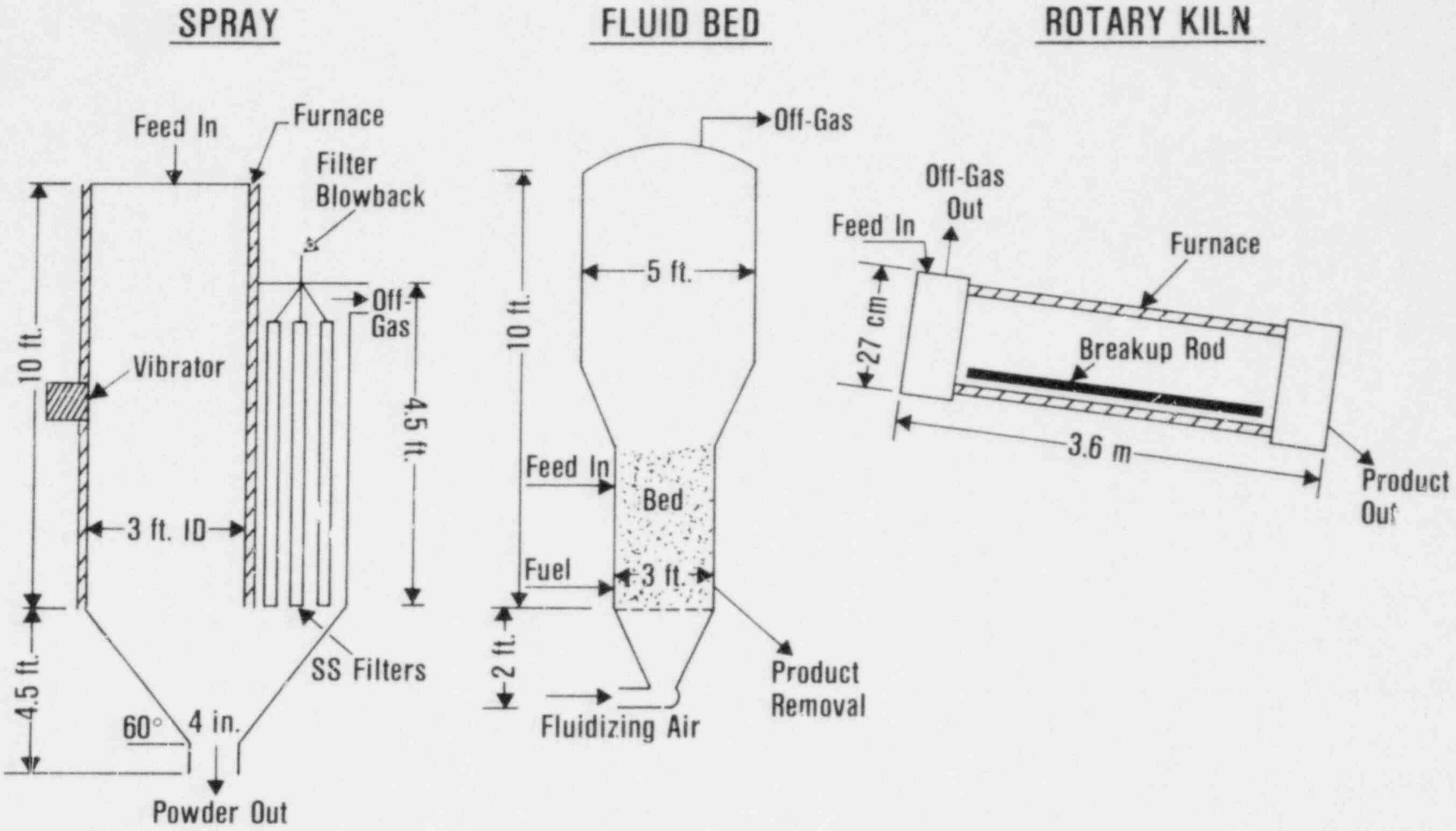

Figure 6. Key Features of Calciners

2.2 Process Heat Input

Two primary methods are used for heat input to a calciner vessel, electric resistance heating and combustion of a hydrocarbon directly in the calciner (fluidized bed only). The spray calciner is normally heated by a multizone resistance furnace; the spray calciner at Karlsruhe has been heated by superheated steam. The rotary kiln is also heated by a multizone resistance furnace. Fluidized beds may be heated by an in-bed heat exchanger or by in-bed combustion of a hydrocarbon fuel (kerosene).

2.2.1 Spray Calciner Furnace. Multizone resistance furnaces have and are being used successfully at Pacific Northwest Laboratories (PNL) to calcine HLLW.[2] A typical production-scale spray calciner chamber would require four zones at approximately 70 kw per zone. A temperature control system is designed to control the temperature of a given zone within the range of 500-1000°C at an accuracy of ±10°C. Radial and longitudinal temperature uniformity on the walls of the calciner vessel do not appear to be required for reliable calciner operation. The furnace is usually held at a temperature of about 700°C during normal operation; some thermal cycling occurs during startup and shutdown. Furnace corrosion is minimized by encasement in a material resistant to vapors and spills of process solution. Advantages of indirect heating are the ability to operate at low temperatures and a lower volume of calciner effluent gases. Disadvantages are the increased complexity of the system for heat input.

2.2.2 In-Bed Combustion. In-bed combustion, as applied to fluidized-bed calcination of radioactive wastes, involves burning a hydrocarbon fuel directly in the bed.[6] To obtain an acceptable combustion efficiency, the fuel is atomized by oxygen and the bed temperature is maintained at a minimum of 500°C. Advantages of in-bed combustion are the relatively simple system, capability of high temperature operation without stressing electrical resistance heaters, and efficient heat transfer within the bed, since no metal heat transfer surface is required. Disadvantages are the inability to calcine at temperatures much less than 500°C, the increased potential for solids agglomeration near the fuel nozzle, and the increased rate of fines generation.

Major problems using in-bed combustion have been selection of nozzle cap materials to assure integrity during operation and decontamination, fuel nozzle design required for high combustion efficiencies, particle size control problems resulting from the increased particle attrition caused by fuel atomization and burning. External mix nozzles with caps of Haynes 25 or 188 alloys have proven reliable. Oxygen-to-fuel ratios from 1800-2400 have been used and combustion efficiencies have ranged from 85 to 91%. Particle size for less attrition-resistant calcines is controlled by decreasing the feed nozzle air ratio; particle size for attrition-resistant calcines is controlled by increasing the feed nozzle air ratio.

2.2.3 Rotary Kiln Furnace. Process heat for the rotary kiln is provided by an electric resistance furnace.[3] The furnace is divided into four independently controlled heating zones. The first two zones have a heating rate of 20 kw each, and are used primarily to evaporate the liquid waste. A heat input rate of 10 kw each is provided in the last two zones where most of the calcining occurs.

2.3 Feed Introduction

Both the spray and fluidized-bed calciners require feed atomization; feed to the rotary kiln is by gravity.

The spray calciner is highly dependent on proper feed atomization for successful operation. Experiments at PNL have shown that a droplet mean diameter of ≤ 70 microns is sufficient for calciner operation using LWR-type waste. An external mix nozzle supplied by Spraying Systems Company has been used to obtain the required particle size. An acceptable wear rate of the nozzle air cap was obtained by using an alumina insert.

Ambient temperature air, steam, and hot air were evaluated as atomizing media. Hot air and steam resulted in nozzle plugging from drying the waste in the liquid orifice. Similar plugging was experienced at Karlsruhe, Germany using superheated steam as the atomizing medium.[7] Nozzle plugging at PNL has been eliminated by using ambient air, a screen upstream of the feed nozzle, and flushing of the nozzle before startup and after shutdown.

Spray droplets in the desirable range of 40-70 microns can be generated by using a volumetric air-to-liquid flow rate ratio of about 300. These droplet sizes can be achieved by maintaining the nozzle air pressure about double the liquid feed pressure at the nozzle for feed flow rates > 40 L/hr. At feed rates below 40 L/hr, the nozzle air pressure should be about triple the feed pressure at the nozzle.

A primary requirement for operation of a fluidized-bed calcination process is the ability to maintain a steady-state bed weight within the calciner vessel. A steady state must be reached such that the rate processes of particle growth and seed particle generation are equal to loss of bed weight through particle elutriation and product removal. A key to maintaining this balance is the atomization of the liquid feed and deposition on the bed material. An external-mix pneumatic nozzle has been demonstrated in pilot plant tests and at the WCF to meet the following requirements:

a) Coating of bed particles at a sufficient rate to provide for particle growth.

b) Sufficient production of small "seed" particles to provide nuclei for particle growth.

c) Acceptable production of fines that are elutriated from the calciner.

d) Acceptable rate of atomizing air requiring off-gas cleanup.

e) Capable of atomizing feed solution resulting from recycled off-gas scrubbing solution.

A standard flat-faced 1/2-J nozzle by Spraying Systems Company has proven adequate for feed introduction, particle size control, and production of "seed" particles. During operation of the WCF, nozzle air ratios from 50 to 900 have been used to control the average bed particle size for calcine produced from aluminum nitrate, zirconium fluoride, and blends of zirconium fluoride and 1.5M to 2.0M sodium wastes.

2.4 Calciner Capacities and Feed Compositions

The capacity of a calciner and the ability to process wastes with a reasonable variance in composition are important considerations in the selection of a solidification process for a given waste. Feed components such as sodium nitrate, which is molten over a wide temperature range, can result in solids agglomeration or scale on calciner vessel internals. The unit capacity of a calciner should be compatible with the annual output of the fuel reprocessing plant.

Spray Calcination. Flow rates of 75 L/hr have been verified using a 21-inch ID spray calciner chamber; scale-up calculations show that at least 150 L/hr can be processed through a 3-foot ID by 10-ft-high full-scale unit. At spray chamber diameters in the range of 10-30 inches, the capacity of the calciner increases exponentially with increasing diameter. Also, for a given diameter, increasing the wall temperature from 550 to 700°C increases the capacity by approximately 1.5 .

Scale from calcine deposition can form on the calciner wall and reduce calciner capacity. To increase the reliability of the unit, vibrators located on the vertical center of the chamber and mounted on the furnace shell are recommended. Vibrators have proven effective in preventing scale buildup while calcining sodium wastes and at conditions imposed and known to promote scaling.

Fluidized-Bed Calcination. If an in-bed heat exchanger is used to supply process heat, the rate of heat transfer from the exchanger to the bed limits the capacity; the WCF using an in-bed heat exchanger, had a capacity of 250 L/hr. In-bed combustion has resulted in the present throughput in the 4-ft-diameter unit of nearly 400 L/hr. The WCF throughput is currently limited by the capacity of the off-gas system. Large-scale pilot-plant studies show that a fluidized-bed calciner, heated by in-bed combustion, can process a net throughput of 70-30 L/hr-ft^2 of bed cross-sectional area.

Agglomeration of bed particles and "caking" at feed and fuel nozzles can occur during calcination of wastes containing significant amounts of sodium nitrate. Sodium wastes at the ICPP are now being calcined routinely by blending one volume of sodium waste with 3.5 - 4.0 volumes of zirconium fluoride wastes. Pilot-scale tests using 10-cm and 30-cm-diameter calciners show that a blend of simulated high-level and intermediate-level power reactor wastes (containing sodium) can be calcined using a fluidized bed. Wastes with sodium concentrations less than 0.2M can be calcined in a fluidized bed without the use of an additive. High-level wastes with a sodium concentration of 1.1M can be solidified by fluidized-bed calcination if iron is dissolved in the feed. The maximum sodium concentration calcinable by fluidized-bed calcination has not been defined.

Rotary Kiln. One rotary kiln 3.6-m-long and 27-cm-diameter can calcine between 40-50 L/hr of concentrated high-level wastes. Based on a high-level wastes composition with a reasonably low content of non-fission product salts, 2 or 3 rotary kilns would be required to calcine the wastes generated by a 1500 MTU/yr LWR fuel reprocessing facility. Studies are underway to increase the unit capacity to > 50 L/hr and to evaluate the effect of continuously concentrating the feed by a factor of 1.5 - 2 prior to calcination.

Lower melting components in the calciner feed also contribute to wall scaling and solids agglomeration in the rotary kiln. The equipment and process are designed to break up agglomerates and scale by two mechanisms. An organic chemical, azodicarbonamide, decomposes at 200°C and "acts like popcorn". Also, a long rod inside the kiln is designed to break scale loose from the walls of the kiln.

3. Off-Gas Cleanup

Considerations important to selecting the calciner off-gas system include process requirements, particulate removal devices, volatiles removal requirement, and cooling and condensing of the off-gas.

3.1 Process Requirements

The off-gas system must be capable of obtaining particulate (^{90}Sr) and volatile ruthenium (^{106}Ru) decontamination factors in the respective ranges of 10^5 to 10^8 and 10^4 to 10^7. Off-gas will exit the calciners at approximately 500°C and must be cooled to the approximate range of 150 to 250°C. The off-gas system must accept significant quantities of plate-out products without plugging. It must operate at less than 10 psi ΔP to allow use of a vacuum system at reasonable blower costs; all equipment must adequately resist corrosion for reliable operation.

3.2 Basic Off-Gas Systems

Simplified fluidized bed, spray, and rotary kiln calciner equipment flowsheets developed and used for power reactor waste off-gas cleanup are described.

3.2.1 Fluidized-Bed Calciner Off-Gas System[4,8]. The fluidized-bed calciner off-gas cleanup system based largely on WCF operating experience uses a series of components to remove progressively smaller particles from the calciner off-gas. A schematic flowsheet showing the major components of the off-gas system was shown in Figure 4. First, a cyclone removes the larger particles and discharges them into a pneumatic transport system that transports the solids to storage or to a waste form conversion process. Next, the wet scrubbing system contacts the off-gas with scrubbing solution in a venturi scrubber, then collects the spray with a vaned swirl separator followed by a wire-mesh separator. The scrubbing system also contains a quench tower, which cools the off-gas entering the venturi scrubber; other equipment collects, cools, and recirculates the scrubbing solution. After leaving the scrubbing system, the off-gas goes through beds of silica gel (or equivalent) which are designed to adsorb volatile ruthenium; the adsorption beds also collect particles. Finally, the off-gas is superheated and passed through HEPA filters which filter essentially all of the remaining particulate solids from the off-gas.

3.2.2 Spray Calciner Off-Gas System[5]. During the radioactive demonstrations of the WSEP program, vapors from the sintered metal filters were routed through an extensive effluent treatment equipment train. As described by McElroy et al.,[9] vapors passed sequentially through a tube and shell condenser, the fractionation tower of an acid fractionator, a third condenser, an air heater, HEPA filters, a caustic scrubber and final filtration prior to discharge.

As a result of the Waste Fixation Program, the following off-gas treatment system is receiving strong consideration. After the sintered metal filters, the off-gas passes through a venturi scrubber, a knockout pot and a condenser; final particulate removal is by HEPA filtration. The primary volatile fission product of concern is ruthenium; studies to date have shown that 1-2% of the ruthenium in the waste can be present in the calciner off-gas. The most efficient method for volatile ruthenium removal is solid adsorption. There are two basic adsorption techniques: with and without sorbent regeneration. Packed beds containing silica gel, ferric oxide, or a hydrous zirconium oxide gel are candidate adsorbents. Regeneration of an adsorbent requires that the acid regenerant be recycled to the calciner feed.

3.2.3 Rotary Kiln Off-Gas System. Details of the rotary kiln off-gas system are not available. However, the general flowsheet (Figure 3) indicates a wet scrubber, dust recycling vessel, and condenser are included. Volatile ruthenium is removed by solid adsorption.

3.3 Particulate Removal Devices

Cyclone Separators. Cyclones are in common use in conjunction with wet scrubbing systems. Particulate DFs in the order of 2 to 5 are attained.

Sintered Metal Filters. Sintered stainless steel filters have found broad use in the nuclear industry in applications requiring high-efficiency filtration of thermally hot and/or highly radioactive vapors. Experience in spray calcination development[5,9] during the last 15 years has demonstrated high reliability and high particulate removal efficiency at practical operating conditions. During operation, routinely less than 0.1% of the calcine particulates penetrates the filter.

Due to the large filter pore size relative to the calcine particle size, some calcine initially passes through the filter; filtration efficiency improved after a calcine coating had collected on the filters. During the first five WFP spray calcination runs. the filters were undisturbed, and the effect of calcine buildup was observed. During the first run, the average filter particulate DF was about 700. During each successive run, the DF steadily improved until during run 5, the DF had improved to 13,000. Following this run, tests with filter washing were initiated which reduced the DF to near the clean filter efficiency. Since filters will normally not be washed, it is anticipated that in an operating plant, the calciner sintered metal filter DF for particulates will be well above 10^3.

Wet Scrubber. Wet venturi scrubber systems are in common use with fluidized-bed calciners.[1,4] Particulate DFs in the order of 800 to 1000 are attained. Pressure drop requirements are approximately 15 kPa. Operation is reliable; however, some corrosion and erosion occurs.

Condenser. The DFs reported for the spray calciner are $\sim 10^3$ per stage.[9]

Adsorbers. Silica gel adsorbers result in particulate DFs of 6 in the fluid-bed calciner off-gas systems.

HEPA Filters. High-efficiency particulate air (HEPA) filters result in particulate DFs of 10^3 per stage.

3.4 Off-Gas Cleanup

Volatiles Removal[10]. The most troublesome radiochemical contaminant in the off-gas stream from a solidification process is ruthenium, which may be present both as a stable gaseous species or as fine solids. Experience at the WCF indicates that if the off-gas cleanup system removes ruthenium effectively, the other radionuclides present no problem. Ruthenium can be volatilized in at least two forms: as RuO_4, and probably as some form of nitrosyl complex. The amount of volatile ruthenium in fluidized-bed calciner off-gas varies widely depending on the temperature of calcination, type of heating, and composition of waste.

Between 350 and 600°C, ruthenium volatility decreases as the calcination temperature of an indirectly heated calciner increases. Increasing calcination temperature from 500 to 570°C using in-bed combustion does not decrease ruthenium volatility. At a given calcination temperature (500°C), calcination of aluminum nitrate or zirconium fluoride wastes using indirect heating produces more volatile ruthenium than when using in-bed combustion. The major proportion of ruthenium produced using in-bed combustion heating is produced as fine solids; indirect heating produces mostly a stable gaseous species of ruthenium. Ruthenium volatility during calcination also decreases as the total nitrate concentration of calciner feed is decreased below 6$\underline{M}$. Chemicals such as formic acid or phosphorous added to a waste help keep the ruthenium fixed in the calcine during calcination.

A conceptual off-gas cleanup system for a fluidized-bed process for solidifying power reactor wastes, along with decontamination factors for particulate (as fine solids) and volatile (as a stable gas) ruthenium projected across each cleanup device of the system, are given in Figure 7. The projected DFs are based primarily on WCF operating experience. Expected particulate ruthenium DFs are: 10 across the calciner and cyclone, 600 across the quench tank and venturi scrubber, 8 across the silica gel adsorbers, and 10^6 across two HEPA filters, for a total DF of 5×10^{10}. Expected volatile ruthenium DFs are: 10^4 across the calciner and cyclone, 10 across the quench tank and venturi scrubber, 800 across the silica gel adsorbers, and 1 across two HEPA filters, for a total of 8×10^7. The conceptual off-gas cleanup system is based on in-bed combustion heating at a minimum bed temperature of 500°C. The waste feed is assumed to be Barnwell-type waste that is one-year cooled from the reactor and generated from 35,000 MWD/MTU fuel. The daily calcination rate is equal to the waste from processing 7.5 MTU.

3.5 Cooling and Condensing

The fluidized-bed wet off-gas scrubbing system uses a quench tower, a venturi scrubber, and spray separators to cool the off-gas and remove fine particles. The dust removed from the off-gas is collected in the scrubbing solution that drains continuously from the quench tower and the de-entrainment separators to the scrubbing solution surge tank. Scrubbing solution is continuously recirculated from this tank to the quench tower and venturi scrubber by a pump. The heat removed from the off-gas and gained by the scrubbing solution is removed from the scrubbing solution by the scrubbing solution cooler. Nitric acid is used as the scrubbing solution in order to dissolve the collected solids. The scrubbing solution is usually kept at an acidity of 2N and a density of 1.25 g/mL.

The 1.68-m-diameter quench tower cools the off-gas from about 450 to about 75°C by contacting the off-gas with cooled scrubbing solution that is sprayed from four spray nozzles in the spray ring countercurrent to the gas flowing up the tower. Although the primary purpose of the quench tower is cooling, it also collects some of the larger particles.

The spray calciner uses condensers, and particulate DFs of 10^3 are reported.

3.6 Decontamination Efficiency

Fluidized-Bed Calciner. The predicted flow of solids through the off-gas system and the estimated airborne solids concentrations is shown in Figure 8. The most sensitive cleanup dvices in the off-gas system are the HEPA filters which can deteriorate in service due to age and in contact with moisture. If filter performance is monitored, and deteriorating filters are replaced when necessary, a set of filters in series can probably provide essentially any required collection efficiency. The basis for the assumed filter-system DF of 10^6 is: (1) the filter system contains a pair of HEPA filters in series followed by a backup filter system containing another HEPA filter, and (2) two of the three HEPA filters are in good condition providing a DF of 10^3 each. The DF values for the other off-gas components are based

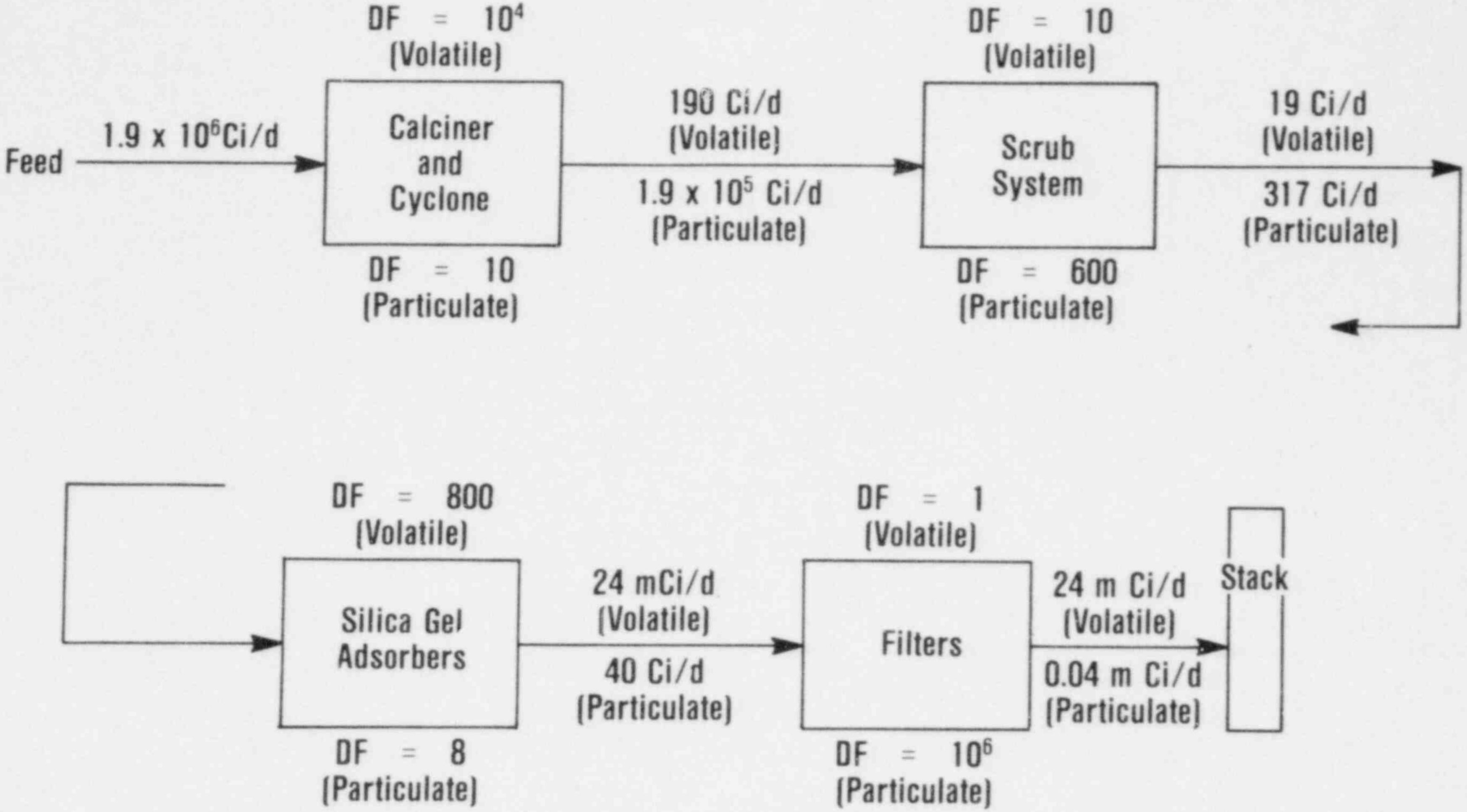

Figure 7. Flow of Volatile and Particulate Ruthenium Through Candidate Off-Gas System

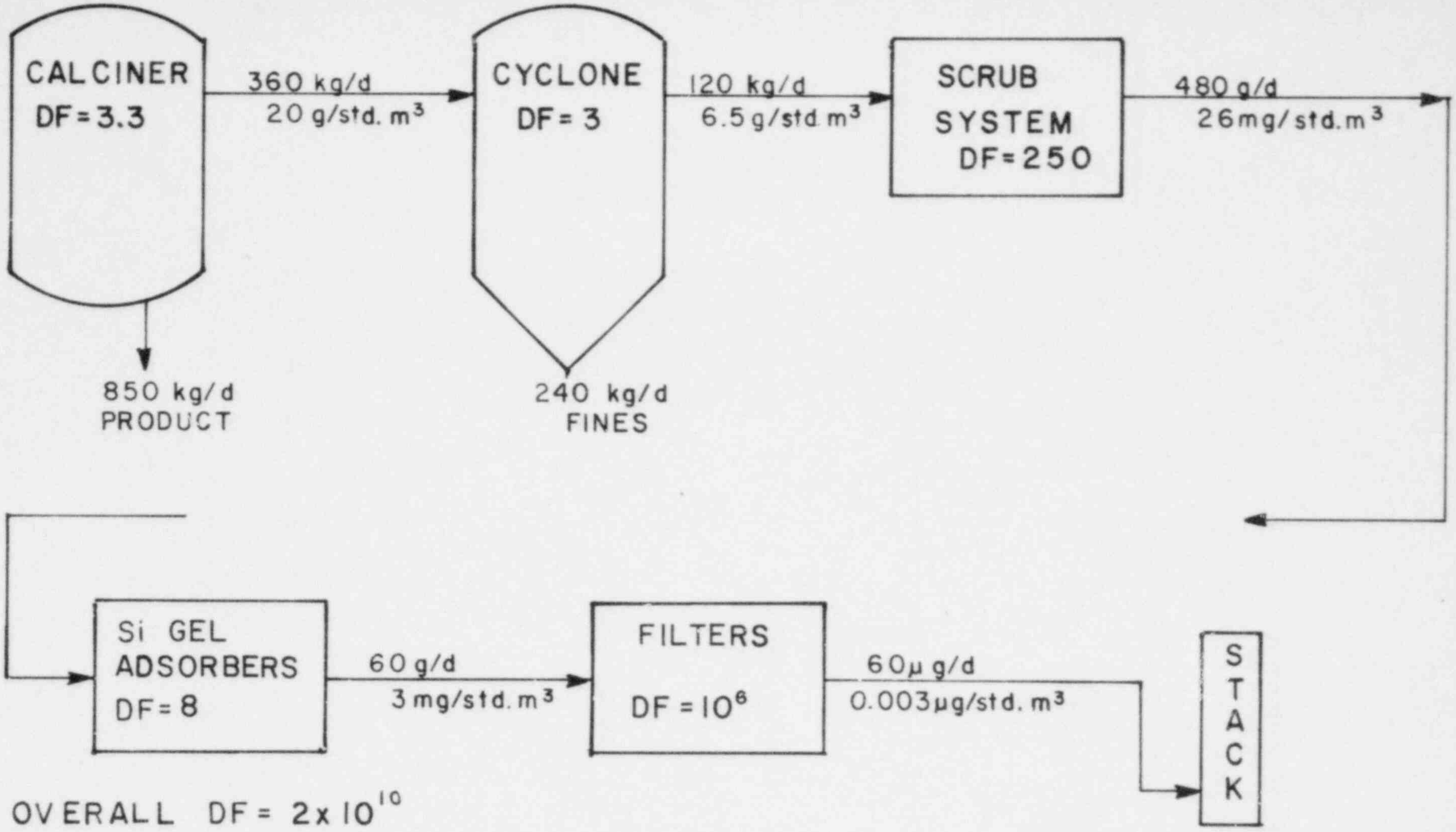

Figure 8. Flow of Solids through Candidate Fluidized-Bed Off-Gas Cleanup System

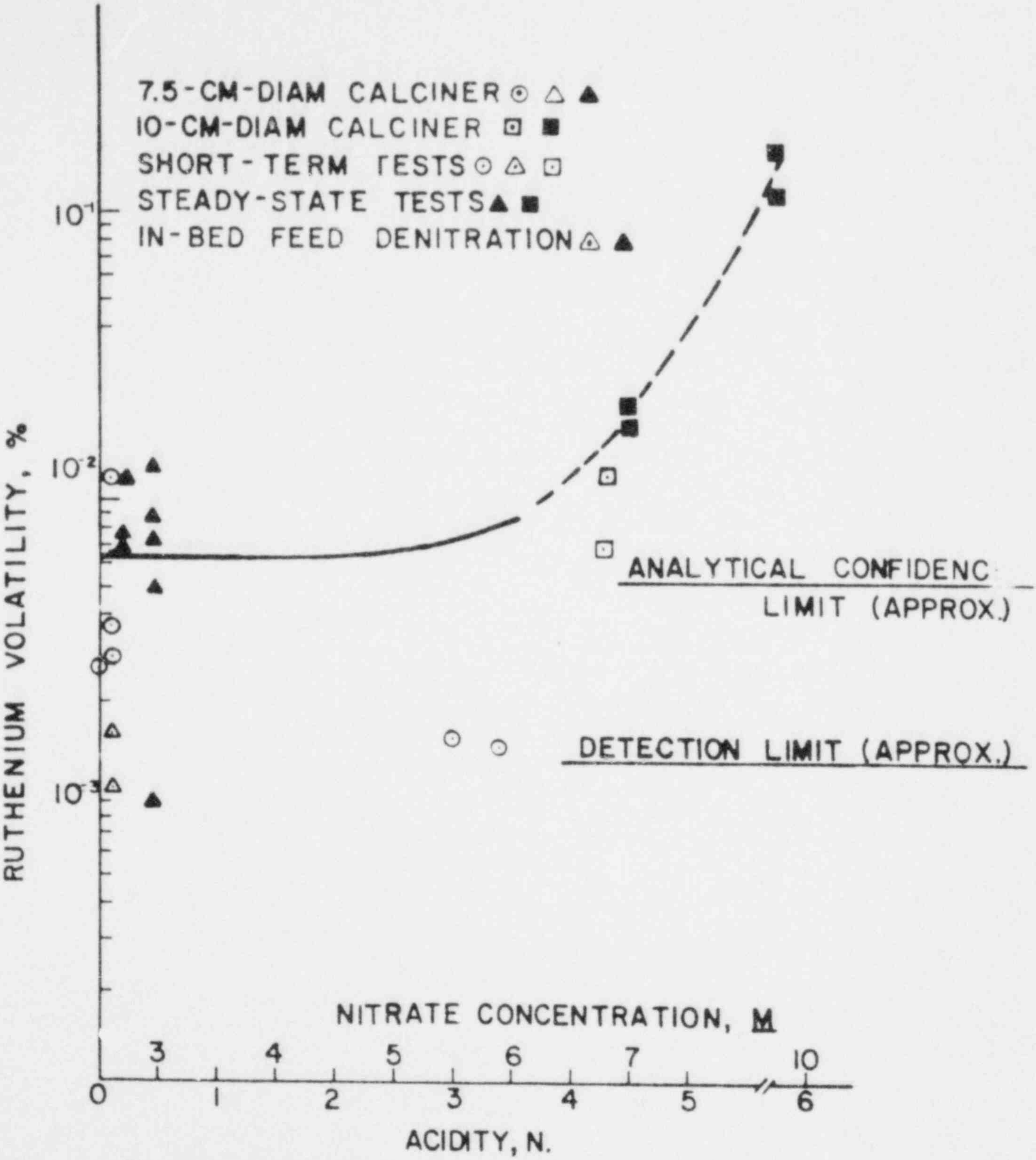

Figure 9. Ruthenium Volatility during In-Bed Combustion

4. Materials of Construction

Recommended candidate materials of construction, based on present experience, for calcination of power reactor wastes are generally Nitronic 50 and in some cases, 304L for the feed system, 347 for the calciner vessel, Nitronic 50 for the off-gas and solids transport equipment, and 304L for storage of calcined solids.

Materials recommendations will vary with the type of calciner. Waste characterization of the ILLW is required and the entire calciner systems should be evaluated for the method and types of decontamination required to maintain and operate the system.

Tests of candidate materials for pneumatic transport piping and bends showed Nitronic 50 to have acceptable corrosion and weldability characteristics, and superior resistance to erosion. Nitronic 50 showed a three-fold increase in erosion resistance over 304L, which were the original materials used in the WCF. Based on these tests, Nitronic 50 was recommended for replacement and future applications.

5. Calcination Experience

Methods for calcining liquid radioactive wastes generated during fuel reprocessing have been under development since the early 1950s. Those processes receiving the most emphasis have been spray calcination, fluidized-bed calcination, and rotary kiln calcination. Spray calcination work has been primarily at PNL and at Karlsruhe in West Germany. The basic spray solidification process was developed and proven as a part of the WSEP program at PNL from 1967 to 1972. A total of 33 demonstrations were completed and more than 50 million Ci of radionuclides were processed. As a part of the total program, the spray calcine was converted to glass and stored in 33 canisters. The WFP began at PNL in 1972 and has continued to the present.

Spray calcination, both in the United States and West Germany, has been shown to be a practical process for the calcination of liquid wastes. The process has been in development at PNL for over 15 years. Aqueous wastes that can be dried to form oxides can be solidified by spray calcination. Operation of a spray calciner heated by superheated steam has been demonstrated at Karlsruhe in West Germany.

Practical feed systems, calciner operating variables, and off-gas cleanup systems have been investigated sufficiencly to reveal no major technical problems using spray calcination.

Fluidized-bed calcination has been studied extensively at the ICPP since 1952; development work was also undertaken at PNL and Japan. Based on development work at ICPP from 1952 to 1958, a Demonstrational Waste Calcining Facility (DWCF) was placed on-stream in December 1963. The unit was originally designed to calcine aluminum nitrate wastes at a throughput of 230 Lph; process and equipment modification has resulted in the present WCF which routinely processes zirconium-fluoride wastes and blends of 1-2$\underline{M}$ sodium wastes. Since 1963, the WCF has calcined greater than 11×10^6 litres of radioactive wastes. The volume reduction factor has averaged approximately seven. Though major design changes would be required for processing power reactor wastes, the basic applicability of fluidized-bed calcination to such wastes has been demonstrated.

Beginning in 1974, pilot-plant studies were conducted at ICPP to verify the fluidized-bed calcination of simulated power reactor wastes. The reference waste composition was a blend of HLLW and ILLW as proposed for the Barnwell plant. Greater than 1200 hours of pilot-plant operations revealed no major technical problems.[7]

Rotary kilns have also been extensively studied for the calcination of high-level wastes. Early work in the 1950s and early 1960s was done at Hanford and Brookhaven National Laboratories in the United States. Currently, the rotary kiln has been selected as the calcination unit in the French continuous vitrification process. Prior to 1971, approximately 5000 hours of testing were completed on a prototype rotary kiln calcination unit. A full-size industrial rotary kiln was designed and built and testing initiated in 1972. Over 8000 hours of operating experience has been obtained during the last three years. Gear and seal lifetimes of 3000 hours have been demonstrated. Currently, a fully radioactive plant is on-stream at Marcoule. Experience to date with the rotary kiln shows that the process is practical for the calcination of LWR-type power reactor wastes.

6. Calcination Technology Assessment

All of the calcination processes discussed above are practical for the calcination of power reactor wastes. Technical problems that would prevent the confident design of a production-scale calcination facility, based on any of the processes and the testing to date, do not exist. The particular process chosen for a given fuel reprocessing plant must be based on compatibility with the total waste management program, economics, safety, and cost considerations.

Refinements can be made in all the calcination processes; however, the process and equipment technology for feeding calciners, operation of the various calciners, and cleanup of the off-gas have been adequately verified. Existing feed systems tested in pilot-plant units or in actual operation (WCF), are reliable. Improvements are needed in metering of feed, flow rate control with minimal plugging, and the ability to manage undissolved solids in the feed.

The ability of the various types of calciners (spray, fluidized-bed, or rotary kiln) to calcine liquid wastes has also been verified. Process heat input by electrical resistance heaters for the spray and rotary-kiln calciners is acceptable. The fluidized bed can operate using either an in-bed heat exchanger or in-bed combustion. All of the calciners have the ability to evaporate, dry, and calcine the liquid wastes and generate a product for feed to other waste form conversion processes. Unit capacities need to be better defined and increased where practical; the fundamental behavior of the various calcination processes should be studied to further increase unit throughput and the ability to calcine various waste types; efforts are also required to decrease capital equipment and operating cost, and increase the safety of a production-scale operation.

Though off-gas cleanup systems proposed and tested for the various processes are adequate, further work is justified to both simplify and decrease the cost of off-gas cleanup. Also, materials of construction for all process steps (feed, calcination, and off-gas cleanup) should be better defined to increase plant reliability. The status of technology of the calciners discussed herein is shown in Table I.

IV. CALCINE MANAGEMENT

1. Calcine Storage

The greatest heat generation rate for high-level waste is during the first 10 years of decay time after reactor discharge, with ∿90% decrease in heat generation rate occurring during the first 5 years.[11] The conditions for storing a solidified high-level waste depend on the method of cooling, container configuration and wall temperature, product heat generation rate and thermal conductivity. The very high initial heat output of power reactor wastes (defense wastes are generally a fiftieth to one-hundredth as much), the low thermal conductivity (∿0.24 W/m-K) and storage temperature limits (∿700°C) of calcined waste dictate the conditions for storing calcine.[12] Calcined waste is restricted to about 700°C in storage temperature, due to potential migration of fission products such as Cs and potential agglomeration much above 700°C. Assuming a mixture of high-level intermediate-level power reactor waste as proposed,[12] about 91.2 kg/MTHM of calcine would be produced. Heat generation rates were based on a fuel burnup of 33,000 MWD/MTHM. To store this calcined waste within a reasonable time period in convection-cooled containers in air or water, long small-diameter cylinders or annular cylinders are required. The number of canisters required annually for calcine storage from a 1500 MTU/yr plant are shown in Figure 10. Limiting conditions assumed for storing calcined waste in air or water were, 43 and 21°C cooling media temperature, and 300 and 60°C maximum canister wall temperature, respectively. Container length assumed was 305 cm.

