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SOLIDIFICATION OF HIGH-LEVEL RADIOACTIVE WASTES

Final Report

National Academy of Engineering
National Academy of Sciences

Prepared for
U. S. Nuclear Regulatory Commission

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Final Report

National Academy of Engineering
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NOTICE

The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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PREFACE

In September 1976, the U.S. Nuclear Regulatory Commission (U.S. NRC), which is responsible for developing performance criteria for high-level radioactive solid wastes, requested that the National Research Council (NRC) conduct a study of the scientific and technological problems associated with the conversion of liquid and semiliquid high-level radioactive wastes into a stable form suitable for transportation and disposition. In response, the NRC established a Panel on Waste Solidification under the Committee on Radioactive Waste Management. The Panel consisted of experts in each of the major inorganic solidification technologies: glass, ceramics, metals, and cement and concrete; and experts in materials science, radiation effects on solids, mineral stability and weathering, and nuclear technology. As a result of President Carter's decision on April 7, 1977 that the United States would indefinitely defer all civilian reprocessing of spent nuclear fuel, the Panel broadened the scope of its study to include consideration of spent fuel as a potential solid waste form.

The Panel's early deliberations in 1977 were assisted by briefings from personnel of the U.S. Energy Research and Development Administration (ERDA). These briefings, augmented by various ERDA documents and reports, acquainted the Panel with the research and development on waste solidification being conducted in the United States. To familiarize the Panel with research and development activities abroad, the Chairman and three Panel members visited solidification facilities abroad and discussed the present state of the art with their colleagues in the U.S.S.R., France, West Germany, the United Kingdom, Belgium, Sweden, and Denmark. The opportunity for this Panel to communicate and exchange information during these visits proved very valuable.

Using the information obtained from these sources, the Panel performed the following tasks.

- Analysis of the role that the properties of different solid forms play in determining selection of the form appropriate to a particular total radioactive waste management (RWM) system.

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- Evaluation of information currently being used as a basis for developing different forms of solid waste, and comparison of this information with information available from the most advanced research on materials considered for use as waste forms.

- Examination and evaluation of management of R&D for solidifying radioactive wastes.

- Evaluation of the research done so far, and recommendations for the future.

- Formulation of recommendations to federal agencies concerning solid form options currently or potentially available as part of the total RWM system.

The following subjects were beyond the scope of this report:

- Quantitative risk analysis of waste solidification, because such analyses are not very useful if they do not examine the complete RWM system.

- Selection among isolation or emplacement alternatives.

- Transportation technologies.

- Incorporation of gaseous radioactive wastes into solid forms.

- Analysis of economic, social, or political issues affecting a decision to permanently dispose of spent fuel.

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. For 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.

PART I
RADIOACTIVE WASTE SOLIDIFICATION

CHAPTER 1

NATURE OF THE PROBLEM

THE ENERGY/ENVIRONMENT CONTEXT

This report is being written at a time when the world is acutely aware of the crucial importance of energy in the economies of developed and developing nations. For the first time, curtailment and eventual exhaustion of supplies of oil and natural gas are perceived as real possibilities in the not-so-distant future. In every nation, political leaders and their technical advisors are casting about for alternative sources of energy. Nuclear fission is one such energy technology with the proven potential for augmenting oil and gas as a means of generating electricity.

In some countries, decisions are already being made to move toward a nuclear energy economy. In the United States, the decision for or against a large expansion of the nuclear industry still hangs in the balance.

One of the considerations that weighs against the nuclear alternative in the United States is the fact that the nuclear fuel cycle has not been closed; that is, spent fuel pins from commercial power production are accumulating, and no final decision has been made about their ultimate disposition. Opponents of nuclear power interpret the situation as evidence that the necessary technology is lacking; proponents reply that the technology is available--all that is required is a policy decision to go ahead. Policymakers sense that both viewpoints may be influenced by the special interests involved. The public, meanwhile, which has become increasingly aware that there is no such thing as a risk-free mode of life, is particularly suspicious of technologies that are unfamiliar.

The policymakers' task will be easier if the purely technical issues surrounding the safe management of fission-power wastes can be clearly identified and evaluated. Foremost among these technical issues is the management of the spent fuel pins and high-level liquid wastes that result from reprocessing spent fuel. The objective of waste management is to ensure that the radioactive components in these wastes are effectively prevented from reaching the biosphere. To accomplish this objective, a safe, worldwide system must be developed for the reprocessing, solidification (or treatment of spent fuel pins), transportation, and ultimate isolation of nuclear wastes. An important component of this system is solidification.

It is the basic assumption of the Panel that eventually all high-level liquid wastes (HLLW) will be solidified. This report analyzes the alternative solid forms that can be used.

REASONS FOR SOLIDIFICATION

Nature of the Wastes

Nuclear reactors, whether used for research, generation of electricity, or production of material for nuclear weapons inevitably produce radioactive wastes. After nuclear fuel has been irradiated for an appropriate amount of time (three to four years for nuclear power reactors), it is removed from the reactor in the solid form termed spent fuel assemblies (SFAs). The SFAs are made up of spent fuel pins (SFPs) (see Figure 1.1) which are in turn composed of metal clad ceramic pellets approximately 1 cm in size. These pellets contain unburned uranium as well as substances that are produced during irradiation of the nuclear fuel such as plutonium, other actinide elements, and highly radioactive fission products.

Reprocessing of spent fuel is essential to the production of plutonium used in nuclear weapons. SFPs from the military program are therefore dissolved to allow the recovery of uranium and plutonium. The residual liquid contains the fission products and a very small fraction of plutonium. For spent fuel from the civilian nuclear power industry, however, current U.S. policy does not permit reprocessing; hence the radioactive fission products and the plutonium from commercial reactors are contained in the SFPs themselves. Because the current United States policy is to defer commercial reprocessing, the Panel has considered SFPs as one of the potential solid forms for ultimate disposal.

At present, large amounts of the radioactive wastes resulting from military reprocessing and research (commonly referred to as DOE wastes) are being stored in tanks as a complex mixture of liquid, sludge, and salt cake ("semiliquid"); should U.S. policy change to allow reprocessing of wastes from commercial reactors, these amounts will be augmented. Moreover, the fresh single-phase, liquid wastes likely to result from commercial reprocessing will be more radioactive (one- to two-year-old commercial wastes may contain hundreds to thousands of

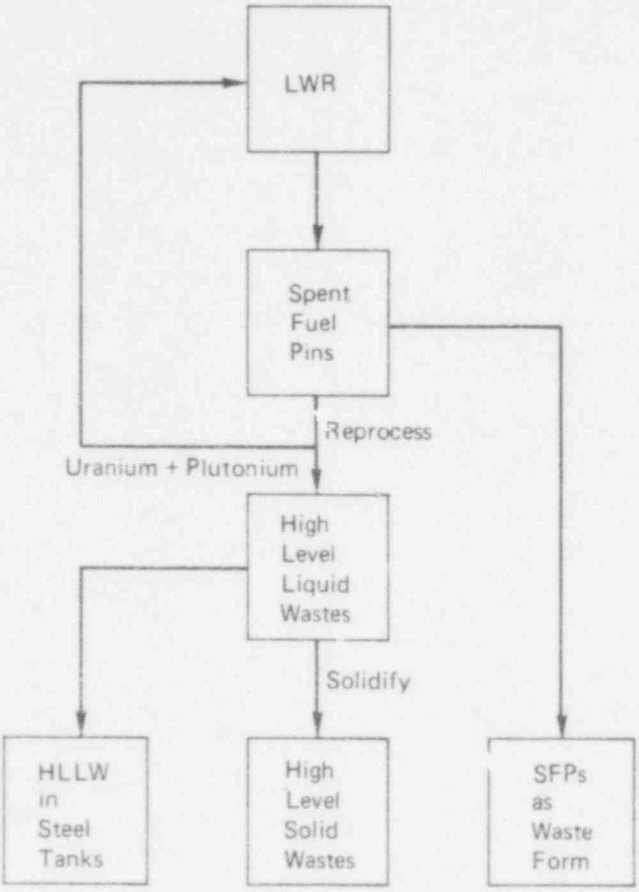

FIGURE 1.1 High-level wastes from light-water reactors (LWR).

curies per liter) than the older multiphase, semiliquid military wastes.

Storage of radioactive wastes as liquids or semiliquids may be an acceptable temporary measure; it is unacceptable, however, in the long term, because radioactive wastes are a long-lived source of radiation and because, in liquid or semiliquid form, they are dispersible and chemically reactive. The orderly management of the nuclear fuel cycle requires that existing HLLW from research and military operations be solidified, and that acceptable methods be developed for solidification of possible future commercial wastes.[1]

Amounts of Stored Wastes

The vast majority of radioactive wastes from military and civilian reactors, exist as HLLW[2] or in SFPs. In the United States, approximately 265,000 m^3 of HLLW are stored in large steel tanks ranging up to 5,000 m^3 in size. These tanks are located at three principal sites (Hanford, Savannah River, and Idaho Falls) and are officially designated as having been derived from military and research operations. Together with 1,480 m^3 of solid waste in the form of calcine--an anhydrous oxide powder--(see Chapter 2, section on calcine), the liquids at these sites constitute the sum total of noncommercial high-level waste now in existence.

The total inventory of commercial spent fuel assemblies, which are stored in basins near or at the reactor, is, as of October 1977, some 2,268 metric tons. If processed by current techniques (U.S. ERDA 1976b) they would yield approximately 2,000 m^3 of high level liquid wastes.[3] The total radioactivity content in the commercial SFAs currently exceeds that in the DOE wastes. Some of the SFAs have only recently been removed from the nuclear power reactors, however, and their radioactivity level will decay rapidly (see Part II, Chapter 11, section describing light-water reactor fuel assemblies). In addition to these SFAs, a fairly small amount (see Table 1.1) of HLLW derived from the reprocessing of commercial spent fuel is now stored at West Valley, New York.

As Table 1.1 indicates, the volume of military wastes presently in storage greatly exceeds that of the commercial wastes. Nevertheless, because of the potential growth of nuclear power in the United States, this situation could change in the future. A current projection used by the DOE (1978) is that by 1995, 60,800 tonnes of spent fuel will have been discharged from commercial nuclear power reactors. If processed by current techniques (Purex processes) these would be expected to yield 52,000 m^3 of HLLW,[3] still not as

TABLE 1.1

Total Inventory of Spent Fuel and High-Level Wastes in the United States

	DOE		Commercial	
	Amount	Activity (curies X 10^6)	Amount	Activity (curies X 10^6)
High-Level Liquid Wastes in Tanks	265,000 m^3[a]	450[b]	2,300 m^3[c]	31[d]
Unreprocessed Spent Fuel			2,268 tons[e] (2,000 m^3)[f]	3,400[e]
High-Level Solidified Wastes	1,480m^3[g]	51.8[g]		

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[a] About half of this volume is in the form of salt cake and sludge (U.S. DOE 1978).

[b] Quantity of ^{90}Sr and ^{137}Cs (F.P. Baranowski, U.S. Energy Research and Development Administration, personal communication to M. Willrich, Massachusetts Institute of Technology Energy Laboratory, October 27, 1976).

[c] Waste is estimated to be 5 percent sludge, by volume (U.S. NRC 1976).

[d] Quantity of ^{90}Sr and ^{137}Cs as of 1973 (U.S. NRC 1976).

[e] Alexander et al. (1977).

[f] Projected amount of HLLW produced from reprocessing current inventory of commercial SFPs. Based on an estimate of 850 liters/MTU (U.S. ERDA 1976b).

[g] These wastes are in the form of calcine (U.S. ERDA 1977b).

great as the present volume of military wastes. It should be kept in mind, however, that such reprocessed commercial wastes will be much more radioactive and have higher rates of heat generation than the military wastes (see Table 1.1).

FUNCTIONS OF SOLIDIFICATION

Solidification of HLLW is an essential factor in minimizing the possible release of radionuclides during the transportation or disposal of radioactive wastes. The solid waste form is defined for the purpose of this report as the total unit which, as the product of a solidification process, will be transported to and emplaced in a repository, for permanent storage or retrieval. The solid form can provide both primary and secondary levels of containment for the radionuclides within the waste. Figure 1.2 and Table 1.2 illustrate schematically the nature of the solid waste form and the two levels of containment. As can be seen from Figure 1.2, the solid waste form itself is buttressed by additional barriers against the release of radionuclides, such as the waste container and the geologic formation in which the waste has been emplaced.

Primary Containment

In any solid waste form, the radionuclides are first contained at an atomic and molecular level. Virtually all materials that act as the immediate host for these radionuclides are ceramics--i.e., high-temperature inorganic nonmetallics. As Table 1.2 indicates, there are four different types of crystalline (or partly crystalline) primary ceramic hosts to contain the radionuclides, and one noncrystalline form which, because of the terminology used in this field, is referred to separately as "glass." Except for significant quantities of dry strontium fluoride (SrF_2) and cesium chloride (CsCl) that are being stored at the Hanford Reservation in Washington State, all crystalline forms are mixtures of oxide phases that have well-known crystal structures. An oxide glass is merely a variant of this theme, wherein ideally the single phase host can accommodate all the ions. In practice, glasses with high loadings of waste often have small percentages of crystalline phases and/or are separated on a microscopic scale into two glassy phases.

Secondary Containment

Many, but not all, proposed waste forms involve composites of one of the primary forms bound together in a matrix of a second material (see Figure 1.2). This matrix may be a low-melting metal, such as lead, a high-melting

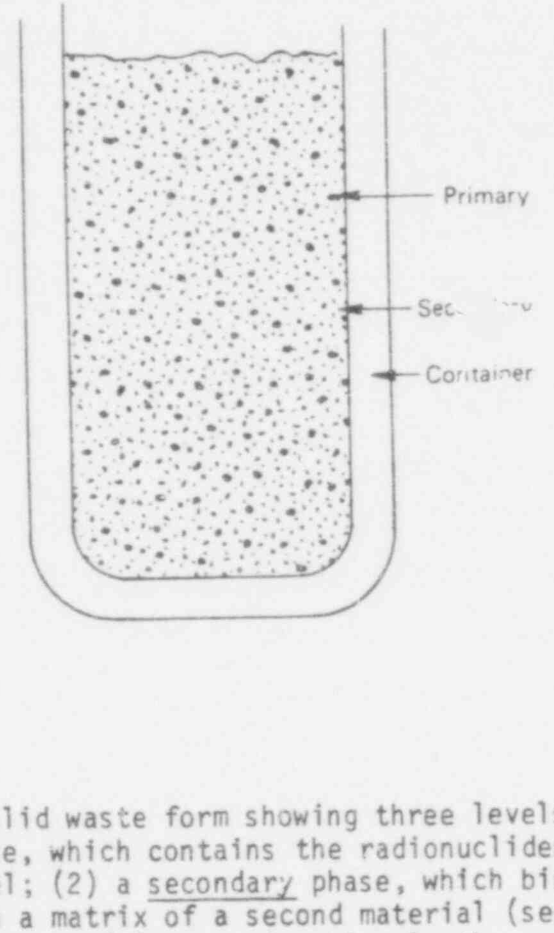


FIGURE 1.2 The solid waste form showing three levels of containment: (1) a primary phase, which contains the radionuclides at the atomic and molecular level; (2) a secondary phase, which binds the primary phase particles in a matrix of a second material (see Figure 10.1 for an actual example); and (3) a tertiary level, the container.

TABLE 1.2

Solid Form Containment Options

Primary	Secondary	Container
Ceramic materials	Metals	Mild steel
Supercalcine		
Low-temperature ceramics	Cement	Stainless steel
High-temperature ceramics	Glass	Titanium
Fuel pellets		Copper
Glass		Concrete
		Alumina or other ceramics

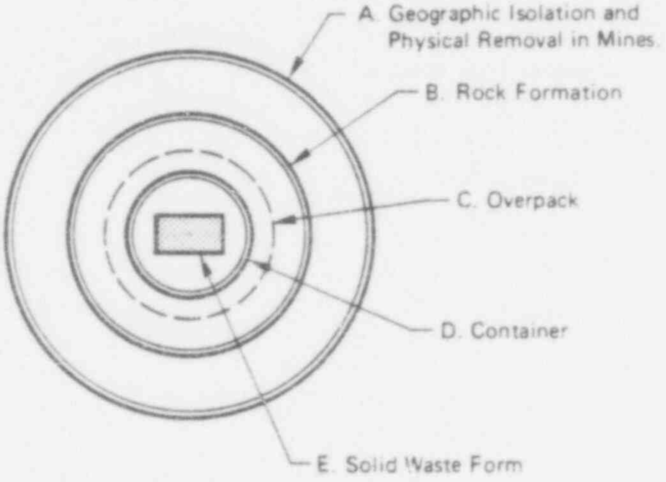
metal, such as titanium, or a concrete that has set at ambient temperature. The matrix provides both a physical and chemical barrier that prevents solvents from reaching the radionuclides. However, the metallic secondary containment materials are unable to incorporate the waste ions into their structures, and the other secondary containment materials can only do so for specific ions in small amounts.

ADDITIONAL FORMS OF PROTECTION

Protection against possible release of radionuclides goes beyond the two levels of containment provided by the solid form itself. A satisfactory method for disposing of high-level nuclear wastes will be one that uses a sequence of multiple barriers (see Figure 1.3).

The outermost protection against exposure is the physical isolation provided by deep emplacement in a remote geological formation. The first barrier to release of radionuclides into the biosphere is the geological formation itself, which eventually becomes the real container. Through careful selection of both the geological formation and the solid form, release of radionuclides brought about by the interaction of the host rock with the high-level solid wastes (HLSW) can be limited. The second, much more temporary barrier, is the canister. The canister, made of metal or ceramic, was originally designed to provide mechanical convenience and safety during transportation. Currently it appears that the intended function of the canister will be to provide an effective chemical barrier for a period of time ranging from five to one hundred years. An additional chemical barrier can be supplied by an overpacking material, consisting of a mineral powder capable of adsorbing radionuclides ions, and/or a metallic shell or casing that prevents the canister from coming into contact with the host rock.

The innermost barrier is the solid waste form itself. Before permanent emplacement and particularly during transportation, the physical and chemical properties of the solid waste form are important elements that can help protect the public from inadvertent exposure to radiation.



A. The outermost protection is provided by geographic isolation and physical removal in mines or excavated vaults.
B. The rock formation will, in most cases, react chemically and physically with the waste to form the long-term container.
C. The waste is separated from the rock by an optional overpack, which can be a metallic cylinder or a mineral powder that adsorbs radionuclides.
D. The container provides protection, particularly during shipping and during the retrievable phase after emplacement.
E. The solid waste form is a major barrier during transportation, after emplacement, and also after reaction with the host rock.

FIGURE 1.3 Multiple barrier concept for disposal of nuclear wastes.

NOTES

1 Most of the radioactive gaseous elements of concern such as ^{85}Kr, ^{129}I, tritium, and ^{14}C, will be released when fuel elements are chopped and dissolved during fuel reprocessing. These gases will either be diluted and dispersed to the atmosphere or recovered for eventual disposal. A number of processes have either been developed or are under development to handle this problem (see ERDA 1976b).