Based on the above conditions, undiluted calcine can be stored under water at 4 or 8.5 years in 20- or 30-cm-diameter cylinders, respectively. For storage in 20- or 30-cm-diameter air-cooled cylinders, the waste would have to be 6 or 12 years old, respectively. Calcine less than 4 years old can be stored in a cylindrical container if diluted with a nonradioactive material such as silica sand. Interim or prolonged storage of calcine, therefore, is

TABLE I

STATUS OF TECHNOLOGY FOR CALCINERS

CALCINER	HEAT INPUT	PRODUCT	FEED INTRODUCTION	WASTE LIMITATIONS	CAPACITY	EXPERIENCE	PROCESS IMPROVEMENT WARRANTED
Spray	External multizone resistance furnace	Powder	Pneumatic atomizing: 70 um droplets	Low melting point solids	∼5 mtu/ day plant	15 years pilot-scale	Reduced scaling: Eliminate solids bridging:
Fluid Bed	In-bed combustion or in-bed heat exchanger	Powder and granular material	Pneumatic atomizing	Low melting point solids	∼5 mtu/ day plant	15 years Plant-scale on defense waste	Predictable particle size control; reduce bed agglomerates; minimize fines generation
Rotary Kiln	External multizone resistance furnace	Powder and granular material	Gravity feed	Low melting point solids	2-3 units for 5 mtu/day plant	15 years	Increase unit capacity; Increase kiln life

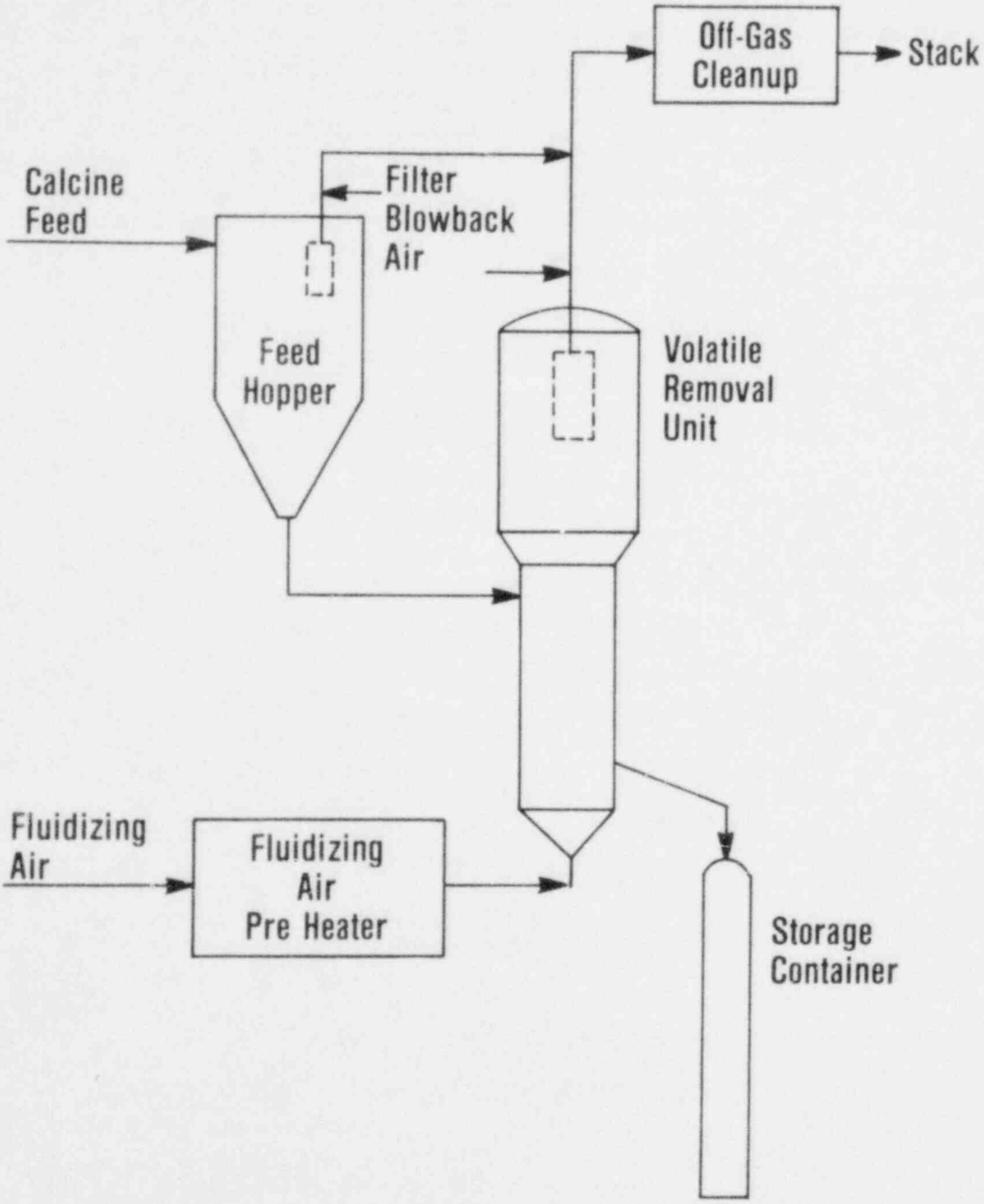

Figure 10. Schematic Diagram of Volatiles Removal Process

practical in containers similarly sized to those proposed for other high-level waste forms, although the decay time before final storage may have to be 3 to 5 years more, because of repository heat generation limits.[13]

2. Calcine Stabilization

To store calcined power reactor calcine in sealed containers will require that the calcine be stable to temperatures of at least 700°C for the first few years after preparation. Calcine usually has residual nitrates of 0.3 to 10 wt%, depending on the method of calcination and the type of waste. Volatiles such as H_2O and CO_2 are also present. These volatiles should be removed prior to sealed storage to prevent pressure buildup to unacceptable levels in storage canisters. Experiments have shown it is possible to sufficiently stabilize (remove volatiles) calcined waste for sealed container storage.[14] The process used to remove volatiles from fluidized-bed calcine is shown in Figure 11. The experiments used a simulated power reactor calcine prepared by a fluidized-bed process. Stabilization was also carried out in a fluidized-bed system, but at low air velocities (6-15 cm/s) to minimize carry over of fines. The fluidizing air was preheated and the fluidizing bed was heated with a resistance heater placed in the bed.

The rate of NO_x liberation and the residual amount of nitrates remaining in the calcine were measured to determine when the calcine had reached stability with regard to volatiles liberation. Stabilization was considered complete when the limits of nitrate detection (< 0.06 wt%) in the calcine was reached. Denitration time varied from 18 to 32 minutes at 725°C for initial nitrate percentages of 1.5 and 9.4, respectively. Time required to reduce nitrate content to < 0.06 wt% varied from 30 to 43 minutes at bed temperatures of 720 and 620°C, respectively, for a calcine initially containing 9.4 wt% NO_3.

At the above stabilization temperatures, no Cs or Ru was volatilized, but at temperatures above 750°C, Cs started to volatilize. Calculations on potential pressure buildup with increasing temperature, due to complete volatilization of 0.02 wt% NO_2 or 0.006 wt% H_2O from the calcine, indicate that at 700°C a pressure of ~275 kPa (40 psi) or 207 kPa (30 psi), respectively, could result. If both NO_2 and H_2O are present at the prescribed amount, a theoretical pressure of 483 kPa (70 psi) could result. In practice, such pressures would not occur because of chemical equilibrium. Stabilized calcine stored at 700°C for two weeks in a sealed container indicated no pressure buildup. Properties of stabilized calcine are shown in Table II.

3. Interface with Conversion Processes

Calcine is often considered as a starting material for conversion to more leach resistant and less dispersible waste forms. The leachability of alkalies in calcine is high and radioactive cesium and strontium will leach rapidly. Leachability of other fission products and actinides is generally low.[5] Due to the large surface area of the calcine, the weight percent leached per unit time is generally higher than, for example, a glass.

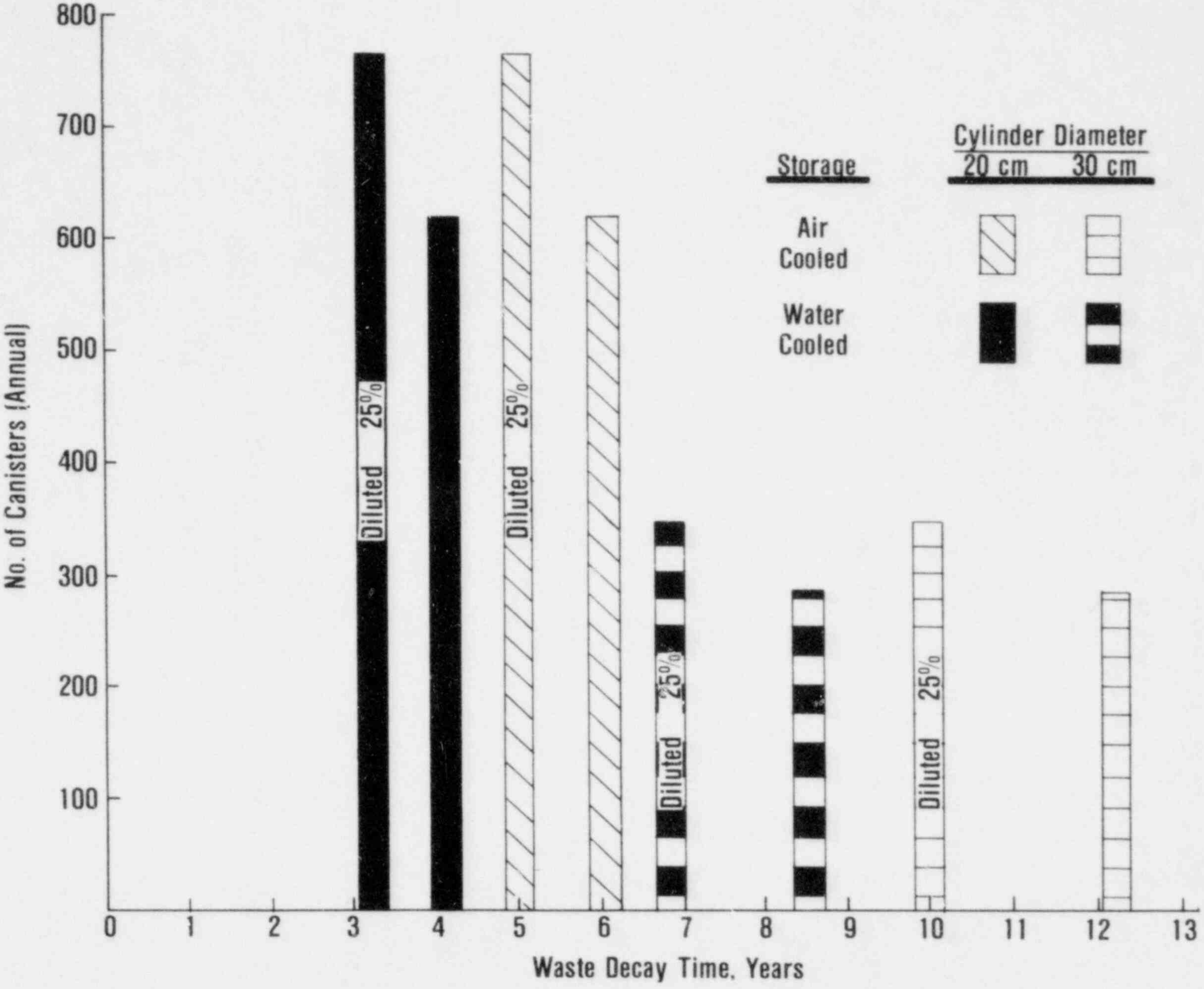

Figure 11. Practical Storage Times for High-Level Calcined Commerical Waste

TABLE II

PROPERTIES OF SIMULATED COMMERCIAL CALCINE

Density, g/cc	2.2
Thermal conductivity, W/m · K	~ 0.24
Volume, m^3/MTHM	0.03 - 0.05
Maximum Permissible Storage temp. °C	~ 700
Percent Volatiles (after volatiles removal stage)	$<$0.06
Leachability	
CS-Sr	High
Alkalies	High
Other elements	Low to Intermediate

	Fluid-Bed	Spray	Rotary
Particle size, mm	0.01-0.5	0.001-0.1	0.01-Flakes

To convert calcined waste to other waste forms such as glass, calciners are often directly coupled to the conversion process. The spray calciner as developed by Battelle Northwest Laboratory is directly coupled to either an in-can glass melting process or to a joule-heated ceramic melter.[6,7] Fluidized-bed calciners can be either directly coupled or coupled to temporary storage prior to coupling to either of the above processes. The rotary kiln calciner is normally directly coupled to a glass melter.

In cases of direct calciner coupling to a conversion process, provision is made to feed the product forming materials, such as glass frit, to the output of the calciner, or to the liquid feed as in the case of Supercalcine,[18] or the bed of a fluidized-bed calciner.

4. Waste Forms Requiring Calcine as Starting Material

Calcine is required as a starting material for conversion of high-level waste to several waste form alternatives to glass including pellets, pellet-metal matrix, and sintered ceramics.[19,20] Although a direct liquid-to-glass conversion process has been tested, this process is not perfected; therefore, for all practical purposes calcine is also required as a starting material for a glass waste form.

Calcine is very practical for use in preparing the above waste forms, because it is a concentrated particulate solid with a low percentage of volatiles and it can be easily metered and mixed to form the desired waste form. The percentage of calcine incorporated into these waste forms varies from ∿25 to over 70 wt%, and the resultant volume increase is generally between 25 and 100%.

V. CONCLUSIONS

1. Calcination

Based on the documented pilot-plant studies and plant performances, calcination technology is available for processing power reactor high-level and intermediate-level wastes. Plant throughputs, product properties, and effluent releases are compatible with fuel reprocessing plant waste production rates, waste form conversion processes, and ALARA effluent release guidelines.

2. Calcine Management

Pilot-scale studies have shown that technology is available for long-term storage of calcine or coupling of the calcination process with candidate waste form conversion processes.

3. Future Needs

Emphasis should be on the following:

- Refinements to and fundamental understanding of candidate processes.
- Establish specific criteria for final waste forms.
- New calcination techniques to increase simplicity and safety and to decrease cost.
- Large-scale demonstrations using radioactive feed to those processes most compatible with candidate waste forms.

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Discussion Following

CALCINE PRODUCTION AND MANAGEMENT

Presented by Bill R. Dickey

Larry Penberthy - Penberthy Electromelt International, Inc.
Comment:
Most of the compounds shown on your slide are compatible with glasses. At Hanford, cesium is being separated as the chloride. Chloride is not very compatible with glasses in general, the limit being 1 to 2 percent solubility. If feasible, I suggest that sulfate or carbonate be the anion if later incorporation into glass is a possibility.

Dickey
Response:
Chloride also presents problems in the off-gas cleanup system of any of the calcination processes. If you have a significant amount of chloride, you are faced with corrosion problems in the wet off-gas cleanup systems of all these processes.

Properties of Spent Fuel

M. D. Houston

U.S. Nuclear Regulatory Commission

TABLE OF CONTENTS

Abstract

The properties of spent fuel from current commercial nuclear power plants are discussed. These fuel rod designs utilize Zircaloy tubular cladding filled with uranium dioxide (UO_2) pellets. During reactor operation, various chemical and physical changes take place in the fuel and cladding due to neutronic and thermal processes. The processes and changes are reviewed. The major topics are as follows: fission product formation, fission product relocation and release, pellet cracking and relocation, fuel-to-cladding interaction, and Zircaloy growth and embrittlement. The chemical and physical properties of reactor fuel after achieving its designed irradiation exposure are described. The integrity of spent fuel rods is discussed as it relates to short and long term storage.

I. Introduction

In practically all light water reactors (LWRs), the fuel designs utilize uranium dioxide (UO_2) fuel enclosed in Zircaloy cladding. The UO_2 fuel is in the form of sintered cylindrical pellets. The fuel is of high chemical purity--typically a total impurity level of 1500 ppm maximum--and is slightly enriched in U-235 (∿1 to 4%). The pellets are sintered to a high physical density (about 95% of theoretical) and may have flat or dished ends. The cladding is a zirconium alloy, Zircaloy-2 for boiling water reactors (BWRs) and Zircaloy-4 for pressurized water reactors (PWRs). A schematic diagram of a typical fuel rod is shown in Figure 1. Spatial arrays of multiple fuel rods are held together with spacer grids, guide tubes or tie rods, and end fittings to form the fuel assemblies. A photograph of such an assembly is shown in Figure 2.

The fuel material, fuel pellets, and Zircaloy cladding undergo various and complex changes during reactor operation due to irradiation processes and to exposure to the pressures and temperatures encountered in the reactor core. These changes and processes are characterized in general terms as follows: fission product formation, fission product relocation and release, fuel densification, pellet cracking and relocation, fuel-to-cladding mechanical and chemical interaction, Zircaloy growth, and Zircaloy embrittlement. Most of these attributes have both an irradiation exposure and a temperature dependency. The following discussion will consider these changes and processes in more detail.

II. Discussion

A. Uranium Dioxide Fuel

The chemical, physical, and mechanical changes incurred in UO_2 fuel and Zircaloy cladding during reactor operation are due primarily to fission and thermal processes. The fission process generates both fission products and thermal energy within the fuel pellet (1,2,3). The changes that occur will depend upon the concentration and nature of these fission products and the fission rate or rate of heat generation.

The exact amount of each fission product present in the fuel at any given time is a function of the power history. However, a reasonable approximation can be obtained from the cumulative yields of the long-lived and stable isotopes. The expected identity and yield of these fission products is given in Table 1 (4). The nature and behavior of these products will be discussed later.

The fission process also generates thermal energy within a UO_2 pellet, and this generation is fairly uniform across any radial plane. This distribution of fissioning coupled with the low thermal conductivity (2,3) of the UO_2 produces high centerline temperatures and steep temperature gradients in the fuel pellets. A typical radial temperature

Table 1

STABLE (OR LONG LIVED) FISSION PRODUCT YIELDS FOR THERMAL FISSION OF U-235(4)

	% Yield*		% Yield*
Se	0.4	Sn	0.1
Br	0.3	Sb	0.1
Kr	3.8	Te	2.5
Rb	1.3	I	1.0
Sr	6.2	Xe	20
Y	4.8	Cs	20
Zr	36.9	Ba	6.7
Pu	23	La	6.6
Mo	25	Ce	12.3
Tc	6.1	Pr	5.9
Ru	9.3	Nd	20.5
Rh	4.9	Pm	2.3
Pd	1.4	Sm	1.9
Ag	0.2	Eu	0.2
Cd	0.1		

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* Number of atoms per 100 fissions

profile for a fuel rod operating at 12 kw/ft is shown in Figure 3. These temperatures and gradients have a major effect upon the operational behavior of the fuel. Specifically, thermal processes are involved in fission product migration and release, fuel densification, fuel restructuring and grain growth, pellet cracking, fuel-cladding interaction, and the removal of crystalline lattice damage.

Since the UO_2 pellets are finite-length cylinders, the ends have more freedom for thermal expansion under the characteristic temperature profile than do the midplanes. Also, the pellet ends possess a higher physical density than do the midsections because of the pressing and sintering techniques applied for fabrication. These attributes cause the pellet to change from a straight cylindrical shape into an hourglass configuration during reactor operation (5). As the pellet ends become more flared at higher gradients or power, tensile forces are developed within the pellet. Ceramic materials are characteristically weak in tension, thus these forces are relieved by crack formation. The cracking pattern is expected to be random although some aspects of crack patterns can be related to operating power, temperature, and fuel plasticity (2,6-11). Typical transverse and longitudinal cross sections of cracked pellets are shown in Figures 4, 5 and 6. It is believed that most pellet cracking occurs during the first few ramps to power. Thus, these open pathways are probably available for fission product migration over the lifetime of the fuel. Some crack healing may occur during operation and additional cracks may form during cooling.

Extreme distortion of the fuel pellets as might occur during a large power ramp may close the fuel-to-cladding gap and result in pellet/cladding mechanical interaction (PCI) (12,13). Here, the flarred ends of the pellets push outward on the cladding to cause ridging, commonly referred to as bambooning (14). At the same time, the pellet is expanding longitudinally so, with the mechanical lockup at the end edges, the cladding can be stretched in the axial direction. Some PCI is expected during the fuel lifetime and will not cause problems or failures in the fuel cladding if the strains are maintained at a low level.

Fission product formation was discussed previously. As a result of the steep temperature gradient in the fuel, some fission products can move away from the location of the fission event that produced them (3,15). Because of the broad range of physical and chemical properties of the fission products, the extent of migration and the mechanism by which it occurs is peculiar to each species. Some can be transported by thermal processes, namely, vapor migration and diffusion. The mobility of a particular fission product may depend on the properties of its precursor in the fission decay chain as well as its own properties. Thus, the migration of cesium is undoubtedly influenced by the fact that the precursors of this species are gaseous xenon isotopes, some of which have appreciable half-lives. The precursors of molybdenum, on the other hand, are zirconium and niobium isotopes, which are not particularly

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mobile in oxide fuels. The fission products that form oxides that are soluble in the fuel matrix show little tendency to migrate in the temperature gradient. Solid fission products that remain in the fuel contribute to fuel swelling. It is found that this swelling is linear with burnup at a rate of approximately 1.0 volume percent per 10,000 MWd/tU.

The fission products that are present as a gas phase coalesce into bubbles, which diffuse to grain boundaries, cracks, or interconnected porosity in the matrix from which they escape to the open spaces in the fuel rod (16-19). The amount of fission gas generated is approximately 3.5 volumes of gas per volume of UO_2 per 10,000 MWd/tU (20). At end-of-life conditions (∿35,000 MWd/tU), it is anticipated that 5 to 10% of this gas will have been released from the fuel (21).

The details for the chemical elements found on the inner surfaces of irradiated fuel rod cladding are only known in a qualitative manner (15,22,23). In an experimental PWR-type fuel rod, a reaction layer or duplex layer was observed (24) between the fuel and cladding and contained the elements U, Zr, Cs, Pd, Ba and Te. A photograph of a typical reaction layer is shown in Figure 7. The following elements were observed (22) at the fuel-to-cladding interface in PWR fuel rods of current design: large amounts of Cs and U, smaller amounts of I and Te, and lesser amounts of Cl, Mn, Fe, Ag, Si, Ba, Cu, Na and Ca. The appearance of these deposits, some circular in pattern, is shown in Figure 8. In these and other studies, cesium and/or iodine have been reported to concentrate at pellet-to-pellet interfaces.

Throughout the fissioning process, the UO_2 lattice structure exhibits a high level of stability. Some lattice damage is observed at fuel temperatures below 400 C (1). At temperatures of 500 C and above, which correspond to the minimum fuel operating temperatures, no significant change in the lattice structure has been observed for exposures up to 140,000 MWd/tU (1). X-ray diffraction studies also show no significant line broadening. The absence of a change during irradiation was ascribed to the migration of the fission products to grain boundaries and lattice defects. Thus, it is concluded that the lattice structure of UO_2 is unaffected by irradiation at temperatures in excess of 500 C, apparently because of the mobility of the fission-produced defects and fission product atoms at these temperatures.

Densification and grain growth complete those changes that occur in the fuel during reactor operation. Fuel densification is caused by similar diffusion and mass transport mechanisms encountered during the sintering of pellets, but densification is enhanced in the radiation environment (25,26). The process of in-reactor densification is active from the initiation of fuel operation and is virtually complete in the burnup range from 5000 to 10,000 MWd/tU. Above 10,000 MWd/tU, fuel swelling from the fission product accumulation is dominant. The amount of densification will depend upon the thermal stability of the as-manufactured fuel. Most current UO_2 fuel is fabricated to about 95% of its theoretical density and, at most, will only densify to 96-97% T.D. Stable fuel of lower density has been demonstrated but has not been widely applied in reactor loadings. Grain growth processes are closely related to those for densification although the two do not necessarily have to occur simultaneously. Current fuel as fabricated has an initial average grain size in the range from 2 to 4 microns; see Figure 9. Grain growth is usually observed only in those regions of the fuel that experience temperatures in excess of 1200 C. Final average grain sizes in the range from 6 to 10 microns are common for these regions; see Figure 10 (27).

B. Zircaloy Cladding

While the above behavior is taking place in the fuel, the Zircaloy cladding is also being altered. The alpha-zirconium matrix, which is dominant in Zircaloy, has a hexagonal crystal structure and, as such, shows a pronounced anisotropy in its mechanical properties. These properties for Zircaloy cladding are influenced by texture, heat treatment and other metallurgical variables (28). During the neutron irradiation, several material properties of Zircaloy are changed. The most pronounced effects are associated with strength, fracture behavior, and creep. In general, the mechanical strength increases significantly while the elongation or ductility decreases. These changes saturate early in the fuel operating cycle and are essentially completed at an exposure of 5000 MWd/tU (29). As an example of the magnitude of these changes during irradiation, the yield strength for annealed Zircaloy-4 has been reported (30) to increase from 70,000 to 90,000 psi while the total elongation decreased from 20 to 5%. The effect on creep depends on other factors, such as texture or metallurgical state, and can be enhanced or retarded by irradiation (31,32). The physical reason for all of these changes is thought to be related to the production of vacancies, interstitials, defect clusters, and dislocation loops. The size and distribution of the lattice defects have been found to depend on irradiation temperature, neutron fluence, and chemical composition.

Another phenomenon observed with Zircaloy in a radiation field is stress-free growth (31-34). The mechanism for this growth is complex and not completely understood. The current explanation (35) is based on the formation of vacancy loops on the basal planes, interstitial loops on prism planes, and differential drift of interstitials and vacancies to suitably oriented segments of grain boundaries. Fuel rods and assemblies are designed with sufficient clearances to accomodate this growth.

Other changes associated with the Zircaloy cladding are due to its chemical behavior. During the operational lifetime, the cladding is exposed to various sources of oxygen, hydrogen and iodine. The largest single source of oxygen and hydrogen is the reactor coolant, water or steam, which interacts to form a corrosion layer of ZrO_2 on the external surfaces of the cladding with the liberation of hydrogen. Under normal operating conditions with controlled coolant chemistry, the final corrosive product is a thin, black, adherent layer that protects the cladding from further chemical reaction. Some of the released hydrogen diffuses through the oxide layer and is dissolved in the Zircaloy. The solubility limit for hydrogen at operating temperatures is about 150 ppm, but this reduces to a few ppm at cold conditions (5). At reactor shutdown, any excess hydrogen in the cladding is precipitated as a zirconium hydride phase in the shape of platelets; see Figure 11. The orientation of the platelets depends on the texture and the stress relationships of the metal. Since hydrogen embrittels the Zircaloy cladding, it is desirable to maintain a low hydrogen content and to assure that precipitation occurs in a circumferential orientation.

The internal surface of the Zircaloy cladding is exposed to those elements that are released during the fission process. Each fission event annihilates a uranium atom, releasing two oxygen atoms that are available for redistribution. Most of this oxygen reacts with other fission products or is taken into solution in the UO_{2+x} lattice. A small part of the released oxygen reacts with the cladding to form a ZrO_2 layer (23). In the early history of Zircaloy application, numerous fuel rod failures were caused by localized regions of massive hydriding (2). This hydrogen came from hydrogenous impurities introduced in the fuel during fabrication. Higher purity fuel with special attention to hydrogen (2 ppm limit) has eliminated these failures. Another internal reaction involves iodine, an element that reportedly initiates stress-corrosion cracking in the Zircaloy (36,37). Iodine migrates from the hotter region of the fuel as CsI and deposits in the fuel-to-cladding gap. Here, the cesium iodide can be decomposed by gamma radiation to liberate iodine that may react with the cladding under certain stress conditions. Although this is a recognized mechanism for cladding failure, operating restrictions have succeeded in keeping the number of such failures very low.

C. Spent Fuel Storage

The recent policy decision to defer reprocessing of spent fuel has made it necessary to consider the extended storage of spent fuel assemblies in various wet or dry repositories. These assemblies after achieving their design burnup in the range from 28,000 to 35,000 MWd/tU and undergoing the complex fuel and cladding changes discussed previously, possess, for the most part, a high integrity and are free of fuel rod failures. Storage of spent fuel assemblies in water pools has been standard practice over the past 35 years. Zircaloy-clad fuel has been stored in this manner for periods up to 19 years without evidence of cladding degradation (38). Such performance is expected since the cladding is designed to operate for several years in water at 300 C yet the cladding temperatures for discharged fuel will be a maximum of approximately 60 C, and these temperatures will diminish with storage time.

Several hundred fuel assemblies having rods that developed cladding defects during reactor exposures are also in pool storage. Radioactive gases were expelled during reactor operation to the coolant, but gaseous releases have not been observed from these cladding defects during pool storage. However, nongaseous fission products have been observed in the pool water. Steady-state radioactivity concentrations in the pool can be maintained in the range 10^{-3} to 10^{-4} μ curies per milliliter with ion-exchange and filtration.

The dry storage of spent fuel assemblies after a residence of 5 years in a water pool has been considered (39). Fuel rod degradation in this condition is assumed to occur from stresses caused by end-of-life internal fuel rod pressures (up to about 1120 psia at 25 C) and by stress corrosion cracking. On the basis of a preliminary assessment, a maximum allowable cladding temperature of 380 C was recommended with a caution that stress-corrosion cracking considerations could lower that limit. The expected maximum temperature in dry storage for a fuel assembly after ten years of decay was reported (40) to be 240 C. Oxidation of the cladding could be expected at this temperature, thus the assemblies would have to be protected by an inert atmosphere.

III. Summary

The properties of spent fuel pellets, rods, and assemblies have been discussed. The changes brought about by fission, thermal, and chemical processes have been described. End-of-life fuel rods will contain columns of cracked fuel pellets. These pellets will have densified early in their operating cycle and then expanded due to fission product swelling. A small portion of the fission products, mostly gaseous species, will have been released from the fuel pellets to other internal regions of the fuel rod. The Zircaloy cladding becomes stronger due to radiation processes but loses much of its ductility. Oxygen, hydrogen and iodine form corrosion products with Zircaloy, whenever these elements are present. The expected behavior of fuel assemblies in wet or dry storage is discussed. Problem areas are specified that will require considerations for successful storage.

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Footnote a.: Available for purchase from National Techncial Information Services, Springfield, Virginia 22161

V. ATTACHED FIGURES

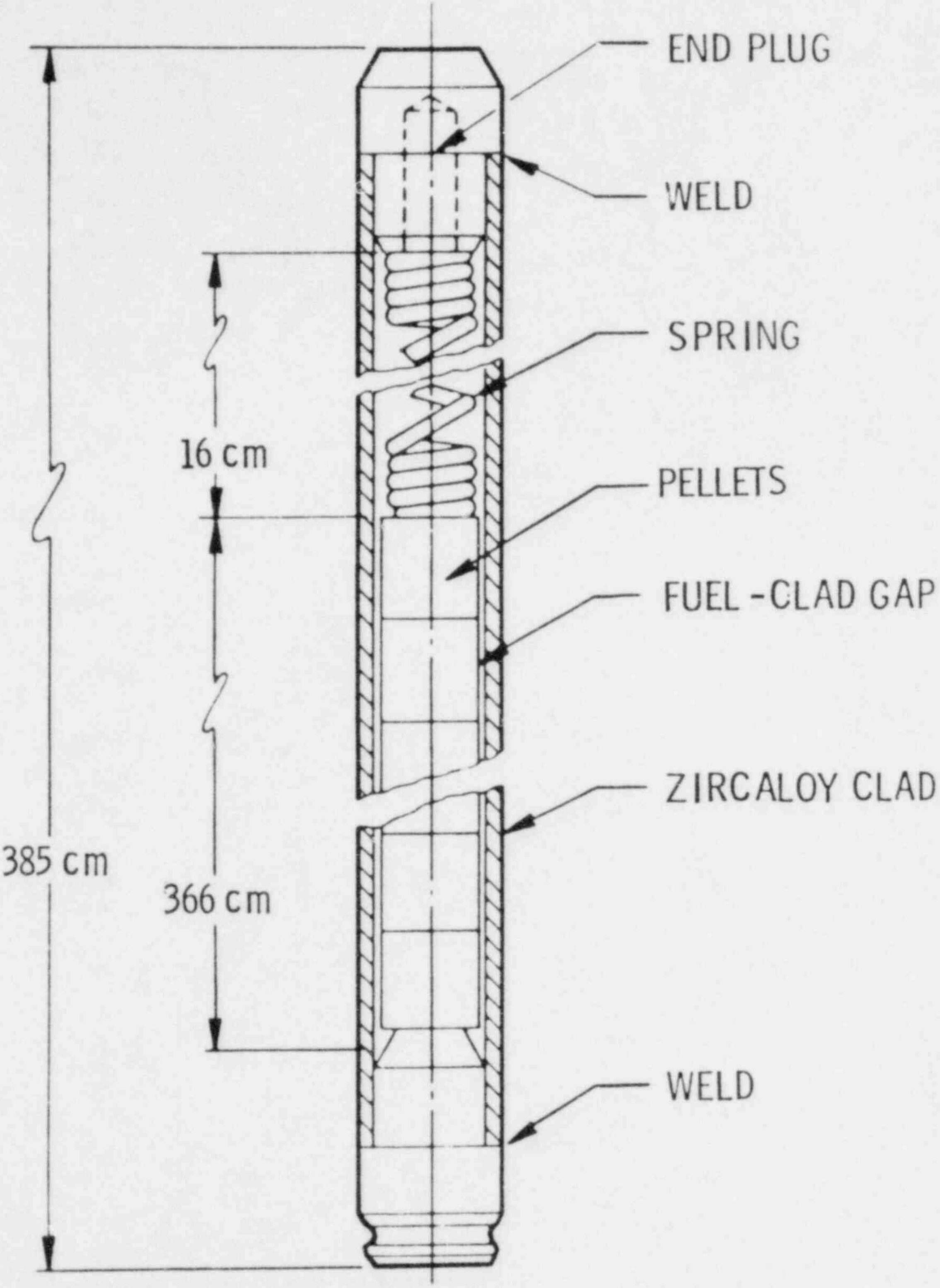


FIGURE 1. TYPICAL PWR FUEL ROD

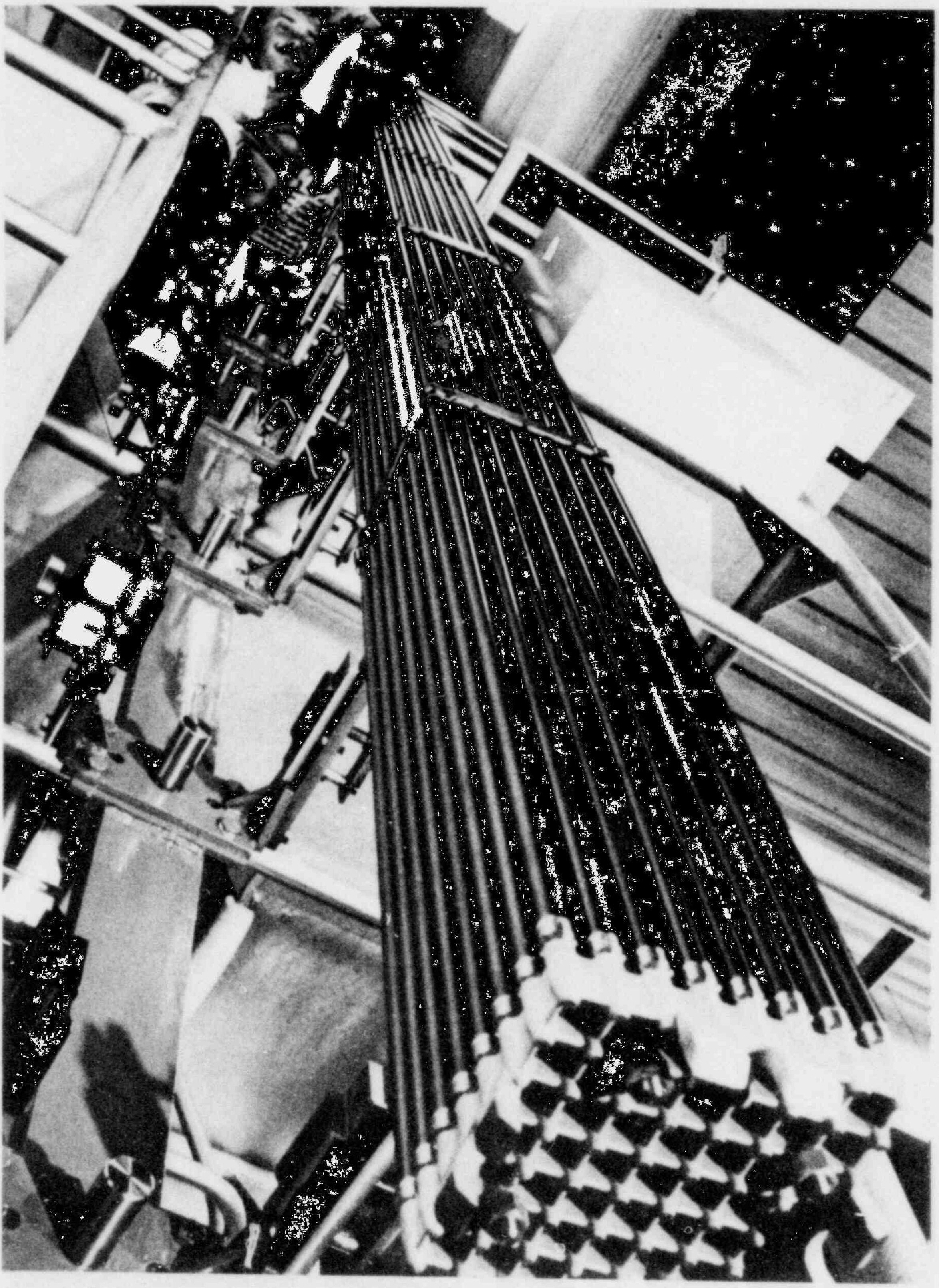
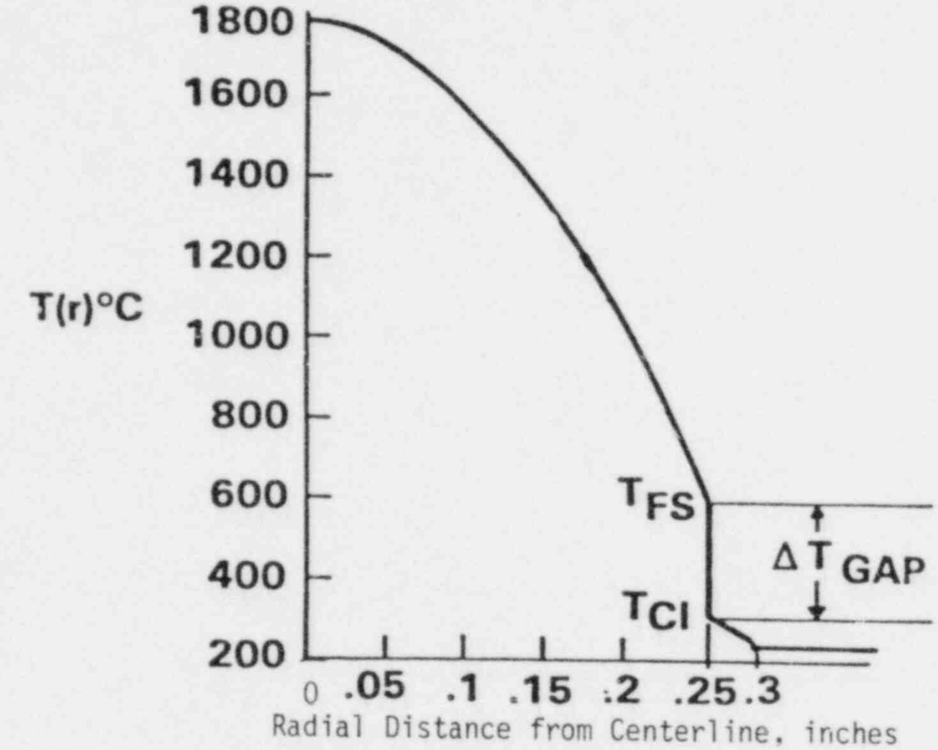