2 DOE wastes, although referred to generically as "liquid," contain various solids (see previous section).

3 Although HLLW is expected to be generated from Purex reprocessing at about 5,000 liters/metric ton of uranium processed (MTU), the volume will be reduced to between 600-1,100 liters/MTU for interim storage (U.S. ERDA 1976b). The estimates of 2,000 m^3 (from the present inventory of SFPs) and 52,000 m^3 (1995 inventory) are based on a choice of 850 liters/MTU.

CHAPTER 2

SUMMARY OF ANALYSES OF INDIVIDUAL SOLID FORMS

The major technical work of the Panel has been to study and evaluate the various solid forms and the methods that have been proposed for incorporating high-level liquid wastes in them. The resulting detailed analyses of the individual forms and methods are presented in the Technical Analysis section (Part II). This chapter, after briefly outlining the general characteristics of solid forms that affect their performance in the multibarrier system, summarizes the technical analysis of each form.

CHARACTERISTICS OF THE SOLID FORM

The relative importance of particular properties of the solid form will vary according to the needs of each stage in the waste-management process. Dispersibility and leachability, for instance, are key characteristics during processing and transportation before emplacement in a geological repository. If, for example, an accident were to occur during the processing, handling, or transportation of radioactive wastes, the least dispersible waste form would pose the least risk to public health and safety. And if water were to come in contact with the wastes, the solid form least subject to leaching would afford most protection because the rate of dissolution of the radionuclides contained within the waste is determined by the leachability of the solid form. Following emplacement, on the other hand, chemical and thermal interaction of the solid form with the host rock become more important considerations than dispersibility and leachability of the original form. For example, if water were to enter the repository after 100 years and come in contact with the wastes, the dissolution of the hazardous radionuclides contained within would be governed not by the leachability of the original solid waste form, but rather by the leachability of the solid product formed by the waste/rock interaction. The nature of this product can be determined by choosing a solid waste form whose chemical composition, crystal structure, and thermal characteristics are compatible with the host rock.

Because of the high heat generation rate of some radioactive wastes, thermal stability must be considered in choosing a solid waste form. Some solids change their form when subjected to high temperatures; for example, glass may crystallize. Others lose their mechanical strength. Furthermore, as a result of chemical changes brought about by high temperatures, properties such as leachability may be altered.

In addition to thermal stability, thermal conductivity is an important factor in choosing a solid waste form. The thermal conductivity of the waste form--along with its rate of heat generation--will in part determine the temperature both at the center and surface of a waste canister. This is an important consideration in designing a repository for spacing of containers, overpacking, and so forth.

Concern has been expressed that many solid waste forms will be adversely affected by irradiation from the alpha particles, beta particles, gamma rays, and neutrons that are emitted by the radionuclides within the waste (see Chapter 12 for a detailed discussion of radiation effects). In general, effects of five types can result.

The most significant of these effects is radiochemical. Beta- and gamma-induced ionization and decomposition of water and nitrates can lead to the production of gases (hydrogen and oxides of nitrogen) that build up pressure inside canisters. (Concrete is of particular concern in this respect, because it contains significant quantities of chemically bound water, which accentuate the potential for buildup of pressure in the sealed canister. This propensity requires further study.)

A second effect consists of lattice expansion and dimensional changes that are caused by accumulated atomic-scale strains associated with lattice and network defects (see Chapters 7 and 8 on Glass and Ceramics). At the total fluxes of radiation expected from the radionuclides in waste, however, this type of radiation damage will be negligible or very minor.

A third effect, sudden release of stored energy, could in principle cause a rapid temperature rise. For the waste forms currently under consideration, however, both the amount of stored energy and the length of time necessary for release of that energy are such that sudden release of stored energy poses no danger.

The increase in internal energy resulting from radiation damage might produce a fourth effect, enhanced chemical reactivity. The amount of energy involved is so low, however, that this phenomenon will contribute little measurable increase to the rates of reaction.

As radionuclides in waste decay, they are replaced with daughter products (transmutation) that may or may not be compatible with the crystal structure of the waste form. Although there is no evidence to show that the chemical-structural effects of transmutation, as distinct from radiation damage, will have serious consequences, the possibility needs to be examined and evaluated. It has been almost totally neglected so far.

PRIMARY CONTAINMENT FORMS

Primary containment forms are solid forms that contain the potentially hazardous radionuclides found in radioactive waste at the atomic or molecular level. Some primary waste forms have excellent properties: low leachability, low dispersibility, high thermal conductivity, and so forth. In general, they appear to be suitable for both transportation and disposal without being further processed or converted to another solid form. We shall denote these forms _potential final forms_. It is possible to convert them into even more desirable final forms. Other primary waste forms do not, in the Panel's opinion, have sufficiently good properties to qualify them as _potential final forms_. Instead, further processing will be required to convert them into suitable forms. We denote these _intermediate_ forms.

Intermediate Forms

Calcine

One of the simplest methods for converting high-level liquid wastes into solids is to evaporate and partially decompose the liquids at temperatures above 500°C; this process typically yields a fine powder, generically called "calcine." Several variations of the process have been developed including spray, fluidized-bed, and rotary-kiln calcination. All produce essentially the same product, a poorly crystalline or noncrystalline powder in the 10 micrometer to 100 micrometer size range (or granules up to a few millimeters in size) consisting principally of refractory oxides and residual nitrates that have not been decomposed. Since 1963, the solidification program at the Idaho National Engineering Laboratory (INEL) has routinely produced and now stores about 1,500 m^3 of calcine. This calcine is the only significant amount of processed high-level solidified waste in existence in the United States.

At present, calcine is not considered suitable as a final waste form because it is soluble in water and highly dispersible, and its poor thermal stability can lead to the volatization of various radionuclides (including cesium and ruthenium). Therefore, several processes are being considered that incorporate calcine into a composite or transform it into a different solid form. Thus far, glass made from calcine has received the most attention. (See Chapter 6 for a detailed discussion of calcine.)

Supercalcine

To improve the properties of simple calcine, the composition of the high-level liquid wastes can be modified, before calcination, by the addition of carefully selected materials such as nitrates of calcium and aluminum. The liquid mixture is then calcined, resulting in a powder--called supercalcine--with significantly improved properties. The solubility of supercalcine can be five to six orders of magnitude lower than that of calcine, and the volatility of certain components can be two to four orders of magnitude lower. Nevertheless, because it is highly dispersible, the Panel does not regard unconsolidated supercalcine as a suitable final waste form, but as an intermediate form to be converted or incorporated into final forms such as glass, ceramics, or various composites. For example, consolidation of supercalcine with other material, such as portland cement or low-melting metal, has resulted in a less dispersible product. Thus, it is generally still considered an intermediate waste form. (See Chapter 6 for a detailed discussion of supercalcine.)

Supersludge

The DOE wastes stored at the Savannah River Plant (SRP) and the Hanford Reservation contain significant amounts of radioactive "sludge" (i.e. a mixture of HLLW and HLSW) at the bottom of their storage tanks. A promising method for dealing with this type of waste, somewhat analogous to the conversion of calcine to supercalcine, is to add slurries of materials (such as clays and other aluminosilicates) that are selected to make a product that is much less leachable--a "supersludge." Like calcine and supercalcine, "supersludge" is regarded by the Panel as an intermediate form. It can either be further treated to form a low-temperature ceramic or incorporated into a cement/concrete matrix for grouting (pumping into hydrofractured geological formations several hundred meters below the surface) or for disposal in drums. (See Chapter 6 for a detailed discussion of supersludge.)

Encapsulation of ^{137}Cs and ^{90}Sr

To reduce the rate of heat generation of the wastes at Hanford and thus prolong the life of the HLW storage tanks, a decision was made in the mid 1960s to separate out the main heat-producing isotopes--^{137}Cs and ^{90}Sr. (The U.S. Atomic Energy Commission [AEC] was hopeful, at one time, of finding uses for the radioactive isotopes present in the Hanford wastes.) To date, about 80 percent of the ^{137}Cs and 65 percent of the ^{90}Sr have been separated from the bulk of the wastes (NRC 1978). Of these separated wastes, about 90 percent are currently stored as liquids in stainless steel tanks equipped with cooling coils. The remaining 10 percent has been converted to solid CsCl and SrF_2 and is being stored in stainless steel and nonferrous nickel alloy capsules in a cooled water basin. These capsules are sources of intense heat that, if emplaced in a repository excavated from basalt, would probably melt the adjacent rock. Alternatively, the capsules could be incorporated in a chemically and thermally resistant metal matrix, such as titanium, for permanent isolation in a geological repository. The capsules placed in each waste canister would have to be few enough so that the thermal loading of the canister would not overheat the host rock.

Research is necessary to develop techniques for converting the ^{137}Cs and ^{90}Sr liquid wastes to stable ceramic or concrete forms. Such techniques could replace the current practice of converting the solutions to solid CsCl and SrF_2. The stable solid forms, their waste loading and the size and shape of the canisters used to contain them could be selected and designed to prevent overheating of the host rock after emplacement.

Potential Final Forms

Ceramics

Ceramics are highly insoluble, inorganic, nonmetallic materials. As a solid waste form, they are primarily composed of crystalline oxides and could range in size from small briquettes (several centimeters) to isostatically pressed monoliths 0.5 m x 1 m.

Ceramics are of interest as a waste form because of their ability to contain all the hazardous radionuclides, such as ^{137}Cs and ^{90}Sr, in thermodynamically stable crystalline phases. Furthermore, their crystalline nature permits the structural environment of any nuclide to be precisely determined; hence, a given nuclide can either be left in a particular crystal environment or the composition and the processing of the waste can be modified to produce new, more desirable phases.

Several methods of making ceramic waste forms have been studied. However, research into these materials has so far been very limited, and the necessary process engineering has not been developed. Until more information is available about the ease and efficiency of producing ceramic waste forms, ceramic production cannot be compared with that of other waste forms, such as glass.

Five major techniques are currently available for making a ceramic waste form (1) Hot pressing--supercalcine itself, or a mixture of it with glass frit, is consolidated under conditions of high temperature (1,000°C) and high pressure (130 to 260 kg/cm^2). A variant of this technique is hot isostatic pressing in which an evacuated metal container filled with supercalcine is hydrostatically stressed by compression of argon gas to produce large dense monoliths. (2) Sintering--pure supercalcine or mixtures of calcine with additives are consolidated through use of high temperatures (1,200°C) alone. (3) Fusion casting--a mixture of calcine and various additives is melted at about 1,400°C and then cooled to promote controlled crystallization, which results in a strong coherent solid. (4) Glass-ceramic--supercalcine or a mixture of calcine plus glass frit and a nucleating agent is melted and cooled rapidly to produce a glass that is then carefully heated to promote controlled crystallization throughout the solid. (5) Adsorption/densification--the high-level liquid wastes are directly sorbed onto preformed ceramic "bricks" of inorganic ion exchange materials. The bricks are then heated at 1,000°C to fix the radionuclides of interest in stable crystalline phases.

Of all primary solid waste forms, ceramics are the most thermally stable and the most resistant to leaching and radiation damage. Furthermore, some ceramic forms are capable of greater waste loading per unit volume than any other form except calcine.

The major disadvantage of ceramics as a waste form does not derive from their properties, which in the view of the Panel are superior in many respcts to those of other forms, but from the relative complexity of some of the high-temperature processing methods required to create them. Of the processes examined, the adsorption/densification process is particularly promising, because it is relatively simple, involves relatively low operating temperatures (compared to glass and other ceramic processing), and is relatively low in cost. Hot isostatic pressing is a recent commercial technology that offers some attractive features--principally low temperature sealing and the formation of large separate units by a batch process. (See Chapter 7 for a detailed discussion of ceramics.)

Glass

Glass is defined as "...an inorganic product of fusion which has been cooled to a rigid condition without crystallization." Radioactive wastes in glass form generally consist of one noncrystalline monolithic phase. In some cases, this could be 3 m long x 0.5 m in diameter, in others, centimeter-size pellets. In practice, radioactive wastes in glass form are based either on a silicate or phosphate network, contain high percentages of waste ions (which render them relatively instable), and often contain significant amounts of crystalline phases dispersed as submillimeter-sized impurities.

Glasses containing radioactive wastes are usually produced by feeding a mixture of calcine and glass-making components into a vessel where they are melted. In some cases, the melting vessel itself serves as the final waste container (In-Can Melting; HARVEST Process--see Chapter 8); in others, the molten glass is drained from the melter into a metal canister. Recently, the use of refractory-lined melters heated by immersed electrodes has become favored. Such melters should probably be incorporated into any vitrification process that may be undertaken. Knowledge gained from the large store of existing industrial experience in the design and operation of electric melters could be used advantageously toward this end.

Glass has many features that make it an attractive form for solidifying nuclear wastes. It can dissolve nearly all metallic oxides, in reasonable concentrations, into a single phase. Furthermore, well-homogenized silicate glasses tend to be insoluble under ambient conditions in the laboratory, have a high thermal conductivity (as compared to calcine, for example), and are resistant to radiation damage. Despite these advantages, it is not clear to the Panel why glass has come to be regarded, worldwide, as the form of choice for solidifying high-level liquid wastes, since glass has a number of disadvantages. The choice appears to result from the assumption that the single criterion of solid-waste performance is low leachability. While some high-silica glasses can have very low solution rates according to conventional tests, glass is definitely not the best form in this respect. Its metastable nature invites physical and chemical changes by phase separation, devitrification, and hydrothermal decomposition.

In terms of processing, glass is probably the least desirable of solid waste forms. The conversion of liquid wastes into glasses involves the handling of gases, vapors, dust, and hot (1,050°C), corrosive, volatile fluid glass. Requirements for total confinement, remote operation, and infrequent maintenance make vitrification plants very difficult to engineer. (See Chapter 8 for a detailed discussion of glass.)

Spent Fuel Assemblies

After LWR fuel has been irradiated for three to four years, it is removed in the form of spent fuel pins from the power reactor. This spent fuel contains actinides (uranium, plutonium, neptunium, americium, curium), fission products, and tritium. Light-water reactor (LWR) spent fuel pins are long sections of zircaloy tubing (about a centimeter in diameter, and four meters long) filled with ceramic pellets that consist mainly of a solid solution of uranium dioxide and plutonium dioxide[1] together with other radionuclides. The fuel pins, when held together in a geometric cluster by end pieces and element spacers, are known as spent fuel "assemblies."

Current United States government policy is to defer indefinitely the reprocessing of commercial spent nuclear fuel. Because of this action, the Panel decided to consider spent fuel assemblies as a potential waste form to be placed in a geologic repository. Of course, SFAs differ from other solid waste forms in that they are not the product of a solidification process involving high-level liquid wastes. Furthermore, the amount of uranium and plutonium in SFAs greatly exceeds the amount present in other waste forms. Nevertheless, the same factors that determine the suitability of other waste forms will also affect the suitability of SFAs as a waste form.

Preliminary analysis suggests that spent fuel assemblies may be a suitable waste form, but further studies and experimental work are necessary to establish feasibility firmly and define the method of preparing the assemblies for retrievable storage or ultimate disposal. Little is known about the phases present or likely to be formed as a result of hydrothermal reaction in various rocks. It appears essential at any rate to encase the spent fuel assembly in an outer metal can to facilitate handling and increase safety at the repository.

Spent fuel has three advantages as a disposal form: it is less costly than other forms; it requires less processing on the surface than other forms, and is therefore less hazardous in the near term; and it eliminates the need for processing and handling a variety of low- and intermediate-level wastes.

The heat generation from solid waste is the principal factor in determining the spacing of solid waste containers in a geologic repository. The greater long-term thermal power of spent fuel (see Chapter 11, Figure 11.4) results in one of the major disadvantages of spent fuel as a disposal form: the lower maximum heat loading in a repository. DOE (1978) estimates that 66 to 99 kW/acre of spent fuel can be stored versus 100 to 150 kW/acre for high-level waste from a processing plant. The second disadvantage is that spent fuel introduces into the repository far larger quantities of plutonium and uranium than would be introduced by other forms. Hence, spent fuel must be judged a greater long-term potential hazard. Also, in a salt repository, the presence of plutonium and uranium make the remote possibility of criticality a concern if the repository were breached, water were to enter and dissolve the salt, and the fissile material were somehow arranged in a suitable configuration. The disadvantages associated with permanently disposing of the energy resources represented by the uranium and plutonium in spent fuel are beyond the scope of this study. (See Chapter 11 for a detailed discussion of spent fuel assemblies.)

SECONDARY CONTAINMENT FORMS

Secondary containment forms are solid materials that serve as a matrix for incorporating various primary waste forms.

Metal Matrix Composites and Metal Containers

Metals can be used in the solidification process in two ways: (1) as a secondary containment matrix for any of the primary forms (especially supercalcine or glass), and (2) as the outer container for transportation of the solid form. The principal advantages of metals as a matrix material are their high thermal conductivity (lowering the steady-state center-line temperature) and their ability to resist leaching attack by external solutions. Use of metals for the outer container provides mechanical strength, important during transportation, and corrosion resistance, important principally in a retrievable emplacement phase. For these reasons, metals are generally considered the best material available for outer containers even though, on a geological time scale, all but the noble metals would be much less stable than ceramics such as alumina.

The metal matrix form is designed at present to consist of large solid metal cylinders of lead or aluminum, typically a meter or so in length and 10 to 20 cm in diameter, that contain uniformly distributed beads or granules of the primary containment form (either glass or supercalcine[2]) throughout the metal matrix. The primary containment form represents 25 to 50 percent of the total volume of the metal matrix.

A preference for introducing the metal through low-temperature melt technologies has led to extensive research on the use of lead but little on the use of aluminum and titanium. As a possible matrix material, lead has received an inordinate amount of attention. The prospects for titanium are good, and further study on this metal seems warranted. (See Chapter 10, section on metal properties).

Three methods are currently available for processing metal matrix composites: (1) immersion of waste particles in molten metal, (2) sintering of a mixture of glass or supercalcine with metal powder, and (3) compacting and then sintering a mixture of the primary phase beads and metal powder. A rather different technology, which warrants more attention, is cold isostatic compaction, in which metal powders are blended with glass beads into a metal container that is evacuated, welded shut, placed in an argon-filled chamber, and stressed pneumatically by compressing the argon.

Technological development of molten metal matrix composites has depended almost entirely on the efforts of a multinational European operation, Eurochemic, in Belgium. To date, these composites have been demonstrated up to the pilot-plant stage. (See Chapter 10 for a detailed discussion of metal matrix composites.)

Cement/Concrete Composites

Concrete is a widely used, well-understood class of inorganic composites made up of sand, gravel, crushed rock, or other aggregates held together by a hardened paste made of cement (primarily calcium silicates and aluminates) and water. In work on high-level solid wastes, supersludge or supercalcine containing the waste ions are typically incorporated in place of the sand or gravel. Upon hydration of the cement (which has the major processing advantage that it can take place at ambient temperatures and pressures), concrete becomes comparable in strength, hardness, and leach resistance to many types of natural rock.

Cement-based composites are a promising medium for containing radioactive wastes. Although it is possible to add liquid wastes directly to cement or concrete (thereby forming new, poorly studied primary containment phases), most of the cement-based composites that are being considered consist of primary solid waste forms, such as granules or fine powders of supercalcine or supersludge, added as the aggregate to the cement. The resulting plastic waste form now offers a unique advantage: it can be pumped (grouted) underground into thin (10 to 40 centimeter) sheets within suitable geological formations, or it can be cast into large cylinders (1 m high x 1 m diameter) for ultimate disposal.