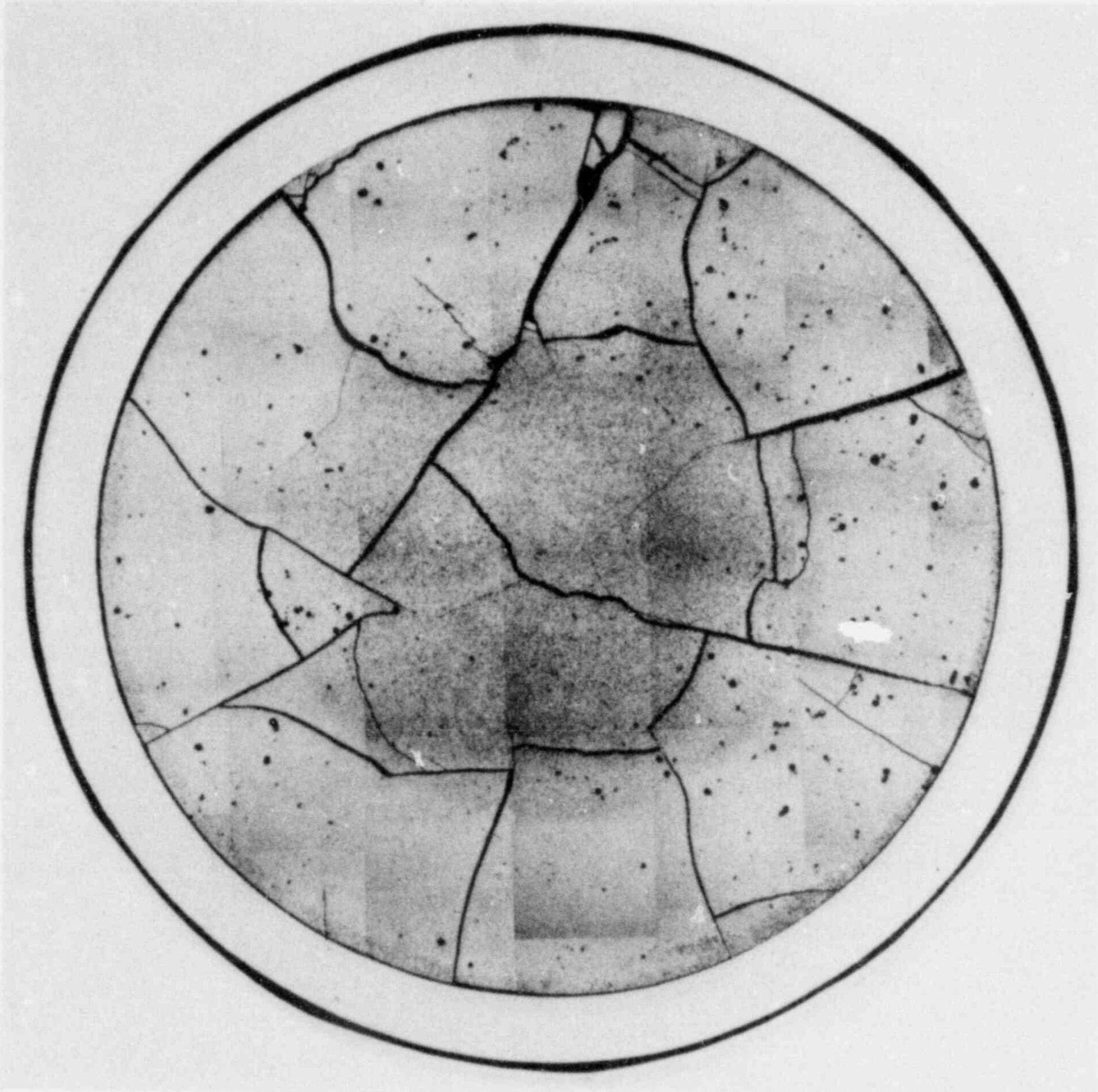
FIGURE 2. BWR FUEL ASSEMBLY



T_{FS}= Fuel Surface Temperature

T_{Cl}= Inner Cladding Temperature

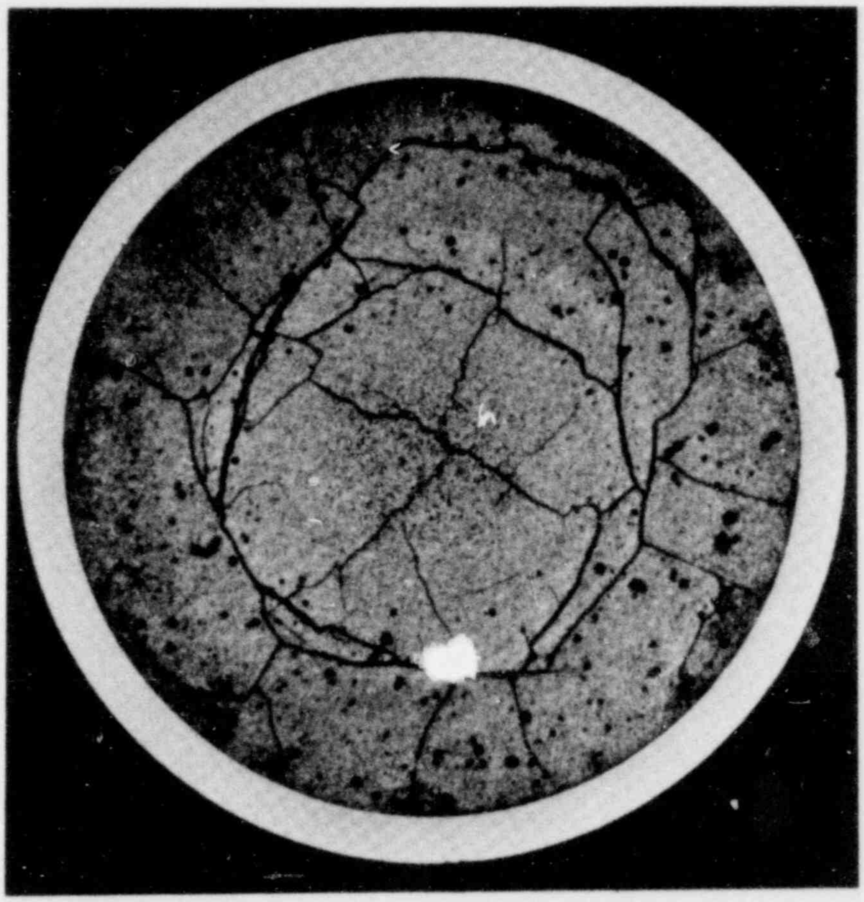
FIGURE 3. TEMPERATURE PROFILE FOR FUEL PELLET AND CLADDING OPERATING AT 12 KW/FT



21,000 MWd/tU

15X

FIGURE 4. RADIAL CRACKING PATTERN FOR LWR FUEL (9)



30,000 MWd/tU 10X

FIGURE 5. RADIAL CRACKING PATTERN FOR LWR FUEL (10)

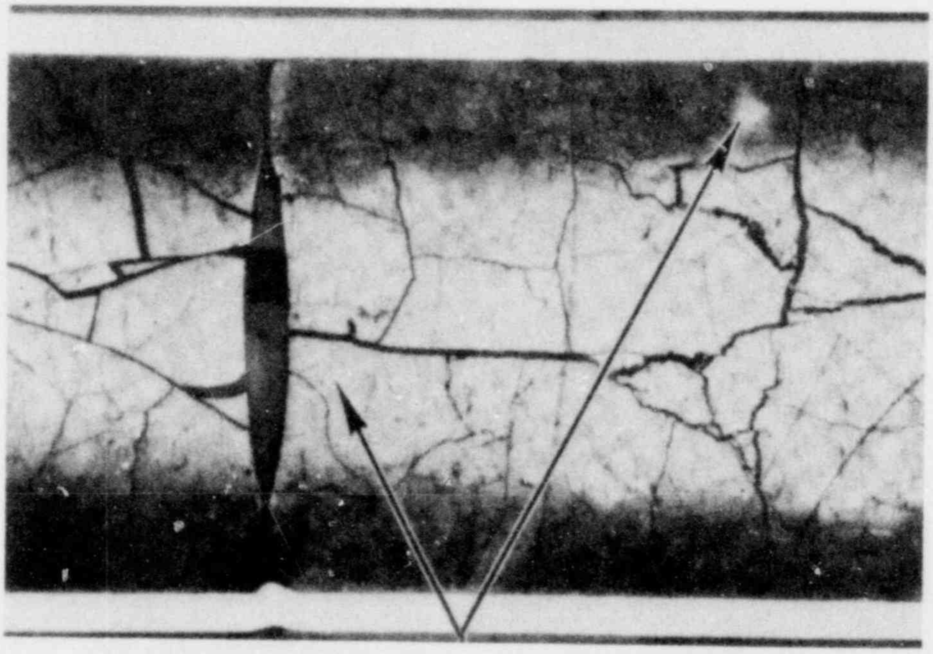


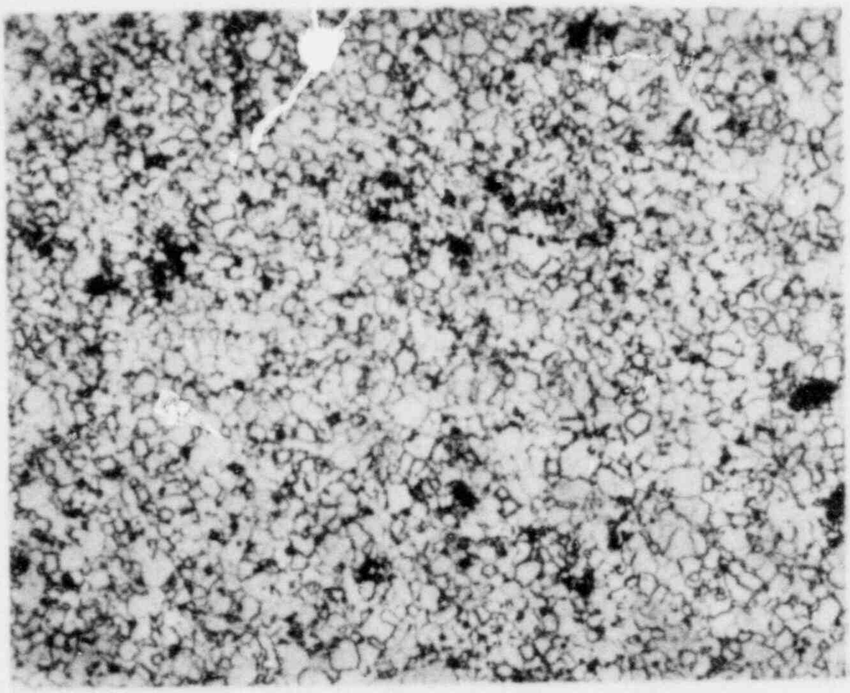
FIGURE 6. AXIAL CRACKING PATTERN FOR LWR FUEL (11)

21,000 MWd/tU 225X

FIGURE 7. BONDED REGION BETWEEN FUEL AND CLADDING (9)

21,000 MWd/tU 225X

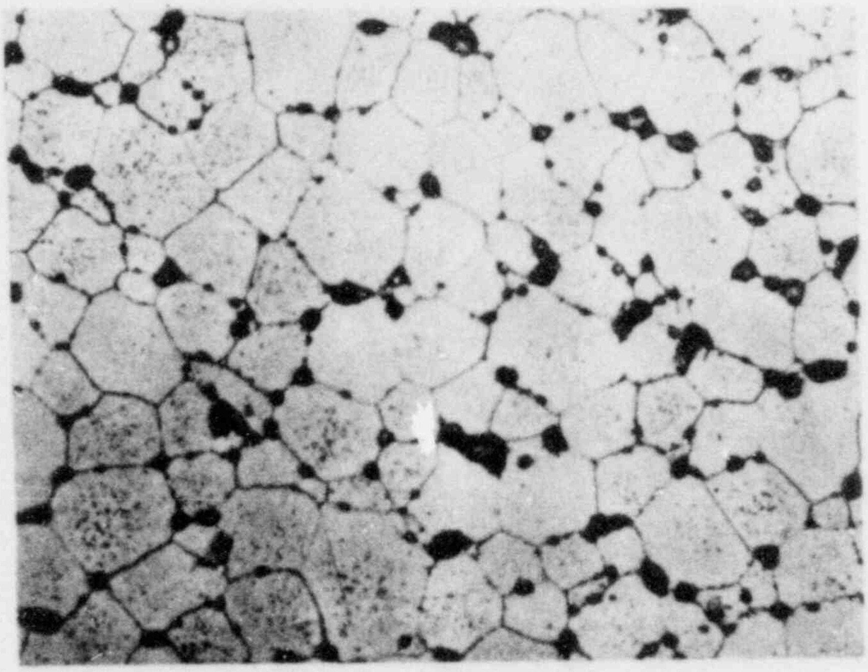
FIGURE 7. BONDED REGION BETWEEN FUEL AND CLADDING (9)



As-Sintered 500X

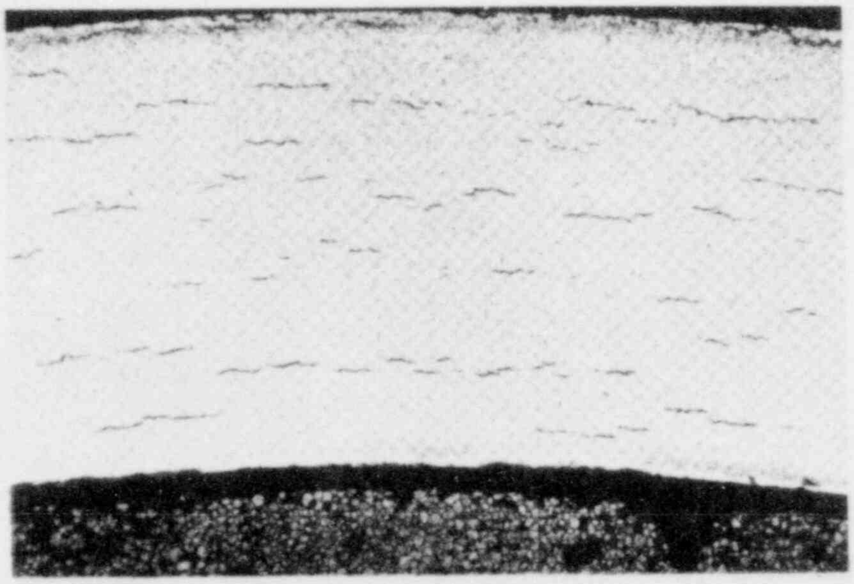
(Average grain size = 1.7 microns)

FIGURE 9. TYPICAL AS-FABRICATED UO_2 GRAIN STRUCTURE (27)



8100 MWd/tU 500X
(Average grain size = 6.8 microns)

FIGURE 10. TYPICAL EQUIAXED GRAIN STRUCTURE IN IRRADIATED UO_2 (27)



30,000 MWd/tU 100X

(Hydrogen content = 55 to 65 ppm)

FIGURE 11. CIRCUMFERENTIAL ZIRCONIUM HYDRIDE PLATELETS IN ZIRCALOY (10)

Discussion Following

PROPERTIES OF SPENT FUEL

Presented by M. Dean Houston

Donald Cameron - Atomic Energy of Canada
Question:
You stated that approximately 1 percent of solid fission products are released into the gap. But, the elements which are released constitute a relatively small fraction of the total fission product inventory. What fraction of cesium, molybdenum, iodine and tellurium are released?

Houston
Response:
I do not believe that has been fully characterized.

Robert Pohl - Cornell University
Question:
I may have missed it. Could you briefly tell us what the burn-ups (in megawatt days per ton) were for the fuel elements that you showed us?

Houston
Response:
I believe they were fairly low. Around 13 to 15 thousand.
(NOTE added upon review of this transcript: Photos were of fuel irradiated to 20 and 30 thousand which is not low.)

Pohl
Question:
Have any pictures been taken on burn-up that are 10 times higher, because you did mention 140 thousand later on in the talk?

Houston
Response:
I do not really believe that would make a large effect upon the nature of the cracking. The nature of the cracking is more a thermal effect than a burn-up one. It depends more on the thermal profile across the pellet than on the burn-up itself.

Pohl
Question:
That is your feeling, but you do not really know of any pictures that have been taken?

Houston
Response:
There may be some. I do not have them here.

Pohl
Comment:
That might be very interesting.

Michael Raudenbush - Stoller Corporation
Question:
Could you or someone from NRC briefly tell us about programs to study the effects of fuel rods in a geologic repository?

Houston
Response:
That is not in an area in which I am involved. I do not know if someone is here from the NMSS office of NRC that could address that question.

Raudenbush
Comment:
Is that on the program? I did not see it if it is. In that case, I would make a comment. In view of the IRG report and other initiatives regarding non-proliferation and the throwaway fuel cycle, I think that should perhaps receive more emphasis in future programs.

J. van Geel - Eurochemic, Mol, Belgium
Question:
The central temperatures in the fuel rods reach 1800°F, if I recall. Are those figures before or after the cracking of the pellets? Do you have data on the thermal conductivity as a function of the degree of cracking?

Houston
Response:
There is some benefit from cracking and relocation when you close the gap and contact the cladding. I do not believe it will make more than perhaps something of the order of 100° C difference in the centerline. This particular profile that we show here is a very idealized thing. I am sure it does not consider relocation. It considers an open gap and the pellet being solid.

Edward E. Pilat - Energy Research Group
Comment:
I think I have part of an answer to that question. I believe the temperatures you showed there were not typical, but were appropriate for the maximum or accident temperatures that would be assumed. For example, you quoted that those temperatures were appropriate to 12 kilowatts per foot, whereas the average kilowatts per foot in a light-water reactor is more like 5. So those temperatures are not the typical ones. The typical ones would be more like 1200 to 1500° F.

Houston
Response:
Right, these are the peak levels.

Chauncy Kepford - Environmental Coalition on Nuclear Power
Question:
You mentioned burn-ups and potential burn-ups. Do you have any idea

what the typical industry burn-up is, as far as fuel goes?

Houston
Response:
The current field designs are scheduled for 27,500 megawatt days per ton for boiling water reactors and about 33 to 35 thousand megawatt days per ton for pressurized reactors.

Kepford
Question:
But what is experienced and what is typical?

Houston
Response:
They have achieved those burn-ups. It is typical of some lead batches. It is not typical of the entire industry.

Kepford
Comment:
I would like to second the comment of the gentleman from Stoller Corporation. It would seem to me that if we are going to a spent-fuel disposal system, that it would be imperative, for instance, to find out the reactions between uranium oxide and salt at elevated temperatures.

Houston
Response:
I agree.

Fred Schmidt - Univesity of Washington
Question:
Do you have any rough statistics on the failure rate of fuel rods during, let us say, the past five years, when we have had heavy use of these fuel rods?

Houston
Response:
Well, up to about 3 to 5 years ago there were quite a few failures due to internal hydriding and there were failures due to pellet/clad interaction (PCI) where the cladding was split. Since the reason for internal hydriding has been eliminated, and since reactors have been given operating instructions to stay away from the PCI problem, there have been very few fuel rod failures during the past 2 to 3 years. If this trend continues, I think we would see less than a tenth of 1 percent as failures.

Jack McElroy - Battelle Pacific Northwest Laborabory
Comment:
For the record, I want to comment on questions that were put forth by two of the gentlemen before me. The DOE has had a spent fuel package program at Rockwell Hanford for over one year. More recently the program has been put under the jurisdiction of the Office of Nuclear Waste Isolation, a DOE program at Battelle. This program is studying the packaging

of spent fuel with the potential of eventual disposal in a repository. Therefore, studies are underway on spent fuel isolation in a waste repository.

Rustum Roy - Pennsylvania State University
Comment:
I wanted to second what Jack McElroy said. A part of that program is going on at Penn State to look at uranium dioxide in contact with brine. That is not the point, though. Our problem is that material scientists have a lousy characterization of spent fuel at the nanostructure and microstructure level. That is a nontrivial problem. I wonder if there are programs on that. Do we have any research, for example, at the national labs? It is a tough problem to determine what phases exist. It is ludicrous to proceed on trying to simulate spent fuel until we know that. I am just trying to find out, maybe there is someone in the audience that knows what is presently known at any decent material science level of characterization.

Houston
Response:
I am not really sure they are looking at grain sizes, grain distribution---

Rustum Roy
Response:
Just phases, just phases---

Houston
Response:
---and phases. There are programs--the ones that I am aware of--that are looking at the stress corrosion cracking phase--looking at the fission products in the gap. Those might get into what you are looking for. Those are being carried out at Stanford Research Institute, and I think that is a very active program supported by the Electric Power Research Institute.

Rustum Roy
Question:
But are there no papers out yet as to what is actually present in spent fuel?

Houston
Response:
There are papers--there are reports in that field, yes.

Rustum Roy
Response.
Well, maybe somebody should determine that. That seems like an elementary question.

Houston
Response:
We shall get those to you.

Jack McElroy
Comment:
Spent fuel leaching studies have been underway for about three years (with actual spent fuel) at PNL. Groundwater, seawater and distilled water were used at room temperature conditions. Higher temperature tests are planned. The results have been reported by Y. B. Katayama and J. E. Mendel, "Leaching of Irradiated LWR Fuel Pellets in Deionized Water, Seabrine, and Typical Groundwater." Transactions of the American Nuclear Society, Winter Meeting, November 1977, San Francisco.

Uranium Oxides in Ores and Spent Fuels

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Cambridge, Mass. 02138

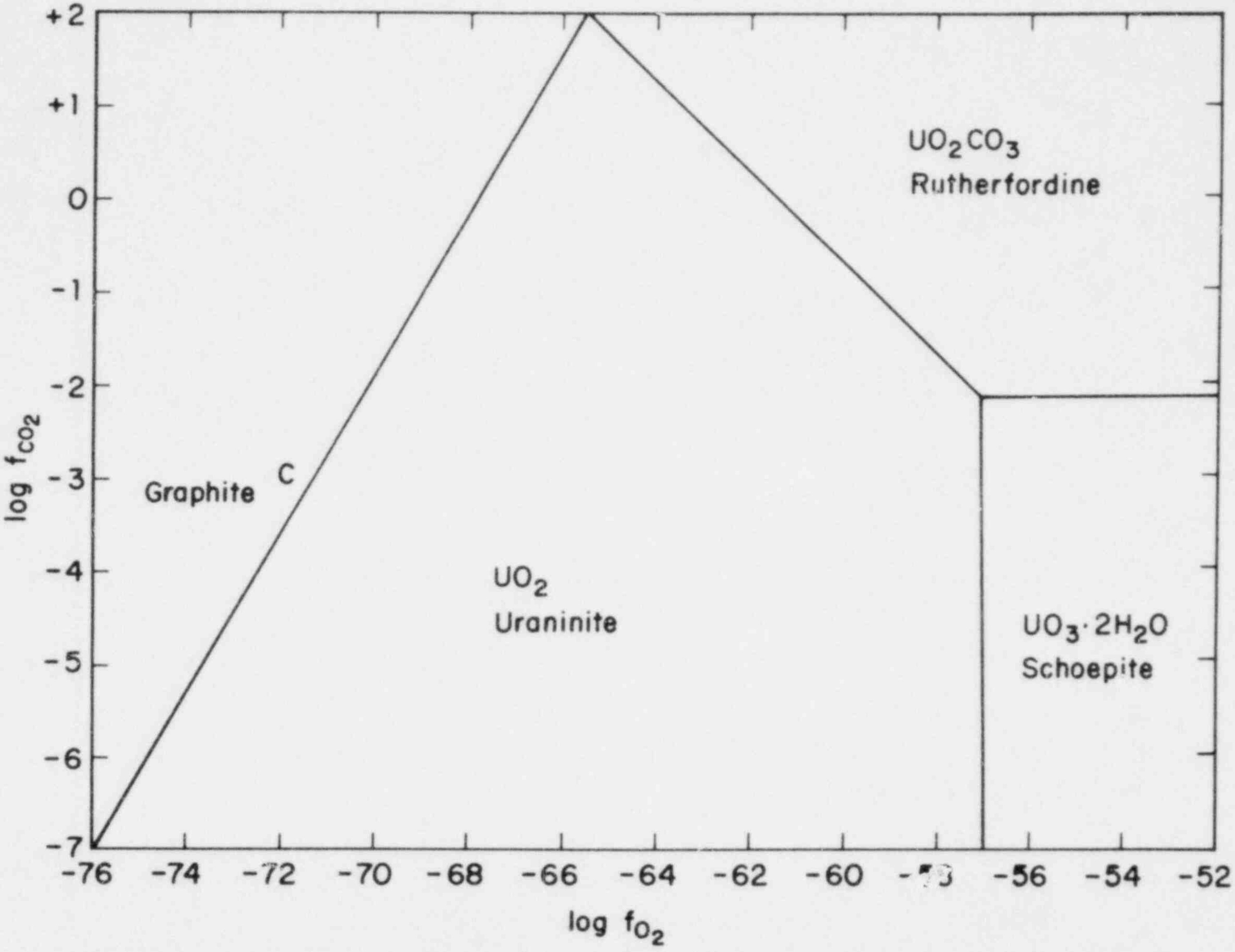
This paper can be regarded as a direct sequel to Houston's (1979) paper, and as a rather preliminary answer to the questions raised at the conclusion of his paper regarding the storage of spent fuel element assemblies. It is well known that even very delicate objects can be stored without noticeable deterioration for several thousand years. Tutankhamun's tomb is a spectacular example of such successful storage. The tomb was designed as a permanent disposal site, and was closed in about 1325 B.C., i.e. ca. 3303 years ago (Edwards, 1977). It was apparently violated within 200 years of its closure, but was resealed and yielded a magnificent assemblage of objects that included linen draperies, leather goods, and a profusion of rush baskets and wooden objects.

The storage of spent fuel element assemblies is more difficult than the storage of such objects because the temperature of the assemblies and of their surroundings is considerably greater than ambient. However, the maximum likely temperatures (see for instance Cohen (1977)) are much less than the temperatures attained during power production. It should, therefore, be possible to store suitably encased spent fuel rods safely in dry, stable environments for any desired length of time.

This is probably not possible where mechanical disturbances can lead to the breakage of fuel element containers and where aqueous solutions can gain access to the fuel elements. The effects of such solution access can be divided into two groups: effects related to the solution of uranium oxide fuel pellets, and effects related to the interaction of solutions with gases and with elements and compounds which reside on grain boundaries and on other surfaces within the fuel rods. This paper deals largely with the first group of effects.

The composition of the stable uranium oxides at temperatures up to a few hundred degrees is still not well understood (see for instance Rich, Holland, and Petersen, 1977). In hydrothermal uranium ore deposits uranium oxides have a composition within the series $UO_{(2+x)}$ where $0 \geq x \geq 0.67$. It is not known whether the entire range of composition from UO_2 to U_3O_8 is thermodynamically stable. In the presence of free oxygen at room temperature $UO_{(2+x)}$ oxidizes to UO_3, which hydrates to schoepite in the presence of liquid water. In the presence of free oxygen and at CO_2 pressures in excess of ca. 10^{-2} atm rutherfordine, $(UO_2)CO_3$, is stable. Relationships between these phases are shown in Figure 1. The diagram is somewhat schematic, because the thermodynamic data for the UO_2-U_3O_8 series and for the various forms of $UO_3 \cdot nH_2O$ are presently inadequate. In spite of these shortcomings the diagram is useful in the discussion of the effect of aqueous solutions on spent fuel elements.

Fig. 1. Log f_{O_2}-f_{CO_2} diagram for relevant solid phases in the system U-O-C-H at 25°C (Rich, *et al.*, 1976).

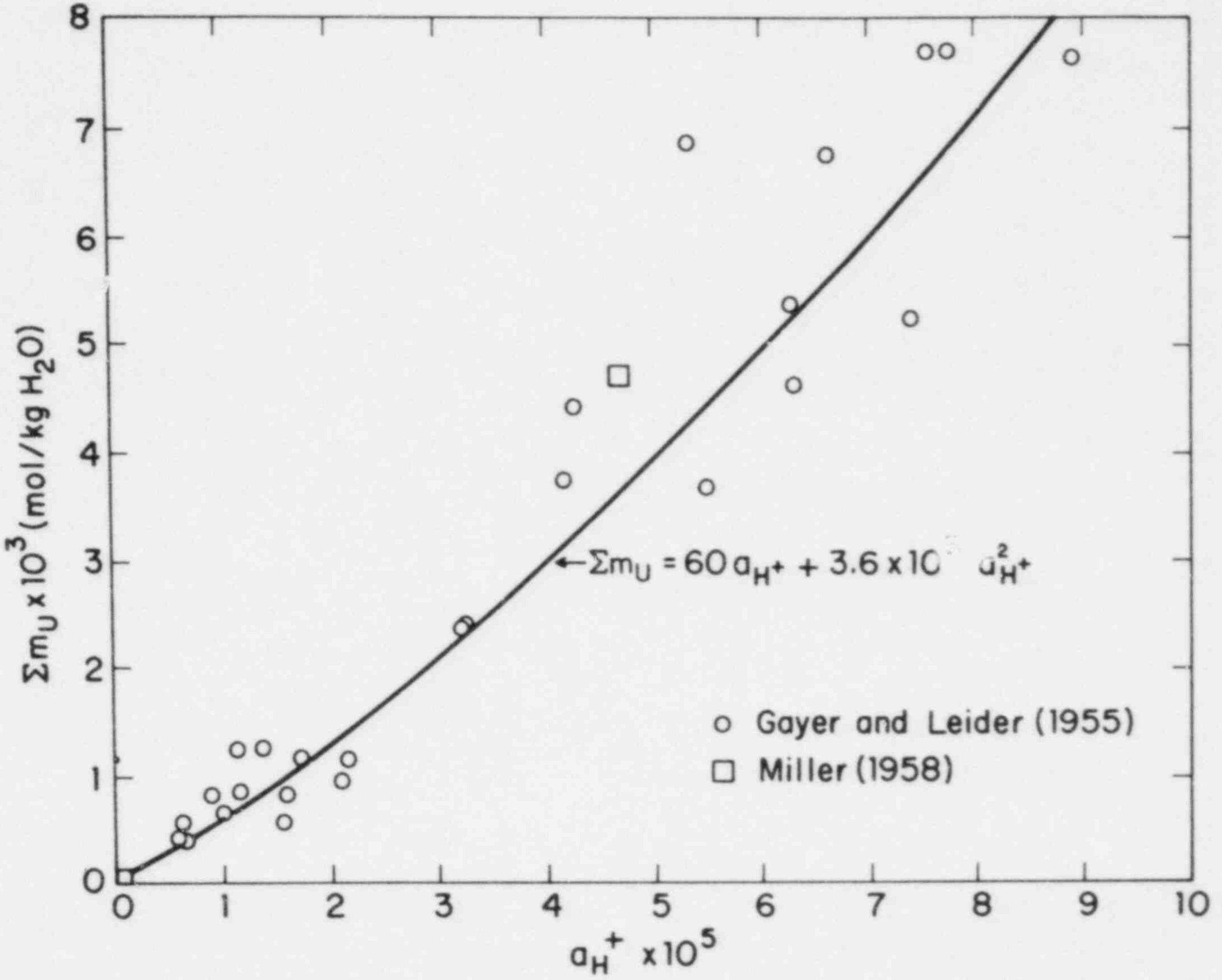

+2
+1
0
-1
-2
-3
-4
-5
-6
-7
log f_{CO_2}
-76
-74
-72
-70
-68
-66
-64
-62
-60
-58
-56
-54
-52
log f_{O_2}
Graphite
C
UO_2
Uraninite
UO_2CO_3
Rutherfordine
$UO_3 \cdot 2H_2O$
Schoepite

Langmuir (1978) has summarized the available data bearing on the solubility of UO_2 in aqueous solutions at 25°C. Although these data are somewhat incomplete, it is likely that in reducing solutions, where U^{+4} and its complexes are dominant and which are saturated with respect to UO_2 at 25°C, the concentration of uranium is less than ca. 0.1 μg/kg solution in the pH range 5-8 even in the presence of a variety of complexing agents. It is likely that uranium concentrations in reducing solutions in equilibrium with UO_2 at 200°-300°C are not much larger (G. McCarthy, personal communication). At first glance it therefore appears that the dissolution of uranium oxide pellets can be maintained at very low levels by buffering the environment of spent fuel elements at low values of the oxygen fugacity. However, this may not be possible. Such buffers may remove free oxygen in solutions which gain access to spent fuel elements, but radiolysis of the solutions adjacent to the highly radioactive spent fuel is apt to produce local oxidants which may well oxidize UO_2 to UO_3. If so, the behavior of the pellets will be governed by the solubility of U^{+6} rather than by that of U^{+4} compounds.

Data for the solubility of these compounds are still very sparse. Figure 2 shows the available data for the solubility of $UO_3 \cdot 2H_2O$ at 25°C. At a pH of 5 the concentration of uranium in an aqueous solution saturated with respect to schoepite is ca. 0.5 x 10^{-3} moles/kg, (120 mg U/kg), i.e. more than three orders of magnitude greater than the solubility of UO_2 in reducing solutions where only U^{+4} and U^{+4}- complexes are present. At 90°C the solubility of

602

Fig. 2. Concentration of uranium in solutions saturated with respect to $UO_3 \cdot H_2O$ in 25°C (Rich, et al., 1977).


$\Sigma m_U \times 10^3$ (mol/kg H_2O)
0
1
2
3
4
5
6
7
8
0
1
2
3
4
5
6
7
8
9
10
$a_{H^+} \times 10^5$
$\leftarrow \Sigma m_U = 60\, a_{H^+} + 3.6 \times 10$ [illegible] $a^2_{H^+}$
○ Gayer and Leider (1955)
□ Miller (1958)

schoepite is smaller than at 25°C, but it is still much greater than that of UO_2 in reducing solutions. Figure 3 is a somewhat preliminary diagram showing the solubility of schoepite at 90°C in dilute aqueous solutions as a function of pH. Above a pH of ca. 6.5 the solubility is apparently independent of pH and is probably determined largely by the stability of the complex $UO_2(OH)_2^{\circ}$. Between pH 4 and 6 the solubility of schoepite increases linearly with respect to the activity of H^+, and is probably controlled largely by the stability of the complex $UO_2(OH)^+$. Below a pH of 4 the solubility of schoepite increases with the square of the H^+ activity, and is probably controlled by the stability of the complex UO_2^{+2}.

If spent fuel rods are stored in salt domes, solutions which might gain access to the spent fuel are apt to be highly saline. Figure 4 shows the presently available data for the solubility of schoepite at 90°C in 1 m NaCl solutions. As might have been expected on the basis of activity coefficient calculations, the solubility of schoepite in 1 m NaCl solution in acid solutions is greater than in NaCl-free solutions at the same pH. It is likely that the solubility of schoepite in more concentrated NaCl solutions at the same temperature and pH will be similar to or slightly greater than in 1 m NaCl solutions. In the near-neutral pH range the effect of NaCl addition will tend to be quite small, since the influence of salts on the activity coefficient of neutral species is much smaller than their influence on the activity coefficient of charged species.

Fig. 3. Solubility of schoepite, $UO_3(H_2O)_x$ at 90°C in NaCl-free solutions.

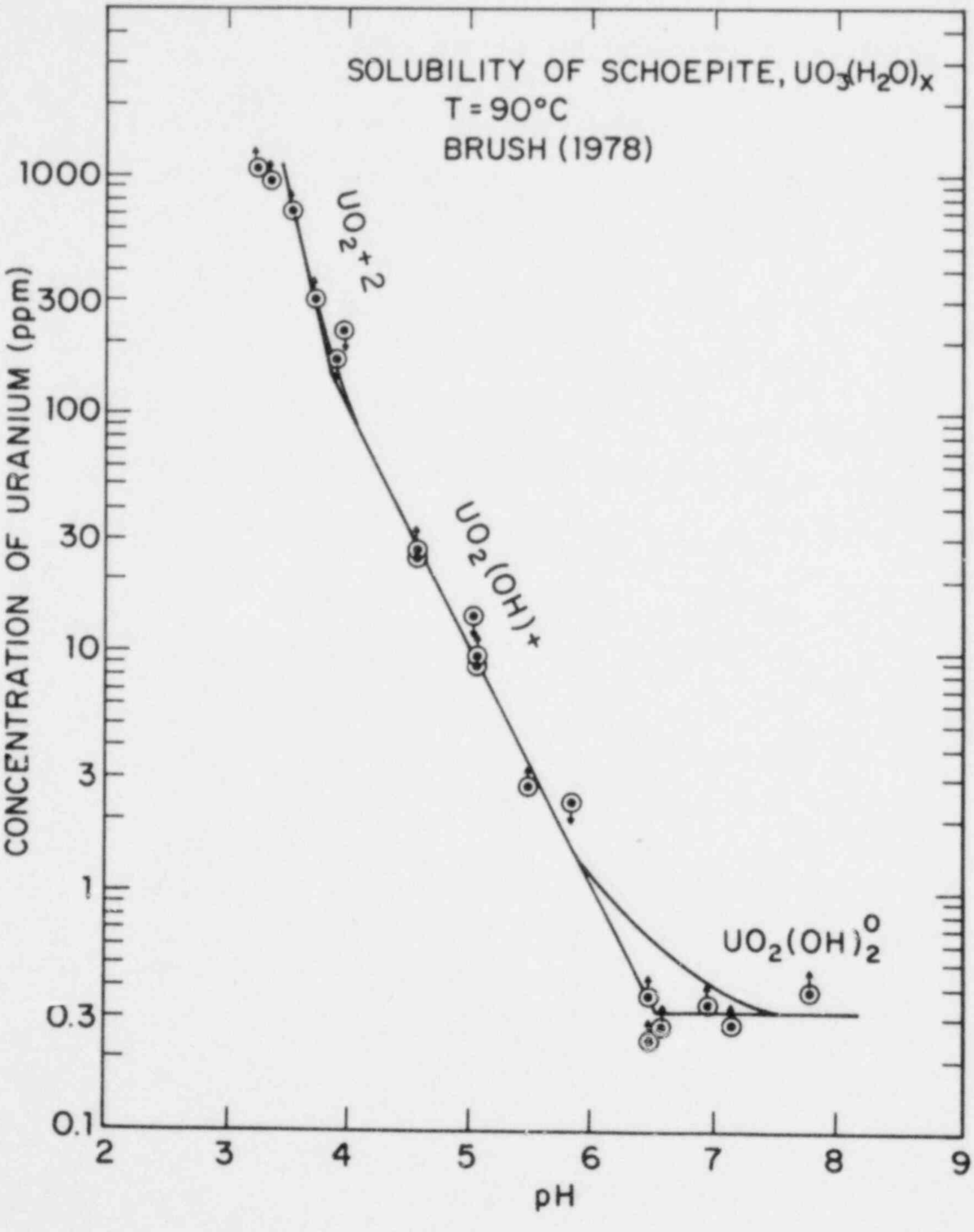
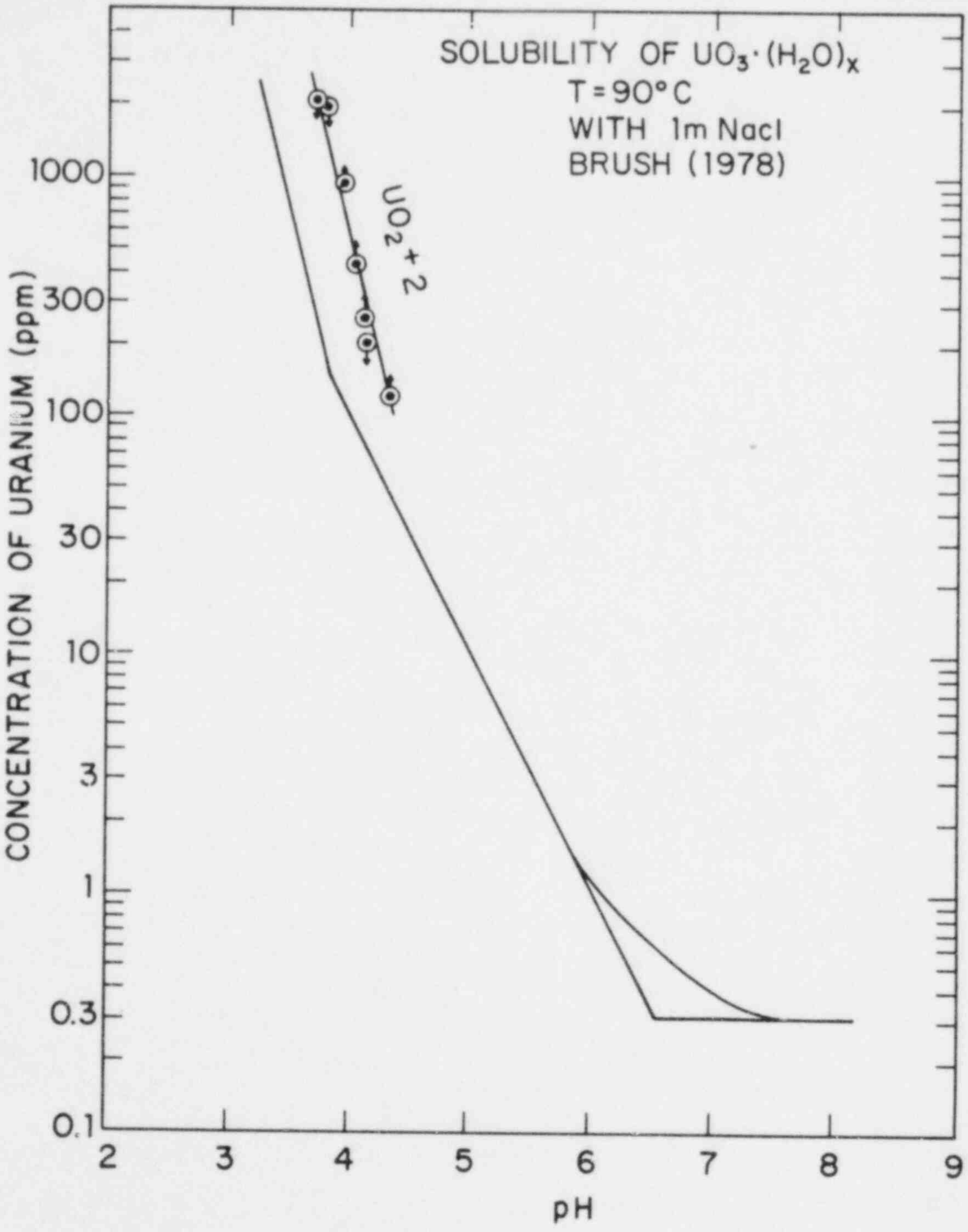

SOLUBILITY OF SCHOEPITE, $UO_3(H_2O)_x$
T = 90°C
BRUSH (1978)
UO_2^{+2}
$UO_2(OH)^+$
$UO_2(OH)_2^0$
CONCENTRATION OF URANIUM (ppm)
1000
300
100
30
10
3
1
0.3
0.1
2
3
4
5
6
7
8
9
pH

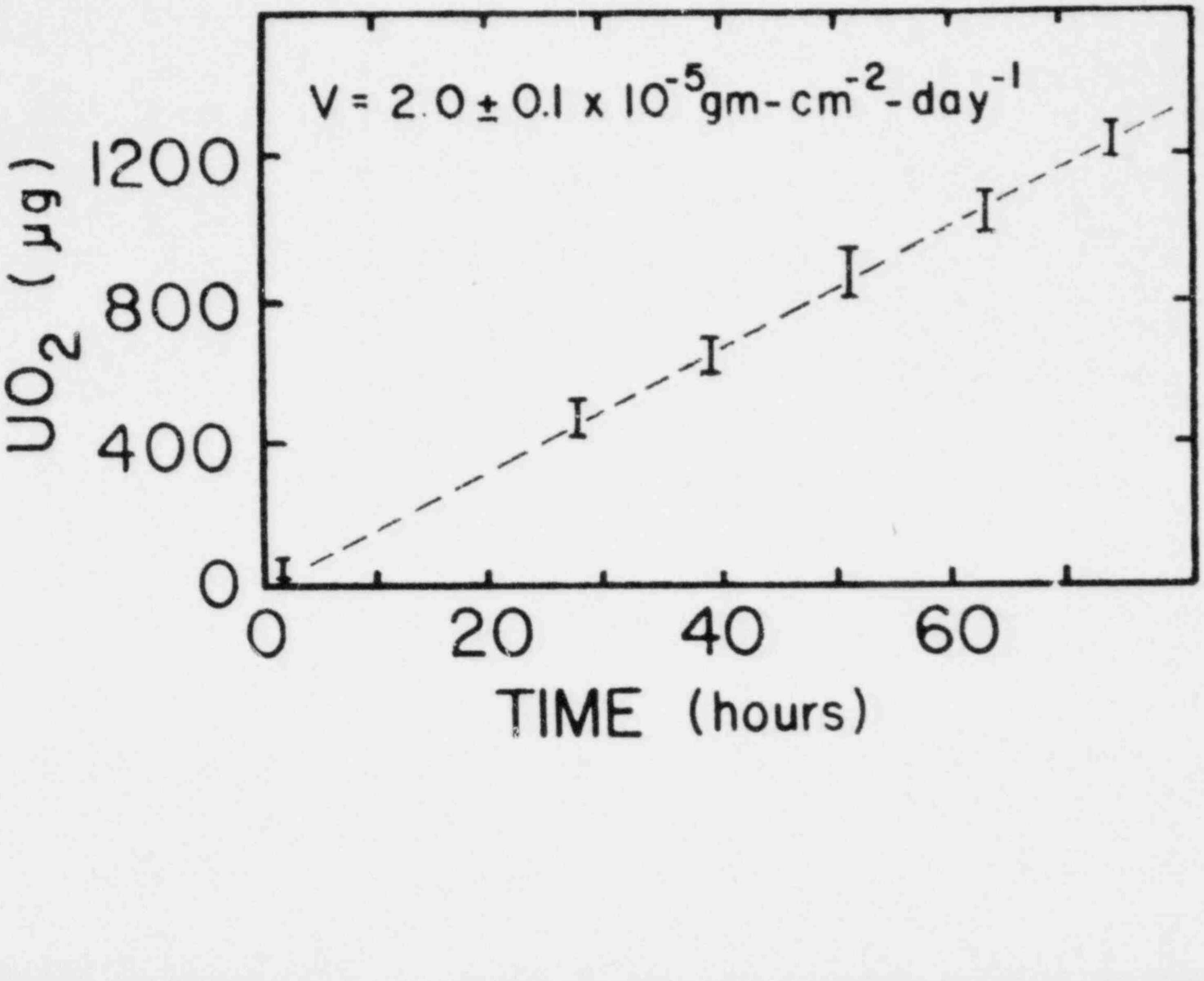
Fig. 4. Solubility of schoepite, $UO_3(H_2O)_x$ in 1 molar NaCl solution at 90°C; solubility in NaCl-free solution shown for purpose of comparison.