The cement/concrete form, as well as providing the major advantage of simple processing at low temperature, has surprisingly suitable properties. For example, the leachability and dispersibility of supercalcine-concrete composites are probably comparable to those of glass. In addition, the amount of waste that can be loaded into a cement-based composite is similar to the amount that can be loaded into a glass or metal matrix waste form. The thermal stability of concrete is acceptable if temperatures do not exceed 300°C, but if temperature reach the range of 500-900°C a complete loss of strength can be expected. Cement composite forms therefore appear to be promising for the relatively old and dilute DOE wastes, but somewhat less attractive for the fresh commercial wastes that have a high rate of heat generation.

The most significant unknown regarding the encapsulation of cement-based composites in a sealed canister is the possible buildup of pressure as a result either of the radiolysis of water and nitrates or of the conversion of water to steam. Further research is needed, therefore, before the use of cement composites in sealed canisters can be judged suitable. If radiolysis does not prove to be a significant problem, a cement-based composite is likely to be the preferred waste form for the solidification of DOE wastes. Initial studies in this area are currently under way (Bibler and Orebaugh 1977, Tingey and Felix 1977). Although no detailed cost analysis has been made, the use of supersludge and "supergrout" compositions, combined with the well-developed grouting technology, could well provide the most cost-effective forms and methods for waste solidification. (See Chapter 9 for a detailed discussion of cement and concrete composites.)

NOTES

1 LWR fuel initially contains only uranium. The plutonium present in spent fuel is produced during irradiation. Should commercial spent fuel eventually be reprocessed in the United States, the plutonium could be recovered and used with uranium as a mixed oxide fuel.

2 Current design of metal matrices uses supercalcine and glass, but other solids could be used as well.

CHAPTER 3

SELECTING A SOLID FORM

To select a suitable solid form for disposal of radioactive wastes, the characteristics of the individual forms, outlined in the preceding chapter, need to be considered in the context of the radioactive waste management system as a whole. Choice of the mode of operation at each stage will affect choice of the waste form, and vice versa. Further, choices made at each stage will affect those made at succeeding stages. Clearly, once adequate data are available, common-sense tradeoffs are called for; in one instance operations may best be modified to accommodate the exigencies of the form, whereas in another case the demands of operations may constrain the choice of a form. Since a number of different options may be available to achieve the given objective of adequate safety, cost, reliability, and simplicity of processing become important factors in selection once the safety criterion has been met.

The present chapter discusses the selection process in terms of the interactions between the form and the system, and the influence on both of cost.

THE RADIOACTIVE WASTE MANAGEMENT SYSTEM

Relative Risks During Operation of the System

The Radioactive Waste Management (RWM) system is defined to include a range of operations that begins with the removal of spent fuel pins from the reactor and ends with the permanent emplacement of spent fuel pins or high-level solid waste in a repository. The major components of the system, as illustrated in Figure 3.1, are storage, reprocessing, solidification, transportation, and isolation. The options available for both the solid form and the isolation medium are illustrated in Figure 3.2. In principle, the system could require five facilities and four transportation steps to accommodate either storage and final disposal of the SFPs themselves, or reprocessing of the

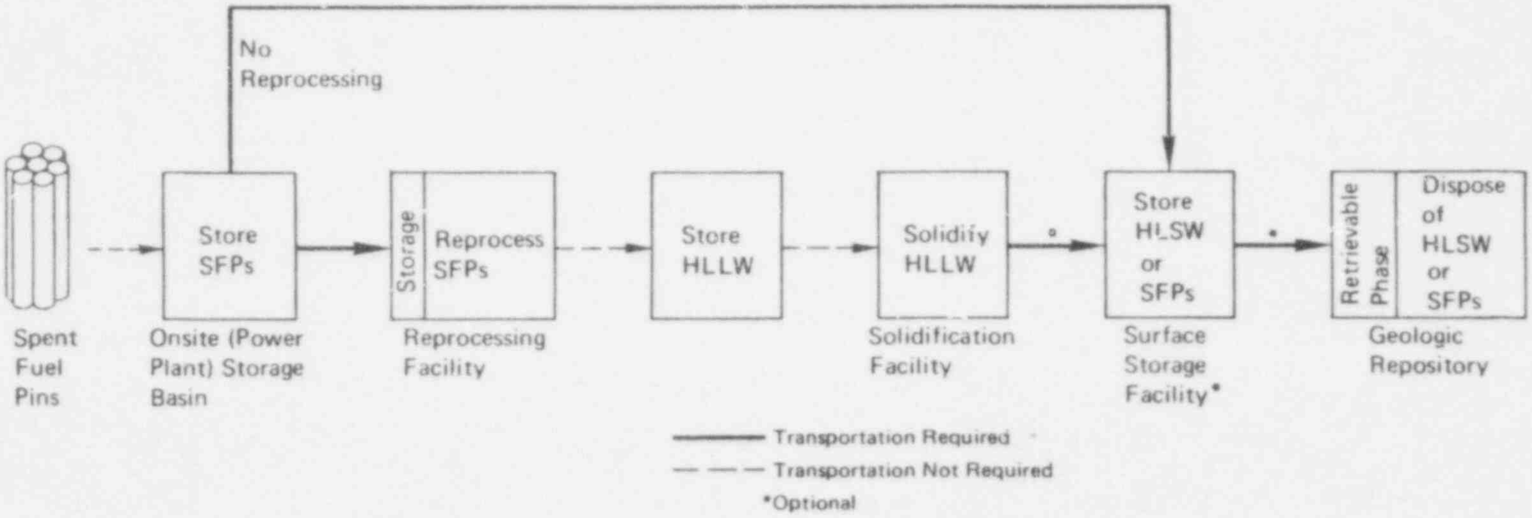


FIGURE 3.1 The radioactive waste management system.

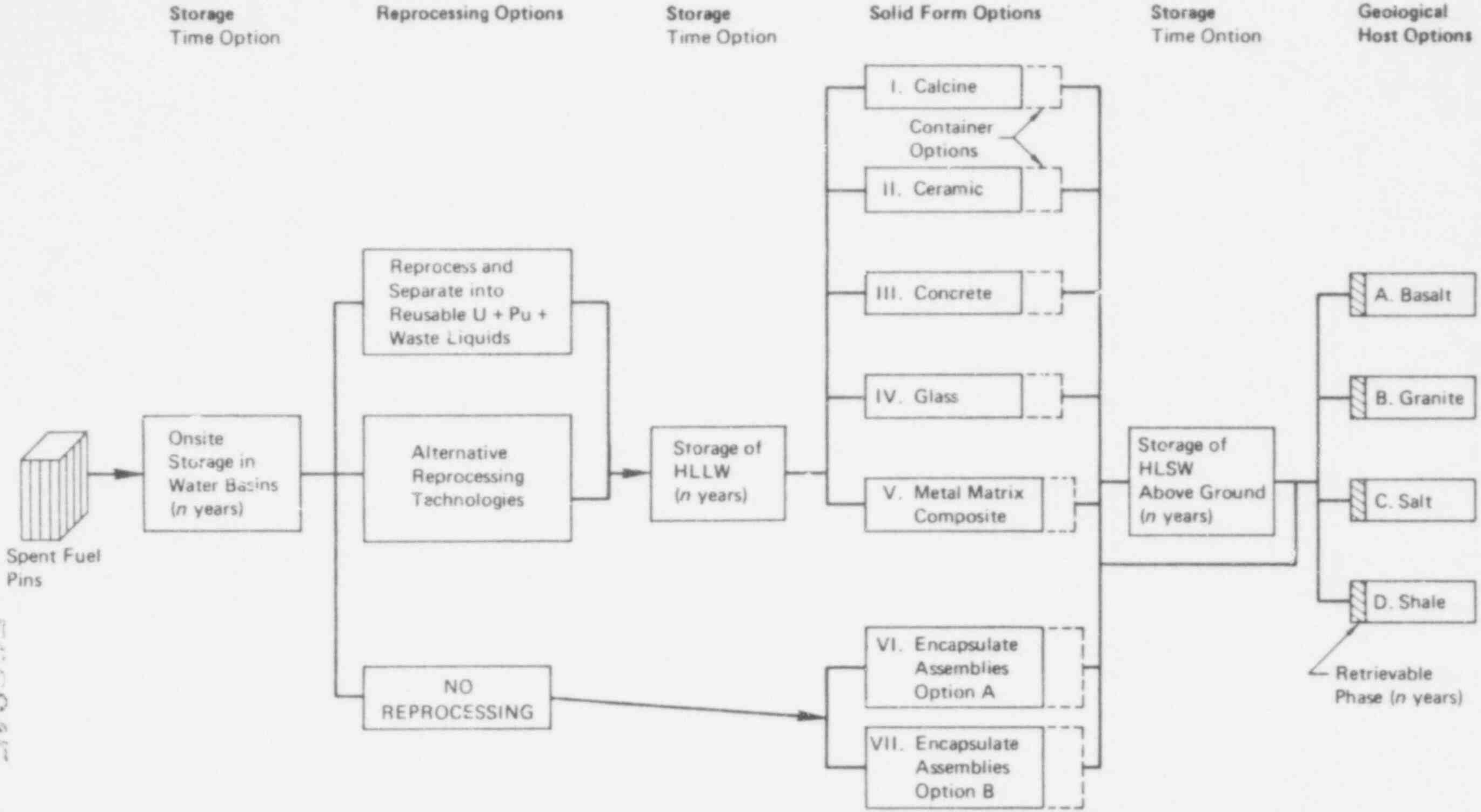


FIGURE 3.2 The radioactive waste management system showing options at each stage. The system is defined by (1) selecting the amount of time that the waste will be stored at different stages in the system, and (2) selecting among the various options for reprocessing, solidification, and emplacement.

SFPs, storage of the resulting HLLW, solidification, and disposal of HLSW.

The focus of this report is the group labeled "Solid Form Options." However, because these options and the other groups of options shown in the figure are interrelated, all the components of the system need to be examined to determine the extent to which each affects selection of a solid form. Furthermore, the time intervals between the various components--fuel discharge, reprocessing, solidification, and emplacement--are important factors in the overall radioactive waste management strategy. To simplify discussion, we have divided the system into three basic steps: processing, transportation, and emplacement. Table 3.1 shows the demands made on the solid form at each step, and the physical and chemical properties of the solid form required to satisfy those demands.

Processing

Processing liquid wastes into solid form must be done in a way that minimizes the exposure of workers to radioactive material and at the same time ensures that no radioactive material will be accidentally released to the environment. We believe that these purposes are served by using processes that are as simple to operate as possible, that avoid high temperatures and highly dispersible products, that are adaptable to remote operation and maintenance, and that provide for quality-control inspection.

Except for dispersibility, the properties of the solid form are relatively unimportant during processing. Studies done at the Savannah River Plant (U.S. ERDA 1977c) indicate that the differences in risk to the public between processing high-level wastes to concrete, glass, or dry powder are insignificant. Furthermore, the risks associated with processing appear relatively minor in comparison with those associated with transportation.

Transportation

During transportation the waste is closer to larger numbers of people and is in a less secure situation than during processing or emplacement. Therefore, the safety measures required for transportation appear to be greater than those for other phases of the RWM system (see Dryoff et al. 1977, U.S. ERDA 1977c, U.S. NRC 1977).

Risks of accidental dispersal of radioactive material are greater during transportation than during either processing or emplacement, as are risks of sabotage and terrorism, although the latter are small in absolute terms.

TABLE 3.1

System Demands on the Solid Waste Form

	Processing	Transportation	Emplacement	
			Retrievable	Nonretrievable
Objectives	Minimize hazard to worker Minimize hazard during storage	Minimize hazard during transportation	Maximize stability in canister for possible retrievability Maximize stability versus rock and groundwater attack	Maximize stability in equilibrium with host rock
Properties of Solid or Process Characteristics	Process should be simple, adaptable for remote operation Solid not too dispersible	Low solubility, low dispersibility, good thermal conductivity, good mechanical properties against accident, minimized volume	Low solubility, good thermal conductivity, low reactivity with rock and water	Yields phases with minimum solubility in equilibrium with host rock
Demand on Solid Properties	Solid properties unimportant	Maximum demand on solid properties	Container properties important; knowledge of thermal properties significant	Physical properties no longer important; insolubility of post reaction phases important

Therefore, the number of transportation steps entailed by any particular system (Figures 3.1 and 3.2) will be important in determining the demands made on the solid form. It is during transportation that it is most important for the solid form to have a low solubility in typical surface waters and be nondispersible.

It should, however, be noted that the increased precaution required during transportation is short-lived. Some RWM plans, moreover, particularly those for DOE wastes, call for on-site disposal of wastes, thereby obviating the need for transportation. If the transportation step were eliminated, demands on the solid form might be significantly reduced.

Transportation risks affect selection of a solid form in two ways. First, the degree of risk depends, to some extent, on how much material is being transported; therefore the amount of waste that can be incorporated into a given solid form (waste loading) is a consideration in choosing or rejecting that form. Second, the physical properties of the solid form such as leachability, dispersibility and volatility, might render it less or more hazardous after a transportation accident. Transportation risks for three solid waste forms have been calculated and compared in a recent study by The Analytic Sciences Corporation (1978). The results indicate that the metal matrix form is superior to glass which, in turn, is superior to calcine. Furthermore, the calculated risk from transporting either glass or metal matrix forms appears to be small in comparison to risks incurred during other stages of the LWR fuel cycle (Nuclear Energy Policy Study Group 1977). Risk analyses such as those performed for metal, glass, and calcine have yet to be made for <u>all</u> the solid forms discussed in this report. Such analyses are essential for determining the suitability of the various forms.

For the policymaker concerned with public acceptance of a particular waste form in a particular system we can point to a helpful comparison. By examining the properties of spent fuel pins and their vulnerability during handling and transportation, future risks from high-level solidified wastes can be compared with those now being taken.

Emplacement

Of the various methods that have been proposed for permanent disposal of nuclear wastes, emplacement of the solid form in a geological formation on land is currently favored in the United States. There is some confusion about the nomenclature of such formations. Technically each geological formation is a particular rock type. Hence, the terms "host rock" and "geological formation" may be used interchangeably. Frequently, a misleading distinction is made between salt, shale, and "crystalline" rocks. All the candidate host rocks considered for RWM are composed of crystalline materials. Therefore, the only terms used in this report are the proper rock names: salt (bedded or dome), shale, granite, basalt, and so on.

Recent analyses (Dryoff et al. 1977, U.S. NRC 1977) indicate that risks after emplacement are smaller than during transportation or processing, and that the nature of the solid form, in particular its solubility, makes a minor difference to an already relatively small risk. The APS study (1978), on the other hand, indicates that if a leach rate of 10^{-7} g/cm^2/day or lower were "reliably achievable," the waste form itself could provide a meaningful barrier to radionuclide release. It should be noted that the above studies have not examined the range of waste forms considered here; nor have they considered in detail the significance of the interaction between waste and rock, although a particular waste/rock interaction, under appropriate hydrogeological conditions, might be desirable, and could therefore be an important consideration in selecting a solid form.

During geological emplacement, there may be a relatively short phase when the waste is retrievable, during which the integrity of the container will be important but the solid form itself will be relatively unimportant. The final "geological time" phase, however, will provide an opportunity for substantial interaction of the solid waste with the host rock. After 100 years, the physical properties of the original solid may become relatively unimportant, while the chemical properties produced by the interaction could become significant. This interaction, which may prove desirable, will be very strongly affected by the presence of water and by the high temperature of the waste.

Insofar as a repository is designed to assure isolation of the wastes for a few half-lives of plutonium (1 half life = 24,360 years), one must consider the nature of the containment system after the high-temperature, radioactive waste has reacted with the rock. Although a suitable repository is expected to be failsafe, regardless of the characteristics of the wastes stored within it, the concept of "multiple protection barriers" requires that the final solid forms have a minimum solubility and thus a minimum rate of release of ions.

Research on waste/rock interaction has only just been funded (Pennsylvania State University 1977), so that direct data on the topic are not as yet available. Several generalizations can, however, be made on the basis of the related, rather extensive, geochemical literature.

1. Under the conditions expected near the waste canisters within a geological repository, i.e. temperatures from 200 to 800°C, modest pressures of 1 to 300 bars, and the presence of water (from cavities, hydrated minerals, and so on), extensive interaction and alteration of the original wastes is certain.

2. Such interactions will affect glass more than any of the crystalline forms.

3. Salt will be more reactive (because of the differences in free energies) with oxide wastes than will granite or shale.

4. Not all interactions between the waste and the host rock lead to products inferior to those originally present in the waste form. However, extensive studies will be necessary to determine what is likely to occur in each particular case.

5. Because common minerals of soil, shale or granite can fix radionuclides through sorption, studies should focus on this process as well as on reaction.

Although, it is not feasible to wait for a thousand years or more to verify experimentally the long-term stability of high-level solid waste forms, an examination of various natural minerals (especially those containing ions found in radioactive waste) that are a quarter of a million or more years old can be instructive. For example, certain natural minerals contain decaying radionuclides that influence the crystal structure and weathering behavior of these minerals. Thus, studies of the phenomenon of metamictization (structural damage in minerals caused by radiation or particle bombardment) provide some indication of the magnitude of the effects of radiation and transmutation on the crystal structure and stability of various solid waste forms. With respect to mineral phase stability, nature gives a good indication of the specific crystal structures that best resist dissolution, alteration, and weathering under near-surface conditions. Those phases that survive a million years of changing geological history provide assurance that mineral or phase "stability" for a million years is quite common. Thus, the minerals of various beach sands form excellent prototype structures for waste encapsulation at the atomic level. Likewise, they demonstrate that glass, which may be an adequate waste form under particular system conditions (dry, low temperature) is not among the best materials.

Optimizing the System

Protection from the hazards of radioactive waste at various points in the waste management system is provided by a combination of surveillance, isolation, and immobilization.[1] Figure 3.3 illustrates the path of the high-level waste as it moves through five different steps in the system. The shaded volume near the origin represents those situations where an <u>unacceptable</u> degree of risk exists. Optimization of the system requires keeping the path of the radioactive waste as far from the origin as possible, at minimum cost.

As we follow the path, we find: HLLW at the reprocessing plant is highly mobile and requires considerable surveillance. Solidification of HLLW greatly increases immobilization. Transportation to a surface storage facility reduces the need for surveillance, but increases the isolation of the wastes. Emplacement in a deep geologic repository further increases the isolation of the waste while limiting the need for and the feasibility of surveillance. After several decades, if appropriately planned, the reaction with the host rock enhances immobilization and further decreases the need for surveillance.

As explained in Chapter 1, the total RWM system offers multiple barriers against release of radioactive materials. Each of the barriers may be designed to provide as much protection as possible. By maximizing the efficacy of each separate barrier, the effectiveness of the system is maximized.

For example, the transportation cask can be designed or the geological formation selected so that practically any solid form would be satisfactory. However, selection of a system by the decision maker will clearly involve tradeoffs among the various levels of protection and the costs of such protection. The analysis in this report enumerates a full range of options, to provide the decision maker with information essential for a rational choice.

Some examples may help to illustrate the kind of tradeoffs involved in deciding between available options.

The number of transportation accidents is expected to be roughly proportional to the number of shipments made. Based on this assumption, the "best" form would be the one that possessed the maximum content of wastes per unit volume. On the other hand, if transportation were eliminated by locating the disposal site and solidification plant together, less costly, high-volume technologies might be preferable.

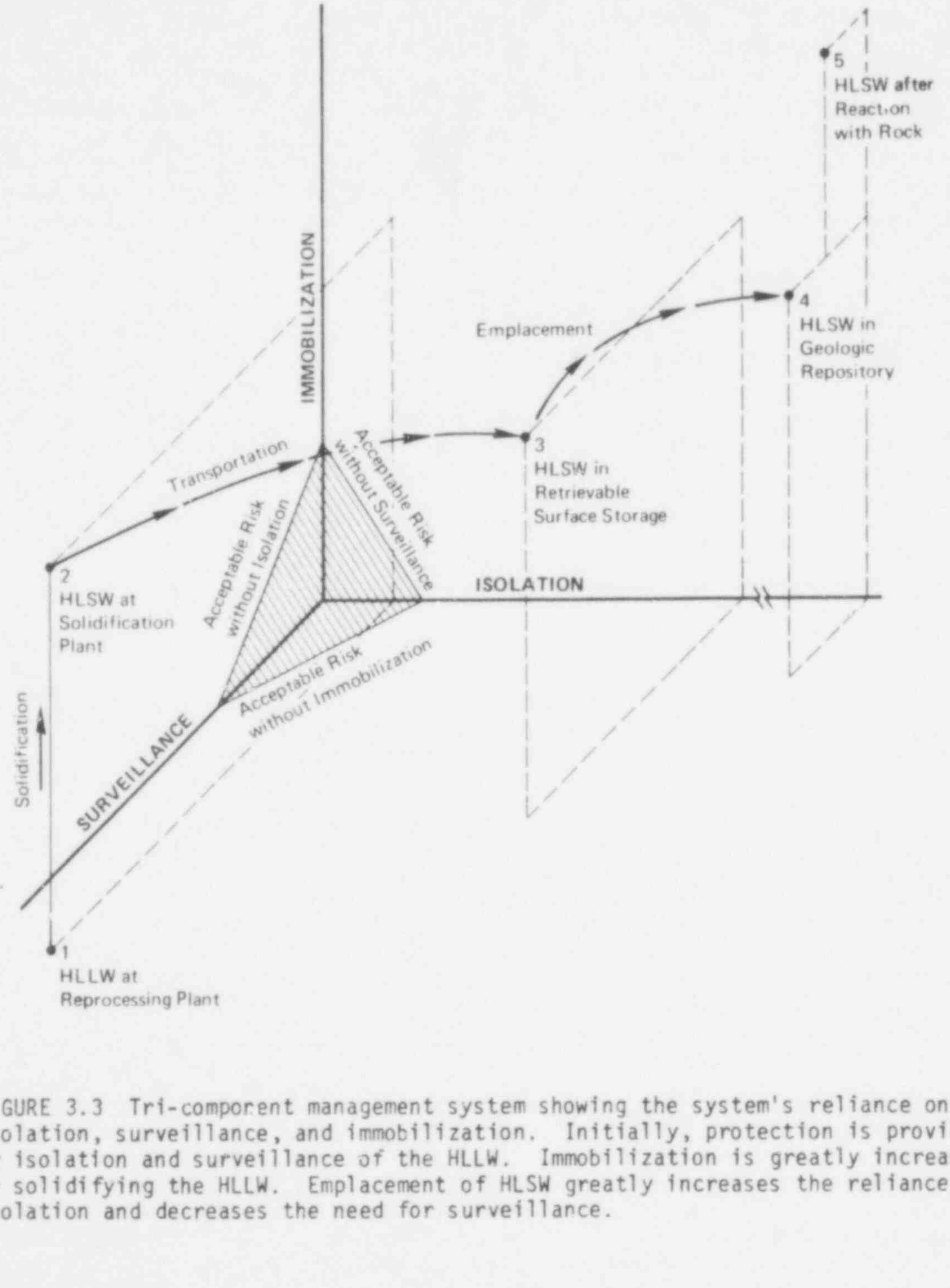


FIGURE 3.3 Tri-component management system showing the system's reliance on isolation, surveillance, and immobilization. Initially, protection is provided by isolation and surveillance of the HLLW. Immobilization is greatly increased by solidifying the HLLW. Emplacement of HLSW greatly increases the reliance on isolation and decreases the need for surveillance.

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The heat generation rate of radioactive wastes is largely dependent on the age of wastes (that is, the time spent in the storage pools) (see Table 3.2). The solid forms most suitable for fresh (one- to two-year-old) wastes will be different from the forms suitable for those wastes (such as the vast majority of the DOE wastes) that are twenty to thirty years old. Furthermore, the acceptable thermal loading of the repository may vary with the characteristics of the geological formation, thereby suggesting use of still a different solid form.

COST AS A FACTOR IN WASTE FORM AND SYSTEM SELECTION

The difference in degree of risk resulting from the various solidification and systems options appears to be relatively small. Indeed, in many cases it may be difficult to choose between two technologies on the basis of safety. In such cases, the cost of each of the options, together with the simplicity and reliability of the process may be the best criteria for choosing among the various options. Although the question of cost has only recently attracted public attention (see, for example, U.S. Congress, House 1977), it will almost certainly become a major factor in future decisions about radioactive waste management.

The determination of how much we are prepared to pay for what degree of safety is a political judgment inappropriate for this Panel to make. Nevertheless, to assist the policymaker who is responsible for making such decisions, accurate information on the costs of alternative waste management strategies must be provided. The Panel believes that this information is of major significance to rational policy planning.

ERDA Cost Estimates

Recently, documents (U.S. ERDA 1977a, U.S. ERDA 1977b, U.S. ERDA 1977c) from each of the three major laboratories (Hanford, INEL, and SRP) have become available that provide preliminary estimates for the total costs of alternative strategies for solidification and disposal of defense radioactive wastes. These costs are further broken down into component costs for each of the steps required in a given strategy, including solidification. In Table 3.3, several of the total cost estimates are listed for illustrative purposes. (The total costs for all alternative strategies considered in these studies are presented in Appendix A; interested readers should also consult the referenced articles for details regarding each strategy listed.) While these attempts to derive cost figures are highly commendable, the Panel believes that the present figures should be regarded as only approximations. Efforts

TABLE 3.2

Rates of Heat Generation from Radioactive Decay of Typical LWR Spent Fuel[a]

Time Out of Reactor	kW/MTU
160 days	18.5
1 year	9.2
10 years	0.86

[a] The values shown are for fuel irradiated at 35 MW/MTU to a total burn up of 25,000 MWd/MTU.

Source: U.S. ERDA (1976b).

TABLE 3.3

Cost and Risk Data for Several Radioactive Waste Disposal Plans at the Hanford Reservation and the Savannah River Plant

Site	Plan Number	Plan Description	Total Cost (million 1976 dollars)	Integrated Population Dose Risk, (man-rem)
Hanford	4	Glass w/RR* in Canisters Disposed of in Off-site Geologic Repository and Bulk Decontaminated Salt Disposed of in On-site Surface Trench.	1,500	2×10^{2}
Hanford	6	Concrete w/RR* in Canisters Disposed of in On-site Geologic Repository and Bulk Decontaminated Salt Disposed of in On-site Surface Trench.	1,400	2×10^{-2}
Hanford	17	Clay wo/RR+ in Canisters Disposed of in Off-site Geologic Repository.	6,000	3×10^{3}
SRP	1	Glass Disposed of in Off-site Geologic Storage and Canned Decontaminated Salt Cake Stored in Outside Surface Storage Facility.	2,700	9×10^{2}
SRP	2	Concrete Disposed of in Off-site Geologic Storage and Canned Decontaminated Salt Cake Stored in On-site Surface Storage Facility.	2,400	9×10^{2}
SRP	12	Concrete Stored in Off-site Surface Storage Facility and Canned Decontaminated Salt Cake Stored in On-site Surface Storage Facility.	3,000	7.3×10^{2}
SRP	14	Dry Powder Disposed of in Off-site Geologic Storage and Canned Decontaminated Salt Cake Stored in On-site Surface Storage Facility.	2,300	9.3×10^{2}
SRP	22	Unprocessed Waste Slurry Disposed of in SRP Bedrock.	180	6.2×10^{4}

NOTE: It is assumed (ERDA 1977c) that the SRP plans listed above will dispose of 60 million gallons (230,000 m^3) of reconstituted wastes having an average activity level of 5 curies per gallon (1,300 curies per cubic meter). It is also assumed (ERDA 1977a) that the Hanford plans listed above will dispose of: 25 million gallons (95,000 m^3) of damp salt cake, containing 7 million curies of radioactive fission products; 11 million gallons (42,000 m^3) of sludge containing about 50 million curies of fission products; and 11 million gallons (42,000 m^3) of residual liquids containing 20 million curies of fission products.

* w/RR means with radionuclide removal.
\+ wo/RR means without radionuclide removal.

Source: Taken from Appendix A, Tables A.1 and A.2.

should be made, therefore, to continuously update such cost figures which are essential for rational policymaking.

Too many uncertainties are involved to allow the Panel to assess the accuracy of the new detailed estimates (the authors, themselves, explicitly mention the limitations). Nevertheless, the fact that each study used a consistent set of assumptions as a basis for deriving cost estimates should allow a reasonable comparison to be made of a wide variety of alternative plans. In addition, these estimates indicate that the <u>total</u> cost for implementing the solidification, transportation, and isolation of the defense wastes will be very large, i.e., as high as 30 billion dollars or more. Implementation costs for the Hanford wastes alone range up to $27.2 billion (U.S. ERDA 1977a:2-4). In light of the magnitude of such costs and the fact that large differences (one to two orders of magnitude) exist in the cost-effectiveness (costs/risk reduction) of competing options, the continued improvement of the initial--"first generation"--waste management system and the development of a more cost-effective--"second-generation"--system could result in significant savings to the public, with relatively small change in risk.

RANKING THE SUITABILITY OF SOLID FORMS

Applying the criteria described above, the Panel has analyzed, in a qualitative manner, the <u>relative</u> suitability of each solid form for three types of waste considered to be most representative. This analysis places the forms in rank order according to their suitability for each stage in the system--Processing, Transportation, Emplacement--and then ranks them in terms of cost. The ranking is summarized in Table 3.4 and provides some of the most important findings of the Panel regarding the science and engineering of waste solidification. In several areas, our knowledge is not yet sufficiently precise for rationally choosing the most suitable solid waste form in a particular system. However, given the expected five- to ten-year period likely to elapse before large-scale solidification of commercial wastes is required, the R&D necessary to improve this situation can, in our opinion, be done adequately.

The types of wastes considered are: Category A, the DOE or "military" wastes (most of these wastes are more than 20 years old); Category B, ten-year old commercial wastes; and Category C, two-year old commercial wastes. For many purposes the distinctions between B and C are relatively small, and therefore, the table categorizes them together as "commercial."

TABLE 3.4

Relative Desirability of Solid Waste Forms During Processing, Transportation, and Emplacement and Relative Costs of Processing[a]

	DOE: Category A	Commercial: Categories B & C
Processing (simplicity, efficiency, and reliability of process)	Supersludge/Cement Matrix Supersludge/Ceramic Supercalcine/Metal Matrix (cold) Supercalcine/Cement Matrix Supercalcine/Ceramic Supercalcine/Metal Matrix (hot) Glass Supercalcine/Glass Glass/Metal Matrix (hot)	SFPs (?) Supercalcine/Metal Matrix (cold) Supercalcine/Metal Matrix (hot) Supercalcine/Ceramic Supercalcine/Cement Matrix (?) Glass Supercalcine/Glass (?) Glass/Metal Matrix (hot)
Transportation	Metal Matrix Ceramic (high temp) Glass Cement Matrix Supercalcine	Metal Matrix Ceramic (high temp) Cement Matrix (?) Glass SFPs Supercalcine
Emplacement		
A. Retrievable	No differences in form. Containers of titanium, copper to be studied.	Metal Matrix, Ceramic, Glass, Cement, SFPs, Supercalcine, Supersludge/Cement
B. Permanent (different ordering in different rock formations)	Ceramic (low temp) Ceramic (high temp) Ceramic/Metal Matrix Cement Matrix Glass	Ceramic (low temp) Ceramic (high temp) Ceramic/Metal Matrix Glass/Metal Matrix Cement Matrix (?) Glass SFPs (especially in presence of O_2)
Process Costs		
(Estimates based on complexity)	Supersludge/Cement-grouted ("Super Grout") Supersludge/Cement in containers Ceramic (low temp) Supercalcine/Ceramic Glass Supercalcine/Glass Metal Matrix	SFPs (?) Supercalcine/Glass Glass Supercalcine/Ceramic Metal Matrix

NOTE: (?) designates insufficient data.

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[a] The order of the forms within any box implies a qualitative ranking (top-best, bottom-worst). However, the resolution is such that not too much weight should be attached to minor differences in ranking.

TABLE 3.4 (continued)

Legend

Supersludge/Cement Matrix:	A mixture of tank sludge with clays, zeolites, and inorganic gels (supersludge), bound together with cement. This could be grouted or cast into containers or caverns.
Supersludge/Ceramic:	Supersludge fired to a low-temperature ceramic.
Supercalcine/Metal Matrix (cold):	Supercalcine granules dispersed in a cold pressed titanium or similar monolithic billet.
Supercalcine/Cement Matrix:	Supercalcine bound together in cement.
Supercalcine/Ceramic:	Supercalcine sintered to a high-temperature ceramic.
Supercalcine/Metal Matrix (hot):	Supercalcine embedded as granules in molten metal.
Supercalcine/Glass:	Glass made by adding glassification components into liquid stream.
Glass/Metal Matrix (hot):	Glass beads embedded in molten metal.
Ceramic/Metal Matrix:	Ceramic granules embedded in metal.
Ceramic (low temp):	Ceramic forms made by low temperature processes. Includes supersludge/ceramic, aqueous silicate, ceramic sponge (see Chapter 7).
Ceramic (high temp):	Ceramic forms made by high temperature processes. Includes supercalcine/ceramic, fusion cast ceramic, glass ceramic (see Chapter 7).
Ceramic:	All ceramic forms.
Metal Matrix:	All metal matrix forms including supercalcine/metal matrix, glass/metal matrix, ceramic/metal matrix.
Cement Matrix:	All cement matrix forms including supersludge/cement matrix, supercalcine/cement matrix.

Categories of Waste

A. About 265,000 m³ of the DOE wastes are currently being stored at three major federal facilities as a mixture of crystallized salts (such as $NaNO_3$), oxide sludges containing most of the radionuclides, and the supernatant solutions containing much of the ^{137}Cs. Because most of the DOE wastes are more than 20 years old, a large proportion (about 90 percent) of the total activity originally present has decayed, so that the heat generation rate is quite low. Since reprocessing of commercial SFPs is deferred indefinitely, the DOE wastes are the only major class that must inevitably be solidified.

B. Owing to the current national policy deferring reprocessing and solidification of commercial wastes, spent fuel is currently being stored above ground in the form of SFPs. By the time a change in reprocessing policy could raise the prospect of solidification for these wastes, a significant inventory of ten-year-old spent fuel will have been amassed. Moreover, if and when reprocessing does begin, increases in available pool storage should allow some of the future inventory of spent fuel to cool for several years. Such cooling would drastically diminish the thermal output and the activity of the spent fuel, reducing the demands on the solid form and thereby increasing the number of suitable options. Further cooling of HLLW after reprocessing is also a policy option, although it is limited by a Nuclear Regulatory Commission requirement that such wastes be solidified within five years of production. Hence, at least up to the year 2000, there could well be a class of wastes which we shall call generically "ten-year-old commercial." Policy decisions might, however, postpone solidification to the point where these wastes become equivalent to Category A above.

C. In the future, it is possible that increased use of nuclear power will create a situation in which the throughput of fuel is so great, that two-year-old wastes will have to be processed.

Principal Criteria Used in Rankings

As is clear from Table 3.4, the age of the wastes was a major determinant in the Panel's ranking of solidification processes. To understand these rankings, the basic distinction between recommending forms for the DOE wastes and the possible future fresh commercial wastes must be clearly understood. The former consist of neutralized salts, sludges and liquids with low activity and resultant low rates of heat generation. Hence any solid waste form made from DOE wastes and containing 20 to 40 weight percent of the waste will not generate temperatures above approximately 250°C in canisters of the size typically used. Thus waste forms, such as concrete composites and low-temperature ceramics, that are stable to these temperature limits are adequate and preferred on grounds of process simplicity. Use of the Oak Ridge National Laboratory (ORNL) grouting process provides further simplification and cost savings. On the other hand, two-year-old commercial wastes generate centerline temperatures of 500 to 800°C in similar configurations. For these, ceramic forms that possess both thermodynamic and thermal stability are clearly desirable. Glass, especially in metal matrix forms, remains an option; but, as a second-generation solution, the Panel feels that glass is likely to prove less desirable in terms either of cost or of stability.

In ranking solid form options, the Panel considered that, for processing, the form chosen should minimize the exposure of equipment to high temperatures because high temperatures increase the threat to long-term engineering stability and reliability of the system, increase the volatilization of waste components, and increase the need for replacing equipment.

Under the heading of transportation, solid forms were ranked according to their relative fragility, dispersibility, and solubility in surface water at ambient temperature.

Under the heading of emplacement, the principal criterion was the stability of the insoluble form in contact with rock and water under physical/chemical conditions expected in the repository. The ranking of spent fuel in terms of permanent emplacement was influenced by the possibility that, in the future, attempts might be made to remove the plutonium and uranium from the spent fuel pins.

Cost Criteria and Considerations

The principal criterion used by the Panel in deriving its rankings in Table 3.4 was process complexity, knowledge of which was based on industrial experience in producing a variety of technological products for purposes unrelated to radioactive waste management. The costs of transportation and emplacement were not considered since they depend on the choice of a particular disposal plan.

Some of the new ERDA data support the Panel's findings. For example, the study at INEL (U.S. ERDA 1977b) estimates that the cost for processing a metal matrix is greater than the cost for processing a glass-ceramic. As another example, the study at SRP (U.S. ERDA 1977c) estimates that the processing cost for glass is about three times as great as that for cement. However, the study goes on to say that "because of the high cost of containers and storage facilities, the smaller volume glass waste product is not significantly more expensive than the higher-volume concrete product in overall plan costs...." The Panel disagrees with this statement, finding that a cement composite can hold as much waste per unit volume as can a reasonably insoluble glass. (See Chapter 9, section on state-of-the-art review.)

Finally, as recognized in the INEL study (U.S. ERDA 1977b), it is important to note that because the technologies for glass and calcine production have received such a commanding proportion of R&D funds (90 percent since 1950, see Chapter 4, Table 4.2), cost estimates for these technologies are much more reliable than those for other technologies.