SOLUBILITY OF $UO_3 \cdot (H_2O)_x$
T = 90°C
WITH 1m Nacl
BRUSH (1978)
UO_2^{+2}
CONCENTRATION OF URANIUM (ppm)
1000
300
100
30
10
3
1
0.3
0.1
2
3
4
5
6
7
8
9
pH

The presence of other anions, notably HCO_3^- and $SO_4^=$, will increase the concentration of uranium in solutions saturated with respect to schoepite. The effect of HCO_3^- concentration on the uranium concentration in solutions saturated with respect to rutherfordine, $(UO_2)CO_3$, is well documented at 25°C (see Rich, Holland, and Petersen, 1977); comparable data at higher temperatures are still lacking, but it is most likely that the data in Figures 3 and 4 represent minimum values of the solubility of schoepite at 90°C in solutions that may gain access to spent fuel.

The rate at which UO_2 is oxidized and passes into solution has been studied most recently by Grandstaff (1976). The rate of dissolution was found to increase linearly with the surface area of the uraninite grains and to decrease rapidly with increases in their thorium and rare earth content. The rate of dissolution was found to increase linearly with the oxygen content of the solutions, and was less by about a factor of 2.6 at 2°C than at 23°C. Both the pH and the combined concentration of dissolved carbon species were found to have a considerable effect on the dissolution rate. Figure 5 shows some typical data for the dissolution of a reasonably pure uraninite at 23°C in the presence of water which had been equilibrated with air. The observed rate of dissolution, 2×10^{-5} g/cm^2/day is by no means trivial compared, say, to the rate of dissolution of various glasses which have been proposed as receptors for high level nuclear wastes. At this rate and in the presence of a sufficient quantity of fluids the spent fuels described by Houston (1979) could be dissolved in a matter of centuries.

Fig. 5. The progressive dissolution of a sample of uraninite (Grandstaff, 1976).


V = 2.0 ± 0.1 x 10^{-5} gm-cm^{-2}-day^{-1}
UO$_2$ (μg)
1200
800
400
0
0
20
40
60
TIME (hours)

Whether or not a rate of 2×10^{-5} gm/cm^2/day would be characteristic of the dissolution rate of spent fuels is open to question. In any given instance the rate would depend on a host of particulars; some of these are apt to increase while others are apt to decrease the rate of spent fuel dissolution below the suggested level.

The leaching experiments of Katayama (1976) and Katayama and Mendel (1977) have shown that approximately 1% of Cs^{137} can be removed in about 1 day from spent fuel pellets by leaching with Hanford ground water, and that an additional 1% of the initial Cs^{137} is removed by leaching for approximately 1 year with Hanford ground water and with artificial seawater. The release rates of Sr^{90} + Y^{90}, Pu$^{239+240}$, Cm^{244}, Am^{241}, and Eu^{154} are slower than the release rate of Cs^{137}. Mechanisms of element release from these pellets are not well understood, but it seems likely that the rapidly released Cs^{137} was present on the surface of the leached spent fuel pellets, and that the release rate of this isotope after the first day was determined by the rate at which new intergrain surfaces became exposed to the leach solutions. These element release data, and the likelihood of an uncomfortably rapid dissolution rate of UO_2 pellets in the presence of sufficient fluid access to spent fuels suggest that spent fuels should be stored only where the probability of such fluid access is extremely low.

Salt mines are typically very dry. However, there have been accidents in salt mines during which the ceiling and/or the floor were breached, so that large volumes of water from adjacent aquifers gained access to the mine workings (Baar, 1966). Such an accident in a spent fuel site could have unacceptably disastrous effects. The migration of brines in fluid inclusions in salt up thermal gradients poses a similar but apparently less serious threat; the predicted volumes of brine are quite modest, and it seems likely that desiccants can be developed to absorb these fluids. The storage of spent nuclear fuels in dry, mechanically stable areas seems entirely feasible. If stability and dryness cannot be essentially guaranteed in salt repositories, then it may be preferable to store spent nuclear fuels in repositories such as those described by Ahlström (1979).

Acknowledgments

The authors wish to thank Miss Anne Brackmann for her work on the history of disasters in salt mines and the Nuclear Regulatory Commission for support of the research reported in this paper under Contract NRC-04-78-265.

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Discussion Following

URANIUM OXIDES IN ORES AND SPENT FUELS

Presented by Heinrich Holland

Gregory McCarthy - Pennsylvania State University
Question:
Would you not add a buffer, a reducing buffer, as a third consideration of spent fuel storage in light of all you have seen?

Holland
Response:
I think it would be fine if one could be sure that a buffer would prevent radiolysis from oxidizing the UO_2 to UO_3, but it seems to me, that it has not been demonstrated that such a buffer exists. I do not know of one. I do not know there is not such a one. If it could be demonstrated that there is such a thing, it would certainly be well worth exploring.

Robert Leachman - Nuclear Regulatory Commission
Question:
You spoke about the uranium oxides, pointing out that under oxygenated conditions there are solubility problems. I should like to ask a question that extends beyond your talk and your subject matter, but in a related field. I would like to ask a question about other host lattices that might possibly be able to retain similar elements, similar in the sense of ionic radius and valence state. More specifically, I should like to ask the question about host lattices that may be able to retain the long-lived plutoniums, americiums and so forth and still not dissolve under oxygenated conditions. I have heard that the thorianite structure might be one such. Could you comment on that?

Holland
Response:
Well, you are not talking about spent fuel rods any more.

Leachman
Response:
I am not talking about spent fuel. I am drawing on your knowledge of these fluorite structures and how they might hold up under solubility, asking only about how they might be loaded to retain specifically the actinide elements, thinking that perhaps canisters might be the safety feature for the shorter-lived fission products as you somewhat implied when you spoke of canisters.

Holland
Response:
I am not an expert in this field, and I do not really wish to commit myself, especially since this is, I understand, part of the record. However, I think it is quite clear that there are lots of other structures

in which I would much rather see these fission products than UO_2.

Pedro Macedo - Catholic University of America
Question:
I come back to the geological situation. In the Oklo affair, there was a reaction there that occurred millions of years ago, where the containment of uranium in shale is still there. Would that not indicate that we should go to a rock which is definitely reducing, like shale, to bury fuel elements, if we are ever going to bury any of it?

Holland
Response:
I do not really want to cut into the story that we will hear at noontime. I do not think the Oklo phenomenon is terribly relevant. I think it is very clear that if you have a repository, or if you have something where there is no water and where nothing can move in and out, that things do not move in and out. But that is really not the problem. The problem is to design a storage facility. I would like to submit that that is a very different thing from the Oklo phenomenon.

Macedo
Comment:
I thought the situation there was that because of the shale the uranium was at very low solubility and stayed in place, and that is the way you originated the situation by precipitating the uranium from groundwater.

Martin Molecke - Sandia Laboratories, Albuquerque
Comment:
There has been a mention of buffer materials in bedded salt repositories, I believe. I would like to inform you that there is a fairly large development program in progress at Sandia on such materials referred to as getter materials, either chemical or physical sorbtive materials, for use in repositories, if water does intrude and mobilizes either actinides or fission product radioactivities. Also, in a bedded salt repository, you should be aware that the probability of water intrusion is much less than it is in essentially all other rock type repositories.

Holland
Response:
I am familiar with that. I am also familiar with some of the accidents (see p. 11 of my paper and my reference to C. A. Baar) that have taken place in salt deposits. I am simply asking that if a salt deposit is used, that we try to be extremely sure that accidents like that are virtually ruled out. I am not telling you anything new. The advantage of most salt deposits is that they are very dry. The disadvantage is that if a lot of water does get at it, you make a horrendous mess and the question then is whether one goes to a salt deposit or whether one explores, in addition, a sort of repository that Dr. Ahlström described to us yesterday, where the water problem is more severe but where the dissolution problem is virtually absent.

Bob Watt - Los Alamos, private citizen
Question:
I was going to ask basically the same question with a couple of more aspects to it. You have mentioned, of course, the migration of water inclusions to the product. I am wondering how much water would be considered bad. The 1971 environmental statement for the radioactive waste depository at Lyons, Kansas, WASH-1503, for example, gives about 5 or 10 liters per canister. One of the proposals also just mentioned has been to react the water with various kinds of compounds. In the particular case of waste glasses, I have gone through the calculations. The free energies are such that cesium and strontium will take the water from, say, calcium. I am wondering whether uranium is in the same category, and its heat of reaction is such that it will take water from any kind of drying agent that you may have in mind.

Holland
Response:
As I indicated, I do not think that 10 liters per canister represents a serious problem. I am sure that one can put sufficient desiccant about in a repository in salt to sop up that quantity of water. The thing that concerns me most is the intrusion of really large quantities of water such as you would get from a mine failure and the subsequent break-in of water from an aquifer.

Watt
Question:
As to the sop-up, my calculations of the hydrations of cesium and strontium were that it would take the water from any amount of dessicant that you put there, so it would have preferential call on those 5 or 10 liters. Secondly, in the particular case of the WIPP, there is a nearby mine in which water is flowing through the bedded salt. I do not know what the situation is at the WIPP site proper, so I am wondering whether the 5 liters of water would form a significant amount of soluble products if indeed the uraninite can take over the water from any such desiccants. The number of moles of water in those 5 or 10 liters is sufficient to completely react all the cesium and strontium in a normal high-level waste canister. Is this the case with uraninites?

Holland
Response:
This would not be enough water to affect the integrity of the canisters and my suggestion that there be desiccants is simply for keeping the repository really dry. We have seen pictures of the repository at Asse yesterday, where after 12 years you could still read the radioactive danger signs very nicely. It seems to me that that can be done in high-level repositories as well, and I do not think there is any danger from the intrusion of the sort of quantity of water that has been talked about.

Thomas Cochran - NRDC
Comment:
The IRG draft report asked for public comments on several policy options for going ahead with a commercial repository for spent fuel disposal. The one favored by DOE was to move rapidly ahead with a commercial repository in salt while one explores other options. I would like to have your professional opinion as to whether that particular option is a good idea. Do you vote it up or down?

Holland
Response:
I am going to take the fifth amendment, if I may. Let me explain why. From my point of view and from the point of view of a geochemist working in these things, it seems pretty clear that if there is a repository in salt which can be certified to be dry for a very long period, then that is a fine way to dispose of these wastes. If it cannot be demonstrated beyond reasonable doubt that the repository will be dry for a long period of time, then I would say that this is not a good alternative. So I think it hinges on the particular salt repository which is being designed, rather than on the principle, per se.

Cochran
Question:
You have to vote up or down on the program before we pick the site. Now I want you to vote up or down on the program without knowing where the site is.

Holland
Response:
I will certainly vote up on the program, but I will be extremely cautious about choosing any particular site that you may decide should be picked.

Robert Williams - EPRI
Question:
I am at the microphone, in part, in response to Robert Leachman's example in asking about items somewhat beyond the scope of your talk. I think, first, I have to inject a comment on this last exchange, though. From Senator Harrison Schmidt's talk last night, there are two questions. One is the resource potential of the spent fuel; is it a resource or a waste? And then secondly, can we technically dispose of it, if in fact, we decide to dispose of it?

Now the technical question I wanted to get into the record is the issue of using natural getters and barriers to waste. Other people in this room know more about them than I do. Dr. Molecke started to introduce that idea. In particular, I wanted to bring up the subject of anhydrite; i.e., calcium sulfates, and their possible use as a barrier to water in a salt repository. Could you comment on that?

Holland
Response:
I think that anhydrite has two major advantages over salt. One, its solubility is very much lower; if water were to intrude into an anhydrite

repository in large quantities, it would not have the disastrous effect that it would have on a repository in salt. Secondly, the brine migration problem is probably absent because the solubility of anhydrite decreases with increasing temperature, so that one would expect brines to migrate away from heat sources rather than toward them. I find anhydrite an attractive alternative.

Williams
Question:
Do you see a place for using anhydrite as a barrier in a salt repository?

Holland
Response:
Possibly.

McCarthy
Comment:
I can answer that. Refer to the paper by Potter and Clynne, "PTX Relations of Anhydrite and Brine and their Implications for the Suitability of Anhydrite as a Nuclear Waste Repository Medium," in the proceedings (to be published by Plenum, New York, June 1979) of the Boston meeting "Science Underlying Radioactive Waste Management." They went into that in great detail.

CRYSTALLINE AND COATED HIGH-LEVEL FORMS

by

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CRYSTALLINE AND COATED HIGH-LEVEL FORMS

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Abstract

It is in the waste form that one has the best opportunity to apply science to high-level waste isolation. The more stable the waste form is in its isolation environment, the less need be the dependence on engineered and geological barriers to radionuclide release. In this presentation, current work aimed at producing high stability, second generation, primarily crystalline waste forms is reviewed. Existing data on the hydrothermal stability of these forms are summarized. It is noted that partitioning of the waste stream could facilitate further improvements in these products. Research and development needs for crystalline ceramic waste forms are described.

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Introduction

You have heard a lot about glass as a high-level waste form in the last few days, and rightly so. It is clearly the world's leading choice for a first generation waste form and nearly twenty-five years of work have gone into its development. For the record, I would like to make the following statement concerning vitreous waste forms. Glass is an adequate waste form for most disposal circumstances. I am indeed impressed by the progress that has been made in developing it. In those circumstances where it does not perform well, we must endeavor to understand what does happen. My colleagues and I at The Pennsylvania State University (PSU) are working with the Office of Nuclear Waste Isolation and the Rockwell Hanford Operations to understand the behavior of glass and other waste forms in various repository scenarios. I agree with J. E. Mendel (1) and the National Academy of Sciences Waste Solidification Panel report (2) that says glass can be made to work within the system of radioactive waste management. However, as a material scientist with a geochemical background I have believed since 1970 that we can do better than glass as a waste form for geologic disposal if we have to. We have an outstanding opportunity in the waste form to apply state-of-the-art material science and geochemistry to produce solids whose stability can be verified by thermodynamic considerations and reaction rate kinetics. We can also utilize the data provided by nature's most stable and durable minerals to design waste forms that could survive even the most severe repository conditions for as long as it takes any of the radionuclides to decay to harmless levels. These considerations are discussed further in a recent article (3).

In this talk I shall briefly review the world-wide picture on crystalline and coated waste form alternatives to glass. I will be distinguishing between primary containment and secondary containment. The former is the actual phase, such as a microcrystal, in which a radionuclide is fixed, while the latter includes coatings, metal or cement matrices, canisters and so on. The materials to be discussed are anhydrous and have been prepared by processing at high temperatures. D. M. Roy has discussed other, generally hydrated, cement-based ceramic forms in an earlier talk (4) and some of the same stability considerations to be presented below apply to these materials also. Conspicuously absent from this presentation will be tables of "leachabilities" for the various waste forms. Such data are generally sparce for crystalline waste forms, but it can be stated that the leaching resistance of each of the products to be discussed will be at least as high as the best borosilicate glasses. Indeed, if it were not, the research and development on alternate forms would not be worth doing. Finally, in order to save time, I shall not repeat here the material on ceramics and glass-ceramics as high-level waste forms presented at an ERDA workshop in 1977 (5). Only the most recent work on solids for high-level wastes from reprocessing will be reviewed here.

Crystalline Waste Forms

Table 1 lists the crystalline high-level waste forms that have received some attention over the last two decades. I estimate that the total world-wide level-of-effort on these waste forms has been 1-2% of that devoted to developing vitreous forms. The waste forms have been divided into three categories:

- Glass-Ceramics: composites of crystalline and vitreous phases; the crystalline component is not ususally greater than ∿50% by volume in the product;
- Matrix-Isolation: a fine-grained solid with variable properties and crystallinity is isolated in a durable matrix;
- Tailored Synthetic-Mineral: using nature's high stability minerals as guides whenever possible, appropriate compositional modifications are made to high-level wastes so that after a crystallization-consolidation step a ceramic consisting of an assemblage of crystalline, mineral-like phases is produced.

One important point to make about the first two categories is that while the emphasis so far in their research and development has been on the processes, each of the glass-ceramic and matrix-isolation forms has considerable flexibility for tailoring along the lines of the synthetic mineral waste forms.

In Table 1, the waste forms marked with an asterisk have been discussed in detail in the earlier report (5), and will not be discussed further here.

Titanate Ceramic

About five years ago, work was initiated independently at Sandia Laboratories (SLA) in the US and the Royal Institute of Technology (RIT) in Sweden on using sodium-titania-based gels as inorganic ion exchangers for high-level waste liquid ions. Some work with gels based on zirconia, niobia and tantala has also been performed at SLA. Two processes can be applied, continuous column extraction and batch processing. SLA believes that the batch processing may be more practical for acidic waste liquids. The loaded titanate ion exchanger is dried and typically hot-pressed into a largely crystalline, dense ceramic.

Most of the waste ions react with the titania during the hot pressing to form titanates, of which many are refractory, low-solubility phases. However, most of the inertness of the product results from microencapsulation (i.e., encapsulation at the 1-100 μm scale) of the waste species in the rutile-form of TiO_2. This microencapsulation is illustrated in Figure 1. Rutile sits atop most compilations of

TABLE 1. Crystalline High-Level Waste Forms

Waste Forms	Feed	Processing	R&D Site
<u>Glass-Ceramic</u>			
*Conventional Glass-Ceramic	Melt	Cast Glass, Nucleate, Crystallize	HMI
*Sintered Glass-Ceramic	Calcine Frit	Press and Sinter	PNL & INEL
*Fusion-Cast Ceramic	Melt	Cast Glass; Crystallizes on Cooling	PNL
<u>Matrix-Isolation</u>			
*Ceramic Sponge	HLW Liquid	Absorb on Clay-Ceramic, Dry and Fire	LASL
*Ceramic Matrix Isolation	Calcine + Ceramic	Hot Pressing	PSU
Titanate Ceramic	HLW-Loaded Gel	Hot Pressing (preferred)	SLA & RIT
"Cermet" (Metal Matrix)	Ppct. from Molten Urea	Press, Fire under Reducing Conditions	ORNL
<u>Tailored Synthetic Mineral</u>			
"Supercalcine-Ceramics"	Modified Calcine	Pelletize and Sinter or Hot Pressing	PSU-PNL
"Synrock"	Calcine + Additives	Hot Pressing (preferred)	ANU

*See the 1977 ERDA Workshop Report (5).
HMI = Hahn-Meitner Institut, Berlin
PNL = Pacific Northwest Laboratory, Battelle Memorial Institute
INEL = Idaho National Engineering Laboratory
PSU = The Pennsylvania State University
LASL = Los Alamos Scientific Laboratory
SLA = Sandia Laboratory, Albuquerque
RIT = Royal Institute of Technology, Stockholm
ORNL = Oak Ridge National Laboratory
ANU = Australian National University, Canberra

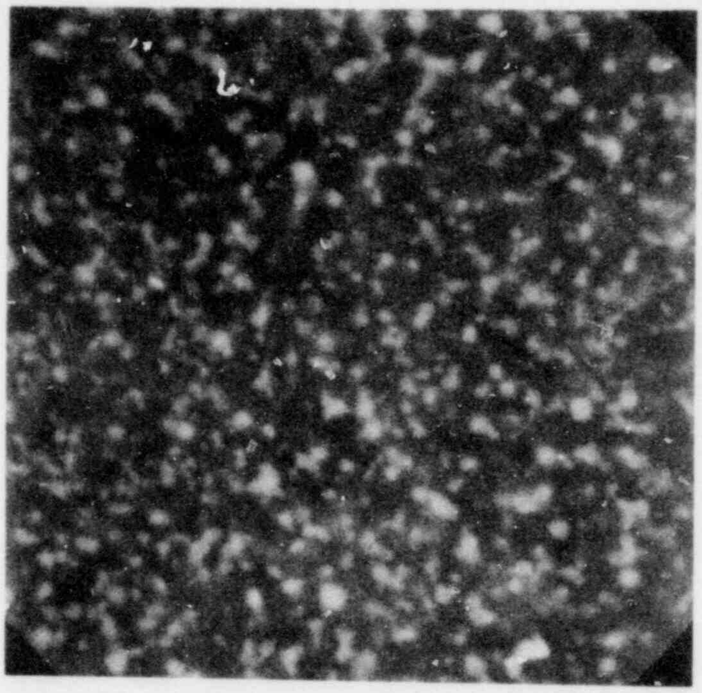

FIG. 1. Microencapsulation of HLW Oxides (white spots) in Rutile (dark matrix) in a Titanate-Ceramic [photo provided by T. Westermark, RIT, Sweden].

weathering-resistant minerals (6), so as long as the microencapsulation is continuous, even an inferior product could be protected (7). Comparisons of the leaching properties of current borosilicate glasses and the SLA titanate-ceramic have indicated that the latter are superior (8).

At the RIT, products with 2-4 wt % simulated high-level waste oxides have been prepared (9) and consolidated by hot isostatic pressing using industrial-scale equipment (10). A demonstration of the SLA titanate-ceramic process using acid PUREX waste has been performed at the Oak Ridge National Laboratory. To date, only tracer-level work has been done on the corresponding product in Sweden.

Primary Containment. Except for the rutile matrix, the size of the crystalline phases in these products is generally smaller than 1 μm. At this level, chemical characterization by routine SEM and electron microprobe analysis (EMA) is not applicable. At SLA, sophisticated scanning transmission electron microscopy (STEM) has been used to characterize both the microchemistry and crystal structure of many of the primary containment phases. The method is illustrated in Figure 2. Table 2 is a list of phases identified to date in the SLA titanate-ceramic product. X-ray diffraction studies have identified the rutile matrix and the pyrochlore-structure $(Ln,U)_2Ti_2O_7$ phase. In some of the high-Sr waste simulations used at the RIT, rutile and perovskite-structure $SrTiO_3$ have been found by x-ray diffraction.

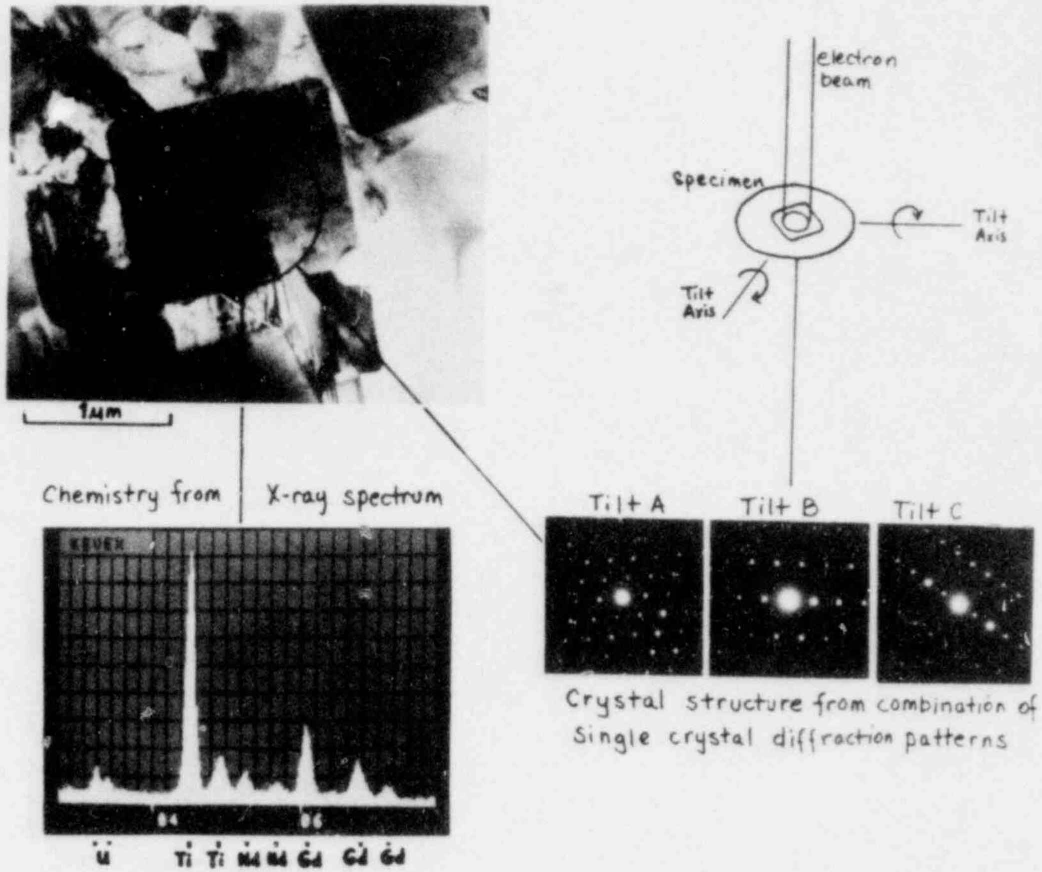

FIG. 2. Example of the STEM Microanalysis used at SLA to Characterize the Crystal Structure and Elemental Chemistry of Primary Containment Phases in the Titanate-Ceramic [photo provided by SLA].

TABLE 2. Primary Containment Phases Identified* in SLA Titanate-Ceramics

Phase	Energy Dispersive Elemental Analysis	Est. Vol. Fraction
TiO_2 (Rutile)	Ti	<50%
Amorphous Silica (SiO_2)	Si (Trace U, Ti, Al, Na)	< 5%
$Cs_2O \cdot Al_2O_3 \cdot 4SiO_2$ (dehydrated pollucite)	Si, Al, Cs (Trace Ti, Rb)	< 1%
$Gd_2Ti_2O_7$	Ti, Gd (Some U, Nd) (Trace Zr, Y)	<10%
Elemental Mo	Mo (Trace Fe, Ti)	< 5%
Elemental Pd	Pd (Some Te and Ti) (Trace Fe, Mo)	< 2%
Cubic-ZrO_2	Zr (Trace U, Si)	< 5%
Amorphous Zeolite, (Na,Cs) Alumino-Silicate	Na, Cs, Al, Si (Trace Ti, U, Fe, Mo, Gd, Sr)	<10%

*At least eight more distinct phases have been detected by electron diffraction and/or x-ray energy dispersive analysis. These have not been identified, but most appear to be titanates.

Status. Work is proceeding at a relatively modest level of effort in Sweden with the emphasis being on leaching studies using tracer methods, microstructure characterization and consolidation by hot pressing. At SLA, research and development on titanate ion exchangers is currently focussed on ^{90}Sr removal from defense high-level wastes at Rockwell Hanford Operations. Some leaching and microstructure studies continue on simulated and actual HLW products made several years ago.

Cermet*

The cermet waste form under investigation at the Oak Ridge National Laboratory (ORNL) (11,12) is designed to fix fission product wastes as small (∿1 μm) particles of oxides or other crystalline host phases, such as aluminosilicates and titanates, dispersed in an iron-nickel base alloy matrix. The alloy is composed of hydrogen reducible metals already in the waste and metal additives from contaminated sources; the alloy is tailored to have high thermal conductivity and corrosion resistance.

The key to the unique properties provided by the cermet waste form is a chemical coprecipitation of waste and additives from molten urea which yields an intimate and homogeneous mixture of all species present (11). Either acid wastes or simulated neutralized sludges have been dissolved in molten urea along with chemical additives or such materials as zeolites. Calcination, hydrogen reduction, forming and sintering or hot-pressing follow in various orders, or in the case of some of these steps, simultaneously. The products are characterized by high thermal conductivity which permits relatively high waste loadings with consequent volume reduction in the solid product.

Primary Containment. To date, there is little direct characterization of the primary containment phases for various radionuclides. Additives such as aluminosilicates to improve Cs-fixation and titania for Sr-fixation have been used and this suggests that such phases as pollucite ($CsAlSi_2O_6$) and $SrTiO_3$ will be identified as primary containment when detailed characterization is performed. The iron-nickel metal matrix constitutes secondary containment.

Status. R&D on cermet waste forms at ORNL has been underway for less than two years, although there is considerably more background in the urea dissolution-coprecipitation and extrusion-forming technologies. Recently a sample of actual commercial HLW from the Nuclear Fuel Services storage tank was processed. Actual defense waste from the Savannah River Plant is also being studied. Leaching tests and a densification process which will lead to a minimum porosity product are currently two priority R&D efforts.

Supercalcine-Ceramics†

The "supercalcine concept" originated at The Pennsylvania State University (PSU). It states that the mixture of elements contained in a

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*Portions of this description are adapted from reference (12).

†Portions of this description are adapted from reference (13). Further detailed information is found in reference (5).

high-level nuclear waste can be modified with chemical additives and thereby tailor-made into an assemblage of refractory and leach-resistant crystalline phases. Wherever applicable, high-survivability minerals are chosen as models for these phases (13-16). Although the concept is applicable to all defense and commercial HLW, R&D to date has been applied only to high-heat, high-loading ceramics of PUREX and THOREX wastes in a joint program between PSU and the Pacific Northwest Laboratory (PNL). Liquid additives (nitrate solutions of Al, Ca and Sr and colloidal SiO_2 in the current ceramics) are mixed with HLLW and calcined to yield x-ray amorphous supercalcine powder. This powder is consolidated and crystallized directly into a ceramic (or "artificial rock") by hot pressing, fusion-casting or by forming followed by a firing step. PNL has developed a disc pelletizer agglomeration method for forming supercalcine powder into "cores" for the multibarrier waste form (13).

Primary Containment. A list of primary containment phases in current supercalcine-ceramics is given in Table 3. The formulae in this table are only nominal. Each of the nominal compositions has been synthesized separately and its x-ray diffraction pattern matched to the corresponding

TABLE 3. Primary Containment Phases in Current Supercalcine-Ceramics.

HLW Ions	Primary Containment Phases	Structure Type
Sr, Ln[b]	$(\underline{Ca},Sr)_2Ln_8(\underline{Si}O_4)_6O_2$[c]	Apatite
Ln, $[PO_4]$	$LnPO_4$	Monazite
Cs, Rb, Na	$(Cs,Rb,Na)\underline{AlSi_2}O_6$	Pollucite
Sr, Ba	$(\underline{Ca},Sr,Ba)MoO_4$	Scheelite
U, Ce, Zr	$(U,Ce,Zr...)O_{2+x}$	Fluorite
Zr, Ce, U	$(Zr,Ce,U...)O_{2+x}$	Tetragonal-Fluorite
Fe, Ni, Cr	$(Ni,Fe)(Fe,Cr)_2O_4$ and $(Fe,Cr)_2O_3$	Spinel Corundum
Ru	RuO_2	Rutile

[a] Te, Pd, Rh, Tc, Pm, Np, Pu, Am, Cm were not included in the simulated waste.

[b] Ln = La, Pr, Nd, Sm, Eu, Gd, Y.

[c] Additive ions are underlined.

reflections in the diffractogram of the complete crystallized supercalcine-ceramic.

The major roles given in Table 3 have been determined from more than 200 crystal chemical and compatibility studies (16), but minor solid solution and partitioning of ions among two or more phases is to be expected. For example, Ln is partitioned between the apatite and monazite phases and a small amount may also be substituting in the fluorite and tetragonal-zirconia phases. The sub-micrometer dimensions of most of the crystals disqualify routine electron microprobe elemental characterization, but STEM is being successfully utilized for direct characterization of elemental distributions in individual crystals in existing products. One important finding is that uranium crystallizes primarily in the high integrity, radiation damage-resistant fluorite structure (uraninite) phase. By analogy, most or all neptunium and plutonium should also crystallize in this phase.

Status. Research on supercalcine-ceramics and supporting synthetic-mineral studies have been underway at PSU for about eight years. Since 1975, several simulated PUREX-type wastes having waste loadings of up to ~80 wt % have been processed into supercalcine-ceramics at PNL. Millimeter-size pellets of these products have been coated (see below) and incorporated into metal matrices to form the multibarrier waste form (13). In addition to the detailed microstructure and microchemistry characterization, current work includes development of THOREX-process ceramics and of high-phosphate aluminosilicate formulations. It is likely that a substantial program of fundamental studies and processing development for "tailored-ceramics" will be initiated in the near future.

Synroc

Another version of a tailored synthetic mineral ceramic waste form was recently introduced (17,18). Termed a synthetic rock ("synroc") by its originator, A. E. Ringwood of the Australian National University in Canberra, it differs from existing supercalcine-ceramics in having much lower waste loadings (<10 wt %) and, in recent formulations, different primary containment phases. Ringwood recognizes that high waste loading (>50 wt %) in a HLW ceramic limits the choices of primary containment phases. His approach is to crystallize HLW ions into preselected assemblages of synthetic minerals as dilute solid solution substitutions rather than as major constituents. This low waste loading gives a greater range of possibilities for primary containment phases. Ringwood asserts that although the much lower waste loadings would mean correspondingly greater volumes of wastes and greater processing costs compared to other ceramic or glass waste forms, this is a minor consideration in overall radioactive waste management (17).

Two routes to synroc processing have been proposed: fusion casting (17) and hot isostatic pressing (HIP) (18). In the former, waste calcine and additives would be melted and cast into a ceramic monolith. More recently (18), Ringwood has indicated that use of the Swedish HIP technology (10) would simplify the processing and allow consolidation of new synroc formulations having very high melting ranges. He has suggested a conceptual process that would utilize this HIP technology. The conceptual flow sheet is outlined in Figure 3. The step in which the powders are mixed could offer processing and control difficulties. I suggest instead that mixing of the HLLW and the synroc-forming additives be accomplished in the liquid phase and be followed by calcination. Experience in the ceramic industry and in the hot-pressing of supercalcine-ceramics (16) indicates that the resulting precursor powder would have far greater (perhaps atomic-scale) homogeneity, would require lower energy inputs for consolidation and would result in better microstructures in the finished ceramic. Additionally, the well-established nuclear waste calcining technologies could be utilized.

Primary Containment. The primary containment phases in a recent synroc formulation are listed in Table 4. Electron microprobe analysis and x-ray diffraction have been used to identify elemental distribution and crystalline structure types.

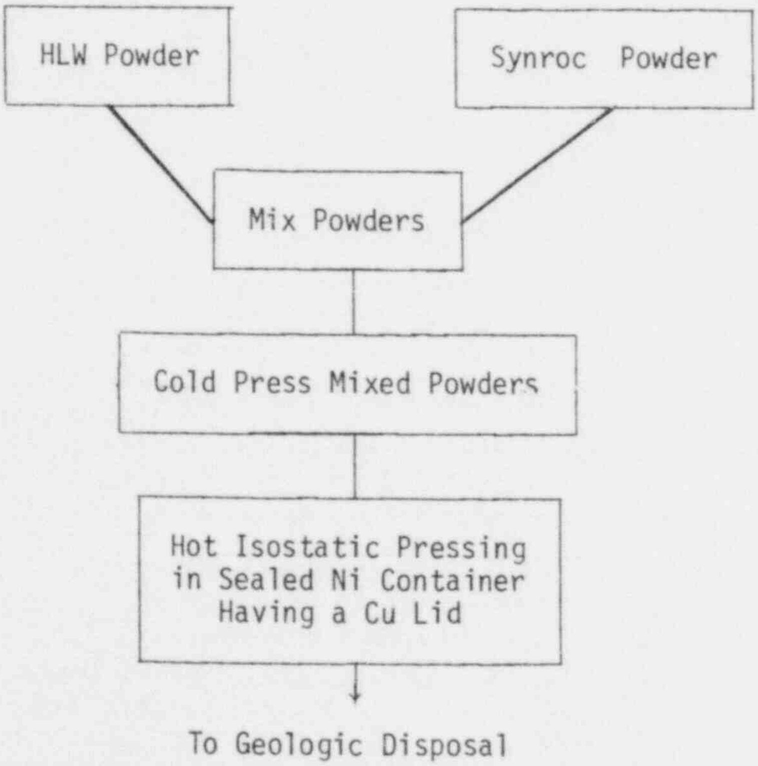

FIG. 3. Conceptual Flow Sheet for Synroc Processing.

TABLE 4. Primary Containment Phases in Synroc B Ceramic.[a]

HLW Ions	Primary Containment Phases	Structure Type
Cs, Mo, Fe, Cr, Ni	$BaAl_2Ti_6O_{16}$	Hollandite
Sr, U, Ln[b]	$CaTiO_3$	Perovskite
Zr, U, Ln, Sr, Na, Cr	$CaZrTi_2O_7$	Zirconolite
[PO_4]	$(Ba,Ca)_3(PO_4)_2$	----
Ru, Pd	Metals	----

[a] After reference (13).

[b] Ln = La, Gd, Y

Status. Synroc products are currently under laboratory-stage development at ANU. Specimens based on several primary containment phase models have been prepared from low-sodium PUREX-process simulated waste calcines.

Coated Waste Forms

Roy (19) has suggested that the well-known concept of "redundant protection" or "defense-in-depth," often used to illustrate the radioactive waste isolation system, be extended to the waste form itself. He termed such a waste form the "Russian doll" after the familiar toy consisting of nesting wooden dolls that are sequentially removed until a tiny inner doll is reached. This inner doll would be the hazardous radionuclide ion and it would be incorporated into a stable crystal at the Ångstrom-level which would be in turn protected by coatings, then by metal or ceramic matrices, then one or more metal or ceramic canisters, and so on. This concept has been reduced to practice in the multibarrier waste forms developed at PNL (20,21). In one of its options having four barriers, 2 mm supercalcine-ceramic pellets were coated and then encased in a copper metal matrix in a stainless steel canister. The development of coatings for supercalcine was pursued to provide an additional protective layer between the radionuclides and the environment. These included a "duplex coating" consisting of a 40 μm pyrolytic carbon (PyC) layer as a barrier to enhance leach resistance and a 60 μm Al_2O_3 layer as a barrier to increase oxidation resistance. Chemical vapor deposition (CVD) in a fludized bed (for PyC) and in a vibrating bed (for Al_2O_3) was employed. Glass coating of supercalcine by frit and glaze, which is a less complex coating process, was also investigated. Although coatings offer a high level of increased inertness, a high level of technological complexity is also required (13).

Primary Containment. The synthetic minerals of the supercalcine-ceramic core are the primary containment phases. The coatings are secondary containment.

Status. The coatings portion of the multibarrier program was recently completed. It produced sufficient coated (simulated) supercalcine-ceramic cores using bench-scale equipment to yield a one liter product when the metal matrix was added (13,20).

Hydrothermal Stability of Crystalline and Coated Forms

Leaching and transport by water is the most plausible mechanism for release of radioactivity from the waste form into the biosphere. A number of the well-developed vitreous waste forms exhibit good leaching resistance in the standard 25°C laboratory tests. However, as the test temperature is increased, to simulate the hydrothermal conditions that could arise from groundwater or brine intrusion during the several hundred year thermal period, vitreous waste forms show vastly increased alteration rates (22-26). (However, as we have demonstrated [22-24], this does not necessarily lead to massive releases of radioactivity.) This alteration is due to the inherent metastability of the vitreous waste form with respect to the minimum free energy crystalline phase assemblage having the same bulk composition.

There are, of course, ways of protecting vitreous waste forms from contact with hydrothermal solutions. One way would be the highly corrosion resistant metal or ceramic canisters envisioned in the Swedish waste isolation program (27). Other methods, including reduced waste loading of the glass and/or the repository, have been reviewed by Mendel (28). However, all of these steps could be eliminated if suitably stable waste forms were used, i.e. waste forms having demonstrated inertness of their primary containment and/or secondary containment phases under the worst conceivable hydrothermal conditions that could occur in a geologic repository.

There is abundant evidence in nature for the extreme stability of crystalline minerals over time scales of literally billions of years (29,3,6,9,17), i.e. orders of magnitude greater than is necessary for all hazardous radionuclides to decay. Some of these even contain substantial amounts of radioactive actinides and show no obvious radiation effects (3,30). We have suggested monazite, one of the supercalcine-ceramic phases, as an ideal candidate for all of these reasons (3).

The testing of the stability of crystalline and coated waste forms under severe hydrothermal conditions has only recently been initiated. Most of the work to date has been done at PSU with some work also at PNL, ANU and SLA. Table 5 summarizes the experimental (and, except for refs. [22-26], unpublished) results to date. The apparent stability of supercalcine-ceramics in any non-salt repository, of synroc in salt at very high temperatures, of the rutile matrix of the titanate-ceramics in salt brines and of duplex coated supercalcine-ceramics in any environment is very

TABLE 5. Hydrothermal Stability Tests on Crystalline Waste Forms

Waste Form	Nature of the Test[a]	Results	Location of the Testing
Supercalcine-Ceramics (SPC-2, SPC-4)	I. Groundwater typical of basalt and deionized water; 100, 200, 300°C/300 bars; 1-24 weeks	No degradation of primary containment phases; enhanced crystallization; only 0.5% of the Cs and 0.1% of the Sr in solution after 4 weeks	PSU (23,24)
	II. Bittern Brine (Ca, Mg, K, Na Chlorides); 200, 300°C/300b; 1-4 weeks	Pollucite and scheelite phases altered; substantial Cs and Sr in solution	PSU (23)
	III. Saturated Salt ("WIPP B") Brine; 250 and 350°C	Most Cs and a small amount of Sr (~3%) in solution after 3 days at 350°C	PNL (25)
Duplex Coated Supercalcine-Ceramic Pellets	Bittern Brine; 400°C/300b; 1-4 weeks	No sign of breach of coating; no detectable Cs in solution; Al_2O_3 outer coating recrystallizes	PSU
Synroc B	I. Deionized water; 400-800°C/1000b, 1 day	No degradation of primary containment phases; no apparent loss of Cs or U from solids observable by electron microprobe	ANU[b]
	II. Brine (10% NaCl); 400-800°C/1000b and 800, 900°C/5000b; 1 day	Same as above until 900°C where Cs extraction and alteration begins	ANU[b]
Titanate-Ceramic	Various brines	Rutile matrix resistant to degradation	SLA

[a] All tests to date have been static tests in sealed noble metal capsules or sealed autoclaves.

[b] Data provided by Professor A. E. Ringwood in December 1978-- to be published.

[c] Observation provided by J. W. Braithwaite of Sandia Laboratories.

encouraging, but must be considered as preliminary until further testing and detailed product characterization are carried out. Yet, based on these preliminary results, it is my opinion that if a waste form exhibiting no measurable radioactivity release away from the immediate repository were required, it could be made.

Value of Partitioning

Each of the waste forms described above would contain all of the species appearing in the HLLW stream. If, however, there were separations or partitioning of the waste stream into two or more fractions, then better "tailoring" or "fine-tuning" of the waste forms would be possible (3). For example, if the vast majority of the lanthanide plus actinide ions were removed from the HLLW by an additional solvent extraction step (31), then monazite or some other actinide synthetic mineral could be used as the host for this long-lived group of radionuclides. The actinide hazard of the remaining fraction could be substantially reduced, but not eliminated because no partitioning is completely efficient. Different repositories having different performance criteria could be used for the actinide and the residual HLW wastes (3). Removing most Cs and Sr from HLLW and forming them into high stability synthetic minerals (or using them as sterilization and heat sources) would vastly reduce the heat output of the residual waste and permit vitreous products to be used without concern for thermal period hydrothermal alteration. It should be emphasized that the costs of R&D and implementation of these partitioning steps would be very great and would thus have to be justified by very severe performance criteria being imposed on the waste form.

General Research and Development Needs

The following R&D needs are common to all of the crystalline ceramic waste forms just described and are not presently receiving adequate attention.

Processing

Powder handling at some stage of a flow sheet is common to the processing of every waste form (except perhaps fusion-casting). More consideration needs to be given to simple, reliable procedures with low dusting potential for remote, continuous operations. This may involve little more than adapting well-established ceramic processing equipment.

Hot pressing, especially the relatively simple HIP technology, is probably the optimum consolidation technology for crystalline ceramic waste forms. The ASEA Swedish technology (10) is a good start, but more experience with hot, remote operation, equipment reliability and quality assurance procedures is needed.

Reproducible consolidation of products that can contain more than ten oxide and metal crystalline and noncrystalline phases and whose components may vary by 50-100% in composition from day to day will need more work. Although this area has received little attention to date, experience in optimizing and characterizing complex ceramics should be quite applicable here.

Products

More studies of optimum primary containment phases are needed. For example, while the Cs-phase in supercalcine-ceramics, titanate ceramics and (probably) cermets is currently pollucite, and in synroc is currently "Cs-hollandite," there may well be other suitable phases that exhibit even better properties. Although there are currently no systematic studies of such optimized phases, one such study is scheduled to begin at PSU in the near future.

Conceptually, radiation and transmutation effects could have more significance for crystalline than for vitreous waste forms because in the former, decaying radionuclides are more likely to be concentrated in a small number of phases. α-Decay in actinide-containing phases could lead to transformation to an x-ray amorphous state (metamictization) (30) accompanied by density changes that could cause microcracking and increase the effective surface area of the product. The threat is that leachability or solubility of the actinides would be substantially increased. α-Decay also produces helium which could be a problem. A similar potential threat could occur from volume changes and structure disruption accompanying transmutation of Cs and Sr into the very different Ba and Zr atoms, respectively. To date, there has not been a single experiment reported in which these potential threats are addressed. Some relevant work has begun at PNL and the University of New Mexico, and will also begin soon at PSU. Note that in the Academy solidification study (2) the potential for radionuclide release in any waste form due to these effects was thought to be minor compared to other mechanisms. Also, some of nature's most durable and insoluble minerals are also metamict minerals (6). This would suggest that their insolubility is not greatly affected by the x-ray amorphous state caused by α-decay. Nevertheless, direct and relevant experiments are still needed in order to access the potential threat from radiation and transmutation effects.

Acknowledgements

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Discussion Following

CRYSTALLINE AND COATED HIGH-LEVEL FORMS

Presented by Gregory McCarthy

Bob Watt- Los Alamos, private citizen
Question:
Are the minerals in either of the two lists you made the most stable minerals under hydrothermal conditions? If not, what are the most stable minerals, and what might be an estimate of the time required to produce them?

McCarthy
Response:
That is an excellent question, and I believe we need a real panel of geoscientists to get together on it. We have done some of this work at Penn State; i.e., a look at the most stable minerals, but certainly not in its full comprehensive form. Even more specifically focused field work would be a big help. Ideas like Oklo can be quite important to us in terms of stability of radionuclides in minerals. Some of these, however, I believe right now are good candidates. In this reprint (G. J. McCarthy, et al., "Synthesis of Nuclear Waste Monazites, Ideal Actinide Hosts for Geologic Disposal," Material Research Bulletin, 13, p. 1239, 1978) we talk about monazite as an ideal candidate for fixation of actinides, especially if these should ever be separated from other constituents. So, we are right at the threshold of getting that question answered.

Larry Hench - University of Florida
Comment:
First of all I think that Gregory McCarthy should be complimented on a very comprehensive talk, especially bringing new data from overseas that otherwise would not be able to be presented. The question is with respect to a point that was emphasized in a couple of talks yesterday, which is the wide variability of existing waste at a couple of the on-site locations. I think you only alluded just briefly to this, so I wonder if you would comment as to the potential for using the procedures mentioned to handle the wide variability without going to such a low average loading as to greatly increase costs.

McCarthy
Response:
I am very glad you asked that. I am happy to expand upon it. I think it is obvious to anyone who saw that slide with the formulation that the more constant the reprocessing of waste compositions, the less demanding is this consideration. However, I feel that built into everybody's crystalline waste forms should be some ability to accept, say, 50 to 100 percent variations in feed composition. As far as applying today's ceramic concepts directly to, say, a Savannah River waste with sludges,

salt cakes, mercury, and so forth, there is a bit of a way to go before one can just apply current concepts to these divergent waste compositions.

Robert Leachman - NRC
Question:
I have been asked by Professor Ringwood to extend apologies that he and his associates were not able to be here. I do thank you, though, Professor McCarthy, for presenting his latest data. Were he to be here, though, I have a suspicion that he would emphasize what he considers to be the distinction between your supercalcine program and his SYNROC program. And as I understand, his distinction is that the supercalcine program is meant to be one competitive in loading with glass, that is, high loading and taking whatever compromises in performance that might come from that. I think that he would go on to say that in his case he is taking deliberately very low loading with the added cost of fabrication, handling, with what he then considers to be something that buys greater public confidence and acceptance and something that he would contend is more compatible with the mineral state. Finally, perhaps it was inadvertent on your part, but you contrasted his program with your well-developed supercalcine program. Is there indeed that much of a difference?

McCarthy
Response
The first two comments you made are appreciated. I believe that I said them, but for the record, let it show that low waste loadings in a wider range of mineralogies is a characteristic of this SYNROC product. Does this represent that much of a difference? No. We can drop our waste loadings tomorrow if someone would give us a good reason to do so. We can also switch to titinate minerals--for example, I would consider using silicotitinate formulations--for compatibility considerations in certain repository rock types. There is a vast difference in extent of development, and I will be happy to elaborate on that privately any time.

THE METAMICT STATE:
RADIATION DAMAGE IN CRYSTALLINE PHASES[*]

by

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ABSTRACT

The long term effect of radiation damage on waste disposal mediums, either crystalline or glass, is a critical factor in the evaluation of the "integrity" of the waste disposal mediums. Natural analogues, such as metamict minerals, provide an excellent basis for the evaluation of radiation damage effects that might be observed in crystalline waste forms, such as the supercalcine or SYNROC.

Metamict minerals are a special class of amorphous materials which were initially crystalline. Although the mechanism for the loss of crystallinity in these minerals (mostly actinide containing oxides and silicates) is not clearly understood, damage caused by alpha particles and recoil nuclei is certainly critical to the metamictization process. The study of metamict minerals allows the evaluation of the long-term radiation damage effects, particularly changes in physical and chemical properties such as microfracturing, hydrothermal alteration and solubility. Comparison of metamict and non-metamict polymorphs, such as thorite and huttonite ($ThSiO_4$), provides a basis for the evaluation of the susceptibility of different structure types to radiation damage. Short term radiation damage experiments of these phases can be validated by comparing the results to long term radiation damage observed in minerals, such as huttonite, thorite and zircon. This report summarizes the pertinent literature on metamictization and proposes experiments that are critical to the elucidation of structural controls on radiation damage in crystalline phases.

PREFACE

Estimates of the long term stability of crystalline (i.e. supercalcine or SYNROC) and glass (i.e. borosilicate glass) waste forms are of paramaount importance in the selection of a waste disposal medium for high level waste. Both crystalline and glass waste forms are subject to a number of effects. Noncompatible crystalline phase assemblages or glasses may undergo undesireable solid state reactions under hydrothermal conditions. Both crystalline and glass waste forms may suffer changes in composition as a result of groundwater leaching. Crystalline phases could become glass-like as a result of radiation damage, while glass waste forms could devitrify (become crystalline) as a result of thermal or hydrothermal conditions. Radiation damage (fission track damage) in glasses is also a possibility. Any waste form may suffer these effects in varying degrees.

All of these effects are temperature and time dependent. While the effect of temperature may be determined in laboratory experiments, the necessarily time-limited laboratory experiments offer only restricted indications of the long term stabilities of the waste forms. For this reason it is important to examine the long term stabilities of natural analogues in order to better estimate the effects of devitrification, recrystallization, alteration and radiation damage. To this end, metamict minerals provide an excellent natural analogue for the evaluation of the effect of radiation damage on crystalline phases.

A part of this work was completed while R. C. Ewing was a NORCUS research associate at Battelle, Pacific Northwest Laboratories, during the summer of 1977.

THE METAMICT STATE
RADIATION DAMAGE IN CRYSTALLINE PHASES*

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INTRODUCTION

Metamict minerals are a special class of amorphous materials which were initially crystalline (1). Although the mechanism for the transition is not clearly understood, radiation damage caused by alpha particles and recoil nuclei is certainly critical to the process (2,3). The radiation damage may result in radiochemical decomposition due to transmutation, changes in structural dimensions, amorphization, compositional changes and mechanical fracturing. The study of metamictization of natural materials allows the evaluation of the long-term effects that result from radiation damage, particularly changes in physical properties. Comparison of metamict and non--metamict crystalline phases speaks to the question of the susceptibility of different bonding and structure types to radiation damage and provides useful insights into defining radiation damage experiments. The purpose this report is to summarize the pertinent literature on metamictization and to propose experiments that are critical to the elucidation of structural controls on radiation damage in crystalline phases.

HISTORY

The term metamict was first defined by Broegger (1) as one of three classes of amorphous substances. Metamict substances are those which were originally crystalline but have become amorphous. The original crystalline state is sometimes indicated by the well formed external morphology of the metamict mineral. While retaining their external crystalline form, they become less dense, optically isotropic and are prone to conchoidal fracturing. Some of the phases listed by Broegger as metamict are gadolinite, euxenite, fergusonite, thorite and zircon. These and other metamict phases tend to contain rare earth elements as well as thorium and uranium. Broegger, however, made no correlation between the presence of U and Th and the process of metamictization.

Prior to the concept metamictization, mineralogists had investigated the thermoluminescence of minerals containing radioactive elements (4) and observed the annealing of radiation damage by optical techniques (5). Hamberg (6) was the first to suggest that metamictization is caused by alpha particles originating from the decay of U and Th nuclides within the crystal structure. Later work (7,8,9,10,11,12)

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supports this theory, but the exact mechanism for the process of metamictization is not clearly understood.

PROPERTIES

The properties of the metamict state have been summarized by others (13,14,15,16,17). The list below is an amplified tabulation of properties listed by Pabst (14).

1. They are generally optically isotropic but may show varying degrees anisotropy. Reconstitution of birefringence with heating is common (18).

2. Metamict phases lack cleavage. Conchoidal fracture is characteristic.

3. Some mineral species are pyronomic, that is, they glow incandescently on heating. In many cases, however, recrystallization may occur without observable glowing (19).

4. Crystalline structure is reconstituted by heating. The metamict material recrystallizes to a polycrystalline aggregate with a concomitant increased resistance to attack by acid (23,23). During recrystallization several phases may form, the particular phase assemblage is dependent on the conditions of recrystallization (e.g. temperature and type of atmosphere) (24). In many cases the original pre-metamict phase may not recrystallize due to compositional changes caused by post-metamict alteration (25).

5. Metamict minerals contain U and Th although contents may be quite variable (as low as 0.41% ThO_2 in gadolinite from Ytterby, Norway). Rare earth elements are also common (in some cases over 50 weight percent). Water of hydration may be high (up to 70 mole percent).

6. They are X-ray amorphous. Partially crystalline metamict minerals display distinct line broadening and decreased line intensities. A shift of lines to lower values of two-theta is observed in specimens with a reduced specific gravity (26,27).

7. Some phases occur in both the crystalline and metamict state, and in these cases there is little chemical difference (14, 28) other than U or Th content.

METHODS OF STUDY

The physical properties of metamict minerals are quite variable. Their variation as a function of degree of metamictization, alteration and hydration are often measured. Among the commonly determined physical properties are refractive index (29), birefringence (30), reflectivity (31), Vicker's hardness (31) and density (32).

The most common methods of analysis of the metamict state are X-ray diffraction analysis of annealed material (33,34,35,36) and differential thermal analysis (37,38,39). Most of the effort by mineralogists has been directed at establishing identification criteria. There has been only a limited effort to use high angle X-ray scattering techniques to examine the short-range structure of the "amorphous" metamict state (40). Other methods of analysis have included optical absorption spectroscopy (41), gamma-ray energy spectrum analysis (42), infra-red spectroscopy (43,44), Mossbauer spectroscopy (45), X-ray absorption analysis (46), electron microscopy (47,48), thermoluminescence (49) and measurement of dielectric constants (50). Elemental analysis is commonly completed by wet chemical means on mineral separates or by standard electron microprobe analysis. The presence of water, both structural and absorbed and the preponderance of rare earth elements make a complete chemical analysis a rarity in the literature. Although radiation damage experiments are voluminous, there have been only limited and unsuccessful efforts to simulate the process of metamictization under laboratory conditions (7,51).

SUMMARY OF OBSERVED METAMICT PHASES

In order to understand the compositional and structural controls on the process of metamictization, it is useful to tabulate naturally occurring phases which are known to exist in the metamict state. Table 1 lists those phases which were described as being partially or completely metamict. This tabulation lists only the major compositional end-members. As one might expect for mineral groups of complex compositions (e.g., compare the A:B ratios for fergusonite and samarskite) which are metamict and much altered, the nomenclature of any single mineral group is quite complicated and much confused by the proliferation of varietal names (56). For a more detailed listing and discussion of the mineralogical literature the reader is referred to Bouska (52). The asterisk by each mineral name indicates it also occurs as a partially or completely crystalline phase. In some cases (e.g. monazite, xenotime and vesuvianite) the inclusion of a mineral phase as metamict is based on a single or poorly documented occurrence. In these instances the critical reference is indicated. In other cases (e.g. rutile) the radiation damage is not due to constituent uranium and thorium nuclides but rather occurred only along grain boundaries where the rutile was in epitaxial contact with radioactive davidite.

For those phases which occur in both crystalline and metamict forms, it is interesting to compare their uranium and thorium contents. Table 2 gives the average U_3O_8 and ThO_2 contents of orthorhombic AB_2O_6-type

Table 1: Systematic Tabulations of Metamict Minerals after Bouska (52)

SIMPLE OXIDES

*Uraninite (UO_2) (53,54)

*Rutile (TiO_2)

Nb-Ta-Ti OXIDES (A = U, Th, REE, Ca, Na, K, Mg, Mn, Fe^{2+}, Pb;
B = Nb, Ta, Ti, Fe^{3+}, W)

Isometric

ABO_3 (Perovskite structure)

*Loparite
Irinite
*Knopite

$A_{2-x}B_2O_{7-Z}$ nH_2O (Pyrochlore structure)

*Pyrochlore
Betafite
*Microlite
Djalmaite
Obruchevite
*Zirconolite

Trigonal

$A_2B_5O_{15}$ (Davidite structure)

*Davidite

Tetragonal

ABO_4 (Fergusonite structure)

Formanite
*Fergusonite
Risorite

Orthorhombic

AB_2O_6 (Columbite structure)

*Columbite (55,56)

Table 1: Continued

AB_2O_6 (Euxenite structure)

- *Euxenite (57)
- Polycrase
- Delorenzite
- *Fersmite

AB_2O_6 (Priorite structure)

- *Priorite
- *Aeschynite
- *Blomstrandine
- Polymignyte

Monoclinic

ABO_4 (Samarskite structure)

- Samarskite
- Chlopinite
- Loranskite
- Yttrocrasite

AB_2O_6 (Brannerite structure)

- *Brannerite
- Thorutite

AB_2O_7 (Zirkelite structure)

- Zirkelite

PHOSPHATES

- *Monazite (58,59)
- *Xenotime (60)
- *Griphite (61)

SILICATES

Neosilicates (Si:O = 1:4)

- *Zircon
- *Thorite
- *Coffinite

Table 1: Continued

- *Titanite (61)
- *Huttonite
- *Steenstrupine - Cerite
- *Britholite group
- *Lessingite
- Karnasurite
- Karyocerite
- Tritomite
- Spencite
- Rowlandite
- Gadolinite

Sorosilicates (Si:O = 2:7)

- Thortveitite group
  - *Thalenite
  - Yttrialite
  - *Hellandite
  - *Rincolite
  - Epidote group
    - *Allanite
    - *Chevkinite
    - *Perrierite
  - *Vesuvianite (62)

Cyclosilicates (Si:O = 1:3)

- *Eudialyte
- Cappelenite (13)

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*May be partially or completely crystalline.

A reference indicates that the mineral is listed in this table based only on a single or poorly documented occurrence. Many of the mineral phases listed are probably alteration products, thus their classification based on calculated chemical formulae may be in error.

Table 2: Uranium and Thorium Content (wt. %) of Non-Metamict and Metamict AB_2O_6 - Type Nb-Ta-Ti Oxides

	U_3O_8	ThO_2
Non-metamict		
euxenite (63)	a	a
fersmite (64)	a	a
aeschynite (65,66)	not detected	0.72
aeschynite (67)	0.25[b]	2.26[b]
lyndochite (68)	0.08[c]	3.75
Metamict		
euxenites (mean value of 28 analyses)	9.31	3.08
aeschynites (mean value of 22 analyses)	1.2	0.73

[a] semiquantitative analysis, no U or Th reported

[b] analysis by R.C.E.

[c] reported as UO_3

Nb-Ta-Ti oxides. Although the data in the literature are limited, in general those specimens of euxenite, fersmite, aeschynite and lyndochite which are found in the crystalline state have distinctly lower uranium and thorium contents than their metamict euxenite and aeschynite counterparts. A similar relation has been demonstrated for zircons (11,70).

Table 3 is a compilation of radioactive minerals which are said to be always crystalline. Comparison of Tables 1 and 3 quickly reveals inconsistencies which are present in the literature. Huttonite is listed as always crystalline (14) and partially metamict (52). Many of these inconsistencies may be resolved by detailed and specific examinations of nomenclature. Also, note that among the phases listed as metamict (e.g. columbite), some structures probably will not accommodate either uranium or thorium. Reports of radioactive columbites are almost certainly mixtures of columbite and metamict microlite (34,71). A number of the phases (bastnaesite and all hydrated phases) are alteration products. The primary phases which consistently occur in crystalline form, even with high concentrations or uranium or thorium, are indicated by asterisks.

Compilations such as those in Tables 1 and 3 provide an empirical guide to crystalline phases that should be avoided in crystalline waste forms, or indicate which phases might actually be preferred. Phases that have appeared in waste form "receipes" for which one might expect long term stability include: monazite, thorianite, xenotime, uraninite and baddeleyite. Suggested hosts for radionuclides that would almost certainly suffer radiation damage include: perovskite, brannerite, zircon, thorite, yttrialite, euxenite, polycrase, fersmite, aeschynite, pyrochlore, betafite, microlite and samarskite.

Radiation damage effects in phases such as pollucite, sodalite, nepheline, scheelite, Ba-feldspar and leucite are difficult to evaluate from natural occurrences as these minerals do not contain U or Th. However, several structural generalizations may be made concerning radiation damage in natural minerals. Metamict minerals tend to have: (1) complex compositions, (2) some degree of covalent bonding, instead of being ionic close packed MO_x structures and (3) channels or interstitial voids which may accommodate displaced atoms or absorbed water. On the basis of these empirical criteria, minerals such as pollucite, sodalite, nepheline and leucite warrant careful scrutiny.

RATE OF METAMICTIZATION

The rate of metamictization of a given mineral is, to a first approximation, dependent on: (1) the inherent stability of its structure and (2) the alpha particle dosage resulting from the presence of uranium, thorium and their unstable daughter nuclides (14).

Table 3: Radioactive Minerals Reported as Always Crystalline after Ueda (27).

autunite** (69,72)	$Ca(UO_2)_2\ (PO_4)_2 \cdot 10\text{-}12H_2O)$
bastnaesite** (13)	$(Ce, La)\ (CO_3)\ F$
carnotite** (69,72)	$K_2(UO_2)_2\ (VO_4)_2 \cdot 3H_2O$
columbite (13)	$(Fe, Mn)\ (Nb, Ta)_2\ O_6$
gummite** (69)	$UO_3 \cdot nH_2O$
huttonite* (14)	$ThSiO_4$
metatorbernite** (69,72)	$Cu(UO_2)_2\ (PO_4)_2 \cdot 8H_2O$
monazite* (7,13,29,59,69,72)	$(Ce, Th)\ PO_4$
stibiotantalite (13)	$Sb(Ta, Nb)O_4$
thorianite* (13,29,72)	ThO_2
thortveitite (13)	$(Sc, Y)_2\ Si_2O_7$
tyuyamunite** (69,72)	$Ca(UO_2)_2\ (VO_4)_2 \cdot nH_2O$
uvanite** (69,72)	$U_2V_6O_{21} \cdot 15\ H_2O$
xenotime* (7,13,29,69,72)	$(Y, U)\ PO_4$
yttrofluorite (13)	Ca_3YF_9
titanite (72,62)	$CaTiSiO_5$
uraninite* (72)	UO_2
baddeleyite* (72)	ZrO_2

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*Primary phases which are invariably crystalline, even with high concentrations of uranium and thorium. Note that in some rare cases even these minerals have been reported as being partially metamict.

**Typically occur as secondary alteration products.

Pabst calculated that a minimum of 110,000 years is required for gadolinite, .4% Th, to become metamict. This figure, which could be low by a factor of 1000 (15,27,69), was obtained by assuming that all of the alpha decay energy was spent in disordering the structure and that this energy was measureable by differential thermal analysis (14).

Most zircons become metamict upon receiving a radiation dose of about 10^{16} /mg (11). Using this dosage criteria, the following table gives estimates of the time required for some radioactive zircons to become metamict.

Initial radionuclide content (wt.%)	Estimated time (yrs)
1% Th	14.0×10^8
1% U	3.3×10^8
10% U	$.32 \times 10^8$
1% Pu^{236} (does not exist in nature)	2.0

There are, however, zircons and thorites (thorite has the zircon structure and is expected to show similar radiation effects) which show anomalous radiation effects. Some zircons which have had radiation doses of only 2.8×10^{15} /mg are metamict (70). On the opposite extreme is a report of a nonmetamict thorite containing 10% uranium that is at least 120×10^6 years old (29). If this age is correct, then the thorite specimen has withstood a radiation dose of about 9×10^{16} /mg. These data suggest that factors other than structural stability and total alpha particle dosage are important in determining the rate of metamictization. Absorbed water, unusual compositions, or alpha particle dose rate are factors which might result in anomalous radiation damage effects.

ALTERATION EFFECTS

Minerals that occur in the metamict state are often severely altered, either as a result of hydrothermal alteration or surface weathering. The resulting complicated compositional variations are in part responsible for the very complex mineral nomenclature. Most of the available data on alteration effects pertains to various Nb-Ta-Ti oxides (25,73) and zircon $(Zr,U)SiO_4$. In both cases alteration may be extensive and followed by recrystallization of phases quite different from the original premetamict phase (74).

For metamict, AB_2O_6-type, Nb-Ta-Ti oxides (A = REE, Fe^{2+}, Mn, Ca, Th, U, Pb; B = Nb, Ta, Ti, Fe^{3+}) primary hydrothermal alteration causes a consistent increase in calcium content, generally a decrease in the uranium and thorium content, a decrease in total rare earth concentrations, a slight decrease in B-site cations, and an increase in structural and absorbed water. Secondary alteration caused by weathering is similar in effect but produces a decrease in Ca content, an increased leaching of A-site cations and a relative increase in B-site cations. Refractive index, specific gravity and reflectance decrease with both types of alteration, but VHN_{50} remains approximately constant. Although alteration effects in these natural materials have been carefully documented, there are no experimental data on hydrothermal alteration effects, solubility as a function of degree of metamictization, or the kinetics of these reactions.

There is an abundant literature on metamictization and alteration effects observed in zircon, $(Zr,U)SiO_4$, a phase commonly used by geologists in U/Pb radiometric dating. A summary and evaluation of this literature is beyond the scope of this report and will be recommended as an important subject of future research. However, despite the abundant literature, little data is available on the effect of metamictization on the solubility of zircons. In general, references in waste disposal literature of changes in the solubility of crystalline phases as a function of metamictization have been cursory (75). Some studies have indicated that the increase in the solubility of metamict zircons is negligible (76,77). Other studies suggest important increases in the solubility and leach rates of cations in metamict zircons (78,79,80). Discordant ages reported for metamict zircons indicate that the U/Pb ratios can be disturbed by metamorphic events (81,82) or by alteration (83). Laboratory experiments involving zircon have demonstrated that altered regions are rapidly dissolved by hydrofluoric acid. Zircons that have become metamict are susceptible to attack by solutions that can cause alteration. Ca, Al, Fe and water are introduced, while Pb is lost (83,84). The experimental data are limited and descriptions of natural zircons are seldom complete. This is an area in critical need of further research.

FUTURE RESEARCH AND DEVELOPMENT

1. Radiation damage effects in natural materials must be evaluated in order to determine the structural controls on the process of metamictization. The most important phases to examine are the $ThSiO_4$ polymorphs, huttonite and thorite (28). Huttonite and isostructural monazite, $(Ce,U)PO_4$, occur only in crystalline form, while thorite and isostructural zircon, $(Zr,U)SiO_4$, are commonly partially or completely metamict. Both phases experience approximately the same alpha particle flux over any given period of time. Radiation damage experiments in which synthetic thorite and huttonite are doped with radioactive nuclides (Pu or Cm) can be used to evaluate structural controls on radiation damage effects. These effects can be monitored by X-ray diffraction analysis, transmission electron microscopy, differential scanning colorimetry and variations in physical properties (density,

refractive index and birefringence). Changes in solubility and susceptibility to hydrothermal alteration should also be determined as a function of degree of metamictization. This work is particularly important as radiation damage effects can be compared to those observed in natural materials of great geologic age. This provides a validation of the short term radiation damage simulation experiments. In addition, crystalline thorium silicates may be compared to similarly doped thorium silicate glasses, in an effort to resolve the relative merits of glass versus crystalline waste forms. This work on huttonite and thorite is presently in progress, supported by Battelle, PNL (Ewing, Contract EY-76-C-06-1830). In addition, experiments examining the process of metamictization in apatite are in progress at Battelle, PNL.

2. Factors affecting the rate of metamictization must be determined. The experiments outlined in the above paragraph will provide empirical data for the thorium silicates; but this data must be placed into a theoretical framework, which presently exists in only a limited form for silicate systems.

3. A careful analysis of the literature and additional experimental work on zircons must be completed. Zircons are the most studied of the naturally occurring phases which are found in the metamict state. This data should provide information on the changes in solubility as a function of metamictization. As zircon is isostructural with thorite, the study of these two phases is an important step in understanding radiation damage in silicate systems. Laboratory experiments on the alteration of synthetic zircon and thorite as a function of alpha particle flux can be compared to the alteration observed in naturally occurring zircon and thorite.

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Discussion Following

THE METAMICT STATE: RADIATION DAMAGE IN CRYSTALLINE PHASES

Presented by Rodney C. Ewing

Robert Williams - EPRI
Question:
I have a very short preamble, which I hope will lead to a constructive suggestion for some research in the area of crystalline waste forms. First, back to Dr. McCarthy's talk where he correctly pointed out the difference in level of R & D effort between the glass waste forms and the crystalline ones. One reason to rationalize that difference is a judgment on the part of industry that a particular course of research and development would lead to a fieldable, practical, operating system ahead of a second waste form, even though the second waste form may be optimum.

Now my constructive suggestion on which I ask that you comment, is as follows: we see a lot of discussion of the leachability of glasses. Once the glass is leached we treat the rest of the earth as a soil column that is a perfect chromatograph, just like something that we have in the chemistry laboratory. Are you aware of any research that is going on, treating the study of crystalline waste forms as a way of looking at natural methods to immobilize the waste that may migrate from glass repositories? It occurs to me that this would be a very constructive adjunct to these programs, which would otherwise appear to require quite a number of more years of work before they would produce a waste form in their own right.

Ewing
Response:
If I understand your suggestion correctly, I think people are already following up on that, particularly in terms of Professor McCarthy's suggestion that the waste form/rock interactions are particularly important. So I think that geochemists are becoming more involved in investigating that type of thing. In a related way, and separate from what I have said here, I think it is also entirely appropriate to look at natural analogs to establish the long-term stability of certain phases, but whenever we do that we have to do it with a great deal of care. This has already been mentioned.

Robert Pohl - Cornell University
Question:
You have talked about thorium and uranium-containing materials that started out crystalline and then turned into amorphous phases, and you talked about problems of leaching of elements out of these amorphous phases. Are there any materials containing thorium and uranium that you think started out amorphous originally and then were left in the ground? Have they been found? Can one say anything about leaching that has taken place from those glasses which were glasses and remain glasses?

Ewing
Response:
First, I do not know of any materials like that. Secondly, it would be difficult to recognize them. If they were initially amorphous and now are crystalline, it would be difficult to determine that they were initially amorphous. But I think getting at perhaps what you are asking, one possibility is to look at uranium and thorium in natural glasses--say volcanic glasses--and radiation damage effects. It would be difficult as uranium and thorium concentrations in natural glasses, say, volcanic glasses, are quite low, and radiation damage effects are minimal. You do see phenomena such as fission tracks. Of course, we can see fission tracks because of differential etch rates in the glass versus the damaged part of the glass.

THE SAGA OF NATURE'S REACTOR
AT OKLO

Luncheon Address By

Etienne Roth, Chef du
Departement de Recherche et Analyse
Saclay, France

December 19, 1979

Nuclear Regulatory Commission

Conference on High Level
Radioactive Solid Waste Forms

THE SAGA OF NATURE'S REACTOR AT OKLO

Etienne Roth*

I first would like to thank the organizers of this conference for providing me with the opportunity to attend, especially Dr. George Cowan who suggested my name to Robert Leachman and Leslie Casey who made this talk possible, and also wrote this title for me.

Now, in the preface of "the Forsyte Saga" - John Galsworthy wrote:

"The word Saga might be objected to on the ground that it connotes the heroic, and that there is little of heroism in these pages. But it is used with a suitable irony..."

This applies perfectly here. But indeed could we expect to find heroism in the history of a scientific discovery based on scientific analysis of natural facts? As far as I am aware of, this kind of analysis was developed first in the mind of a man not at all carried away by the desire to become a Hero.

When Gideon, leader of the Hebrews, received the message that he should fight the enemies of his people, he was seized by the natural desire of a prudent, but not necessarily heroic, general to have his orders confirmed. He asked for the following sign: Should a goatskin be spread before his tent and found wet with dew in the morning, the desert sand being dry, this he would hold as the necessary confirmation. He thus already showed ingenuity in conceiving the idea that sharp differences in effects on neighbouring objects would not be due to accounted for physical phenomena.

But, what makes Gideon the precursor of scientists is that, when he observed the anticipated, although perhaps feared, humidity before his tent, he did not jump all of one piece to any bloody conclusion. Instead he discussed the results. With verbal precautions, but stubbornly, he expressed his misgivings as to the validity of the experiment he had conceived, because this phenomenon could always have occurred that way, unknown to him. So, he asked for a repeat experience, next morning, showing the goatskin to be dry, and the desert sand wet. As you know the request was granted; he fought the battle and won, having made use "en passant" and for the first time of the rule that in nature (or scientific experiments), the same causes should produce the same effects, under the same conditions.

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Luncheon talk at the conference on high level radioactive solid waste forms; DENVER December 20, 1978.

This method of unravelling the meaning behind an uncertain document was profusely used several thousand years later in deciphering the Oklo enigma. In 1972, it was a well established observation that all natural uranium ores exhibited the same ^{235}U concentration within a two per mill range, with a mean .7202 ± 0.007 in atoms percent.

In France the recorded variations were even smaller, and therefore no systematic determination of this ratio was made on material from established natural origin.

So when, on June 7, 1972, in Pierrelatte Mr. Bouzigues found that a natural UF_6 sample, from a container originating from the COMUREX plant, showed a 0.7171 ^{235}U content, the message "beware of anormal natural uranium" was not believed. The messenger (the analyst) was bawled out, contamination was the accepted meaning of the results and repeat experiments asked for. Especially as Pierrelatte was producing depleted uranium, a material error was quite thinkable.

Accordingly, on June 14, a new value, 0.7088, was established and other containers were measured at 0.7097 and 0.7108.

Still unwilling to accept the meaning of these figures, two obvious human failures were discussed, i.e., mixing of natural UF_6

a) with UF_6 from the tails of the Pierrelatte uranium enriching plant, or
b) with UF_6 manufactured from spent nuclear fuels.

The sought for confirmation of the first hypothesis was not obtained. A check of containers of UF_6 tails in Pierrelatte showed that all of them were accounted for, well filed, and sealed.

However the raw material for the "natural" UF_6 was UF_4 produced by the Malvesi plant. It was also checked and found depleted. But, as Malvesi was handling depleted uranium from spent fuel, contamination was still the interpreted message. And by this time (June 15) 700 tons of uranium had been found to be "contaminated".