SOME SOLIDIFICATION PLANS SELECTED BY THE PANEL

The principles developed earlier in the chapter show that there is no "best" form that can be recommended universally. Instead, the waste form chosen for use in one system may not be the most suitable choice in another system. The four solidification plans outlined below have been devised, on the basis of the rankings depicted in Table 3.4, to illustrate some of the more promising (though by no means the only) options. Each treatment described is suitable for a particular type of waste and is compatible with specific rock types and transportation requirements.

DOE Waste

Plan I

1. Flush out tanks and separate sludge from supernate (alkaline liquid fraction of DOE wastes). Wash sludge and mix wash fluids with supernate. Pass supernate over optimized zeolite-clay-gel bed to extract ^{137}Cs and ^{90}Sr and other radionuclides.

2. Combine bed-adsorbents with sludge, and at the same time add necessary components tailored to give total composition of optimized "supersludge-concrete."

3. Either: Cast concrete cylinders in 6 mm titanium or stainless steel cans 1 meter diameter, 1 to 3 meters high. After concrete has set, heat to 150°C, outgas, and weld containers to seal.

Alternatively: Grout supersludge-concrete into bedrock layers or caverns on site using, for example, the ORNL grouting technology.

4. Stack containers in frame for retrievable storage. Add tailor-made overpack materials to form protective layers during retrievable phase, and as an additional barrier during permanent isolation.

5. To keep transportation to a minimum, locate repository on site. At Hanford, for instance, horizontal tunnels could be used in Rattlesnake Hills.

Plan II

1. Centrifuge and separate solids in sludge from supernate.

2. With these solids make supersludge, and from it a cement-composite to be grouted or cast into cylinders.

3. Prepare porous ceramic pre-forms (large bricks) from tailor-made zeolites and related phases specifically to sorb the radionuclides of the supernate.

4. By repeated filtration through pre-forms, remove most of the ions from the supernate.

5. Consolidate ceramics by sintering below 1,000°C to form moderate-strength, crystalline ceramic bricks.

6. Fill canisters with reacted preforms.

Fresh Commercial Waste

1. Locate solidification plant adjacent to reprocessing plant and storage facility to keep transportation to a minimum.

2. Solidify HLLW to supercalcine pellets tailored to contain radionuclides in stable ceramic phases.

3. Blend pellets to 20 volume percent of the charge, the remainder being commercial purity aluminum powder. Contain in an aluminum can. Weld to seal. Isostatically compact at 300°C to near 100 percent density. Dimensions of compacted cylinders: 35 cm diameter and 70 cm in length.

- Volume percent selected to permit continuity of Aluminum matrix, not of pellets.
- Low processing temperature reduces reaction with processing equipment, eliminates volatilization problems.

- Aluminum selected for ease of deformation during processing, thermal conductivity, cost, limited reactivity, and corrosion resistance.

- Size of cylinders selected to limit size of processing equipment.

4. Emplace cylinders in 3 mm thick titanium cylinder and weld titanium container.

- Titanium selected for corrosion resistance, lack of reactivity.

5. Emplace titanium cylinders in salt, shale or granite for retrievable storage or final disposal.

Older Commercial Waste

1. Locate solidification plant adjacent to reprocessing plant to avoid transportation problems.

2. Solidify HLLW to a calcine, mix with a suitably-selected glass frit, and convert continuously to glass in a Pochet-type (see Chapter 8, section on evaluation of current R&D) joule-heated ceramic melter for vitrification.

3. Solidify molten product in titanium canisters.

4. Emplace canisters in salt, shale, or granite for retrievable storage or final disposal.

Costs of Panel's Plans

The systems choices made by this Panel, and enumerated above are sufficiently similar to the alternatives described in the three ERDA documents (See Appendix A) to permit some cost comparisons of solidification plans. For example, the typical plan using concrete envisaged by the Panel for DOE wastes is not very different from the SRP plan number 9 and the Hanford plan number 6. Similarly the plan using "dry powder" (SRP number 14-17) can be compared with the supersludge and low-temperature ceramic options. Furthermore, the pumping of supergrout, an option especially recommended by the Panel for further study, can be compared with one of the lowest cost options discussed in the ERDA documents, that is, SRP plan number 22, which calls for disposing of the liquid wastes without containers in the SRP bedrock caverns. It is surprising however, that a grouting plan such as the one described by the Panel, is not explicitly discussed, since ORNL has had actual experience with this process and cost figures should be available.

SUMMARY

Since the total radioactive waste management system relies heavily on protection provided by a set of multiple barriers, it is important to consider each individual barrier, including the solid waste form. In choosing the solid form for a given system, one must consider its role in the processing, the transportation, and the emplacement stages. Although, among these three stages, the total hazard to the public during transportation appears to be the highest, the hazard is still relatively small and the differences in risk among the individual forms are not well known. In selecting a solid form, therefore, it is important to consider not only which form will perform best in an unlikely transportation accident, but also such factors as cost, and simplicity and reliability of engineering. It is possible that cost, rather than the properties of the solid waste form, may become the more important determinant of selection. The relative weight that should be given to cost and safety, however, is a value judgment which is inappropriate for this Panel to make.

NOTE

1 As the radionuclides in the wastes decay, the wastes become less hazardous and consequently the amount of protection required decreases. The time scale for this to occur is on the order of hundreds of years for the major fission products (^{137}Cs and ^{90}Sr) and hundreds of thousands of years for ^{239}Pu.

CHAPTER 4

RESEARCH AND DEVELOPMENT FOR RADIOACTIVE WASTE SOLIDIFICATION

BACKGROUND

The practice of storing high-level wastes, in their liquid form, in heavy-walled steel tanks was expedient and adequate in wartime. As this practice is extended longer and longer into the postwar era, delay in developing and implementing solidification procedures becomes less defensible (see e.g., Kubo and Rose [1973] and the Nuclear Energy Policy Study Group [1977]). Some of the possible reasons for the delay are worth mentioning here because they provide a perspective for our recommendations.

During the era of big and new science of the 1950s and 1960s, the expansionist emphasis of the nation's science policy was felt particularly strongly in the emerging area of nuclear energy. An important effect of this emphasis was a comparative neglect, reflected throughout that period in the AEC budgets, of the "back end" of the nuclear fuel cycle--including the management of radioactive wastes. Harvey Brooks, speaking at the Denver Conference in 1976, summarized the position thus:

> "In the first years after the war the waste-disposal problem was never attacked with a real sense of urgency. Research and development expenditures were relatively small, and the whole problem had little prestige or glamour among the scientists and engineers who were being attracted to the new and growing field of nuclear energy. The few competent people who chose to work in the field got little recognition for their efforts; for example, so far as I can remember neither the prestigious Enrico Fermi Award nor the more numerous E.O. Lawrence Awards ever went to an 'atomic scientist' for a contribution to waste management" (Brooks 1976).

Given the prevailing focus of science policy during those years, it is understandable that the accepted view of

HLLW management as a minor engineering problem remained unchallenged, and consequently that the relevant expertise in the scientific community was not tapped to research the problem with the vigor it merited. One result of this attitude and policy appears to have been the early acceptance, on slender evidence, of glass as the prime candidate for the solid form. To our knowledge, no research from any of the countries principally concerned--France, Britain, and the United States--substantiated the premise, on which the choice of glass would seem to have been based: that natural glasses are "stable" in natural environments. The data supporting the case for the stability of glass were largely erroneously interpreted: in fact, natural glasses are relatively easily weathered materials, especially when water is present, and only the high-silica phases survive for any significant length of time. In the absence of expert evidence to highlight these limitations, a large proportion of the small effort on solidification of HLLW was concentrated on developing various glasses as the likely solid form.

The disproportionate emphasis on glass meant that, until 1975, the small research expended on the large number of other possible forms was sporadic and uncoordinated. Calcine, because it was regarded as a possible precursor to glass, predominated among the alternative candidates; concrete, ceramics, and various composites were also considered. With the exception of some studies of concrete, however, most alternative solid waste forms have been researched only in the last four years, and the level of effort has been strikingly low. Furthermore, the scientific community in general has not been involved in the problem.

Our present assessment is that, while specific glasses may be an acceptable solid form for a specific waste management system, glass cannot be considered the best or universal choice. Furthermore, to confine virtually all R&D to any single solid waste form, considering the variety of HLW management systems needed, is likely to be extremely wasteful and costly in the long run. The argument that it is best to concentrate on a single technology, even if it is not the best for all systems, is not convincing. Although glass may be adequate as a first-generation solution, parallel work should proceed, at a reasonable level, on alternatives if their promise is substantial. At present, many of these alternatives are possible, but an adequate data base has yet to be developed for choosing among them. The Panel, in fact, feels that a basic scientific understanding of the performance required of the solid form is lacking. Even less in evidence is an adequate plan for R&D on the materials sciences related to solidification. In the absence of such a plan, there has been, for the last decade or two, research on particular favored solutions proposed, engineered, managed, and executed by individual laboratories. Among these, there have been only two "successful" solidification programs in the country.

The INEL calcine program has been producing and storing calcine without much difficulty for many years. The product could be improved (i.e., by making supercalcine), but the process has been well managed. The ORNL grouting program (for low and intermediate level wastes), which also had limited R&D funding, has also produced a functioning system. These programs offer evidence that the problem of waste solidification is tractable. Unfortunately, cooperation and interaction among different waste solidification programs have been weak or nonexistent.

The climate that fostered neglect of radioactive waste management during the 1950s and 1960s has begun to change in recent years. Increasing public concern over the problem has begun to be reflected in actions taken by professional societies and the federal government. For example, the American Physical Society has just completed a major study of the nuclear fuel cycle, including waste management. The Materials Research Society, the American Chemical Society, and the American Ceramic Society are planning to hold symposia on waste management in the near future. Within the government, the Department of Energy has recently placed a high priority on basic research related to waste management (U.S. DOE 1978). In general, there appears to be a growing awareness that the current technical data base may not be adequate to support future decisions and regulatory actions regarding radioactive waste management. This chapter attempts to define past deficiencies and current gaps in information so that, with the advantage of hindsight, future research can be tailored more adequately to the needs of the decision makers.

INADEQUACIES IN KNOWLEDGE AND RESEARCH ON SOLIDIFICATION

During the course of this study, the Panel has reviewed the availability of information that it felt was required to make important judgments (see Appendix C for a discussion of European R&D on Waste Solidification). While in many cases such information was readily available--there are excellent computerized abstracting services, and DOE and contractor personnel provided a great number of reports and other documents--in some areas, the knowledge base was inadequate. Some gaps in knowledge toward which increased research attention should be directed are:

1. As a problem in materials science and engineering, waste solidification would clearly benefit from the systematic approach normally applied to "materials

selection" in most advanced materials industries. Efforts to apply this approach need to be developed.

2. Detailed, developed knowledge of the actual chemical phases present in spent fuel is lacking. In view of the current U.S. government policy on reprocessing and the possible disposal of fuel elements, this information is essential.

3. A great deal of basic research has been done on radiation damage in solids. But, since very few bulk effects that can translate into chemical changes occur at the radiation levels involved (≤0.1 to 1 displacements per atom), the large store of knowledge is of little value in understanding waste solidification. From the relevant data that are available, it is clear that solid-state radiation damage is not a serious problem. On the other hand, two other radiation effects, both inadequately understood, may lead to problems and may be relevant to solidification decisions. The first is the radiolytic decomposition of hydrated phases in the presence of high-surface-area solids and at elevated temperatures. The second is the influence of transmutation on structural stability--a phenomenon that could have an influence in 25 to 35 years on the one- or two-phase solids containing substantial amounts of ^{90}Sr or ^{137}Cs.

4. The science of experimental geochemistry, which has largely come into being since 1950, can be used in developing an understanding of solidification. The experimental tools that have been developed (e.g., high-pressure, high-temperature vessels) allow simulation of virtually any geochemical condition that has ever existed within 100 kilometers of the earth's surface. From experiments of varying duration, application of appropriate theory, and comparison with other mineralogical data, one can predict or explain natural systems where millions of years are involved. Thus, the technique for simulation of the waste-in-rock situation is quite routine. Such simulation experiments under hydrothermal conditions with a variety of solid forms in a variety of rocks will provide a reliable guide to the behavior of radionuclides after emplacement.

5. The design of ceramic materials at the atomic or molecular level is now well advanced in many industrial and university laboratories, but so far the types of materials studied differ considerably from those that might be appropriate for radioactive waste solidification. In particular, one of the major solid forms under consideration, a cement-supersludge composite, relies on the interactions of clays and zeolites (aluminosilicates of the sheet and network families) or noncrystalline gels with complex mixtures of ions to immobilize the radionuclides of

interest. These reactions, as well as those that occur when calcium hydrosilicates or cements are added to the system, are not adequately understood. Yet it is almost certain that solid waste buried in geological formations will ultimately be subjected to conditions where reactions of these types take place.

6. Additional basic data are needed on the adsorption of ions on simple and complex mixtures of natural silicates at low temperatures, including possible chromatographic separation. Again, solid waste buried in geological formations will, at some point, almost certainly be subjected to conditions where interactions of this type take place.

7. The metallurgy of container/waste and container/rock reactions under the appropriate range of simulated emplacement conditions has been inadequately studied. Studies of interaction and corrosion of candidate metals under possible repository conditions are needed.

8. Research on processing of radioactive waste materials has been very narrowly based--essentially limited to developing a miniature glass plant. The goal should be to design simple, remotely controllable processes, that need the lowest temperature, for primary or secondary containment. These processes would range from hot pressing of ceramic pellets or large blocks to cold isostatic forming of metal matrix composites.

9. Because radioactive waste contains at least 40 different elements, the basic research required is rather sophisticated. General answers may not easily be found, but it is clear that any advancement of the fundamental knowledge of complex systems would be relevant to radioactive waste solidification.

These major gaps in our basic scientific knowledge relevant to radioactive waste management developed--in spite of large total AEC budgets for R&D over the years--because of a classic case of targeted, fundamental science falling between two interests. On the one hand, the waste-management group in AEC (and later ERDA) apparently felt a responsibility primarily to develop the engineering for a more or less predetermined solution of the solidification problem. On the other hand, the Division of Physical Research, although possibly following what they were charged to do at the time, supported fundamental research directed to general goals, where relevance to specific AEC objectives was probably not a major consideration, and possibly even a disqualification since it may have been assumed that the waste-management section should fund such work. Thus, some basic research highly relevant to AEC needs appears to have been neglected for two decades. In view of the gaps in information identified above, some change is clearly needed in research policy: either the Division of Waste Management or the Division of Basic Energy Sciences[1] should be specifically assigned the responsibility and allocated the necessary funds for the relevant fundamental research. The Panel is encouraged by a recent report from the Department of Energy (1978), which indicates that they are placing a high priority on waste management research.

SCIENTIFIC PERSONNEL

Research and development on problems as important to the nation as the management of radioactive waste has normally drawn on the talent and relevant expertise available from industry and the universities. Several strategies exist for tapping these sources. For example, by using a "sources sought" in the Commerce Business Daily, existing competence can be identified; indeed, after the early drafts of this document had been written, such a "sources sought" for solidification research appeared on page 3 of the Commerce Business Daily on December 2, 1977. Other groups, especially in universities, can be persuaded by holding appropriate symposia and inviting known experts. Professional societies can also be stimulated to hold meetings on the topic and to publish and widely disseminate appropriate papers. Project managers can invite the nation's leading experts on a topic to submit proposals or respond to requests for proposals.

Until the last two or three years, management of R&D has not generally taken advantage of any of the normal mechanisms noted above. Most of the major conferences that dealt with radioactive waste solidification have been part of more general conferences (such as those listed in Table 4.1), primarily addressed, until very recently, to groups and individuals already working on the problem. There was little professional society involvement or interest in the science and technology of solidification. Similarly, after talking to colleagues most likely to be involved as R&D performers or consultants, the Panel members found that there had been little contact with waste solidification research until 1975, when an accelerated effort began to include a broader range of scientists in R&D on waste solidification. What is most surprising in this brief examination of R&D management has been the failure to recognize the appropriate scientific expertise relevant to the task. The involvement of materials scientists, principally ceramists and secondarily metallurgists, and experimental geochemists or petrologists in the planning of the R&D efforts would have been particularly helpful.

TABLE 4.1

Major Conferences Involving Nuclear Waste Management

First United Nations International Conference on the Peaceful Uses of Atomic Energy. Held in Geneva, Switzerland, 1955. Geneva: United Nations.

Report of Working Meeting on Fixation of Radioactivity in Stable Solid Media at the John Hopkins University, June 19-21, 1957.

Second United Nations International Conference on the Peaceful Uses of Atomic Energy, held in Geneva, Switzerland, 1958. Geneva: United Nations.

Report of Second Working Meeting on Fixation of Radioactivity in Stable, Solid Media at Idaho Falls, Idaho, September 27-29, 1960.

Proceedings of the Symposium on Treatment and Storage of High Level Radioactive Wastes held by the IAEA in Vienna, October 8-12, 1962.

Third United Nations International Conference on the Peaceful Uses of Atomic Energy held in Geneva, Switzerland, 1964. Geneva: United Nations.

Proceedings of the Symposium on the Solidification and Long Term Storage of Highly Radioactive Wastes, February 14-18, 1966. Richland, Washington.

Fourth United Nations International Conference on the Peaceful Uses of Atomic Energy, Jointly sponsored by IAEA, held in Geneva, Switzerland, 1971. Geneva: United Nations.

Symposium on the Management of Radioactive Wastes from Fuel Reprocessing, OECD/IAEA, Paris, November 1972.

Symposium on the Management of Radioactive Wastes from the Nuclear Fuel Cycle, IAEA/OECD, Vienna, 22-26 March, 1976.

Proceedings of the International Symposium on the Management of Wastes from the LWR Fuel Cycle, Denver, Colorado, July 11-16, 1976.

Proceedings of the First Pacific Basin Conference on Nuclear Power Development and the Fuel Cycle, Honolulu, Hawaii, October 11-14, 1976 (edited by Ruth Farmakes, ANS, Hinsdale, Ill.).

IAEA Conference on Nuclear Power and Its Fuel Cycle, Salzburg, Austria, May 1977.

This involvement would have been helpful not only to the AEC, but also to the professional societies and to a lesser extent to the National Research Council.

LEVEL OF SUPPORT FOR R&D

The deficiencies in management of R&D on waste solidification were not entirely due to budget limitations, since many could have been remedied at little cost; however, before 1974, when the total level of effort for waste management was $5 to $10 million per year, it would have been extremely difficult to initiate many desirable projects. And as the budgets have risen to about $30 million per year (beginning in 1976), many of these projects have been started.

The Panel obtained data from the Hanford Reservation, the Savannah River Plant, and the Idaho National Engineering Laboratory on the level of support for waste solidification research, categorized by waste forms. Together, the work done at these three DOE laboratories comprised approximately 90 percent of all recent waste solidification research conducted in the United States (Goetz K. Oertel, U.S. Department of Energy, personal communication, May 26, 1978). The Panel recognized that these data would not be precise, nor could they be separated sharply into categories of basic research, applied research, or engineering. Nevertheless these data, which are summarized in Table 4.2 and Figures 4.1 and 4.2 strongly support the Panel's conclusion that there has been disproportionate emphasis on the development of glass as a waste form,[2] and that virtually no basic research has been planned or executed on waste solidification. Further, the data show a significant fluctuation in the level of funding for R&D on radioactive waste solidification: a twofold increase in one two-year period (1965-1966) was followed by a fourfold decrease six years later (1971-1972).