So, in order to get the final confirmation of this hypothesis one looked for the ^{236}U isotope that is produced in irradiated fuels at the same time as ^{235}U depletion.

And here came the thundering answer: "contamination not confirmed. No $^{236}UF_6$ in the material can be found". So a detailed investigation was decided.

Happily, when UF_4 is prepared in Malvesi, samples are taken and stored. A survey of the collection soon showed a sharp decrease in ^{235}U in all UF_4 produced after May 9, 1972.

Good bookkeeping enabled a trace of the corresponding nitrates, and by June 21 those prepared at the Geugnon plant were identified as responsible for the anomalies.

They had been prepared by COMUF (Compagnie des Mines d'Uranium de Franceville). Here again, thanks to the care with which samples were taken and sent to be stored in France from each lot of ore mined abroad, it took only a few days to ascertain that some minerals that were shipped showed isotopic contents as low as 0.44% in ^{235}U!

Their origin was the open pit quarry at Oklo, and contamination was all the less probable as the richer the ore appeared to be in uranium the lower the isotopic content it had!

From there on, I rely mostly on personal memory recollection.

The analysis of the samples had been carried out with the greatest discretion and now that depletion was established, the cause was to be ascertained.

Firstly COMUF needed to be sure whether mining the quarry could go on, as prospective buyers of uranium ore would probably be reluctant to buy depleted material. And, as new samples had not been taken in the field, fugitive assumptions were even made that mixtures of downgraded materials might have been purposely contrived by malevolent foreign agents!

On July 19th, concerned people and advisers were convened by Dr. Frejacques, head of the Chemistry Division. An animated discussion between participants took place as to the origin of the now well established effect.

Natural ion exchange chromatography process, an extraordinary occurrence of transuranium elements that would have finally decreased into ^{238}U, were among hypotheses enunciated more or less seriously. Finally, fission was mentioned, but in the context of normal, natural, spontaneous fission.

I had come to the meeting bringing with me the routine chemical analysis bulletin provided by the mineralogy department and remarked that, on the basis of those bulletins, fission did not seem probable as the amount of fission neodymium that would correspond to the mean uranium depletion should have been several thousand ppms, and no neodymium appeared on the analytical sheets, while other, scarcer elements, such as iron or boron were listed.

"Mais Monsieur" I was answered, "we never look for rare earths in uranium ores ..." - So it was decided to look for them.

Melle Neuilly of Cadarache asked to spectrochemically analyse the ores, and in my laboratory we would look at them with the same techniques that we were using for spent fuels.

Melle Lucas to whom I handed the samples on the 20th asked. "Am I to look at Neodymium?" I said "yes". And left on holidays. All results were to be kept secret and I was supposed to get a copy of them to issue a report in September. That year I spent a couple of weeks hiking in the Alps around Mont Blanc and had left word that results of the analysis were to be sent to me.

Early in August I simultaneously got two letters from my assistant M. Nief, who, having taken his holidays before, had not been a party to this meeting. The first one, for which I would have wrung his neck, read. "This whole business is probably an analytical artifact". The second read, "It is not an artifact, it is almost certainly a natural fission reactor." Finally, I got a compte rendu of the 19 July meeting that was simply out of tune with what I by now knew and with what I was supposed to report in September.

August 15 is a national holiday in France. By August 19, I was in Paris and in the absence of Dr. Frejacques told his deputy, M. Regnaud, what we thought had occurred in Oklo. In the mean time, I had collected data on the thickness of the uranium layers - richness of the ores, discussed briefly with Dr. Horowitz, former head of reactor design in CEA, and was convinced that it was altogether credible that critical uranium mass might have occurred at Oklo and that it was the only possible explanation of the facts.

Dr. Regnaud then told me that Melle Neuilly had already written a report where she came to the same conclusion from the spectrochemical analysis of rare earths that showed a chemical distribution of abundances identical to that of fission products of ^{235}U.

After discussing those results with reactor physicists such as M. Bussac working with Dr. Vendryes, MM. Frejacques, Vendryes, Bussac, Leveque, Vidal and I finally flew to Gabon to visit the Oklo quarry, discuss on the spot with geologists, especially Dr. Pfiffelman, and with the active head of the uranium plant, M. Guibal.

We all came back loaded with Oklo samples and still shaken by the realization that what we had all been working on so long, harnessing the energy of the nucleus, what we had thought were the results of the most advanced human science and greatest coordinated research and industrial efforts during the 1940-1945 period, had been quietly and mechanically achieved by nature two billion years ago.

In the meanwhile, we were rapidly piling up more data, and by the end of September were publishing results on many more fission elements including noble gases. They corroborated the find and established conditions of its occurrence.

It is interesting to observe that the conclusion, a natural chain reaction had occurred, was announced to the French press with fanfare and, therefore, should have been immediately noted. But, again, the message was only believed by the international scientific community after many months of delay. And this in spite of the fact that the possibility of such an event had been predicted years ago by Dr. Kuroda whose papers I had not only read but even quoted in a 1969 review I had made of uranium isotopes. Also, alas, I had forgotten by 1972*. Kuroda, unfortunately for him, had perhaps overlooked the necessity of studying old enough uranium ores that could have been as rich as 3% in ^{235}U and studied only 600 million year old pitchblende. Even otherwise, he might not have succeeded as to this day the accidental Oklo find is the only known one, although the quarry can now be compared rather to a reactor park as it houses half a dozen units lying next to each other.

After that the study of the phenomenon went on steadily.

In my laboratory we attached ourselves to evaluate, inter alia, the age of the reactor, the duration and intensity of the reaction, and its temperature. We tried to find out whether this phenomenon could have been frequent, or must have remained exceptional, and concluded the second hypothesis.

An effort coordinated by M. Naudet, a well known reactor physicist, was devoted by CEA to study this phenomenon. He investigated the site, unravelled the mechanism by which those reactions were started, propagated, and finally came to an end.

M. Naudet also supplied many laboratories in France, and abroad also, with samples for further studies and analysed their results. The amount of work done by him has been outstandingly put to light by the two international conferences convened by IAEA in Libreville and in Paris.

After telling the Saga of its discovery, here is briefly the Saga of the creation of the reactor for which an article by George Cowan in Scientific American (July 1977) is a good introduction.

Two billion years ago the earth had long gone from a reducing atmosphere, as existing when created, to an oxidizing one. Water flowed freely at the surface--temperature was probably warmer, organic life was

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*It was called back to my attention by Dr. Labeyrie.

developing at that time. In Gabon early minerals containing uranium in a reduced formed started to let it be leached out as oxidized U^{VI} carried away by water. When an active bacterial action occurred uranium was reprecipitated as U^{IV}.

Then those deposits started to be buried by sediments. Now remember that 2 billion years ago the ^{235}U content of uranium was about 3%, and due to the shorter period of ^{235}U it never ceased to decrease down to the present 0.7%. During the burial uranium was reconcentrated by complex exchange with organic material, water was expelled and finally, critical mass was achieved in locations where no natural poison (boron, rare earth, etc.) were too abundant.

From there on, still sinking deeper those reactions even further propagated themselves, burning adjoining poison. And the "reactors" were controlled by a complex thermal circulation of water. Finally they stopped because of fuel depletion, water depletion perhaps, also of continuous burying, and stayed buried and essentially intact for 2 billion years in spite of tectonic movements, and only recently resurfaced.

The duration of operation of these reactions ranges from 100,000 years to about 1,000,000 years.

With respect to the topic of this meeting let us concentrate on what happened to the fission products and transuranium elements. During our studies of the date at which the reaction took place, Dr. Hageman and I tried to extend the well known rubidium-strontium method to the fission produced rubidium-strontium couple, as the first impression we had was that all fission elements had stayed "en place".

To our surprise, and dismay because it ruined a "bright" idea, those particular elements, which were indeed chemically present in about the expected amounts from ^{235}U fission, were isotopically almost normal, in total contradistinction with the previously investigated rare earth fission products. This demonstrated the fact that large migration of some elements had occurred.

M. Frejacques was quick to foresee that much could be learned from the study of the Oklo sites with respect to the stability of elements from stored waste, and systematic investigation was made of many elements to find what proportion had remained in the reactor "core".

The Oklo site provides an up to now unique facility to trace what has become of all fission products. The study showed an exceptional stability of uranium. For many elements, confinement during the last stage of operation was good, probably because, as will be seen, pitchblende turned into uraninite and rare earths were well preserved, although definite differential migration between these elements, buried in a natural site over 2 billion years, can be shown.

Oklo is also informative about long lived alpha emitters, such as plutonium. And this in spite of the fact that, when one studies a fossil reactor, those elements that we are accustomed to finding in spent fuel of man-made ones, or in wastes can no longer be observed, because they have decayed away. For example, ^{239}Pu, which has a half life of about 20,000 years has long ago decayed back to ^{235}U, so has ^{241}Pu to ^{236}U and further to ^{232}Th.

In Oklo, this concerns no small amounts as, in the explored regions of the quarry, 4 to 6 tons of ^{235}U underwent fission, and about half that quantity of ^{239}Pu was formed. If ^{239}Pu produced ^{235}U, ^{240}Pu similarly produced finally ^{232}Th, and ^{241}Pu decayed into ^{209}Bi. We know about these elements from their descendants, as Alice in Wonderland could still know about the cat from his smile long after he had vanished in the tree.

In spite of many efforts and a few false expectations due to mass spectrometric artifacts, no enriched ^{235}U was ever found anywhere in Oklo. This proves, and is substantiated by ion microprobe investigations, that plutonium and uranium in Oklo ores, mostly uraninite in the reaction zones, have truly kept together. The fact that ^{238}U and ^{235}U images at the micro level are strictly identical would not occur if the 50%, due to ^{239}Pu, had migrated. In interpretating the data decay it should be kept in mind that during the nuclear reactions themselves the ores underwent many changes due to radiation. Although fluxes were low, 10^7 - 10^8 n/cm^2/s, integrated fluxes were high, up to 10^{21} n/cm^2.

Thus pitchblende turned into uraninite. Increasing confinement, because of a more regular crystalline structure, is demonstrated by the fact that, outside reaction zones, uraninite is not found but pitchblende is.

Also around those zones, sandstone desilicification occurred due to radiation damage. And clay seems to have but poorly contributed to confinement, except for zirconium. Finally, quartz was found free from fission tracks in the immediate neighborhood of the reactor, probably due to a self annealing effect.

CONCLUSION

What are the lessons of this Oklo story?

1) The first could be the importance of strict analytical procedure and the utmost worthiness of faithful records and of good sample collections. Red tape is not always futile.

2) The second is that while Oklo still remains an isolated occurrence the preservation of such a site is something providential.

In a mine, excavation would, most of the time, start with the richer ores--precisely those that would have reacted if made possible by age, low neutron capture of the soil, water content during ore formation and richness.

3) If depleted ore were diluted in large quantities of normal uranium no tangible effect might have followed its introduction in either an enrichment plant or a fuel manufacturing plant.

4) With respect to storage, the Oklo uraninite was, in spite of tectonic accidents for many of the more difficult elements to store, a good retention medium. But some losses did occur--it is therefore important to carry out further the study of retention to ascertain when losses did occur--during the early operation of the reactions, as flux measurement seems to prove, i.e., before uraninite was formed. But even small effects should be scientifically interpreted.

How would I define such a task. Edward Teller liked to say that an expert is a man who knows from personnal experience all the errors that can be made in a limited field.

I propose that the scientific study should enable us to predict, from our experts' experience in the laboratory, the results that experts' experience in the field would provide, but minimize the errors implied in a pure trial and error method. In this way our hope is that scientific interpretation of Oklo's data will help in the conception and design of high level waste storage.

REFERENCES - Most details on the history of the Oklo reactors, the scientific investigations, and deductions, especially on mineralogy and reactor physics, can be found in the two thick volumes produced by the International Atomic Energy Agency.

1/ The Oklo Phenomenon. IAEA, Vienna, 1975
Proceedings of a Symposium, Libreville, 23-27 June 1975.

2/ Natural fission reactors . IAEA, Vienna, 1978
Proceedings of a Technical committee Meeting, Paris, 19-21 December 1977.

WORKSHOPS

Workshop #1, Criteria for Solid Waste Forms

Workshop #2, Stabilities of Alternative Waste Forms

Workshop #3, Limitations

To initiate each workshop, two short talks presented suggested issues from distinctly different points of view. The chairperson and a rapporteur wrote the results for presentation to their workshop at the beginning of Thursday morning, 21 December.

WORKSHOP #1

CRITERIA FOR SOLID WASTE FORMS

Chairperson: Robert Bernero, NRC

Issue Presenter: Karen Adelson, Westinghouse Electric Corp. - Optimistic

Issue Presenter: Thomas B. Cochran, Natural Resources Defense Council - Cautious

Workshop #1 was set up to discuss the ability of regulators to establish and to adhere to sufficiently meaningful criteria of solids to achieve safe regulation in high-level waste disposal.

1. ISSUE PRESENTATIONS

A. Optimistic Issue by Karen C. Adelson

Ms. Adelson indicated that we do have the means to dispose of high-level radioactive wastes, and that we ought to make decisions and proceed.

Her objectives for establishing specific scientific and technological criteria for disposal of high-level waste include:

- Reasonable short- and long-term environmental impact;
- Acceptable impact on public health and safety with minimal risk to future generations;
- Maximization of resource conservation;
- Maximization of wise resources allocation; and
- Compatibility with the primary economic, political, moral, and ethical goals of society.

There is consensus in the technical community, in that regulators, scientists, engineers, consumers, and concerned environmentalists agree that we should apply current knowledge to dispose of high-level radioactive waste safely.

B. Cautious Issue by Thomas B. Cochran

Dr. Cochran mentioned three aspects of the issue:

- Public attitude about the development of radiation protection standards;
- Formal decision-making; and
- Religious or ethical considerations.

Dr. Cochran covered only the first two items and left the third for discussion in an informal discussion group. He traced the history of the development of radiation protection standards. He argued that the public's attitude toward the environment is one of nondegradation, and the public in its influence on the development of radiation standards has indicated that no amount of radiation contamination is considered "acceptable." The effects of radiation on future generations are of prime importance and cannot be discounted.

Dr. Cochran discussed formal economica decision theory to show that it is possible to aggregate individual preferences in a consistent way into a societal preference function and at a minimum if decisions are to be fair one must have access to everyone's feelings about the outcomes. This line of argument was further developed to show that as a goal for our radioactive waste management program we should strive to be totally neutral with respect to the allocation of risks and benefits to future generations.

In summary, these different approaches to decision-making relevant to nuclear waste management converge to a control thesis: that considerations of fairness and reasonableness require nondegradation of the environment as a fundamental waste management goal.

Dr. Cochran argued that the systems approach as discussed in the IRG report is consistent with the defense-in-depth licensing philosophy, but is being abused by some people to suggest that performance objectives for individual waste barriers (e.g., waste forms) do not have to be met as long as the overall system meets some overall performance objective.

2. OBJECTIVES OF WORKSHOP DISCUSSION

This workshop session started with certain stated objectives for the discussion. As the discussion proceeded some modifications of the objectives evolved. The objectives were to establish a method for setting waste form performance criteria and, if possible, to set specific criteria or elements of such criteria.

3. WORKSHOP SUMMARY

The discussion revealed an apparent consensus limited to approach and the basic structure of the consideration.

A. Apparent Consensus

It was generally agreed that one can't set criteria for waste form alone. One must consider the total objective of waste management. There must be an acceptable performance objective for the disposal system as a whole set first, and then a well thought out analytical methodology to reduce that overall objective to specific waste form criteria consistent with it.

B. Range of Specific Views

The range of specific views can be considered on each of the basic elements of the apparent consensus of structure, namely, the overall performance objective, the analytical methodology, and the waste form criteria.

(1) Overall Performance Objective

Four possible objectives were considered, all related to risk. They are that risk should be no greater than that from:

- the original natural ore bodies
- natural background radiation
- energy-related activities
- man-made risks of all kinds

The proposal to relate to the natural ore bodies (Cochran's Non-Degradation Criterion) suggested that nuclear operations of all types (mining, processing, and waste isolation) should be conducted so the overall hazards to future generations are the same as those which would be presented by the original uranium ore bodies utilized in those operations, assuming they were never mined. It was argued that such an approach obviates the need to discuss whether future generations would accept the risks we would leave them. There were questions about the possible details of using this criterion, whether it was technically realistic. Time did not permit pursuit of these questions.

The use of natural background radiation or a fraction of it was proposed because it too could eliminate discussion of whether future generations would accept the risk.

The relation to energy-related activities is proposed as a means of doing energy system risk-benefit analysis. Some raised questions on whether future generations would accept the same levels of risk, noting that the repository would be difficult, if not impossible, to change. Others questioned whether our regulatory system can apply this objective risk-benefit test to all energy technologies. Some proposed relating the overall performance objective to man-made risks of all kinds, again using the criterion of what this generation will accept. The same argument was made about possible changes in risk acceptability standards.

It was also suggested that the overall performance objective or elements of the system performance be based on two time scales, one the shorter time scale associated with high F. P. activity and the other the longer time scale of actinide toxicity.

The proposal was also made that it would be prudent to make an expeditious choice of the most broadly endorsed performance objective in order to ensure the maximum degree of public acceptance and support.

(2) Methodology

The discussion here was on the proper use or combination of two approaches:

System Analysis (SA) or Defense-in-Depth (DD). Many argued that SA had to be used for an intelligent consideration of all of the parameters, thus enabling tradeoffs between them. SA would also permit tailoring the waste form to the disposal medium and avoid choices of design parameters which would enhance one aspect of performance at the expense of another.

It was argued that economic cost of waste form should be eliminated from the SA consideration or at least made only a secondary factor, since even a two- or three-fold cost change for the waste form had only a small effect on the cost of energy. Some cautioned that good SA would take care of that.

The propoenents of DD argued that it did not eliminate SA but made up for uncertainties in the analysis by overlapping the performance requirements for each element of the system. In this way, error in one element would not lead directly to failure of the overall system. The counter-argument was that the choice of DD broke up good SA.

(3) Waste Form Performance

It was acknowledged that high temperature of the waste form can pose serious problems, but without the other elements of the approach a temperature limit could not be simply chosen. Some suggested that temperature and other specifications for the waste form not be taken as the criteria, the waste form performance criterion should be based on release of the radioactivity from the form and the form's interaction with its surroundings.

4. WORKSHOP DISCUSSION

Summary presented by Robert Bernero, U.S. Nuclear Regulatory Commission.

Eugene Cramer - Southern California Edison Company (see Appendix A for post-Conference communication)
Comment:
I would just simply like to make a clarifying question. I thought when Dr. Cochran proposed what has been called a "non-degradation criterion" that he was speaking of this natural uranium ore body only in relationship to the waste disposal, rather than incorporating the transportation and operation of nuclear reactor fuel reprocessing plants or lack thereof. I just wish you would clarify that with Dr. Cochran.

Robert Bernero - NRC
Response:
I would be happy to do that. In his notes which he used for presenting issues, Dr. Cochran did use the entire cycle. That which we have added are the actual words from his notes. In our original draft it was over-simplified. In Dr. Cochran's original

notes and in his talk he referred to the risk or impact of the entire cycle, starting with mining and going on, and in our original summary we did not include all of it. We just had waste disposal. So we have altered the text of the summary to reflect his original remarks.

WORKSHOP #2

STABILITIES OF ALTERNATE WASTE FORMS

Chairperson:	Leslie A. Casey, U.S. Nuclear Regulatory Commission
Issue Presenter:	Rustum Roy, Pennsylvania State University - Optimistic
Issue Presenter:	Robert O. Pohl, Cornell University - Cautious
Rapporteur:	W. Carl Gottschall, University of Denver

Discussion in Workshop #2 focused on the ability and likelihood of learning the characteristics of alternative waste forms and utilizing these in the choice of the optimum form for actual disposal. Included were: results of the National Academy of Sciences' Panel on Waste Solidification; scientific and engineering properties; present knowledge and abilities; schedules; and costs.

1. ISSUE PRESENTATIONS

A. Optimistic Issue by Rustum Roy (see Appendix B for post-Conference communication)

Up to now, waste management strategies have seriously underestimated the significance of the waste form, by concentrating on the isolation system. In sharp contradistinction to the latter, the waste form offers the possibility of experimental verification, on well-established scientific principles, for geological scale time periods. Furthermore, the use of resistant minerals as the model desirable hosts has not only scientific significance, but special value in public interpretation.

The recent report of the National Research Council has summarized the important consensual findings re the alternative solid forms available for waste solidification (see next page for briefest summary).

- The choice of waste form must be made in the context of (a) the age of the waste; and (b) the final host rock
- Excellent mineralogical and geological models exist to demonstrate the survival of specific phases incorporating particular ions (including the actinides) in a very wide variety of near surface ambients.

ALL SUCH "RESISTATES" ARE CRYSTALLINE

- The existence-theorem of a "safe" solid waste form in a system must be established within the scientific community. This is the ONLY route to getting public acceptance
- The concept of "demonstration" of any system will require 20-30 years as a minimum, and obviously too long to defer any policy decisions on nuclear power
- The use of a "Cadillac" model of a mineral-modeled-ceramic, coated with Al_2O_3 and/or Si_C, and embedded in a metal matrix, is likely to be most important as a test case
- Once the cost becomes evident, especially for DOE (or other old) wastes, the modified Oak Ridge super-grout process, used on-site, will appear increasingly attractive

B. Cautious Issue by Robert O. Pohl

(1) Does the System View leave us with too many options? How can they be reduced?

a. Don't use salt formations for any radwastes.
Less strict requirements for waste forms.

b. Don't use a 40y wait - instead use dilution.
Less strict requirements for waste forms.
Glass may be okay.

c. Ignore costs in selecting options.

d. Don't invest in clearly intermediate solid waste forms; this avoids the temptation to define them as permanent.

(2) Potential Waste Forms: Different wastes will need different waste forms.

a. Glass - the great disappointment; can it be salvaged in the public view? This must teach us caution.

b. Supercalcine, Synrock: basically very appealing. But unknowns remain: I-129.

c. Spent Fuel - the reality of high level waste: far too little is known.

d. Uranium Mill Tailings - an ignored high level waste in need of a waste form.

2. WORKSHOP SUMMARY

It was noted that considerable advance had been made in the development of new waste forms which, together with metal or cement matrices, high integrity containers, and overpack appear to promise the major barrier to radionuclide release.

- The primary concern from the floor was the question of the relation of the waste form to how soon criteria will be set (note: the socio-political climate will not permit a wait of 10-15 years) and on what basis or bases they will be set (e.g., length of durability required). It was stressed that the regulations must rest on the most defensible part of the system and this was felt to be the radionuclide source; e.g., the waste form. This feeling was founded on the general agreement that materials sciences today can meet most specifications that might be set and established.

- For purposes of discussion a benchmark fractional release rate based on a paper by H. C. Clairborne and F. Gera, "Potential Failure Mechanisms and their Consequences at a Radioactive Waste Repository in Bedded Salt in New Mexico," ORNL-TM-4639, 1974, was introduced, and although the proponents of different waste forms (glass, crystals, metal matrix, etc.) did not resolve which form met this rate best, it was generally concluded that" "If a waste form can be made to release an adequately small fraction under repository conditions, then the rest of the waste management system is relegated to being redundant assurance.

- There was general consensus that the U.S. should return to a policy of reprocessing and even a belief that with a change in administrative policy reprocessing will become a reality. This was exemplified by the fact that the discussion centered around the primary barrier being waste forms which only come from reprocessing instead of on high integrity canisters which would be essential if spent fuel were believed to be the accepted solution.

- It was recognized that the mill tailings problem was comparable to the high-level waste problem for time scales beyond a thousand years. One view point stressed as a goal that if mill tailings were placed in a deep continental waste repository the hazard should be contained such that it does not exceed the hazard existing from a natural ore deposit. No consensus was reached as to whether the mill tailings placed in a waste repository should be immobilized further than just using the tailings as backfill. Reference was made to the extensive work performed at ORNL (M. B. Sears et al., "Correlation of Radioactive Waste Treatment Cost and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle for Use in Establishing 'as low as practicable' Guidelines - Milling of Uranium Ores." ORNL-TM-490-4903, 1975) on various mill tailings management options.

3. WORKSHOP DISCUSSION

Summary presented by Leslie Casey, U.S. Nuclear Regulatory Commission. (No discussion ensued.)

WORKSHOP #3

LIMITATIONS IN PREDICTING LONG-TERM PERFORMANCE

Chairperson:	James C. Malaro, U.S. Nuclear Regulatory Commissi.n
Issue Presenter:	Bernard Cohen, University of Pittsburgh/ANL - Optimistic
Issue Presenter:	Terry Lash, Natural Resources Defense Council - Cautious
Rapporteur:	Michalann Harthill, private citizen, Denver, Colorado

Systems analyses which are used to predict long-term performance in waste disposal have led to a dominant reliance upon geologic retention, but an insignificant reliance upon the post-emplacement durability of the waste solids. These predictions are pertinent to the extent that all effects have been anticipated and that the data are measured and accurate. The discussion focused on whether basic reliance should be placed upon such predictions or whether, alternatively, the durability of solids has importance beyond transportation and retrievability.

1. ISSUE PRESENTATIONS

A. Optimistic Issue by Bernard Cohen (see Appendix C for further details.

Dr. Cohen suggested that standards for acceptability of risk in nuclear waste disposal be compared with the risks society is apparently willing to take with other forms of toxic substances.

- Problem associated with high-level nuclear waste is not necessarily as severe as with other forms of radioactive waste; e.g., radioisotope releases associated with coal burning, radon gas emittance from uranium mines
- Nuclear waste is not as persistent as some forms of chemical waste (e.g., as Hg.)
- Risks are associated with all aspects of existence
- Costs to reduce risk from radioactive waste must be justified in comparison to costs to reduce other forms of risk

B. Cautious Issue by Terry Lash

Dr. Lash did not feel confortable with the current amount of research done to effectively dispose of nuclear waste.

- Several institutions are researching various aspects of the problem. A few reports have synthesized results to date
- Emphasis should be placed on a systems approach to isolation and disposal
- "Multiple barriers" is a conservative approach which should be implemented
- Analytic models alone are not capable of demonstrating long-term safety with adequate certainty

2. WORKSHOP SUMMARY

Two major issues were discussed during general commentary. The first, more subjective, is the basis for determining acceptability of risk. Several concepts were considered. Among these were using for reasonably safe exposure, the occurrence of natural radioactive ore bodies, or the radioactive waste from mined coal or phosphate. Strong objection was voiced to the use of radioactive waste from mined coal and potash as a standard on the grounds that risk from these sources may themselves be unacceptable

Another factor to consider is the value placed on human life and the monetary sum (real dollars) required to minimize damage from a probable risk. The concept suggests that spending additional money to meet stringent criteria is a waste if that money could be spent in other ways to save more lives. It was noted that the value of the life in question is subject to change; the value placed on human life varies from one culture to another, and also from one period of history to another within the culture.

A third concept discussed is our responsibility to future generations. Given that this generation does not want to openly expose itself to radwaste, and bearing in mind that the radioactive component of the waste diminishes with time, should we ensure that several generations from now the potential radioactive risk is less than might be expected from natural background radiation?

Although there was no consensus on the above points, there was agreement that these determinations should ultimately be made by an informed public who makes its value decisions based on adequate physical, chemical, and biological and cannonical data generated by scientific investigations.

The second major issue discussed in the workshop was the ability to predict risk over time from geologic disposal of high-level wastes with reasonable certainty. Recent reports including USGS Circular 779, "Geologic Disposal of High-Level Radioactive Wastes - Earth-Science Perspectives," EPA Report "State of Geological Knowledge Regarding Potential Transport of High-Level Radioactive Waste From Deep Continental Repositories," and Interagency Review Group on Nuclear Waste Management "Subgroup Report on Alternative Technology Strategies for the Isolation of Nuclear Waste" [TID-28818 (Draft)], were referred to as evidence that many uncertainties still exist.

Some predictive modeling studies now underway in the UK, Sweden and the U.S. were described briefly. U.S. modeling studies include DOE studies at Battelle (WISAP), Rockwell Hanford Program and TERA (WIPP); EPA studies at the University of New Mexico (AMRAW) and A. D. Little; and NRC studies at Sandia and LLL.

Common to all of the efforts is a series of analytic models which address (1) radionuclide availability (waste dissolution); (2) transport to the biosphere (ground water transport, geochemical retardation); (3) transport through the biosphere; and (4) dosimetry. All models were predicated on the assumption that ground water transport was principal potential transport mechanism. Some models are designed to also consider disruptive events, including intrusion by man.

In the UK it is assumed that only reprocessed waste will be buried as encapsulated glass.

Work performed to date has been principally aimed at developing models with sufficient flexibility to accommodate a variety of possible events so that "what if" questions can be addressed. Models are now being used to determine sensitivity of waste disposal systems to different parameters.

It was generally agreed among those familiar with modeling work being done that modeling capability presently out-strips the availability of data based on adequate field and laboratory tests and that such data inadequacies may be the limiting factor in making predictions.

One member of the group pointed out that the Rasmussen study (prediction of reactor risks) was still subject to much question even though the data base was much larger than that which exists for geologic repositories.

It was generally conceded that little has yet been done in the area of model verification. In Sweden field measurements of Sr^{85} migrations have been made to verify sorption models. The agreement between predictions based on laboratory measurements of K_d-values and the observed migration time was good.

There was a great deal of discussion as to whether reliance should be placed principally on natural geohydrologic barriers or engineered barriers. There was no consensus on the issue. The use of conservatism to compensate for uncertainties was discussed. It was generally agreed this presently would be necessary and that NRC should fulfill its functions. Some expressed the view that because of the apparent uncertainties involved in predicting the effectiveness of any single barrier it would be necessary to rely on a series of barriers which would be shown to be mutually independent (i.e., no common mode failures), and preferably redundant.

The potential for making long-term predictions of the reliability of waste forms was discussed. A number of questions were raised concerning the certainty with which long-term predictions could be made by extrapolation from short-term tests or from "accelerated" or non-integral tests. It was argued that an advantage of such materials predictability studies is the opportunity to compare predicted responses with demonstrated performance of analog materials removed from burial sites from 1-10^6 years. Thus, possible verification of materials predictability models may be achieved in this manner.

There was general agreement that there should be more effective coupling between the geologic model community and materials community in specifying appropriate boundary conditions for laboratory testing of materials and release rates for the geologic models.

3. WORKSHOP DISCUSSION

Summary presented by Michalann Harthill, private citizen, Denver, CO

Fred Schmidt - University of Washington
Comment:
I wonder if you would clarify what you said at the beginning You said something about some members not subscribing to the summary.

Michalann Harthill
Response:
I am not certain what you are talking about. Originally we were to be discussing the systems analyses being developed to predict the long-term performance of waste disposal. However, there were two issues discussed in the workshop. One of them was the acceptability of risk. The second half of the workshop we actually did talk about systems analyses and how we would go about developing those.

Robert Mason - Boulder, Colorado, private citizen
Comment:
I came here because I personally have been concerned about waste disposal for quite some time with particular emphasis on the local issues of uranium mining and milling. There was a problem that was raised during this workshop session that did not get touched on. I would like to raise it here as a comment that many of you ladies and gentlemen are working on. My concern has to do with the sensitivity of these models to problems of scale, and I am thinking in terms of scale in basically three ways. These are problems of scale in individual repositories, problems of scale in terms of the number of repositories, and problems with scale relating to the time dimension. That is to say, the projected total interval over which the nuclear power option might be exercised in something like its present form. I did not hear in any of the discussions any attempt to relate possible modelling problems and analysis problems to this area. I think it is clear that a release rate which might be conceived to be quite acceptable--let us say 60 gigawatts electric per year over 50 years--might be totally unacceptable at 10,000 gigawatts worldwide over 500 years. So it seems to me fairly obvious that these models are at least somewhat sensitive to these problems. If for no other reason than that, the number of acceptable repository sites may turn out to be rather small by the time you applied all of the relevant criteria. I would like to invite your attention to this issue in your further deliberations. I do have, if I may, one additional short comment, a more general one. It has to do with a rather troubling lack of discussion, even by implication, to me as a member of the general public, of the recent work and the recent statements that have been made by people like Karl Morgan and others relative to the new knowledge that is emerging on permissible limits of exposure to low levels of radiation, particularly alpha particles. Dr. Morgan, as some of you may be aware, was out here recently testifying at a trial of . . .

Robert Leachman - U.S. Nuclear Regulatory Commission
Response:
May I interrupt? You perhaps were not here on the first day of the conference. I, as Conference Co-Chairperson, laid out the desire that we go in-depth in certain subjects and, to do that, to leave out other subjects and have those subjects come up in the

evening discussion groups. I think you are in that now. I am not trying to detract from the importance of the subject or your desire to bring it up. I am just trying to play by the Conference rules. I prefer that we do not hear you out because I think that should have been brought up in the Wednesday evening discussion, just as we laid out this whole program.

Harry Landon
Comment:
Let me entertain that you write your comment. We will see that it gets into the record. In view of what our Conference Co-Chairperson has ruled, I think that is the proper procedure. Are there further comments?

William Barnard - Office of Technology Assessment
Comment:
Does it matter if there is any apparent contradiction between any of the Workshop synthesis documents?

Harry Landon
Response:
If you ask my personal opinion, I would say no, but I will again refer to the Conference Co-Chairperson. It was his design and his criteria that we are living to.

William Barnard
Comment:
Maybe I could just elaborate on the point that I would like to make. If you look at Workshop #2 synthesis at the end of the first paragraph, concerning waste form it says that "this feeling was founded on the general agreement that the material sciences today can meet most specifications that might be set and established." I think this implies that the testing of materials can tell us whether they can or cannot perform according to standards. However, if you look in Workshop #3 synthesis near the end, it says that "a number of questions were raised concerning the certainty with which long-term predictions could be made by extrapolation from short-term tests or from accelerated tests." I assume that the accelerated tests were those tests performed on the waste forms. It is my feeling that the testing of the waste form, canister, and overpack materials may provide the key to providing a safe disposal system. I think perhaps some discussion of the validity of accelerated tests may be appropriate here.

Harry Badad - Rockwell, Hanford
Response:
I think I should answer that question. Our concern in Workshop #3 was not nearly as focused as Workshop #2 on the materials of the waste forms, but we were really focusing on how do you test transport characteristics from placement until the materials released might possibly enter the biosphere, as well as how you model the system

and where do we get the long-term assurance. If we test for 30 years--50 years--do we draw upon migration experience at our various sites? How do we tie that into possible requirements for 500 years or longer, in terms of assurance. And we were also asking how does the scientific community develop tests that do extrapolate, rather than focusing on materials.

Harry Landon
Response:
Let me say that our purpose was not to have a global consensus of three workshops. We want to have the talks on these particular subjects on the record as we have achieved them. Are there further comments?

Pedro Macedo - Catholic University of America
Comment:
Just one slight clarification. The speaker asked the question about overpack and containers. We considered the solidification, the overpack, and the container as all one barrier when we were talking in Workshop #2.

Larry Penberthy - Penberthy Electromelt International, Inc.
Response:
It is obviously impossible for us to make a physical test of these systems that will take 500 years and then perform any action today, after we have completed such a test. The way that we went at it in general philosophy in Workshop #2 was to say let us do a very good job of the waste form barrier and let us take a number that we think might be reasonable. That is, we have a 10^{-5} possibility of not having the right choice. We have a good barrier there. Then in addition, we put on the waste canister and its surrounding overpack and that is another 10^{-5}, and then we take the geologic formation and it is another 10^{-5}. 10^{-15} security is good enough.

EVENING DISCUSSION GROUPS

WEDNESDAY 7:30 P.M.

Special concurrent evening sessions on issues related to the Conference theme were chosen and conducted by the Conference attendees. The subjects chosen are listed below.

Group	Subject	Organizer
1	Ethics and Political Issues of Disposal	Michael Hamilton
2	Ocean or Seabed Disposal	Sigurd Nielsen Bernard Cohen
3	ENGINEERING	
	- Repository Interfaces	Ralph Johnson
	- Engineering Barriers	Arthur Bauer
	- Electric Melting of Glass	Larry Penberthy

PLENARY SESSION IV

ASSESSMENTS

HARRY LANDON, U.S. NUCLEAR REGULATORY COMMISSION

CHAIRPERSON

"THE DOE PROGRAM IN HIGH LEVEL WASTE IMMOBILIZATION"

G. K. OERTEL

U.S. DEPARTMENT OF ENERGY
GERMANTOWN, MARYLAND 20545

DECEMBER 20-22, 1978

This symposium has been a valuable educational experience for me. The presentations and discussions have been marked by a general tone of candor, sincerity, and readiness to consider and respect other points of view. The wide spectrum of backgrounds and expertise among the participants has made for lively and useful interactions. The Statesman-like attitude of the participants is encouraging, even on the part of strong advocates of one waste form or another. Those of us who have the jobs of managing and planning nuclear waste management programs will take home new perspectives and ideas.

When I first looked into nuclear waste management some four years ago I noticed a strong tendency towards "programmed responses":

nuclear waste - high level waste
high level waste - glass
disposal - salt repository

The current critical review of glass and salt is therefore healthy. I expect that we will see considerable effort on alternatives to both concepts.

Our strategy for high level waste is summarized in figure 1. Alternatives are assessed for the wastes at each site and their different chemical and physical characteristics. The immobilization program interfaces with the repository development program to assure that the waste form will be compatible with the repository system. A first full scale immobilization plant at one DOE site has been proposed as the initial step towards immobilizing all existing high level waste for placement in a permanent disposal facility. I will address these points in more detail and will highlight recent changes and the outlook.

The high level waste inventories in the United States in 1978 and the forecast for 1990 are summarized in figure 2. Note that the activity content (in Curies) of spent fuel from commercial power reactors now exceeds that of the defense waste inventory. Note also that the spent fuel inventory is given in metric tons of heavy metal (MTHM) while the other entries in the first and third columns are in millions of gallons. I will not address spent fuel further in this paper.

There has been considerable recent emphasis on the repository system. Compatibility with this system constitutes one of the major constraints on high level waste immobilization (figure 3) all of which are intended to protect public health and safety. The repository system may be described as a series of barriers between the waste and the environment (figure 4). It is the goal of the immobilization program to tailor the waste form to the waste type, repository, and geology so that it will be compatible with the respository system. This will be assured through meeting repository acceptance criteria which will be specific to the repository and subject to regulatory approval. If the criteria cannot be met, then the waste form technology must be changed or abandoned. The canister, repository design, and possibly an overpack constitute additional variables that can help assure compatibility with the repository system. Failure modes, such as waste-rock interactions in the presence of corrosive liquids, must be considered.

Transportation is another major constraint (figure 3). Since it is not practical to ship liquid high level wastes in significant quantities it is necessary to plan for as many immobilization facilities as there are locations with high level inventories. Transportation also imposes requirements on the solid waste form.

Processing must be done remotely to reduce processing risks and radiation exposure to personnel. This constraint requires a considerable amount of engineering development before a waste form concept can be applied "full scale" in a radioactive facility.

The high level wastes at most US sites are stored as solids that are not easily retrieved and must undergo chemical processing to concentrate the waste, remove radioactivity from effluents and bulk chemicals, and prepare the waste for immobilization. These activities can constitute about 90% of the total immobilization costs.

The immobilization system must satisfy the regulatory standards and criteria which are still evolving (figure 5). In the interim, technology development and early design must adhere to the best available criteria and standards. Communications with their developers must remain active to assure that DOE's activities remain consistent with the evolving regulatory constraints.

Selection factors for high level waste forms are summarized in figure 6.

The developmental status of a technology determines when it may be ready for use. Figure 7 shows some of the waste immobilization technologies and the times when radioactively cold and hot experience was gained at 'laboratory', 'pilot', and 'full' scales. The entries represent the laboratories and years when such experience was first obtained. Glass and cement are seen as most developed. Most of the alternatives are still in the laboratory development phases. Calcination may be considered as an interim step in the immobilization to glass, certain crystalline forms, and other alternatives. The status of some international immobilization programs is summarized in figure 8.

It is apparent that considerable effort is needed to bring some promising concepts from the laboratory phase to the point where large scale engineering applications with the necessary safety and reliability demands can be undertaken. I will return to this point.

When could immobilization of the high level waste inventories begin? There are two primary options: proceed as soon as possible at each site, or begin at one site and 'phase in' other site programs with a few years delay to assure availability of specialized personnel, learn from the experience with earlier operations, and reduce the peak manpower and funding requirements. Immobilization schedules for these two options are illustrated in figure 9.

Waste form technology has been affected by several recent developments: Measurements have shown that glass will leach rapidly at extreme temperature and pressure in brine and water. The National Academy of Sciences report on high level waste forms (unpublished, but available in draft at the Academy's reading room) favors several alternatives over glass. Synthetic minerals have gained attention as potentially superior, e.g. by the work at Penn State University (Roy, McCarty) and in Australia (Ringwood). The Interagency Review Group (IRG) for Nuclear Waste Management has published a draft of its report to the President which focuses attention on the need to consider the waste form in the context of the repository system, identifies opportunties for developing alternative technology, and stresses the need to get on with the long deferred processing of defense wastes.

The strategy will change in the future (figure 10) as a result of the IRG report. For example, the further definition of the limitations and uses of glass will be emphasized. Alternatives to glass, including 'synthetic minerals' will be developed aggressively. The immobilization program has been modified already to accelerate the development of alternatives and explore new avenues. For example, a hot laboratory scale demonstration of Oak Ridge's cermet process has been performed with waste from West Valley, and Ringwood is assessing the applicability of his Synroc concept to defense waste and may develop a new Synroc formula tailored to defense wastes.

In other new developments, the interface between the repository and waste form development programs, and the testing needs to assure compatibility of waste form with repository acceptance criteria, are being further defined. The Savannah River Operations Office has been established as lead office for high level waste immobilization technology and program planning. They are supported by the Savannah River Laboratories of E.I. DuPont de Nemours.

In summary, I am expecting a 'new look' in high level waste management, including waste form technology. Many of us will probably revisit the high level waste form scene late in 1979.

HIGH-LEVEL WASTE IMMOBILIZATION

PROGRAM STRATEGY

ASSESS IMMOBILIZATION ALTERNATIVES FOR EACH WASTE TYPE AND SITE

INTEGRATE IMMOBILIZATION PROGRAM INTO TOTAL HLW SYSTEM

FIRST FULL-SCALE IMMOBILIZATION PLANT AT ONE DOE SITE

IMMOBILIZE ALL EXISTING HLW AND PLACE IN PERMANENT DISPOSAL FACILITIES

FIGURE 1

SOURCE SITE	PRESENT FORM	1978 QUANTITIES		1990 HIGH EST.		SOLIDIFICATION VOL. OF 1990 WASTES (10^3 CU. FT.)
		10^6 GAL	10^6 CURIES	10^6 GAL	10^6 CURIES	
RHO	ALK. SALT/SLUDGE LIQUOR	50	190	65	230	660
	SEPARATED ^{90}Sr/Y ^{137}Cs/Ba	-	350	-	425	
ICPP	ACID CALCINE	0.42	70	1.3	500	300
	ACID LIQUID	2.4		1.2		
SRP	ALK. SALT/SLUDGE LIQUOR	23	560	22	680	200
NFS	ALK. SALT/SLUDGE LIQUOR	0.6	64	0.6	48	7
	ACID LIQUID	0.01	2.1	0.01	1.6	
LWR	SPENT FUEL (MTHM)	4,400	1,900	34,800	14,000*	460**

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*After at least 6 years' aging.

**Metric tons of heavy metal

RHO - ROCKWELL HANFORD OPERATIONS

ICPP - IDAHO CHEMICAL PROCESSING PLANT

FIGURE 2

HIGH-LEVEL WASTE IMMOBILIZATION SYSTEMS CONSTRAINTS

Variety of Waste Types

- over 20 varieties presently in storage

Waste Removal and Concentration

- up to 90% of processing costs for existing wastes

Remote Processing

- Reduce processing risks and exposures

Transportation

- Imposes immobilization requirements
- Necessitate individual site immobilization plants

Repositories

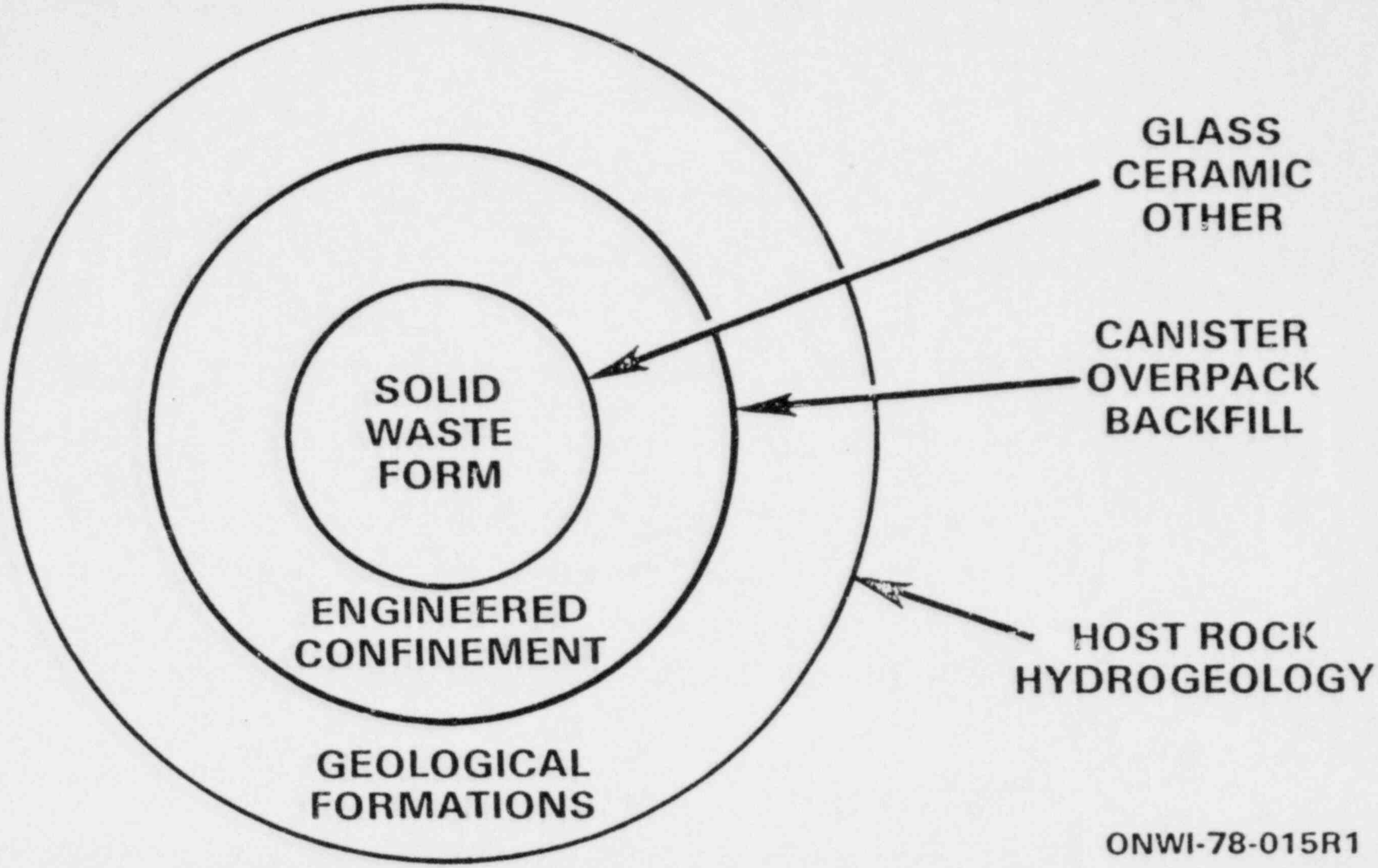
- Form requirements must be matched to repository
- At least five repository types under consideration

Criteria

- Must match to NEPA process, regulatory agencies
- Must demonstrate all criteria are met

FIGURE 3

BARRIERS TO THE ENVIRONMENT



SOLID
WASTE
FORM

ENGINEERED
CONFINEMENT

GEOLOGICAL
FORMATIONS

GLASS
CERAMIC
OTHER

CANISTER
OVERPACK
BACKFILL

HOST ROCK
HYDROGEOLOGY

ONWI-78-015R1

FIGURE 4

HIGH-LEVEL WASTE IMMOBILIZATION: WASTE FORMS

- GOAL: DEVELOP WASTE FORM COMPATIBLE WITH THE REPOSITORY SYSTEM

GEOLOGY - OVERPACK - CANISTER - WASTE FORM
- WASTE/ROCK INTERACTION

- ASSURE THROUGH MEETING REPOSITORY ACCEPTANCE CRITERIA:

IF CRITERIA CANNOT BE MET, THEN THE TECHNOLOGY MUST BE CHANGED OR ABANDONED.

FIGURE 5

HIGH-LEVEL WASTE IMMOBILIZATION FORMS
SELECTION FACTORS

FORM

DISPERSABILITY AND IMPACT RESISTANCE - TRANSPORT AND STORAGE
LEACHABILITY - MATCH TO REPOSITORY CONDITIONS
VOLATILITY - MATCH TO TRANSPORTATION ACCIDENTS
STABILITY - AGING, RADIATION, TRANSMUTATION
SENSITIVITY TO WASTE LOADING AND COMPOSITION
WASTE VOLUME LOADING
DEVELOPMENT STATUS

PROCESS

PROCESS SAFETY - REMOTABILITY
PROCESS SENSITIVITY - QA REQUIREMENTS
FEED PREPARATION REQUIRED ?
PROCESS WASTE GENERATION - OPERATING AND DECOMMISSIONING
CAPITAL AND OPERATING COSTS
ENGINEERING SCALE EXPERIENCE AVAILABLE?

FIGURE 6

WASTE IMMOBILIZATION

HLW SOLIDIFICATION PROCESSES
U.S. STATUS

	LABORATORY		PILOT SCALE		FULL SCALE		
PROCESS	COLD	HOT	COLD	HOT	DESIGN	COLD	HOT
CALCINATION	ANL/55	ANL/59	ID/57	--	ID/58	ID/62	ID/63
VITRIFICATION	PNL/63	PNL/64	PNL/65	PNL/79	SR/78	SR/80	SR/89
CEMENT	SR/74	SR/75	*	*	SR/75	--	--
CRYSTALLINE CERAMIC	PSU/74	PNL/77	PNL/80	--	--	--	--
(INCL. SUPERCALCINE)		SANDIA/75					
CERMET	ORNL/78	ORNL/78		--	--	--	--
MULTIBARRIER							
MARBLES	PNL/78						
METAL MATRIX	ANL/77						

---

* GROUT OF INTERMEDIATE LEVEL WASTE, OAK RIDGE NATIONAL LABORATORY/60 - COLD AND ORNL/66 - HOT.

ANL - ARGONNE NATIONAL LABORATORY

ID - IDAHO

ORNL - OAK RIDGE NATIONAL LABORATORY

SR - SAVANNAH RIVER

PSU - PENNSYLVANIA STATE UNIVERSITY

PNL - PACIFIC NORTHWEST LABORATORY

FIGURE 7

INTERNATIONAL
HLW IMMOBILIZATION STATUS

NATION	PROCESS	STATUS/MAJOR MILESTONE
FRANCE	BOROSILICATE GLASS - "AVM"	.5 TON/DAY HOT PILOT PLANT STARTUP 1978-1979 PRODUCTION PLANT STARTUP 1982-1983
GERMANY	BOROSILICATE GLASS	"VERA" .5 TON/DAY COLD PILOT PLANT OPERATION CONSIDERING FRENCH "AVM" PROCESS FOR LICENSING
EUROCHEM	BOROSILICATE GLASS	FRENCH "AVM" SELECTED FOR PRODUCTION PLANT
	METAL MATRIX	VITRAMET - LOTES) PILOT PLANT VITRAMET - PAMELA) 1981-1982
ENGLAND	BOROSILICATE GLASS	"FINGAL-HARVEST" PRODUCTION PLANT 1990 FRENCH "AVM" UNDER CONSIDERATION
RUSSIA	PHOSPHATE GLASS	COLD PILOT-PLANT WORK IN PROGRESS
INDIA	BOROSILICATE GLASS	.1 TON/DAY HOT PLANT STARTUP 1979-1980
JAPAN	GLASS OR CERAMIC	HOT DEMONSTRATION PLANT 1986
SWEDEN	CERAMIC	LABORATORY STUDIES IN PROGRESS

FIGURE 8

IMMOBILIZATION TIMING

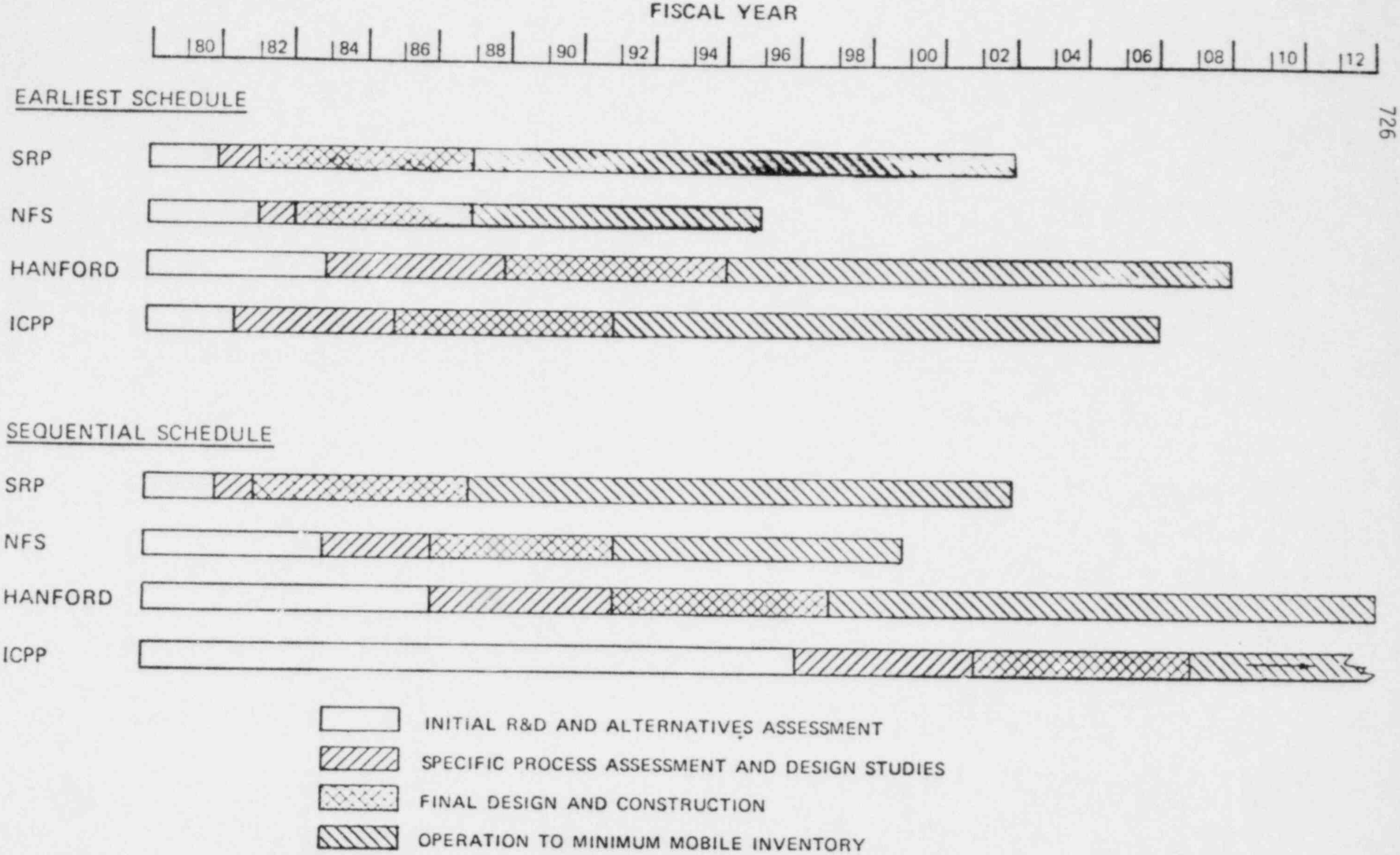


FIGURE 9

HIGH-LEVEL WASTE IMMOBILIZATION: WASTE FORMS

- Technology Status Before IRG:
  - Glass and concrete most developed, seen as adequate for several waste types
  - Alternatives in early R&D phases
- Strategy After IRG:
  - Define limitations of glass
  - Aggressively develop alternatives such as synthetic minerals
  - Formalize interface with repository development
  - Strengthen high-level lead office
  - Evaluate high-level waste form scene again late in 1979

FIGURE 10

Discussion Following

THE DOE PROGRAM IN HIGH LEVEL WASTE IMMOBILIZATION

Presented by Dr. Goetz K. H. Oertel

Robert O. Pohl - Cornell University
Comment:
Dr. Oertel, I think one of the messages that has come out of the meeting here, as well as the meeting in Boston on the same topic, is that salt presents a particularly serious, difficult environment for waste and I am wondering whether it is unwise to pursue salt formations for the first study of waste disposal or whether it would not be a lot more expedient to focus on non-salt media.

Oertel
Response:
The answer here is that we are likely to be in a position to make the tests in salt before we would be able to make them in other media. However, I think you are completely right; there would be a need to look at other media as well and that will be done as soon as that opportunity presents itself. We are not waiting for that opportunity; it is being developed. It will depend to some extent upon whether the strategy 2 or 3 of the IRG Report to the President on Nuclear Waste Management (October 1978 Draft) will be accepted by the President. Anticipating that strategy 3 will be selected, that means that there would not be a commitment to a first salt repository; rather that there would be a considerable expansion in R&D on other media; I would then see considerable emphasis on tests in other media. At the same time I do not see that the geologists who run the geology program are ready to abandon salt as being clearly not appropriate. I don't think that proof is in hand either.

Pohl
Comment:
Except that the Committee on Radioactive Waste Management of the National Academy of Sciences, National Research Council, has expressed itself very clearly on this point and this is the same committee, or at least the successor committee, that in 1957 first led us on the salty path.

Bernard Cohen - Argonne National Laboratory
Comment:
On this program to solidify the defense high-level waste they are spending billions of dollars which would not have to be spent if, say, you would just convert them into cement in the tank. Do you have a number of the dollars spent per life you expect to save in these operations?

Oertel
Response:
No, I think you probably have a better number than I do.

Martin Molecke - Sandia Laboratories, Albuquerque
Comment:
When is the administration's response to the IRG report, the decisions on waste management, going to be made public?

Oertel
Response:
I really cannot speak for the administration on that. I know the comments have been collected and are being collated and I would expect this to come out fairly soon. I would be very surprised personally if it were not out in January, but I do not have first-hand knowledge.

Rustum Roy - Penn State
Comment:
I believe after that nice balanced presentation, that perhaps you should not lose the message of this Conference. I think the message is to alert DOE to the unused potential of the waste form for giving the public the assurance of the ability of the total system. In other words, it is in the interface between your shop and Colin Heath's shop that I think the novelty of the research lies. It suggests that the potential in the waste form has (in the big system's planners) been probably not given the proper weight. Further, the potential of innovative research on the waste form appears to make it possible that verifiable and standardizable standards can finally be laid down, dependent principally in the waste form. In other words, the message is make the waste form one of the major legs in the sequential barriers rather than the minor one that it has been so far. Which simply suggests that maybe your shop becomes equally important with respect to Heath's shop. But I hope that the message is principally that the waste form conflict is about just how good the newer waste forms can become.

Oertel
Response:
I do not want to dispute that waste form is important. After all, I am responsible for developing it in the Department of Energy. And I think I said when I talked about that issue that clearly it would be great if one could come to a point where that in itself is really all the assurance that would be needed. I am just not sure that we should take that one-sided an attitude. Obviously, we will pursue the zero release from the waste form, and if we get that, great.

Larry Penberthy - Penberthy Electromelt International, Inc.
Comment:
As has become apparent already, I am highly partisan for glass, and therefore I hope that you will make a change in your paper, as it will be printed. One slide said that glass deteriorated under thermal conditions, including brine and water. Now there are literally thousands

of formulas for glass, and the glasses that were being tested were what we call a very soft glass. The viscosity, for example, at 1100°C is more or less like strong coffee. At 1100°C pyrex glass 7740 is at least as stiff as bread dough. So you can see there is a vast difference between glasses, even though they are both called boro-silicate. I hope you will distinguish the glass which was disintegrated under those conditions.

Oertel
Response:
I believe I did not mention a temperature at which this occurred. Clearly, for every glass there is a temperature where it will occur and I think I did say that we will explore the limitations of glass, which I think will answer your concern.

Jack McElroy - Battelle PNL
Comment:
I believe a statement on one of your slides needs to be restated. It said that "it has been found that glass leaches rapidly under repository conditions." It should say that glass alters rapidly under extreme repository conditions. The resulting material after alteration is relatively insoluble. Of the radioisotopes present, it has been primarily found that only cesium is readily leached from the altered glass.

Oertel
Response:
I might have also said in the discussion that of course for the glass to deteriorate in an actual repository two things have to go wrong at the same time. One is that the canister has to be breached and whatever containment there is must be breached so that the brine or whatever can get to the waste form, and secondly, this has to occur at an early time when the temperature is still high. This is the specific failure mode that we are talking about.

John Sokol - Westinghouse Electric Corporation
Comment:
We have talked about the solid waste form. The Swedes, the Canadians and a number of other people have investigated different canister materials ranging from copper and lead to very sophisticated ceramics. My question is that in your discussions between yourself and Colin Heath's office, who has responsibility for the design of the canister or is it "falling in the cracks," between the two offices and is that one of the reasons why you are coordinating more closely?

Oertel
Response:
It is exactly on the interface, but let me put it this way. It is my responsibility to see that the waste form is packaged in such a way that it can be transported and accepted at the repository. That does not necessarily mean that the canister that would be the outermost shell of this could be used in the repository as is. It may require an overpack. If an overpack is required, then that would be clearly on Colin's side.

HIGH-LEVEL RADIOACTIVE SOLID WASTE FORMS

CONFERENCE SUMMARY

Hans Frauenfelder

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1.

It is difficult to summarize a conference. During three days highly qualified scientists and engineers describe work on which they have spent many years. To select the most important and relevant aspects from this wealth of information is a challenge even to an expert. I am not an expert, but an outsider with superficial exposure to nuclear power and nuclear waste problems. Rather than describe the technical progress, I will give my personal impressions and concentrate on problems that I believe will determine the future.

Nuclear waste management has many aspects: scientific, technological, environmental, managerial, legal, political, public, and ethical. I will only discuss a few of these. From listening to the talks and questioning many people during breaks, I received the impression that the technical problems are essentially solved, but the scientific background requires more work and only a dedicated effort will alleviate public concern.

Nuclear technology is unique. Technologies usually evolve by trial and error; dangerous side effects such as dam breaks, oil spills, airplane disasters, and the greenhouse effect occur initially on a small scale. The public thus becomes familiar with them and accepts them as an unwelcome but necessary price for progress. Nuclear power started on a large scale and its image is dominated by a mushroom cloud. Public opinion appears to demand unprecedented guarantees with extrapolations to times that no sane scientist can predict with certainty.

What, then, are the problems, where do we stand, and what can we do?

2.

First the background. Let me oversimplify and start with some thermodynamics:

$$F = E - TS \quad .$$

F is the free energy, E the energy, T the temperature and S the entropy. A power plant produces energy, E. The useful energy is F and the two differ by the term TS. The second law of thermodynamics states that the entropy always increases. (A practical example of the entropy increase in our system is the fact that raw minerals must be mined from ever increasing depths.) Even if we keep the free energy use constant, the energy production must steadily increase. However, the efficiency of energy use cannot be steadily increased; conservation only postpones the point in time where either F must decrease and the standard of living be lowered, or where still further energy must be produced. Any power production will produce waste. What do we do with the waste?

In discussing the small part of the overall energy problem that is the topic of the present conference, we must remember the larger picture and realize that optimization is required for the overall situation, and not just for one small part. The question is not: "Is coal, or nuclear power, absolutely safe?", but "What is the cost for society now and in the future for a given mix of energy sources". To answer this question rationally, the advantages and disadvantages of all power sources must be scrutinized. The subproblem addressed here is: "How can high-level nuclear waste be stored?".

3.

Let us first consider the scientific aspects. The solution of a technological problem is found most efficiently if the basic science is known and understood. Solid state electronics is a good example where a sound theoretical basis stimulated technological applications. This logical approach to a technological problem is not always necessary or possible, however. In many cases, theory and application develop in parallel. In some situations, an advanced technique can even stimulate basic research. In nuclear waste disposal, the scientific underpinning was initially weak. A lack of glamour may well have been responsible for the lag in basic research. Clearly a great deal of fundamental work remains to be done. It was encouraging to see a number of beautiful fundamental contributions to this conference. Geology, geophysics, geochemistry, solid-state physics and chemistry, and surface and materials science now take the wast disposal problem seriously.

One problem exists -- the lack of quality standards. Some contributions were excellent, the contents of some were unacceptably weak. As an outsider, I believe that this situation is partially due to a lack of refereed papers. Exposure to the nuclear waste field always results in being buried under an avalanche of long reports. It is much easier to write a 300 page report than a concisely written 15 page paper. I hope that the new "Journal of Nuclear Waste Management and Technology", under the editorship of Dr. Cranberg, will set standards and replace many of the long reports by lucid and convincing papers.

Another remark concerns the interactions among the various communities. Much of the past work appears to have been done in relative isolation. Closer ties among Universities and industrial and government laboratories, and better interaction between the materials and geological sciences will benefit the field. The contributions to the present conference show that such ties are being forged.

4.

The main technological question is not "What is the best solution", but "Which solution is acceptable?". We know from personal experience that it is not possible to wait for the "best". When we buy a hi-fi set or a pocket calculator, we must make a decision at a given point in time, knowing that a better and less expensive model will appear shortly. Similarly, society must make a decision with respect to nuclear waste now. Discussions with many participants give me the impression that there is no technical problem. One geophysicist said: "If you throw a dart at the U.S. map, close to nearly every hit I could build an acceptable repository". All materials scientists and engineers questioned agreed that glass is an acceptable waste form under suitable conditions. The beautiful work in France and Sweden, presented in two exceptionally clear papers, shows that acceptable technological solutions can be realized. In the U.S. all the pieces exist, but the puzzle must now be put together.

Some remarks to individual aspects are as follows:

(i) The waste problem must be solved in an integrated way, as a system. Waste form and repository must be matched.

(ii) Glass will be the first-generation waste form. If the temperature is kept low by low loading and/or long intermediate storage, no serious difficulties are to be expected.

(iii) Alternate waste forms may well be superior as second-generation solution. However, much more work is needed before a decision can be made.

(iv) It is likely that initially spent fuel and reprocessed material will be stored.

(v) Personally I believe that the stored material is too valuable to be thrown away and should be retrievable. We not only have the duty to protect later generations, but also to not impoverish them.

(vi) As a scientist I feel that the repositories should be monitored as long as possible. Valuable scientific and technical data can be gained. Certainly fail-safe experts can design a system that will self-destruct should technical expertise be lost in future generations.

(vii) The multibarrier approach to waste disposal does much to ensure safe storage. A design, however, in which each individual barrier already satisfies all safety criteria may amount to a very expensive overdesign.

5.

To an outsider, the managerial aspects of the U.S. approach appear to lack a clear goal and a well-defined direction. (The talk by Dr. Oertel, given after I had written my summary, dispelled much of my concern.) Appointment of a "waste csar" could speed up waste disposal. It would also be good to for once have a csar with a problem that can be solved.

An important part of the waste problem is an early setting of the criteria.

6.

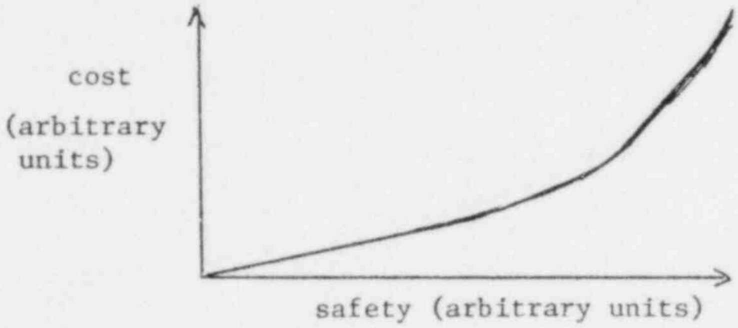
The nontechnical problems are the most difficult ones:

(i) The distrust in nuclear power and waste disposal is deep and emotional. The public sees a monster in nuclear energy. Many of us have been asked: "Would you like to live near a power plant or a repository?". It has taken me some time to understand that people really ask: "Would you feel safe and confident to live near a nuclear plant?". All scientists and engineers that I have asked answer yes without hesitation. I certainly would much rather live near a nuclear plant than below a dam, near a coal plant, or near a harbor with LG or oil tankers.

(ii) A point not made often enough is the fact that of all wastes, chemical or others, nuclear is most easily monitored. Anyone who distrusts the statements of the regulatory agencies can buy a scintillation counter set-up. Private monitoring of radioactivity is possible, but no similar surveillance of other wastes is known to me.

(iii) We must try to continue the dialog on nuclear safety in a rational way. It is not easy. Once, years ago, I talked to a consulting company about helping to solve technical problems. They laughed and said: "Problem solving is easy. It usually takes us an hour to solve the technical problem. We then spend weeks to sell the solution to management." Management in the nuclear power field is Congress and the people.

(iv) One particular aspect of the nuclear power debate troubles me. People talk about "zero release" or "zero danger". Such a statement sounds like sheer nonsense to me, for two reasons. On the one hand, no measuring instrument ever detects a true zero; there is always a limit of error involved. On the other hand, an unlimited effort for nuclear safety must lead to dangers in other fields. To see this, consider the sketch below in which cost (in arbitrary units) are given versus safety (in arbitrary units) for nuclear waste disposal. Obviously, if this curve were all we have to consider, we would move as far to the right as possible. Unfortunately, life is complex and similar curves can (and should) be drawn for coal power, electric power and dams, pollution by cars, chemical waste, air traffic, carcinogens, health care, ... In addition, there exist two conservation laws:



$$\sum \$ = \text{GNP} \quad , \quad \sum T = \text{const, small} \; .$$

The first law says that we cannot spend more than the gross national product on all safety measures. (In fact, we cannot even spend so much.) The second says that the number of talented people who can solve these problems is finite and small. Thus, we cannot look at one problem alone, we must optimize the entire set. At present we probably spend too much on nuclear safety, too little on others. A balanced approach is necessary and we must explain it to our management!

(v) We often hear: "If the scientists and engineers do not even agree among themselves, how should we believe them?". Two points can be made to this question. First, scientists will argue even when they agree. Such arguments do not affect crucial features. Only if there is a real disagreement about an essential point may safety be affected. A second point is more difficult to describe. What do we do if somebody comes and says: "But have you seen the paper by Professor X from Lower Slobovia in which he shows that two alpha particles emitted in the brain of a dog will do permanent damage!". How can we explain that such work is most likely irrelevant if it disagrees with hundreds of well established papers, because science forms a consistent body of knowledge in which a single set of data lying outside the coherent whole is nearly always wrong? I have not found a good way to do so. All we can do is try.

7.

Finally let me summarize the summary. We must continue to establish confidence in science and technology. We have much to be proud of. Technology as a whole works well. As a rule, technology keeps what it promises -- in contrast to many other human enterprises. True, there are side effects, but we must always balance the benefits from technology against disadvantages from the side effects. The writer Meyrink tells the story of a centipede who was asked: "Sir, how do you know which leg to lift after you have moved the 67th, and which after the 13th?". The centipede thought, and thought, and never moved another leg again. We have to be careful not to lose creativity by trying to anticipate everything. We must listen to the thoughtful, knowledgable, and positive critiques and disregard the purely negative ones. If we intend to safeguard the waste for 10^5 years, we must also plan energy production for the same period. Otherwise no humans will be around to benefit from the forethough of the safeguarders. This condition rules out fossil fuels and leaves the sun, fusion, fission, and renewable fuels. My guess is that we will need all.

Discussion Following

CONFERENCE SUMMARY

Presented by Hans Frauenfelder

Bob Watt - Los Alamos, private citizen
Question:
You concluded that if one started with a waste disposal method, there would be a series of changes which would eventually produce the best method. I, at the moment, worry about the process in the following sense. I think that selecting the best method requires (a) that there is an alternative you know to be better; (b) that there are experimental data showing that what you are doing is not good enough; and lastly (c) that there be a willingness to accept the need for change. I submit that there is considerable doubt in my mind that any one of those three can be applied in the case of nuclear waste. You obviously differ. I wonder if you could point out why.

Frauenfelder
Response:
Let me answer indirectly. Anyone who tells me he can take a major technological problem and solve it completely without doing any experiments is either a genius an order of magnitude larger than I have met, or he is insane. It seems to me that one must perform experiments to find the answers to many of the problems by trial and error.

Watt
Comment:
I should have pointed out that the loading life for many of these repositories would be at least 20 years. You probably would not have any significant data as a result in periods less than several decades. And it is for that reason that I think that the in-flow of data may be so slow as to really prevent integration of those new data into the whole process.

Frauenfelder
Response:
It is still a useful feedback. Whatever you do, you will need this feedback.

Watt
Post-Conference Comment Added to Transcript:
I agree completely with Dr. Frauenfelder that all available feedback will be valuable. I simply point out that a comprehensive waste disposal plan will have to be based on basic laboratory data, obtained in experiments simulating nature as nearly as possible. Often this means full-scale waste forms, some with fully radioactive samples. Temperatures,

pressures and other parameters must be duplicated in the laboratory for real time tests. Accelerated tests will often be necessary, with appropriate complementary experiments to test the validity of the accelerated results. My reason for this belief is simply that results from any field test will be obtained too slowly to affect the design of waste management systems.

Bernard Cohen - University of Pittsburgh and Argonne National Laboratory
Question:
On your diagram that had the cost versus risks and so forth, you did not have any numbers on your axis.

Frauenfelder
Response:
Yes, arbitrary units.

Cohen
Comment:
I have recently completed a paper on the amount of money our society and Government are willing to spend to save lives in various contexts. In medical areas you can save lives for tens of thousands of dollars each. In highway safety you can save a life for a hundred thousand or two hundred thousand dollars spent. Yet anything I can calculate for the nuclear waste sounds like we are spending hundreds of millions of dollars to save a life, and with defense wastes it seems to me like we are getting into the billions. The trouble is, this is based on my probabilistic analyses of the number of lives that are going to be lost. And I know there is a tendency not to believe my probabilistic analyses. What we need is for somebody to do probabilistic analyses that will be generally accepted. This would not apply to analyses that come out of Livermore, Hanford, Savannah River or Sandia. And so, what I would like to see is an analysis by Bob Watt, who has a comment on every paper, and Bob Pohl, who has a comment on every other paper, and maybe you can commission the Union of Concerned Scientists--I assume people will believe them. I would like to ask them to come up with an estimate of how many lives are going to be lost, with what probability, if you convert the waste in the Savannah River tank to cement. Or, if we put glass in salt, in a titanium can, with reasonable site selection, how many lives would be lost. If they could come up with numbers on those curves, we could see what ball park we are in.* I really think we are at the point of spending hundreds of millions of dollars to save a life; this really amounts to killing people, because we could spend that money to save lives in other areas and we are not doing it.

*Editor's Note:

Considerable post-Conference correspondence ensued between Pohl and Bernard Cohen on this subject. Interested readers can obtain that correspondence from them upon request. Bob Watt contributed the following on the subject for the record.

Dr. B. Cohen recommended that I (Bob Watt) prepare some cost/benefit analyses on the subject of nuclear waste disposal.

Cost/benefit ratios were the principal subject of my paper at the ANS-AIChE sponsored Topical Conference on "Controlling Airborne Effluents From Fuel Cycle Plants." The conference was held in Sun Valley, Idaho, on August 5 - 6, 1976; my paper starts on Page 18 - 1 of the Proceedings.

For TRU and High-Level waste disposal site-specific features must be considered in calculations of the cost/benefit ratio. Wide variations result from different assumed scenarios and those involving human intrusion (including drilling operations) are likely to yield the largest hazards (costs) for future generations. For the proposed WIPP site an assumed scenario and a rough estimate of potential cost were included in my (privately distributed) paper "Comments on Disposal of High-Level Nuclear Waste in Salt," dated June 1, 1977. Copies can be obtained from:

Dr. Bob E. Watt, 1447 45th St., Los Alamos, NM 87544

Data pertinent to the calculation of possible environmental impacts should be distributed on request to interested persons and included in appropriate Environmental Impact Statements. Essential data are not now available, making cost/benefit analyses for TRU and HLW repositories of limited value. It is my intention to make such comparisons when the data becomes available.

Frauenfelder
Response:
I think you are right, but you miss one variable in your equation. People are not reasonable. This fact is important because out of unreasonableness comes probably all great art and science. It also means, however, that people consider dangers subjectively. And nuclear power is, in the minds of most people, always connected with the mushroom cloud. The important thing is to find a balance among all possible ways to spend money to save lives. There is no completely objective way to determine the best balance and the way people assess the various dangers must be taken into account. Look at another case, the cancer drug laetrile. The best present evidence indicates that it is useless. Nevertheless, it will be tested, not because of sound scientific evidence but because often non-scientific aspects are strong driving forces in a society. If nuclear power is feared more than other possibly much more dangerous power sources, we must build this fact into our equations.

Cohen
Comment:
What you are implying is that there is a technical solution to every problem, but this is a problem where there is an educational solution, rather than a technical solution.

Frauenfelder
Response:
That is what I am saying, basically.

Mike Hamilton - Washington Cathedral
Comment:
Could I follow on that? I should like to suggest that scientists and managers have contributed to the problem of the public distrust. In a "fallen" world, theologically speaking, I have no difficulty in accepting the inevitability of risks, dangers and accidents. And, I believe there is latent within our society such an acceptance available to us. But, one of the reasons it has not been able to be acknowledged is because scientists themselves have been defensive and have contributed to the belief that nuclear energy and waste disposal should be safer than anything else. And the way they have contributed to it, I suggest, is by frankly hiding some of the accidents. It has often been the newspapers or people who are frightened who have ferreted them out. That has contributed to the distrust. I would like to see an openness, a willingness to talk honestly about problems and failures--something which has not always occurred, if you look at the Congressional Records. Is this a fair request--the possibility of a new and more open way of talking about problems and inevitable accidents?

Frauenfelder
Response:
I am a little worried about answering your question because it leads into so many difficult problems. Nuclear power has a special problem because of its close initial ties with the nuclear bomb and because it is something that the average man does not understand. It appears miraculous, or mysterious, or demonic. We can explain much of the basic principles in simple terms, but this takes an enormous amount of time. Most of us are very much pressed for time by conflicting demands. As a result, we do too little explaining and nuclear power remains mysterious. If everything goes well, nobody cares. But if there is some problem, every newspaper picks it up. The problem is usually given much more space than later explanations. Moreover, explanations are usually discounted as coming from "biased" people. Secondly, every large technology, from airplanes to chemical plants, is continuously beset with problems. Problems are part of the normal day and they can nearly always be solved. The fact that a problem occurs and is not widely advertized is not in itself serious. Thus, while I agree with you that openness is needed, I also feel that we need an understanding that the occurrence of problems is natural and not a sign that any particular approach is deeply in trouble.

Judith Johnsrud - Environmental Coalition on Nuclear Power
Comment:
I am here also under the auspices of Friends of the Earth. I would like to add a comment for the record on both Dr. Oertel's talk and yours, and following on from Bob Watt's comment earlier. We have heard a great deal of promise in the papers at this Conference. I am very

much encouraged, and I intend to take this message back to the public interest groups that are concerned with this issue. But, I have also heard a great many uncertainties. I have heard much couched in future terms; I have heard promises. I come away with the sense that there is a great deal of basic, almost fundamental research remaining to be done. Therefore, I want to address what we view as a fundamental problem, namely, the problem of "bounding the problem" of radioactive waste disposal. For the record, I would like to make this recommendation: we are rapidly increasing the quantities of radioactive wastes from the commercial program and to some extent from the defense program. You have spoken, sir, to the small quantity at the present time. It may be that the fundamental research projects that have been proposed here will take a great deal more time than anticipated and that they may run into further questions, and have further difficulties. Therefore, in order to avoid being rushed into the second-rate solution, we would recommend to the Nuclear Regulatory Commission that it exercise its regulatory authority to halt the further production of radioactive waste until the research that is yet to be done has been fully done and the demonstrations have, in fact, proven that these solutions proposed here are indeed workable. I would anticipate that this recommendation to the NRC would be rather unpopular with the industry representatives here. I would also feel that it would be exceedingly popular with those engaged in fundamental research. We certainly support their efforts.