The fluctuating levels of support and the overall inadequacy of funding for waste solidification R&D support the conclusion that the Joint Committee on Atomic Energy and the AEC regarded this problem as being one of low priority. In fact, since a clear conception of the problem was lacking, the AEC management may have assumed that there was no major technical problem worthy of a sustained R&D effort.

RECOMMENDED LEVEL OF R&D

To correct past deficiencies and assist in the development of second generation waste solidification and disposal technologies, increased support for R&D will be required. Costs of such increased support will be a very

TABLE 4.2

Department of Energy R&D Expenditures (in Thousands of Dollars) on Waste Solidification Categorized According to Waste Form

	GLASS	CALCINE	CEMENT	CERAMIC CLAY	ADVANCED FORM[a]	TOTAL
1955-56	200	600				800
1957-58	200	600				800
1959-60	300	1,530	100		20	1,950
1961-62	270	1,400	100		40	1,810
1963-64	440	970	100	500	10	2,020
1965-66	1,620	2,530	100	200	350	4,800
1967-68	2,800	4,400	200	200	700	8,300
1969-70	2,650	4,400	200	360	700	8,310
1971-72	660	1,000	200	90	130	2,080
1973-74	2,480	1,670	1,090	90	290	5,620
1975-76	6,190	3,700	2,320	550	890	13,650
1977-78	41,350	5,620	830	1,220	1,280	50,300
TOTAL:	59,160	28,420	5,240	3,210	4,410	100,440

[a] Includes metal-matrix, supercalcine.

Source: Data provided by the Savannah River Plant, the Hanford Reservation, the Idaho National Engineering Laboratory, the Oak Ridge National Laboratory, and the Division of Basic Energy Sciences.

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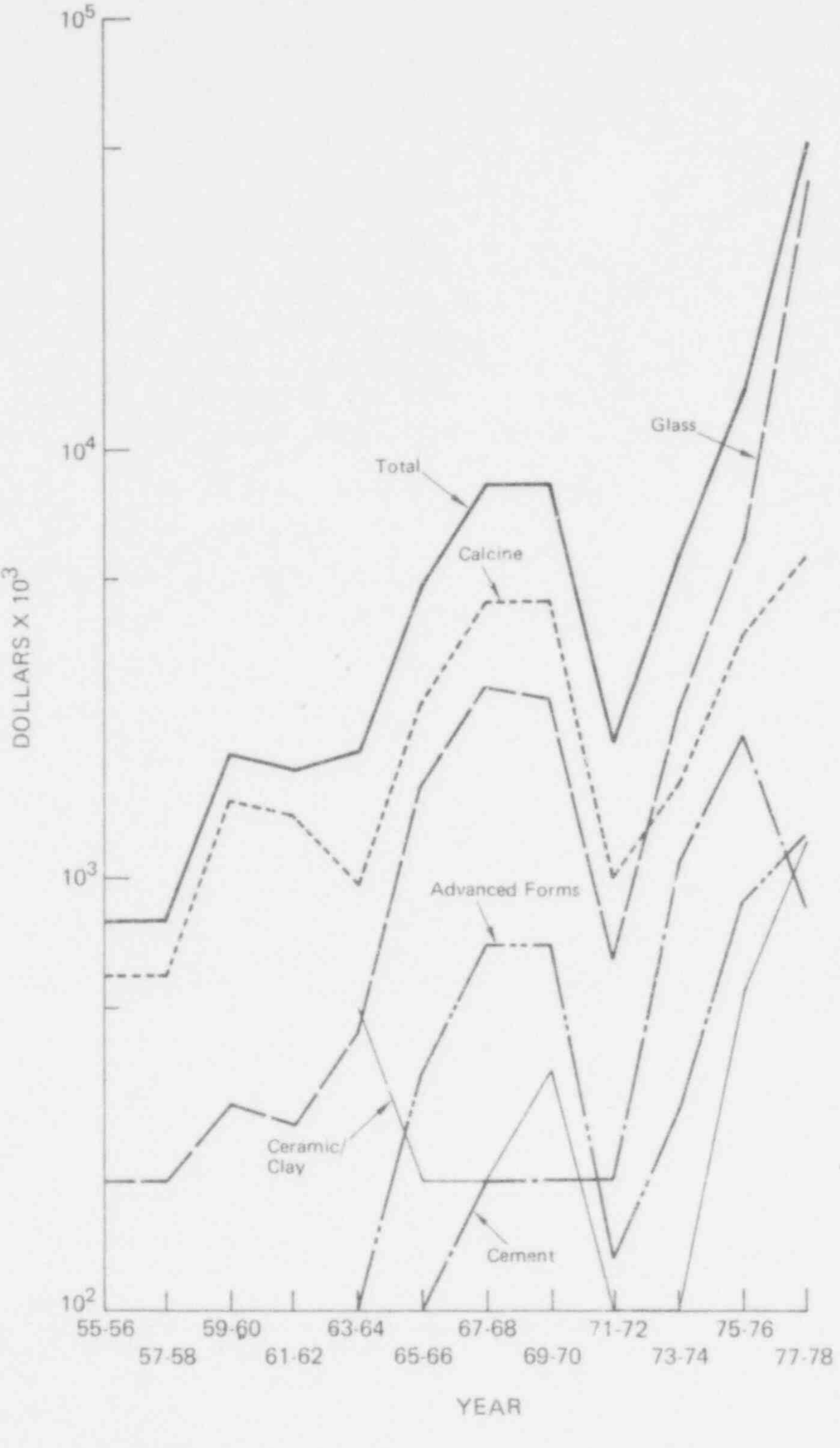
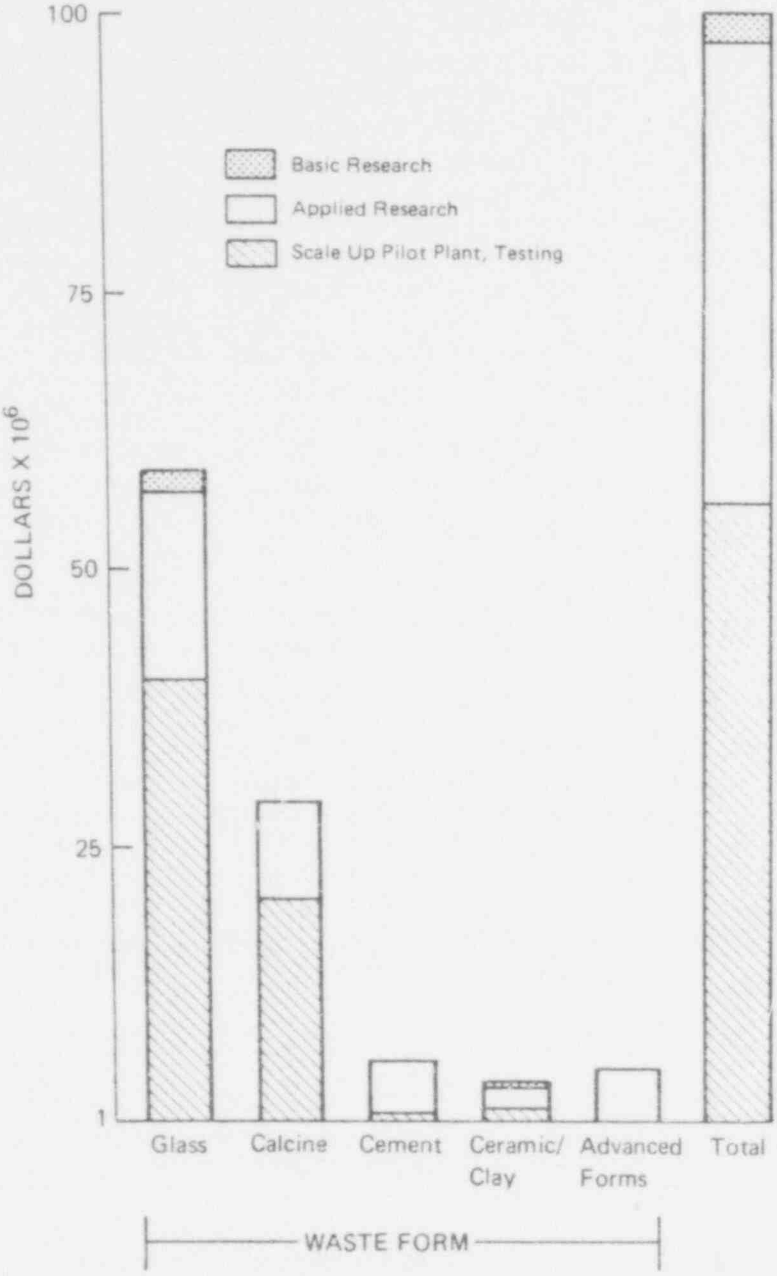


FIGURE 4.1 Department of Energy R&D expenditures on waste solidification categorized according to waste form.

Source: Data taken from Table 4.2.



Source: Data taken from Table 4.2.

FIGURE 4.2 Breakdown of R&D expenditures for different waste forms.

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small part of the total costs of radioactive waste management.

Estimates of the total cost of the solidification and isolation of the weapons waste alone range up to $30 billion or more (U.S. ERDA 1977a, 1977b, 1977c). The large degree of uncertainty associated with projections of future commercial nuclear power capacity precludes firm estimates of the cost of solidification and isolation of commercial wastes. For the limited purpose of estimating a rough level of R&D funding that might be required for radioactive waste management, the Panel is assuming that the volume of commercial waste produced by the year 2000 will be comparable to that of the military wastes (see Dance [1975], Rowe and Holcomb [1974], U.S. Congress, House [1976], U.S. General Accounting Office [1974]). Therefore, if another $30 billion is added for all commercial nuclear power wastes generated until the end of this century, an upper limit of perhaps $60 billion may be required for the management of all radioactive wastes. In high technology industries, it is not unusual for a company to spend 5 percent of its gross revenues on R&D. Similarly, the Panel feels that it would not be unreasonable for the United States to spend 5 percent (or $3 billion) of the $60 billion that may be required for radioactive waste management on R&D. This reduces to an annual budget of $150 million, which, although in marked contrast to the actual amounts (typically in the $5 to 10 million range) spent before 1974, coincides roughly with the level of expenditures planned for FY 1978. Of this $150 million, 10 percent or $15 million spent annually on <u>fundamental</u> research could provide the basis for developing more cost-effective second-generation technologies capable of saving possibly billions of dollars.

NOTES

1 The Division of Basic Energy Sciences was formerly known as the Division of Physical Research.

2 Glass and calcine have received more R&D support than all waste forms combined. Since calcine is itself a precursor to glass, most of the studies on calcine should be viewed as being studies on glass.

CHAPTER 5

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.

- In the interests of relative processing simplicity (and probable resulting low hazard and cost), cement-based composites and low-temperature ceramics should be researched vigorously as the prime candidates for solidification of DOE wastes. In particular, the feasibility of grouting these wastes (suitably modified as "supergrout") directly into appropriate geologic formations needs to be re-examined. (See Chapter 3, section on ranking the suitability of solid forms.)

- Substantial analysis and experimental work are necessary to establish firmly the feasibility of retrievable storage and/or disposal of spent fuel, and to define the method of preparation of the fuel assemblies. As a minimum, it appears desirable to encase the spent fuel assemblies in a metal can to facilitate safe handling. (See Chapter 2, section on primary containment forms.)

- For wastes of high specific activity and thermal power density, research and development of waste forms other than glass should receive greater emphasis. Metal-matrix composites involving glass or supercalcine, and high-temperature ceramics are principal candidates. Cement-based composites are not ruled out, but cannot be fully evaluated here owing to the lack of relevant data on radiolysis. (See Chapter 3, section on ranking the suitability of solid forms.)

- Continued research and development of vitrification of high-level wastes should emphasize the development of the refractory-lined melter as compared to the in-can melter. (See Chapter 2, section on primary containment forms.)

- The Panel sees no justification for continuing to convert high-level liquid wastes into unmodified calcine for storage. Until a decision is made on a final waste form, the Panel recommends that a change to supercalcine be effected as soon as possible. (See Chapter 2, section on primary containment forms.)

- The Panel recommends research and development of techniques to convert the ^{90}Sr and ^{137}Cs salt solutions stored at the Hanford Reservation to stable ceramic or concrete forms. The techniques would replace the current practice of converting the solutions to ^{137}CsCl and ^{90}SrF$_2$ and storing them as solids in stainless steel capsules. (See Chapter 2, section on primary containment forms.)

- The stainless steel capsules containing the CsCl and SrF$_2$, now being stored at the Hanford Reservation, should be incorporated into a chemically and thermally resistant metal matrix such as titanium, for permanent isolation in a geological repository. (See Chapter 2, section on primary containment forms.)

Needs for programs for research and development of specific aspects of waste solidification have been identified throughout this report. In particular, research should address:

- the susceptibility of sealed containers of waste cement composites to pressurization by radiolysis of water and nitrates (see Chapter 2, section on secondary containment forms);

- the chromatographic retention factors for HLLW ions in typical host rocks under the expected conditions of temperature and pressure. (see Chapter 4, section on inadequacies in knowledge);

- the interaction of potential canister materials with candidate solid waste forms and host rocks, at relevant temperatures, to determine how suitable the *canister material is for use during the retrievable storage phase* (see Chapter 4, section on inadequacies in knowledge).

Research and development are also needed on:

- *optimum stable crystalline or noncrystalline forms as radionuclide hosts, through the use of ceramic molecular engineering* (see Chapter 4, section on inadequacies in knowledge);
- *glass compositions that will retain radionuclides in insoluble crystalline phases after hydrothermal reaction with the host rock and water*;
- *special additives for cement/concrete waste solidification technology to fix each radionuclide in a low solubility crystalline phase* (see Chapter 4, section on inadequacies in knowledge);
- *remote process engineering on the waste solidification technologies that are serious candidates for possible adoption* (see Chapter 4, section on inadequacies in knowledge);
- *optimum overpack (adsorption layer) material with maximum fixation capacity for HLW ions.*

MANAGEMENT ISSUES

Findings
(See Chapter 4)

The technology for solidification and disposal of high-level wastes has not kept pace with nuclear reactor technology. The cause is not technical difficulty, but the low priorities assigned to the problem. Nevertheless, the Panel finds that the development of waste solidification technology, in general, is adequate to proceed with DOE's plans for first-generation demonstration and implementation, namely the WIPP project and a pilot plant for geological disposal of commercial wastes. DOE's timetable is flexible enough to allow the results of recommended research and development to be phased into its longer range plans.

Specific findings on deficiencies in management are:

1. A comprehensive and coordinated plan for research and development on waste solidification has been lacking. Although particular areas of waste solidification technology have received attention and funding, there has not been a balanced research and development program designed to

develop the capabilities and understand the requirements of a broad range of solid waste form candidates.

2. Little effort has been made to assemble a team of scientists and engineers, drawn from a variety of institutions, to work continuously and cooperatively on the waste solidification problem. There has been a general failure to involve two relevant national scientific communities--materials sciences and experimental petrologists--and relevant industry in the planning and conduct of waste solidification research.

3. Research and development have been concentrated far too heavily on glass, which may, in many systems, be much less desirable than other solid waste forms.

4. In the recent past, because of limited funds and the need to demonstrate any feasible solution quickly, there has been a tendency to neglect alternatives while pushing glass technology to engineering and pilot plant stages. Steady support for research and development of alternative, second-generation technologies has therefore been neglected.

5. Relatively little research and development would be required to provide the options needed to assure that optimized or second-generation methods for solidifying various types of high-level liquid radioactive wastes are available. Stable support over a relatively short period of a decade would suffice. Technically optimum methods could probably be selected for DOE wastes in a shorter time, perhaps five years.

6. The United States has neither initiated nor taken full advantage of any cooperative multinational research and development programs, similar to those supported, for example, by the Commission of the European Communities (see Appendix B for a discussion of European research and development of waste solidification).

Recommendations

In view of the management problems just identified, the Panel makes the following recommendations:

- Responsibility and authority for all radioactive waste management operations (including solidification research and development) should be centralized. Basic and applied research would then be most directly translated into engineering and production. In addition, a single agency could conduct negotiations on behalf of the United States in the international area in matters of waste handling, reprocessing, solidification, and so on.

- A comprehensive and stable research, development, and demonstration program, of limited duration should be established for second-generation waste management technology. The Panel estimates that an annual total of $150 million ($15 million for basic research), over a period of about ten years, would be required to fund a successful program of this type.

- All future research programs should be designed to draw continuously on the personnel, experience and research capabilities not only of the government-owned, company-operated facilities or the national laboratories, but also of the nation's industries, universities, and non-profit laboratories.

- The authorities in the United States responsible for managing radioactive waste should take the lead in organizing coordinated international research programs and information-sharing mechanisms to avoid needless duplication of effort, and to hasten a convergence of the various national technologies and criteria for waste disposal.

- Because United States programs on storage and disposal of spent fuel are all new, international workshops, colloquia, and perhaps joint development programs should be used to mobilize the best available talent in support of the new objectives recommended in the previous section.

PART II
TECHNICAL ANALYSIS

CHAPTER 6

CALCINE, SUPERCALCINE, SUPERSLUDGE

INTRODUCTION

Definitions

Calcine is the general name for unconsolidated powder or granules made by the single-step process of evaporation and partial decomposition of high-level liquid wastes. Although calcine was for some time considered acceptable as a final solid waste form, it is now principally considered an intermediate form before consolidation to, or incorporation into, some other form. Calcine is relatively easy to prepare, can serve as a precursor to glass, and could be recycled to recover potentially useful radionuclides. Throughout the world, processed high-level solid wastes exist in significant amounts in only one waste form--calcine.

Supercalcine[1] is a crystalline assemblage of phases tailor-made for desired properties of solubility, and thermodynamic stability in contact with other assemblages as needed. As prepared by calcination (and where necessary, annealing), supercalcine is similar in appearance to calcine, with a crucial difference: its solubility has been lowered five to six orders of magnitude, and the volatility of certain components reduced two to four orders of magnitude. This change is effected by adding specially composed liquids to the HLLW stream before the waste is evaporated and decomposed. The principles of crystal chemistry are applied to make the final solid consist exclusively of highly insoluble crystalline phases that are thermodynamically mutually compatible. At many of the nuclear waste research sites, the HLLW stream has been modified with additives, the objective being improved processing, not improved products. At this time, only the Pennsylvania State University/Battelle Pacific Northwest Laboratories (PSU/PNL) and, to some extent, the Eurochemic/LOTES ("low-temperature solidification") products qualify as supercalcines.

Supersludge[1] is used in this report to describe a product that is a modification of "sludge" (a solid/liquid slurry of high-level wastes). It is considered here because part of the DOE wastes now exist as sludge. A supersludge is a compositionally tailored form, produced by specific additions (liquid, solid, or both) to the sludge to achieve minimum leachability in the product. The supersludge can be dried and heated at a low temperature (<500°C) to form a low-temperature ceramic, or may be handled as a two-phase slurry. In the latter case, "supersludge" becomes simply the term for a chemically and structurally optimized grouting mix such as that used at Oak Ridge. Such "super" materials contain each of the hazardous radionuclides in an identifiable phase that is highly insoluble. The assemblage of such phases is designed to approximate thermodynamic equilibrium at the pressure and temperature conditions to which the form will eventually be exposed.

Background

The obvious advantage of making solid calcine is that it is the direct product of a one-step process, and requires no innovation in science or engineering. Calcine has two major disadvantages. Its physical form--typically a fine powder--is relatively highly dispersible, and, because of its chemical composition, it is very soluble in water. These combined properties are likely to rule out calcine as an acceptable final solid form.

The second disadvantage has been eliminated in supercalcine, and innovations such as the granulation process developed by the Eurochemic Corporation have markedly reduced the original dispersibility. Whether, under certain circumstances, 3mm to 10mm granules of supercalcine approximating the solubility or leachability of glass would be acceptable as a final solid form is a matter for future decision.

Tables 6.1 and 6.2 list several typical actual and potential calcine compositions in the United States. They can be divided into two composition groups: those made up largely of refractory oxides (and fluorides) with only traces of fission products (e.g., Tables 6.1 and the Mol LOTES calcines), and those wastes from reprocessing of commercial fuel, a major portion of which are fission products (Table 6.2). A "clean" commercial waste consists of fission products, processing chemicals, equipment corrosion products and traces of unseparated uranium and plutonium. A "dirty" commercial waste is high in Na and phosphate from additions of intermediate-level liquid wastes (ILLW) to the HLLW stream.

While the chemical composition of calcines is almost always known, it is striking that very few organizations report the phase compositions. This information is

TABLE 6.1

Weight Percent Composition of High-Level Waste Calcine Produced at the Idaho National Engineering Laboratory, Idaho Falls[a]

Oxide	Wt% Aluminum Waste (Nonfluoride Waste)	Wt% Zirconium Waste (Fluoride Waste)
ZrO_2	-	21
Al_2O_3	89	22
CaF_2	-	54
N_2O_5	4	2
H_2O	2	1
Na_2O	2	-
HgO	3	-
Fission Product Oxides	0.6	?
Cs^{137}	0.017 (0.015 Ci/g)	0.005 (0.0044 Ci/g)
SR^{90}	0.009 (0.013 Ci/g)	0.002 (0.0035 Ci/g)

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[a] As of January 1974, 42,500 ft^3 (approximately 1,600 metric tons).
Source: Slansky (1976).

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TABLE 6.2

Weight Percent Compositions of Potential Commercial Reprocessing High-Level Waste Calcines

Oxide	PW-4b (Clean)[a]	PW-7a (Dirty)[b]
Na_2O	-	9.1
P_2O_5	1.6	8.3
RE_2O_3	31.8	30.5
ZrO_2	12.1	6.5
MoO_3	12.6	6.8
Tc_2O_7	3.2	1.7
RuO_2	7.3	3.9
PdO	3.6	2.0
Cs_2O	7.0	3.8
Rb_2O	0.9	0.5
SrO	2.6	1.4
BaO	3.8	2.1
U_3O_8	2.9	15.4
PuO_2	0.2	0.1
Others	10.4	7.9

[a] J.E. Mendel, Pacific Northwest Laboratories, personal communication. Several tons of PW-4b-like calcine were produced (as an intermediate step to glass or phosphate ceramic products) during the period 1966-1970 at Hanford, Wash. as part of the Waste Solidification Engineering Prototypes program (Blasewitz et al. 1973). PW = Purex Process Waste; "Clean": fission products, residual U and P and some equipment and fuel pin assembly corrosion products (Fe, Ni, Cr).

[b] Adapted from McElroy (1975). "Dirty": a waste to which high sodium and phosphate intermediate-level waste has been added to the HLW; PW-7a is typical of the projected Allied General Nuclear Services, Barnwell, S.C. flow sheet.

important, since the crucial question of the solubility or leachability of hazardous radionuclides is principally determined by the phase into which they are incorporated. Thus Sr^{++} in $SrCl_2$ is over a million times more leachable than Sr^{++} in $(Sr, Ca)\ Al_2Si_2O_8$. X-ray studies of some calcines (McCarthy and Davidson 1975) suggest that the typical calcine is a mixture of two or three phases, each poorly crystallized or nearly noncrystalline. McCarthy and Davidson (1975) have shown that crystalline phases can be formed in calcines that are heated briefly to temperatures above 900°C. However, much or all of the Cs, Rb, Na, Mo, Ru, and Te in the calcines is volatilized during these firings. This poor thermal stability is a third disadvantage of ordinary calcine. Although it is not a critical property for routine handling of calcine, it would be important in a transportation accident involving fire.

Definitive leachability measurements are difficult to perform on unconsolidated calcine, but some data have been reported. For the calcine in storage at the Idaho National Engineering Laboratory (INEL) at Idaho Falls, it has been found that 60 percent of the ^{137}Cs and 40 percent of the ^{90}Sr are removed after 2,000 hours of continuous leaching by water at 25°C (U.S. ERDA 1976b). Mendel and McElroy (1972) reported that 20 to 25 percent of the constituents in typical commercial calcines dissolve readily in a 25°C leaching test. Fission product leachabilities of Eurochemic oxide calcines have been measured at 10^{-1} g/cm^2/day, at 25°C, in a standard International Atomic Energy Agency (IAEA) test (van Geel et al. 1976). This means that all of a particular constituent of concern could be leached in 15 minutes from a typical 100 cm^2/g powder. Leachabilities of the modified aluminum phosphate granular Eurochemic calcines are 10^3 lower (van Geel et al. 1976) than the oxide calcine, i.e., 10^{-4} g/cm^2/day. Leachabilities of DOE powder supercalcines produced by PSU/PNL have not been measured, but in a severe test with boiling distilled water, consolidated supercalcines (more comparable to other forms) have both bulk and Cs leachabilities of 10^{-5} to 10^{-6} g/cm^2/day (McCarthy 1977), in spite of the fact that they contain 30 times more Cs than the Eurochemic modified calcines.

There are two other problems with using simple calcine powders as commercial HLLW solids: their thermal conductivity is low, and they contain residual volatilities such as H_2O and NO_x that could form gases by radiolytic decomposition. The low thermal conductivity means that containers of calcine would have to be of small diameter to prevent unacceptably high centerline temperatures. The removal of residual volatiles would require an extra (800 to 900°C) bake-out before canister sealing (U.S. ERDA 1976b).

Present Calcine Inventory

For 14 years, ERDA has been routinely solidifying wastes from U.S. Navy nuclear-powered ships and research reactors. Some 2,000 tonnes of calcine, one of the largest quantities of solidified high-level wastes in existence, are now contained in underground storage bins at Idaho Falls, Idaho. The Eurochemic inventory in Mol, Belgium, is approximately 40 tonnes of aluminum-rich calcines. There are also appreciable quantities of SrF_2 and CsCl salts[2] that have been separated out from the HLLW stored at Hanford and sealed into metallic capsules. The disadvantages of unmodified calcine as a waste form (i.e., high dispersibility and high solubility) are identical to those of CsCl and SrF_2.

Calcine as a Precursor for Glass and Composites

It has been realized for quite some time that calcine is far from ideal as a HLW solid. Hence, for almost two decades laboratories around the world have been exploring processes that would either convert calcine into a glass-like solid or isolate and protect it in a more inert matrix. Table 6.3 summarizes some of the typical processes and products that include the making of calcine as an intermediate step. The vitrification processes using calcine as an intermediate are covered in another chapter of this report. Several vitrification processes currently under investigation aim to eliminate the calcining step altogether.

PRESENT STATUS OF ENGINEERING

All current demonstration plants for glass making and many of the research programs use a calcine step (see Chapter 8), which is consequently a familiar process. The INEL program has clearly demonstrated the viability of a full-scale, hot-cell process of calcination. The French effort at Marcoule, the German work at Karlsruhe, and the hot-pilot operations at Hanford between 1966 and 1970 show that calcining can be done effectively on a laboratory and pilot-plant scale. In these latter cases handling of the powdered calcine is minimized, since it is fed more or less directly into the furnace for glass melting. At INEL, on the other hand, the powder is handled routinely and "blown" directly to the storage tanks. This process demonstrates that even a very fine powder of relatively soluble materials can be handled safely. At Eurochemic the granulated calcine is normally feed for the glass method, but it has also been directly incorporated into a lead matrix. Table 6.4 summarizes the status of current work on calcine.

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TABLE 6.3

Calcine as a Precursor for Glass and Composites

Product	Process	Site
Borosilicate Glass	Rotary-kiln calcination Glass production (Metallic melter)	Marcoule (van Geel and Eschrich 1975)
Borosilicate Glass	Spray calcination Glass production (In-can melting)	Pacific Northwest Laboratory (U.S. ERDA 1976a), Larson and Bonner 1976)
Borosilicate Glass	Spray calcination Glass production (Metallic melter)	Karlsruhe (Blasewitz et al. 1973)
Borosilicate Glass	Pot calcination Glass production (In-can melting)	Windscale (Clelland 1973)
Phosphate Glass (beads in metal matrix)	Fluidized-bed calcination[a] Glass production (Metallic melter) Metal matrix production (casting)	Mol (Clelland et al. 1976)
Calcine/Glass Composite	Press and fire blocks of calcine-glass mix	Idaho National Engineering Laboratory (Berreth et al. 1975)
Calcine/Ceramic Composite	Hot press calcine/crystalline ceramic mix	Pennsylvania State University (McCarthy and Davidson 1976)
Calcine/Metal Composite	Granulate or pelletize calcine, cast in metal matrix	Mol (van Geel and Eschrich 1975, Clelland et al. 1976) Idaho National Engineering Laboratory (Clelland et al. 1976)

[a] Also uses direct feed of slurry into melter as an alternative to calcining.

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TABLE 6.4

Status of R&D on Calcine

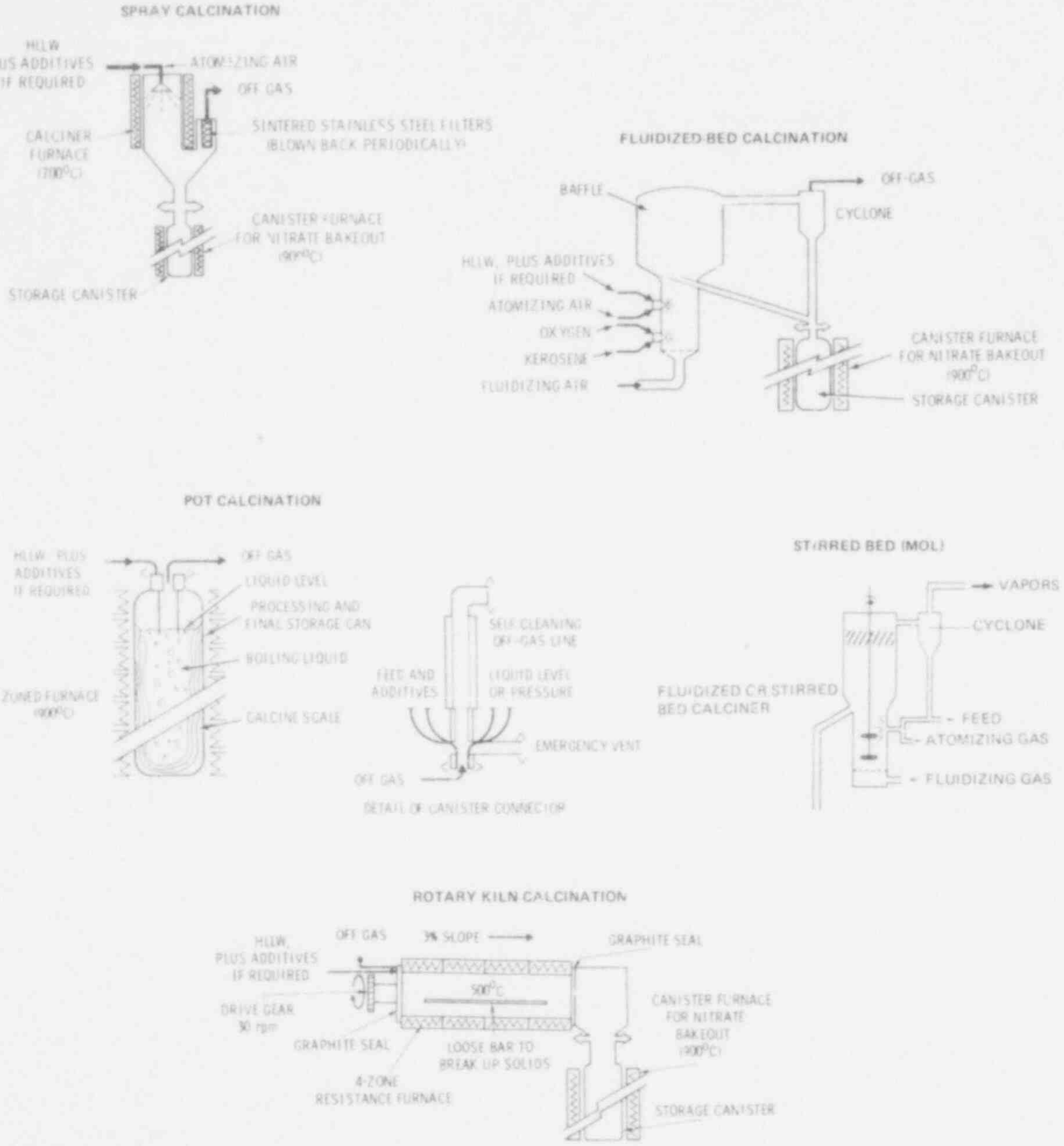
Site and Process	Lab-Scale Research	Pilot Plant		Routine Production	Storage
		Cold	Hot		
Idaho National Engineering Laboratory - Fluidized Bed					
Defense HLW	X	X	X	X	X
Commercial HLW	X	X			
Pacific Northwest Laboratory - Spray Calcination	X	X	X		
Pacific Northwest Laboratory - Fluidized Bed	X	X			
Marcoule - Rotary Kiln	X	X			
Windscale - Pot Calcination	X	X			
Karlsruhe - Spray Calcination	X	X			
Eurochemic - Stirred Bed	X	X			X
Eurochemic - LOTES	X	X			

Process Description

In the United States a great deal of engineering research has gone into alternative methods for calcine production. Two families of technologies have emerged: spray calcination and fluidized-bed calcination. Both of these are now rather routine; they are illustrated in Figure 6.1. In fluidized-bed technology, there is an additional and basic complication: the nature of the starter material and possible reactions between this bed material and the calcine. The stirred-bed calciner developed by the Eurochemic Corporation at Mol is a modification of the spray calciner and achieves granulation very simply (see Figure 6.1). Another calcining method, pot calcination, is a batch process in which the storage container is also the crucible for a boil-down/decomposition operation. It has been dropped from consideration in the United States (U.S. ERDA 1976b), but is still the first stage of the rising-level, in-pot vitrification processes in the United Kingdom (Clelland 1973).

ERDA (1976b) provides concise summaries and descriptions of the two current United States calcination processes and the French rotary kiln process:

> "Spray Calcination
>
> Final Product Form: A very fine powder. Most particles have a diameter in the range of 2 to 5 μm.
>
> Process Description: The HLLW is pumped to an internal mixing pneumatic atomizing nozzle in the top of the heated (700°C wall temperature) spray calciner barrel. The atomized droplets (nominally <70μm in diam) are flash dried and calcined as they fall through the hot barrel. The finely divided powdery product is separated from the off-gas by sintered stainless steel filters.
>
> Applicable Wastes: All aqueous wastes which can be evaporated and dried or calcined to form oxides (excludes Hg, for example). Any pumpable waste concentration can be calcined. Wastes containing 2M Na can be readily calcined.
>
> Development Status: The process has been in developoment at PNL for over 15 years. Thirteen fully radioactive engineering-scale runs (about 50 hr each) with the spray calciner were made in the Waste Solidification Engineering Prototypes (WSEP) program. Over 1,000 operating hours with simulated waste at feed rates up to 75 liters/hr have shown spray calcination to be a simple reliable operation. A large-scale calciner



Source: U.S. ERDA (1976a), van Geel et al. (1976).

FIGURE 6.1 Five calcination processes.

566094

is currently under construction to demonstrate spray calcination at higher feed rates.

Fluidized Bed Calcination

Final Product Form: A mixture of granules and powder in the size range 0.05 to 0.5 mm and generated at a rate of 40 l/MTU processed. The product can be stabilized (denitrated and dehydrated) for storage, or the calcine is a suitable feed to a glass melter.

Process Description: Wastes are atomized into a fluidized bed of inert oxides, heated by inbed combustion, operating at a bed temperature in the range 500 to 600°C. Evaporation occurs on the surface of the original bed particles and results in a product consisting of granular bed material and powdered calcine, both of which are removed from the calciner. Stabilized calcine product can be stored in canisters, or the calcine can be converted to other waste forms (e.g., glasses, metal matrices, sintered glass-ceramics).

Applicable Wastes: Wastes (liquid or slurries) consisting of HLLW, HLLW-ILLW, radioactive concentrates from evaporation processes, and organic spent solvents from fuel reprocessing.

Development Status: Process flowsheet has been verified on cold pilot-plant scale at feed rates up to 2 liters/hr; similar process and equipment operability has been demonstrated on a full radioactive scale using ERDA wastes at routine processing rates in the range 400 to 500 liters/hr. This corresponds to 2 to 3 times the projected output from a 5 MTU/day plant. The ERDA wastes for which high processing rates have been demonstrated are mainly composed of aluminum or zirconium nitrate, whereas commercial HLLW is predominantly fission product nitrates.

Rotary Kiln Calcination

Final Product Form: A relatively free flowing finely divided oxide powder.

Process Description: The rotary kiln calciner is an externally heated (500°C) rotating cylinder operating at a slight angle so that deacidified HLLW introduced at the upper end is dried and almost completely denitrated before it exits the lower end. A loose bar keeps the calcine free-flowing and prevents deposits sticking to the wall. The off-gas is scrubbed with water to remove entrained particulates, which are recycled by combining the scrub solution with incoming HLLW. The calcine product is heat treated to assure total decomposition of nitrate.

<u>Applicable Wastes</u>: All aqueous wastes which can be evaporated and dried or calcined to form oxides (excludes Hg, for example). The alkali metal contents of the waste should be stabilized by the addition of stoichiometric amounts of a stable anion such as sulfate or phosphate.

<u>Development Status</u>: The process has been in develoment for over 10 years in France for use with a continuous HLLW vitrification process. For much of that time an engineering scale unit has been in use with simulated nonradioactive waste. There has been no radioactive experience" (U.S. ERDA 1976b).

Limitations on, or Difficulties with, Calcination

Several recurring problems in calcination processes are described below:

1. Decomposition of the nitrate during calcination requires the highest temperatures (500 to 1,000°C) involved in the process. Some European laboratories (Mol, Karlsruhe, etc.) use formic acid or formaldehyde to denitrate the liquid before calcination.