Frauenfelder
Response:
Let me try to answer your suggestion. First of all, the fact that problems surface does not mean that the technology is in difficulties. In every endeavor it is our job to look for problems. If we do not find problems, we invent them. For instance, I think if you saw what problems occur with airplanes, you would never use one again. But to come to your proposed shut-down of all nuclear power plants I believe that would be one of the most disastrous things we could do. If we were not to replace the lost power at all, it would affect the lives of a very large number of people and clearly lead to excess death. On the other hand, if you replace the nuclear plants by coal plants, you would very likely increase the number of deaths by about a factor of 100. What you are saying is let us kill a hundred times more.

Johnsrud
Comment:
I said no such thing, and I do not like that characterization of what I said, sir. No, indeed.

Frauenfelder
Response:
I am sorry, but it is implied in what you said. There is only one other solution, a lowering of our standard of living. That is implied.

Johnsrud
Comment:
Nor have I implied lowering a standard of living. This is your reading.

Frauenfelder
Response:
But you are violating some rules.

Johnsrud
Comment:
What I am saying to you, sir, is that we are dealing with a rapidly compounding problem in terms of quantity of radioactive wastes. What I am saying to you is that the political pressures to resolve that problem using less than the best technology we are now close to being capable of will increase very rapidly and thereby prohibit the best job that can indeed be done.

Frauenfelder
Response:
I think where we disagree basically is that I feel that if you have a good solution, then that is good enough. You can never, in science or technology, have the best solution. There is always a better one. The crucial question is whether the solution that we can do is acceptable; does it satisfy all criteria? If it does not, then it should not be done. If it does satisfy the criteria, then the fact that there may be a better solution around the corner is irrelevant. Postponing that solution because there may be a better one will hurt everyone, including you. I think there is no way out of that. I am not in any way tied to the nuclear power industry. It is simply that I have spent the last two years looking at the problem. At some point you have to come out with an opinion. The industry representatives may think differently. That is irrelevant to me. If I look at the problem, I see no other choice. You have to realize that within the next 2 or 3 years we may also not get the oil that we have been getting. There is just no alternative.

Johnsrud
Comment:
Then I will say one last thing to you--and to this Conference. You have spoken of assurances to the public. If you continue to present that view to the public, you are not going to get their concurrence with the approaches with which you propose to rush ahead. The only way to do it is through good, honest science and engineering. And I ask that of the NRC and of those present here.

Frauenfelder
Response:
I think nobody disagrees with your last statement. Let me make one point again at the end. I believe that you can never have a best solution. You can only have good, acceptable solutions.

Ed Pilat - Energy Research Group
Comment:
I notice, sir, that you said you were very impressed with the Swedish and the French programs for high-level waste. Yet it seems to me that

the Swedes and the French have spent a lot less money than the United States has and that they have been working on it for a much shorter time than the United States. I wonder if you would be so rash as to give us some thoughts on why you think they have been able to do this impressive work.

Frauenfelder
Response:
What should I say to that? I think I have given the answer during my talk, and I will not repeat it.

APPENDIX A

POST-CONFERENCE COMMUNICATION FROM

EUGENE CRAMER

COMMENTS ON NATURAL URANIUM ORE AS A REFERENCE OBJECTIVE FOR NUCLEAR FUEL CYCLE RISKS

Dr. Tom Cochran proposed[1] that the risk of the completed nuclear fuel cycle activity including waste disposal should be no greater than the risk from natural uranium ore bodies that had never been mined. This was done because of the difficulty in deriving numerical criteria which would take into account a changing population, societal expectations and knowledge over centuries; as well as the need to establish an overall objective before considering the more specific secondary criteria such as a temperature limit for a waste form.

This idea of setting an overall objective such as this has sufficient merit that it should be discussed, as in the following.

(1) A more general criterion needs to be established to protect against inadvertently destroying another energy form. I propose "that no energy criterion or objective shall be made so severe for one energy form as to rule out another energy form when rationally applied."

For example, it is well known that the Radioactive toxicity of coal ash exceeds that of nuclear reactor waste after about 1000 years decay (1). To accede to excessive isolation of nuclear waste as a means of public acceptance may make the use of coal as an energy source uneconomic due to the considerably larger quantities of waste.

As a second example, the recent Canadian study by Inhaber establishes that the societal risk from solar electricity is about 100 times that of nuclear electricity. Thus to require that electricity sources have no more risk than nuclear could eliminate solar electricity completely.

(2) The objective is stated entirely in terms of risk, and does not allow for balancing of risk against benefits.

For example, the United States accepts 50,000 deaths per year from the automobile in exchange for some perceived benefits of increased mobility. Restriction of the risk of automobiles to that risk of buried iron ore would no doubt eliminate the automobile--at the same time eliminating its benefits.

More directly, requiring an energy form to have no more risk than its untouched fuel supply would eliminate <u>any</u> energy form, because the objective asks for the nonexistent "free lunch"--i.e., that an entity have all benefits and NO RISKS.

(3) The objective would have some merit if properly stated in relationship to waste disposal alone: for example, "the risk of a waste repository should be no greater than the risk of an equivalent uranium ore body."

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[1] During a NRC Workshop December 20, 1978 on Solid Waste Forms.

In this formulation, a major portion of the benefits of the use of the fuel may be applied to cancel the risks of this use, so that only a minor portion of the benefits applied to cancel some short-term risks of the disposal.

Accepting for the moment a very rigorous application of the objective, let us see what this implies with respect to repository and waste form criteria:

- The waste form and package should give reasonable assurance against escape of radioactivity to the geological structure until the waste toxicity and ore toxicity are approximately equal.
- The repository should be sited in a relatively remote area as is the ore body.

If we use as a first approximation the relative toxicities of the ore and waste (2), then the performance objective for waste form and package would be:

- For reprocessed fuel, the waste form and package should essentially retain all fission product radioactivity for a period of about 1000 years. (2, 3)
- For spent fuel disposal, the fuel element and package should essentially retain all radioactivity for a period approaching 1,000,000 years. (4)

These times are approximate, of course, since the calculations have NOT been made with the specific objective of comparing the spent fuel, waste and ore toxicities.

However, there is some indication that a properly stated objective of waste isolation relative to the original ore body would show:

- Removal of actinides significantly reduces the time required for the waste form to guarantee radioactive retention.
- Removal of cesium and strontium would allow their placement in waste forms most suitable to higher heat loadings.

Thus it would seem desirable to extend past calculations to those specific situations.

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(1) T.H. Pigford, Transactions of the American Nuclear Society, 30, 293 (1978).
(2) NUREG-0116, Suppl. 1 to WASH-1248 "Environmental Survey of the Reprocessing and Waste Management Portions of the LWR Fuel Cycle," October 1976.
(3) Fig. 7B1, Rev. Mod. Phys. 50 (1978).
(4) Fig. 7B2, Rev. Mod. Phys. 50 (1978).

APPENDIX B

STABILITIES OF ALTERNATE WASTE FORMS

RUSTUM ROY

STABILITIES OF ALTERNATE WASTE FORMS

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Abstract

The most significant advance in recent research in Radioactive Waste Management has been the development (definitive in concept and already partly verified in the laboratory) of solid waste forms of such stability that the RWM system may place a much higher fraction of its total reliance on these forms. The additional unique advantage of relying on the solid form, is that for the first time since RWM received national attention, there is hope that verification of standards and the meeting of criteria may be accomplished <u>in the laboratory</u>.

The theory which lies at the center of this advance is the mineralogical evidence on the survivability of specific crystalline phases in any of a very wide variety of near surface terrestrial environments. Thus a suite of mineral model phases can be selected which can accommodate all the 40 odd radionuclides in reprocessed fuel. An optimized, polyphasic, polycrystalline, ceramic material, especially surrounded by a metal matrix or durable ceramic or metal container constitutes a major step function advance over the previous "reference waste form" of monolithic glass in stainless steel. The waste form itself combined with the container and overpack can be specifically tailored for minimum reaction, in any particular host rock and for any age of waste.

Introduction

For some time the author and his colleagues(1) have attempted to describe explicitly the 'systems' nature of Radioactive Waste Management, and to clarify the different components in the system which provide the redundant barriers in the Russian doll model.(2) To date in models of radioactive waste management, the release from the waste form is often assumed to be relatively high and more or less a 'given.' In this respect, therefore, the vast majority of the discussions on the system ignore the potential of engineering this <u>primary</u> containment of the radionuclides. This is even stranger since the waste form is the only component which is unavoidable in any system. This neglect of the role of the waste form has been universal. In all nations - until 1976-77 - the developers of atomic energy agencies appear to have settled on a "reference" waste form - an oxide glass - rather early, and made no serious attempt to develop alternatives. The scientific communities in charge of these decisions were singularly weak in the relevant - geological and materials - sciences. The U.S. National Academy's Committee on Radioactive Waste Management did not comment on this component of the system for over twenty years. The Panel on Waste Solidification was established under the chairmanship of the author only in 1976.

This paper will be divided into two parts. The first will summarize by verbatim abstract some of the findings of the NAS Committee. The second will present in brief the author's personal views on the most important research findings of the last two or three years, which impinge on the role of alternative waste forms.

INSERT HERE TEXT FROM NATIONAL ACADEMY REPORT - enclosed at end of paper

Recent Advances in Waste Form Science

Existence of Alternatives to Glass

While there has been a rather widespread interest in alternative waste forms on the part of many individuals, the vast majority of every national R & D effort (except for the U.S.S.R. and recently, Sweden) has been devoted to glass. The fundamental case against glass as the most stable waste form has been made by McCarthy, Roy, et al.(2-4) Both thermodynamics, and empirical mineralogical evidence, allow no room for debate. Glasses are by definition metastable states; they have by definition a higher free energy (and hence total solubility) than the crystalline assemblage with the same composition. No glasses survive geologically in the wet and warm environments - even those corresponding to the lowest rank metamorphism - of nature. And these are precisely the likely conditions in a repository failure. As we have stated repeatedly none of this rules out glass as a possible waste form. It most certainly has ended the era of the unexamined push to use glass as the solid waste form. Appropriate engineering adjustments could be made to make it possible to utilize glass, but the resulting system, including the volume of the diluted waste form, area of repository, etc. would have to be compared with one using alternative solid forms.

The Alternatives

a) High Temperature (Crystalline) Ceramics modelled on natural mineral resistates.

The principal contribution of the Penn State effort by McCarthy,(4) Roy,(1) et al.(2-5) has been:

1) To use as the models for the ultimate crystalline phases to contain the radionuclides, the mineral structures which have survived in near surface conditions in the earth for hundreds of millions of years. (This leads first to the typical heavy mineral phases of beach sands, ilmenite, perovskite, monazite, apatite, etc. in addition to quartz and rutile). This concept also appears in an early paper by Isaacson.(6)

2) To molecularly engineer the waste stream composition by liquid phase additions, to locate each radionuclide in a specific phase in the final desirable alternate crystalline assemblage; the consolidation of the crystalline powder being achieved by sintering or hot pressing.

Moreover, the proposed use and the justification of the superiority of ceramic (= crystalline) as opposed to glassy forms is quite general. Thus the glass-ceramic work at HMI has been in progress for some years.(7) The Sandia titanate process,(8) and early Swedish work(9) also result, of course, in crystalline assemblages, though not with the fine tuning of the PSU work. Most recently, Ringwood,(10) has proposed two other sets of phases to be added to this list of candidate alternative crystalline assemblages.

b) Composites - Metal Matrix forms

The metal matrix forms - incorporating small (0.1-1.0 cm) ceramic or glass beads in a metal - offer three substantial advantages to the monolithic glasses. The mechanical properties towards impact are improved. The chemical durability in near surface environments can be vastly improved and the important buffering to a very low E_h is of great significance in immobilizing the actinides.

The Belgian group at Mol, under van Geel and Detilleux,(11) are the pioneers in this work. They have incorporated both crystalline and (principally) glassy beads in Pb matrices, and carried the process through a pilot plant stage. Recent work at Oak Ridge(12) suggests a very different approach to the same product, with the phases being much more finely dispersed. There can be little argument that a metal matrix form is superior in most respects (except resource use) to monolithic glass; whether it is worth it or not will need much more careful analysis of trade-offs of numbers of containers, dilution in glass, areas of repositories required, etc.

c) Coated Multibarrier forms

The use of CVD coating technologies (well-known in the nuclear industry) to give an additional layer of several microns of chemically impervious Al_2O_3 or SiC around ceramic pellets is another new technique. Embedding such coated ceramics in metal gives a remarkably resistant waste form.(13)

d) Composites - Low Temperature Ceramics, Cement Matrix forms

The alternative solid form most studied in the U.S. has been the "concrete waste form." Other low temperature ceramics such as the "aqueous silicate" process at Hanford(14) and the "ceramic sponge" have not been researched sufficiently as yet to be compared effectively. The concrete work to date suffers from an insufficent scientific appreciation of the nature of the problem. (e.g. It is not clear in what phases the radionuclides are incorporated.) The work of Stone(15) at Savannah River Laboratories, and Moore at Oak Ridge,(16) and D. Roy(17,18) at Penn State, clearly demonstrate that such cement forms are roughly the equal of the typical glassy forms with respect to the usual "leachability" tests. The alleged radiolytic generation of gases in cement forms has been based on poorly defined experiments, and at present there is no evidence to show that concrete (free of occluded H_2O) would generate any hydrogen at all, since recombination is so rapid on the fine particle surfaces.

New developments such as the incorporation of crystalline ceramic powders containing the radionuclides in a concrete matrix, or making special high density concretes using pressure, clearly make cement matrix forms as leach resistant as typical glasses, while the room temperature processing has many obvious advantages.

e) High Temperature Ceramic-Composites

One of the most interesting recent developments is that by the ASEA group in Sweden(19) where they have essentially made a composite of chopped fuel elements in Alumina, or have canned coiled elements in a hot isostatically pressed 1" wall alumina container and sealed it into a 1m x 2m Al_2O_3 monolith. With the well-known chemical durability of Al_2O_3 (rubies and sapphires in nature) the superiority of such forms should be obvious. Again, however, while such extreme measures may not be needed in the long run, it is quite clear that such state-of-the-art science will be extremely important in convincing the public that waste radionuclides can be immobilized for geologic times.

Processing, Containers and Emplacement

New developments in these areas will be longer in coming, but the directions are clear. While up to now only glass-making had been considered, today the full panoply of modern ceramic technologies are being considered, including hot pressing and sintering. The advantage of the substantially lower processing temperature than is used in glass-making, is not lost on anyone designing such a totally remote facility.

With regard to containers, new active research has sprung up on alternate container materials. Copper and titanium are both serious alternatives to stainless steel. The corrosion studies at high temperature and pressure, and especially the development of the full-size ASEA corundum (Al_2O_3) container show that the technology is available to make this barrier formidably stronger than conceived earlier.

In the emplacement area, Soviet experience with pumping of liquid wastes(20) (or sludges) and the Oak Ridge grouting process(21) of hydraulically injecting a slurry of waste liquid + adsorptive silicates + cement, offer radically cheaper technologies. The waste form produced may be adequate for many purposes, especially older wastes. Moreover, new developments of tailored overpack(22) instead of natural silicate additives, promise to make such "supergrout" forms even more resistant. Furthermore, these calcium silicate assemblages will be much closer to equilibrium with various silicate rocks. The key to the effective use of such forms is finding the proper geological conditions - a factor consistently emphasized by Spitsyn$^{(20)}$ and his colleagues. The push towards such forms will be driven principally by the cost advantage, the simpler, lower or room temperature processing, and hence lower worker exposure.

Summary

At the end of 1978, waste form research had been recognized for the first time as a major - possibly the most important single - barrier in the RWM system.

The technical community agrees that many forms, crystalline and glassy, low temperature and high temperature ceramics, metal matrix and cement matrix composites can each be utilized in a particular system. Comparisons between forms is meaningless unless the total system is specified. The principle of using crystalline minerals which have survived in the earth's leaching environment for hundreds of millions of years, as models, can be effectively interpreted to the public, and most congently argues the survival superiority of the properly selected crystalline assemblages.

Two examples, a "Fort Knox" and a "Brinks Truck" version serve to illustrate the variety of options available (for details, see ref. 23).

A. The "Fort Knox" solid form: This would consist of pellets of nearly theoretically dense ceramics (prepared by modern sintering or hot pressing methods) composed of 4-5 phases each modelled on a highly resistant mineral phase like monazite. The pellets would be coated with a layer of CVD SiC and/or Al_2O_3. These pellets would be embedded in a lead matrix, and sheathed in an outer layer of 1-2 cm of pure lead along the lines of the Mol technology. Alternatively, the pellets could be hot pressed in a Al_2O_3 matrix with an outer skin of 1-2 cm of Al_2O_3 using the ASEA hot isostatic pressing technology.

This solid waste form is now so chemically resistant that the releases which can be obtained under any conditions in the surface 1000 meters of the earth probably cannot exhibit significant amounts of radioactivity.

B. The "Brinks Truck" model: If it is argued that especially for older (defense) wastes the Fort Knox may be unnecessary in the long run (although its value in the short run in helping satisfy the public is enormous) one could turn to a simpler model.

This model would process all wastes on site. To defense sludges one would add highly optimized superoverpack (developed by Penn State), mix with cement, and use Oak Ridge grouting technology to emplace in suitable geologic strata on site.

Two slight variations are possible.

Modification (B'): The sludges are all converted to the tailored ceramic (artificial crystalline mineral) powder which is added (instead of the defense sludge) to universal overpack and cement.

Modification (B"): Instead of pumping the grout into the ground, it is put back into the tanks (especially at Hanford) which then becomes a mass of solid concrete containing insolubilized oxides and oxyhydroxides. The entire tank is then concreted over and under with "plain" supergrout.

Acknowledgement

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SUMMARY

The solidification of high-level liquid radioactive wastes from nuclear fuel reprocessing plants is a key element in most proposed radioactive waste management systems. The primary function of solidification is to minimize migration of radionuclides from the waste to the biosphere; the first requirement of the solid waste form, therefore, is that it be capable of furnishing a major barrier to that migration. In addition, the solid waste form selected must be suitable for all phases of waste management, including processing to produce the solid form, possible temporary storage, transportation, and emplacement in the repository.

Because a variety of system options is currently available and because different systems will make varying demands on the solid waste form, the choice of an appropriate solid form cannot be made without considering the specific radioactive waste management system in which the form will play a part. Furthermore, it is likely that a solid form chosen for use in one system will not be the most suitable choice for another system. The age of the waste, how much transportation is involved, and the geologic medium chosen for construction of a repository will be important determinants in selecting a solid waste form; other critical considerations will be the relative safety, reliability, and cost of the various methods used to process the solid.

Quantitative performance criteria for solidified high-level radioactive wastes are currently being established by the U.S. NRC. Until that procedure is complete, the Panel cannot judge whether any or all of the waste forms considered in this report are "acceptable." Existing government regulations on the storage, handling, and transportation of spent fuel assemblies (SFAs), however, might assist the policymaker in determining the acceptability of other solid waste forms.

On the basis of its detailed study of the relative advantages and disadvantages of individual solid forms, the Panel has reached the conclusions and developed the recommendations summarized below. Fo a more detailed listing of findings, see Chapter 5 of Part I of this report, which concludes Part I's discussion of the problems relating to the solidification of high-level liquid radioactive wastes. Technical evidence in support of the Panel's findings is contained in Part II.

1. The Panel finds that many solid forms described in this report could meet standards as stringent as those currently applied to the handling, storage, and transportation of spent fuel assemblies.

2. The Panel concludes that solid waste forms should be selected only in the context of the total radioactive waste management system. Considerations affecting this choice include the age of the waste, the hazards involved in processing, the amount of transportation entailed, and the characteristics of the geological formation in which the solid will be emplaced.

3. The Panel finds that many solid forms are likely to be satisfactory for use <u>in an appropriately designed system</u>, (see Chapter 3, section on the radioactive waste management system). Furthermore, at least one form--glass--because of an extensive developmental effort, is currently adequate for use in a first demonstration system consisting of solidification, transportation, and disposal. For the implementation of a large-scale solidification program, glass may also be adequate, but, on the basis of our analysis, <u>it cannot be recommended as the best choice</u>, especially for the older DOE wastes. In fact, a modest R&D effort may well provide alternative first or second generation solid forms whose long-term stability and ease of processing are superior to glass.

4. The Panel finds that the current United States policy of deferring the reprocessing of commercial reactor fuel provides additional time for R&D on solidification technology for this class of wastes. During this time special attention should be given to waste forms other than glass, which have received inadequate attention to date. The additional information thus developed may also be applicable to DOE wastes.

5. The Panel concludes that defense wastes which are relatively low in radioactivity and thermal power density can best be solidified by low-temperature processes, such as those used to produce cement-matrix and some ceramic forms.

6. For solidification of fresh commercial wastes that are high in specific activity and thermal power density, the Panel recommends that, in addition to glass, the use of fully-crystalline ceramics and metal-matrix forms be actively considered.

7. Preliminary analysis of the characteristics of spent fuel pins (SFPs) indicates that they may be eligible

for consideration as a waste form. However, before disposal can take place, SFPs must be characterized in detail and a system must be developed for packaging them.

8. Because the differences in potential health hazards to the public resulting from the use of various solid form and disposal options are likely to be small, the Panel concludes that cost, reliability, and health hazards to operating personnel will be major considerations in choosing among the options that can meet safety requirements.

9. The Panel recommends that responsibility for all radioactive waste management operations (including solidification R&D) should be centralized. The expertise existing in industry, universities and nonprofit institutions, which the Panel feels has been neglected in the past, must be more fully drawn upon through use of scientific symposia, professional society meetings and R&D contracts. Funding for R&D should be stabilized to provide sustained support (for example over a ten-year period) for long-term research. Regular communication and cooperation among major contractors working on radioactive waste management should be mandated.

FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

TECHNICAL ISSUES

Findings

From the Panel's examination of the technical issues involved in selecting options for disposal of radioactive waste (see Part I, Chapter 2) the following general findings and conclusions emerged:

1. High-level liquid radioactive wastes can be incorporated in several solid forms. These are:

    a. Supercalcine and calcine

    b. Glass

    c. Low-temperature ceramics

    d. High-temperature ceramics; glass ceramics

    e. Cement and concrete composites

    f. Metal-matrix composites

    g. Various combinations of the above

The Panel finds that many of the forms listed above are likely to be satisfactory in an appropriately designed system, and that at least one form--glass--is currently adequate for incorporation into such a system as a full scale demonstration of solidification and disposal.

In view of current policy, spent fuel pins are another solid form that needs to be considered for disposal.

2. The suitability of a solid waste form can only be determined in the context of the specific waste management system in which the waste form will be used (see Chapter 3, section on the radioactive waste management system). The important elements of this system are: <u>processing</u> (to form

the solid phase), storage, transportation, and emplacement (both retrievable and permanent).

a. For processing, low-temperature technologies, such as cement composites and low-temperature ceramics, are probably preferable to those requiring high temperatures.

b. For transportation, unconsolidated calcine and supercalcine are the least desirable solid forms because of dispersal hazards.

c. After emplacement in a well-selected continental geological formation, the performance of the system is more dependent on the chemical and thermal interactions of the solid form with the host rock and especially with the volatile components contained therein than it is on the original properties of the solid form.

3. The large difference in thermal power density between existing DOE wastes and possible future commercial wastes indicates that a single solidification technology may not be best for both. The following conclusions give some guidance on promising candidates for selection in specific instances, and on useful directions for research:

a. The preference for glass as a waste form has been mistakenly based largely on the assumption that low leachability is the major criterion for solid waste performance, and on a misreading of the "stability" of glass under repository conditions. Nevertheless, two vitrification technologies have matured to the point where either could be engineered into systems for the full-scale demonstration of high-level solidification and disposal. (See Chapter 2, section on primary containment forms.)

b. Research, development, and demonstration of alternative solid forms is essential in order to optimize the form (in terms of safety and costs) to be used in a disposal system. (See Chapter 4.)

c. DOE wastes are now relatively low in both specific radioactivity and thermal power density; accordingly, a wide range of solidification options is available for use in a first generation RWM system (see Chapter 3, section on ranking the suitability of solid forms). If current research indicates that buildup of pressure from the radiolysis of resident water and nitrates at the activity levels and temperatures present in the DOE wastes is not limiting, cement composites and ceramic forms made at low temperatures appear to be extremely promising candidates. (See Chapter 2, sections on primary and secondary containment forms.)

d. The Panel finds that, before emplacement, the effects of radiation damage (excluding radiolysis of water and nitrates) can in no case pose a major problem. After emplacement, effects caused by transmutation and radiation damage could somewhat alter interactions between wastes and rock. Further research is necessary to evaluate this possibility. (See Chapter 2, section on characteristics of the solid form.)

e. The reprocessing of spent commercial fuels is not current policy; however, if reprocessing is resumed at some future date, it will eventually be necessary to dispose of liquid wastes with high specific activity and high thermal power density. These characteristics will probably narrow the range of solidification options to those with high thermal stability. (See Chapter 3, section on ranking the suitability of solid forms.)

f. The amount of uranium and plutonium present in spent fuel poses a potential long-term hazard greater than that associated with other solid waste forms. Preliminary analyses indicate, however, that the radionuclides of concern (both actinides and fission products) may be contained in relatively insoluble phases with the spent fuel. If the results of research and development confirm these initial analyses, spent fuel would be eligible for consideration as a solid waste form.

APPENDIX C

LIMITATIONS IN PREDICTING LONG-TERM PERFORMANCE-OPTIMISTIC

BERNARD L. COHEN

LIMITATIONS IN PREDICTING LONG-TERM PERFORMANCE-OPTIMISTIC

Bernard L. Cohen
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Can we prove that a repository will be acceptably safe? This depends on what we mean by acceptable: safe compared to what?

If we compare it with perfection -- which seems to be the common practice -- the answer is obviously no. Nothing in this world can pass that test.

It seems more reasonable to compare it with other waste disposal problems that are considered acceptably safe. One of these is the solid radioactive waste from burning coal. People worry about the air pollution from coal-burning, but there has been no serious complaint about the solid radioactive waste from burning coal (due to its uranium content). For average coal, this is 1/10 as hazardous as nuclear waste (from the same energy production) after 500 years, and the ratio increases to 1/4 at 1000 years, 1.0 after 15,000 years, 3 after 1 million years, and 12 after 10 million years. Some commercially used coals have 35 times higher than average uranium content; their hazard equals that of the nuclear waste after 400 years and is 100 times higher after a million years. The phosphate rock mined in this country leaves a radioactive waste (from uranium) which is 20 times higher than that from coal if all our electric power were derived from coal. Thus, this radioactive waste hazard exceeds that of nuclear waste after 450 years, and is 5 times higher after 1000 years, and 60 times higher after a million years. There has been some consideration of covering phosphate waste to reduce radon emissions, but no one has claimed that the solid waste is not acceptable because of its own radioactivity.

The most logical hazard index is "hazard-years," the magnitude of the hazard multiplied by its persistence time. This depends on the period of integration, but for 100 to 1 million years, the hazard-years for nuclear and for average coal radioactive wastes are equal, and for 0 to 100 million years, the hazard years for coal radioactive wastes are 10 times higher. For high-uranium coal and phosphate mining wastes, these numbers are 35 and 20 times higher respectively than for average coal.

Since these other waste hazards are considered acceptable, we propose that a reasonable criterion for a nuclear waste repository is that it be at least as safe at all times as phosphate mining waste disposal. This works out, after some simplification, as follows:

Probability for escape of an atom of waste to the surface:

$< 0.1\%$ for first 100 years

$< 1\%$ from 100-200 years

$< 10\%$ from 200-400 years

No requirements after 400 years.

This does not consider the more logical "hazard-years" index, so it actually makes the nuclear waste much less hazardous than the phosphate waste.

Moreover, no credit is given for surveillance; this is a bonus which would again make nuclear waste very much less hazardous. Some estimate of the hazard involved with our criteria may be obtained by assuming that all of the waste is released into rivers, and then has the same chance of being ingested with drinking water as other materials in rivers. This gives 0.5 fatalities/GWe-yr. Assuming it is mixed through the soil gives a similar result.

One might ask why these criteria should not be made more stringent. To do so would be a violation of the ALARA principle. Everyone seems to agree that spending more than about $1 million per life saved is inconsistent with the R - "reasonably" - in ALARA. Typical estimates of costs of our present nuclear waste disposal program are about $2 million/GWe-yr. If this investment can satisfy our criteria, it is not consistent with ALARA to spend more than 25% more to do better. Stated more meaningfully, spending additional money to meet more stringent criteria is wasting money that could save more lives if used in other ways, as, for example, by improving highway safety or improving medical care. Actually, lives can be saved in those areas at a rate of about $100,000 per life, so our case is grossly under-stated. Even more importantly, any honest assessment of the value of saving lives should be discounted into the future -- we could invest money to draw interest, giving us much more money to be used to save lives with improved medical care or highway safety in the future. Typical discount rates are 4-5%, but even if we discount at 1% per year real interest (after inflation), saving a life 70 years in the future is worth only half as much, and saving a life 500 years in the future is worth less than 1% as much. Clearly, then, spending more money to improve on the above criteria is a violation of ALARA.

We now consider the various reasons to believe that current technology can satisfy the above criteria. This is most easily shown in terms of time delays, even assuming no protection from the waste form - i.e. assuming it is dissolved and dispersed through the rock formation in which it is buried (by entrapped water or water of crystallization). We still have the following time delays:

1. The waste will be buried in a rock formation with no circulating ground water, and in which geologists are quite certain there will be no ground water for "at least a thousand years, and probably very much longer" - quoting from the NAS Committee.

2. If circulating water does enter this rock formation, it must dissolve X% of the rock in order to dissolve X% of the waste. This might seem easiest in salt, but in the Carlsbad (NM) region, if all the water flowing through the ground were diverted to flow through the waste, it would take 50,000 years to dissolve away the salt enclosing one year's waste. Typical water-saturated rock lasts for many millions of years.

3. If waste is dissolved in circulating ground water, in all ordinary circumstances there is a delay of typically 1000 years before that water reaches the surface.

4. The radioactive material does not move with the ground water; in all ordinary circumstances it is "filtered out" by adsorption in rock and soil and consequently moves hundreds or thousands of times slower than the water.

In view of these time delays, it is obvious that the criteria we have outlined will be very easily satisfied.

I now turn to the question of long term security, beyond 400 years, even though this is not necessary to make a repository acceptably safe. By this time, buried waste resembles other rock. Its heat source is gone and waste-rock interactions are largely completed. It seems reasonable at this stage to make a comparison with average rock.

The life expectancy of an average rock at 2000 ft depth is about 50 million years. In a previous paper (Rev. Mod. Phys. 49, 1(1977)), I demonstrated this by use of radium, but it can be checked with any of several other elements. An even simpler procedure is to estimate average erosion rates from the total solids (dissolved or suspended) carried into the oceans each year by rivers. There is no question but that, if the waste behaves like average rock, there is nothing to worry about.

How is buried waste different than average rock? There are a few ways:

1. Being emplaced artificially rather than by natural processes, the waste is not in chemical equilibrium with the surrounding rock. But this is true of thorium and radium formed by decay of uranium, and to a large extent it is true of any trace element in the ground. Yet the transfer probability per year for these from the ground into human food is no larger than for major elements. In most cases it is less.

2. Repository construction requires making bore holes and shafts from the surface down to the waste horizon, and these may provide a release pathway. However, all groups that have studied this problem have concluded that these holes can be sealed so as to be at least as secure as the original rock. A demonstration of bore hole sealing is expected in the next year or two.

3. The waste is initially quite hot, and there is a wide range of thermal effects which could possibly lead to early release. However, these have been studied intensively for many years, and no important difficulties have turned up. These studies are continuing and should continue until the experts are satisfied.

If difficulties should appear, they can generally be handled by more dilute emplacement. If there should be extreme problems, the waste can be stored for a long enough time to eliminate them. A 100 year delay reduces the heat source by a factor of 10 and maximum temperature rises to about 20°. An additional factor of 10 can be achieved by waiting 200 years, and a third factor of 10 is obtained by a 300 year wait. This would bring maximum temperature rise down to a small fraction of 1 degree, which would certainly eliminate thermal problems.

As one last thought before closing, I think it should be pointed out that no one has produced a probabilistic analysis that indicates that a repository does not provide adequate containment of nuclear waste. I consider this fact to be highly significant.

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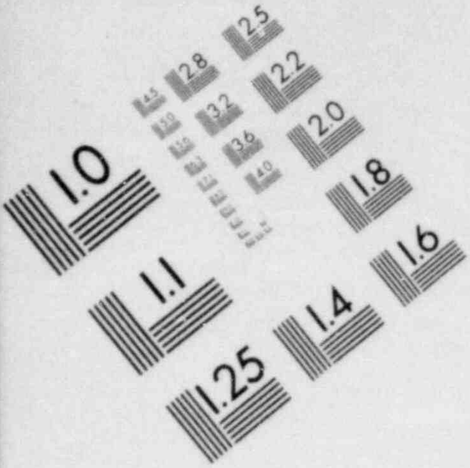

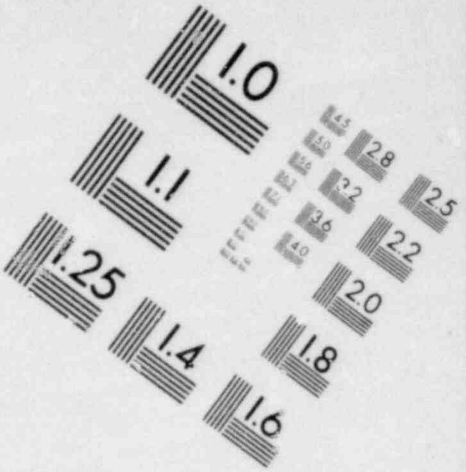

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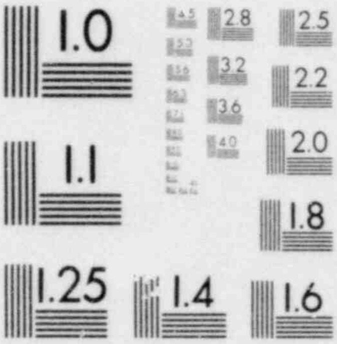

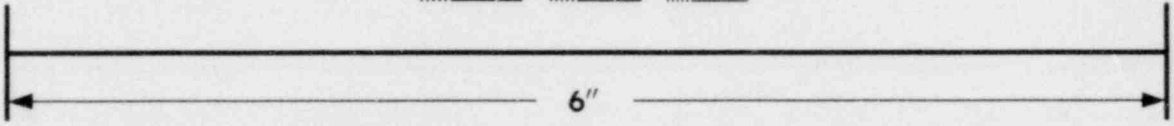

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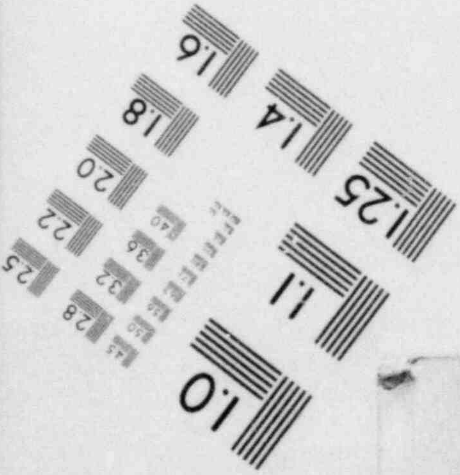

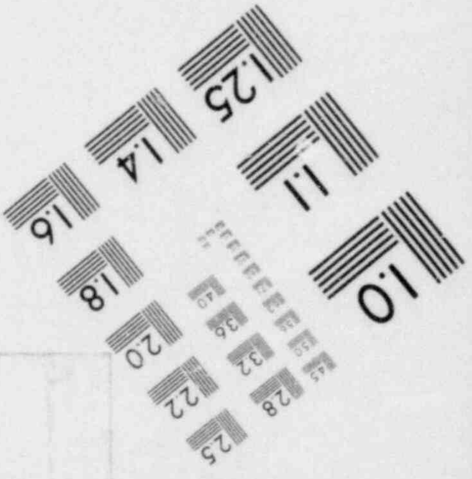

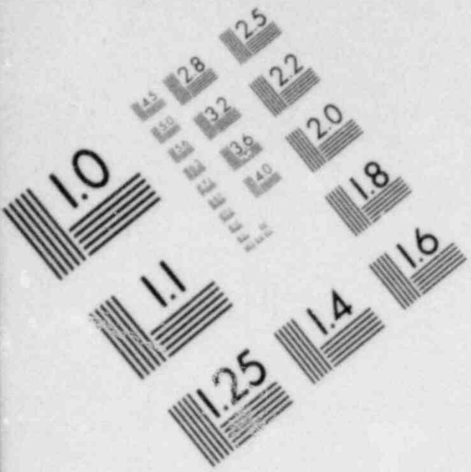

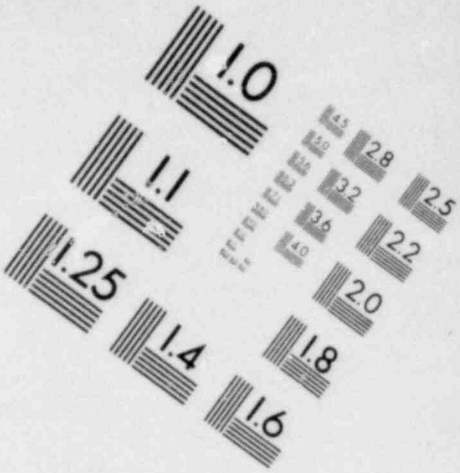

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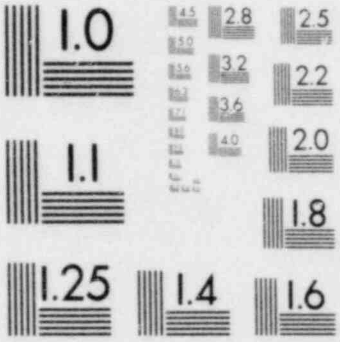

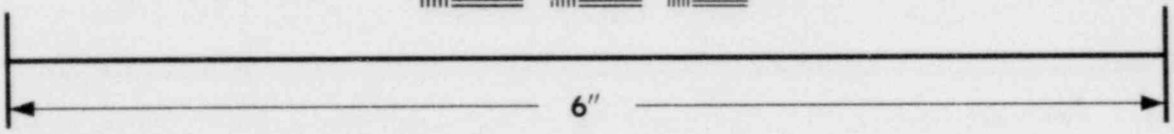

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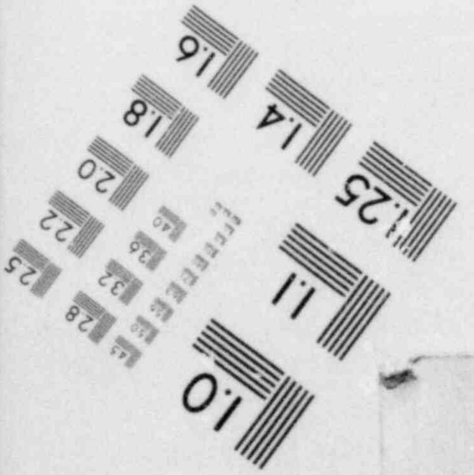

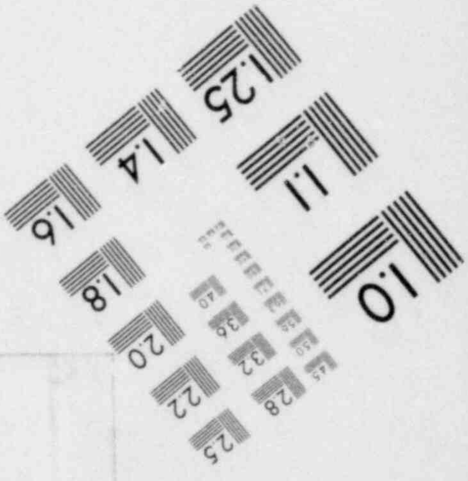

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This report contains the proceedings from the Denver Conference on High-Level Radioactive Solid Waste Forms. The Conference presentations and discussions involved the full range of materials sciences as applied to solidification of wastes, their canisters and potential buffering overpacks. Prominent spokespeople presented an in depth discussion of current research in their fields. Workshops focused on implementing new technologies into possible policy decisions.

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