2. Waste volatilization, primarily of Cs and Ru, is a fundamental problem. High Cs volatility--one disadvantage of the pot calcination process--was suppressed by additions of stable anions such as sulfate or phosphate. Loss of the higher oxides of Ru can occur during concentration of HLLW before calcining as well as during calcining of the highly oxidizing nitrate solutions. Careful control of processing temperatures reduces Ru volatilization. Any abnormal condition in a calciner that would permit the self-heating calcines to reach temperatures above 800°C could cause serious waste volatilization problems. Gray (1976) has measured the following volatility weight losses on simulated clean commercial calcine (PW-4b) that has undergone 12-hour heating at several temperatures:

800°C - 0.5 wt% 1,100°C - 7.0 wt%

1,000°C - 2.8 wt% 1,200°C - 12.8 wt%

The major volatile constituents were Cs, Ru, Rb, Mo and Te.

3. Until recently, it was difficult to calcine high-sodium acid wastes in a fluidized bed because of the sluggish decomposition of molten $NaNO_3$. As a result, additions of metallic iron were required to promote decomposition. At present, the problem appears to be under control and both INEL (Slansky 1977) and PNL (Bjorklund 1976) have been successful in engineering-scale, fluidized-bed calcination of the high-sodium "dirty" HLLW. Here again, prior denitration may solve the problem.

4. Because the product of spray calcination is a very fine powder, the off-gas filters are an essential part of the equipment. PNL has had some 15 years of experience with sintered stainless steel filters <u>in parallel</u>, each of which routinely lets less than 0.1 percent of calcine particulates penetrate the filter. A pulsed blowback of air cleans the filters (Bonner et al. 1976).

PRESENT STATUS OF RESEARCH

Standard Calcine

While there has been considerable work on engineering design for new calcines and fluid-bed reactors, described in the preceding section, there appears to be virtually no current activity that could be called fundamental research on calcine. As a result, knowledge of the compositions and structures of the individual phases comprising calcine is lacking. Furthermore, there appears to be little effort to develop novel methods of preparing calcine, despite the interest by workers in the ceramics field in fine powder preparation.

Supercalcines

During the last few years, following the introduction of the supercalcine concept, greatly increased activity in research on supercalcine has brought about major advances. Although the groups discussed below may not have recognized the affinity of each other's work, all are in fact working towards the same goal.

Pennsylvania State University/Battelle Pacific Northwest Laboratories

The clearest conceptual basis for supercalcine has been provided in the Pennsylvania State University work by McCarthy and coworkers (Chapman 1976). They were the first to select (on the basis of fundamental crystal chemistry) specific highly insoluble phases that can contain one or more of the undesirable radionuclides. To produce supercalcine, it is then necessary to adjust the total composition by making additions to the liquid stream that will yield such phases. A further condition is that these phases should be in, or close to, thermodynamic equilibrium with each other. In a 25 to 30 component system, this is clearly a formidable task in phase equilibrium research, but one well within the capabilities of modern molecular engineering.

PSU/PNL have succeeded in developing effective formulations for converting both clean and dirty HLLW (see Table 6.2) into thermodynamically compatible assemblages of refractory and leach-resistant phases. Table 6.5 lists these phases and structure types. The assemblage of phases changes somewhat with major changes in waste composition. Nitrates of Ca and Al plus soluble forms of silica are added to the HLLW. These additions cause a dilution of only 20 to 40 wt% of unmodified HLW calcine. To date, three engineering-scale demonstrations of supercalcine preparation by spray calcination have been performed at PNL. Spray supercalcine is X-ray amorphous and must be heated briefly above 950°C to "develop" the assemblage of crystalline phases. ERDA (1976b) states that, "if an unconsolidated calcine continues to be an acceptable waste form, supercalcine formulation concepts can be introduced into flowsheets immediately which would improve the stability and insolubility of some of the radioactive waste constituents." This pronouncement summarizes the minimum potential of the process.

Eurochemic

In the LOTES engineering process developed by Eurochemic (also see below), the addition of phosphate to the HLLW results in the formation of metal phosphates and substantial amounts of aluminum phosphate, which acts as a secondary containment. This helps to fix many of the hazardous ions and yields products with leach rates reduced by a factor of 1,000 compared to oxide calcine (van Geel et al. 1976). Phase analysis has not yet been done in detail, so it is not clear which ions are tied up in which phases. However, it is clear that the product is a supercalcine that has been made without the conscious science-based design of the Pennsylvania State University process.

Supercalcines as Precursors

For Glass or Glass-Ceramics

Since the composition of supercalcine is infinitely adjustable, and since most calcines are now seen as precursors to glass making, an important research objective

TABLE 5.5

Primary Containment Phases for Principal HLW Radionuclides in Supercalcine

Constituent	Fixation Phase	Structure Type
Cs,Rb	$(Cs,Rb)AlSi_2O_6$	Pollucite
Sr,Na,Mo	$(Ca,Sr)_2[NaAlSiO_4]_6(MoO_4)_2$	Sodalite
Sr,Ba,Mo	$(Ca,Sr,Ba)MoO_4$	Scheelite
Sr,RE* $[PO_4]$	$REPO_4$	Monazite
	$(Ca,Sr)_2RE_8[SiO_4]_6O_2$	Apatite
Ce,U,Zr	$(Ce,U,Zr)O_{2+x}$	Fluorite
	$(Zr,Ce)O_2$	
Fe,Ni,Cr	$(Fe,Ni)(Fe,Cr)_2O_4$	Spinel
	$(Fe,Cr)_2O_3$	Corundum
Ru	RuO_2	Rutile

*RE=rare earths, particularly La, Pr, Nd, Sm, Gd (and probably Am, Cm).

would be to convert an appropriate supercalcine directly into a glass, a glass-ceramic, or a melt-formed (fusion-cast) crystalline ceramic form.

Some work in this area is planned for FY 1978 at PSU/PNL that will use the high-temperature PNL ceramic melter technology (Chapman 1976). This work has a direct bearing on the glass process, since it is a faster way to avoid addition of frit and to make more homogeneous glass.

For Ceramics

Most of the work done by the McCarthy group to date has been aimed at preparing highly insoluble phases that can be fully crystallized by heating and then rendered into larger ceramics bodies by hot-pressing, sintering, or other processes. These processes have produced the densest thermodynamically stable solid waste form produced so far in the laboratory (see Chapter 7).

For Composites

Some current R&D on calcine or supercalcines has as its final product goal a composite waste form of pellets or granules encased in a metal, cement, or glassy matrix. PSU/PNL supercalcine forms the core of a particularly exotic multibarrier waste form under development at PNL. Eurochemic/LOTES supercalcine granules are formed into a metal matrix. These two composite products are discussed in detail in Chapters 9 and 10.

For Supersludge

The radioactivity in the large volumes of DOE wastes stored in tanks at Hanford and Savannah River is contained mainly in a solid/liquid "sludge" at the bottom of the tanks. Any process to extract and process the material from the tanks will deal directly with these sludges.

A little work has been done at Hanford (Wodrich 1976) to treat these sludges by addition of slurries of very fine clays and other aluminosilicates (see Table 6.5). The goal of such work was to prepare low-temperature ceramics. However, these mixed, fluid slurries are in many ways analogous to the mixed liquid stream in the supercalcine process. By adding the clays and other aluminosilicates, the total composition can be adjusted--and this has to some degree been done--to yield, after low-temperature drying or calcination, a desirable set of phases. We are terming this mixed tailor-made slurry, whether dehydrated or not, "supersludge."

It may be desirable not to react or bake the sludge if the final form will employ cement as the secondary containment either as "supergrout" or for making monolithic blocks. On the other hand, if the final form is a ceramic, other shaping and forming processes are called for (see Chapter 7). Thus supersludge is a precursor for two or three other composite waste forms.

Consolidation Technologies

Since the major physical drawback of calcine and supercalcine is their dispersibility, efforts to consolidate these fine powders into pellets or larger granules are increasing. Methodology for converting many tons of powder into pellets is certainly well established in the ceramic and pharmaceutical industries. However, the equipment may be too complex and cumbersome, and the hydraulic fluids too unstable, for the remote, automatic or semiautomatic, high-radiation environment operations required for HLW processing. On the other hand, the familiar disc pelletizer has the potential to overcome each of these objections, and both PNL and INEL (Slansky 1977) have under way significant engineering-scale evaluations of this apparatus. Garrett (1976) has described the operation of the disc pelletizer in use at these sites.

It has also been recognized for many years that a fluidized-bed calciner can be adjusted to produce millimeter-size granules, but a consistent problem has been the simultaneous production of "fines," or unsatisfactorily fine powder. At Eurochemic in Mol, Belgium, modifications of the fluidized-bed equipment and chemical modification of the high-aluminum wastes have allowed the production of "large" granules. A description of this LOTES engineering process has been given by van Geel et al. (1976):

> "To the HLW feed solution a stoichiometric amount of phosphoric acid, with respect to the metal ion content, is added together with sufficient aluminium phosphate to obtain a final product containing 30 wt% of the original waste compounds. The solution is sprayed into the stirred bed reactor which is electrically heated at 150-500°C and prefilled with aluminum phosphate particles of about 3 mm in diameter. The optimum temperature is a function of the composition of the HLW feed solution. High amounts of sodium nitrate require temperatures above 500°C while for low amounts relatively moderate bed temperatures can be used. At equilibrium conditions, the particle growth is balanced by the formation of new seed particles and the removal of the product by overflow. Granular crystalline products of a hard and dense appearance

could be obtained. By adjusting the stirrer speed, the dimensions of the granules could be varied between 3 and 15 mm."

POTENTIAL OF R&D

Process Research

In principle, it would appear that there is little justification in research or in technology to continue to work on unmodified calcine. Instead, <u>all research and development on calcine should henceforth properly be focused on the category of supercalcine</u> as defined above.

In the general process research area, it would certainly be worthwhile to explore all new technologies that would permit lower temperature reaction, including denitration, to produce a fine powder. These should include the new kerosene droplet method of Reynen and Bastius (1976), freeze-drying, microwave heating, etc. All these processes offer the potential of obtaining a fine homogeneous powder at the lowest possible temperatures.

Supercalcine Research

Basic research on supercalcine is clearly essential to the development of all final ceramic forms. At present, there are major gaps in our knowledge including: (a) the phases in which each ion (present in 0.1 to 1 percent concentrations and above) is contained in the variety of calcines made, and (b) the series of host phases that are the most desirable (i.e., least leachable) for each ion. A good beginning has been made by McCarthy and co-workers on the latter, and all the essential data can be obtained rapidly with a very small investment. These can then form the guidelines for any solidification program that yields crystalline phases.

It would be desirable to have a master list of a few optional phases to contain each of the 30 to 40 radionuclide ions in an assemblage compatible with other likely phases. Then for a particular HLLW composition, the additive stream could be tailored virtually automatically to yield an acceptable total composition and thence the desirable phase assemblage. While this may sound like a difficult problem, the physical limitations on closest packing of ions in most oxide crystal structures leave us with only a handful of candidate phases: fluorite, apatite, perovskite, pyrochlore, scheelite, monazite, spinel, corundum, and a few network aluminosilicates such as pollucite, nepheline, and sodalite. If the composition of the wastes were to change, an appropriate adjustment could be made in the composition of the additives to yield a final product with a suitable mixture of desired phases. Since each of these phases can contain a wide variety of ions in true crystalline solution, it is possible to design the total assemblage so that only the desired phases appear.

Supercalcine and Supersludge Composites

Whereas the incorporation of supercalcine or supersludge into various composites appears to have excellent potential, these options have not been vigorously pursued in the United States and other Western countries. Concrete-matrix composites, metal-matrix composites, and graphite-calcine composites, the latter two made by powder metallurgy and/or hot isostatic or uniaxial forming, appear to be very promising. The concrete matrix supersludge in the form of a grout is a highly specific waste form for which expansion of basic and applied research would appear to be worthwhile. This research should focus on defining the desired phase compositions and the means of obtaining them.

Supersludge Composition

The composition tailor-making already done on supercalcine should be carried out for supersludge. Because inorganic ion sieves--both crystalline clays and zeolites, and noncrystalline gels--have great potential to adsorb ions, it should be quite feasible to develop compositions highly stable to leaching. These should be designed so that reaction to form insoluble phases occurs at the lowest possible temperature.

NOTES

1 The prefix "super" signifies a waste form in which the chemical composition has been altered so that all radionuclides are accommodated in known, relatively insoluble phases.

2 At present about 80 percent of the total ^{137}Cs and 65 percent of the ^{90}Sr have been separated from the bulk of the Hanford wastes. The encapsulation program is less than 10 percent complete; however, 240 out of a projected 3,500 capsules have been produced (NRC 1978).

CHAPTER 7

CERAMICS

INTRODUCTION

Ceramics have been defined as inorganic nonmetallic materials formed at high temperatures. For purposes of the current discussion, we shall restrict the use of the term "ceramics" to those materials that, in contrast to glasses, are predominantly crystalline in nature. The many product types range from porcelain and chinaware to sophisticated solid state electromechanical components.

Ceramics can be prepared by several processes, including consolidation of solid particulates by either sintering or hot pressing (with or without the presence of a liquid phase). Temperature is the driving force for the sintering process, which is characterized by the reduction of particle surface area via particle coalescence, and by shrinkage due to reduction of porosity. The sintering process generally occurs below the point at which major compositional constituents melt; distortion of shape and gross modifications of microstructure are thus avoided.

Ceramics have also been prepared by melt-solidification processes: raw materials are melted and reacted while solidification rates are controlled to develop the desired microstructure and properties. Products made by this process include fusion-cast refractories for glass and metals industries, single crystal boules for gem stones and optical applications, and, indirectly, glass-ceramics.

Ceramics are being seriously considered as a form for nuclear waste solidification because they potentially provide atomic level (primary) structural containment with the greatest thermodynamic stability. Ceramics are also more resistant to low-level radiation damage than other primary[1] monolithic waste forms, exhibit the highest thermal conductivity and leaching resistance, and are capable of greatest waste loading per unit volume. Furthermore, because ceramics, unlike glasses, are crystalline, X-ray and electron diffraction can be used in combination with scanning electron microscopy to pinpoint precisely the crystal structural environment of any nuclide. Judgments can then be made on whether to leave a nuclide in a particular crystalline phase or to modify the compositions and processing to produce new, more desirable phases. If insufficient data on such phases are available, the phases can be synthesized and evaluated individually for their relevant properties (leachability, thermal stability, susceptibility to radiation damage, and so on).

Ceramics and ceramic processes present some characteristic disadvantages for waste solidification. The high process temperatures usually involved present facility stability and longevity problems. Control and containment of particulates during processing, especially by the sintering or hot-pressing routes, are considered to be an additional complication. Ceramics are also possibly sensitive to transmutation effects.

STATE-OF-THE-ART SURVEY

Studies on crystalline ceramics as waste forms have received only a very small fraction (perhaps 0.1 to 1 percent) of the funding support that glasses have been given. This emphasis probably resulted largely from the fact that the glass-forming process appeared to be less complicated and easier to manage than many ceramic-forming processes. However, as discussed in Chapter 8, the glass-forming process has its own complications. Furthermore, there are problems with the stability of the product.

Whatever the reason, research efforts have been limited and development virtually nonexistent in the processing of ceramic/glass-ceramic HLW forms. The studies on ceramics are summarized in Table 7.1.

TABLE 7.1
Studies on Ceramic High-Level Waste Forms

Product	Site	Reference
Fusion-Cast Ceramic	PNL (WSEP)	Mendel and McElroy (1972)
Ceramic Sponge	LASL, Sweden	Christenson et al. (1964) and Hultgren (1977)
Low-Temperature Silicate	PNL, INEL, SRP	U.S. NRC (1976)
Stable Hot Pressed Ceramic	Penn State	McCarthy (1973) and McCarthy and Davidson (1976)
Sintered Calcine-Glass	PNL & INEL	Ross (1975) and Berreth et al. (1977)
Glass-Ceramic	HMI (Berlin)	De et al. (1976)
Titanate Ceramic	SLA	Schwoebel (1975)

Fusion-Cast Ceramic

Fusion-cast ceramic was one of the HLW solids evaluated in the Waste Solidification Engineering Prototypes (WSEP) program. A crystalline ceramic was prepared by casting a melt consisting of ortho- and pyrophosphates into a storage canister. The product crystallized when cooled below 800°C. It proved unsatisfactory because its leachability in water was 10 to 10^3 times that of HLW borosilicate glasses. However, it was the least dispersible HLW solid evaluated in the WSEP program. No effort seems to have been made to optimize the ceramic composition to decrease solubility, which would seem to be a routine task.

Ceramic Sponge Process

In the ceramic sponge process, HLW liquid is sorbed into porous bisqued clay bodies, which are then dried and fired at 1,200 to 1,300°C to partially vitrify the bodies and fix the HLW species. The products in the LASL effort had very low Cs but high Ru vaporization losses on firing and had low Cs and Sr leachabilities. The ceramic sponge work was performed at LASL in the early 1960s; it was then discontinued, and has only recently been included again in HLW programs, e.g., National Council for Radioactive Waste Management (PRAV), Sweden.

The aim of the Swedish program is to develop inorganic ion-exchange materials and techniques that will selectively remove waste nuclides, e.g., Cs and Sr, and long-lived actinides. Efforts are being made to develop ion exchangers that can subsequently be transformed to stable ceramic or glass materials via an in situ heat-treatment process. The successful removal of very long-lived actinides would drastically reduce the storage time necessary for decay of the remaining waste. Ion-exchange materials under consideration are zeolites (crystalline, hydrated aluminosilicates), nonzeolites (e.g., pyrochlor and Group IV phosphates), and arsenates with structures containing interconnected void channels suitable for cation absorption. This process of sorbing HLW liquid into stable crystal forms is recognized as the least complex and potentially the lowest cost ceramic process.

Low-Temperature Silicate

One of the lowest temperature ceramic forms conceived goes under various names, one being "aqueous silicate." In a variant of this concept, HLLW ions are adsorbed onto a mixture of silicates; this mixture is then reacted to create a set of relatively insoluble phases, some hydrated and some anhydrous. The high-sodium, DOE wastes have been studied in this manner. Another possibility is to mix the oxy-hydroxide sludges in the DOE wastes with mixtures of clays and zeolites. The resulting mixture can then be briquetted and reacted at low temperature (near 500°C). This reaction temperature could be increased with a corresponding increase in density and crystallinity of the product.

The ceramics produced by the techniques just described have not been characterized in any detail, but, despite their high porosity, their leach resistance will probably be nearly as good as that in most of the other ceramic forms. Their mechanical properties will naturally be much poorer than those of glass and hot-pressed ceramics, but will be similar to those of ceramic sponge.

Ceramics from Calcine

The ceramic product that has been least studied so far is one made from supercalcine. The original objective of the PSU development of supercalcine was to transform it by hot pressing or sintering without any additive to a thermodynamically stable assemblage of four or five crystalline phases in a ceramic monolith.

Three other products involving calcine or supercalcine--hot-pressed ceramic matrix, sintered calcine-glass, and glass-ceramic--are similar to one another and to ceramic sponge in that they are designed to protect HLW calcine, a product inferior in terms of strength, leachability, etc., by encasing it in or reacting it with a superior glass or ceramic matrix. Partial vitrification of the product is used to promote sintering and densification.

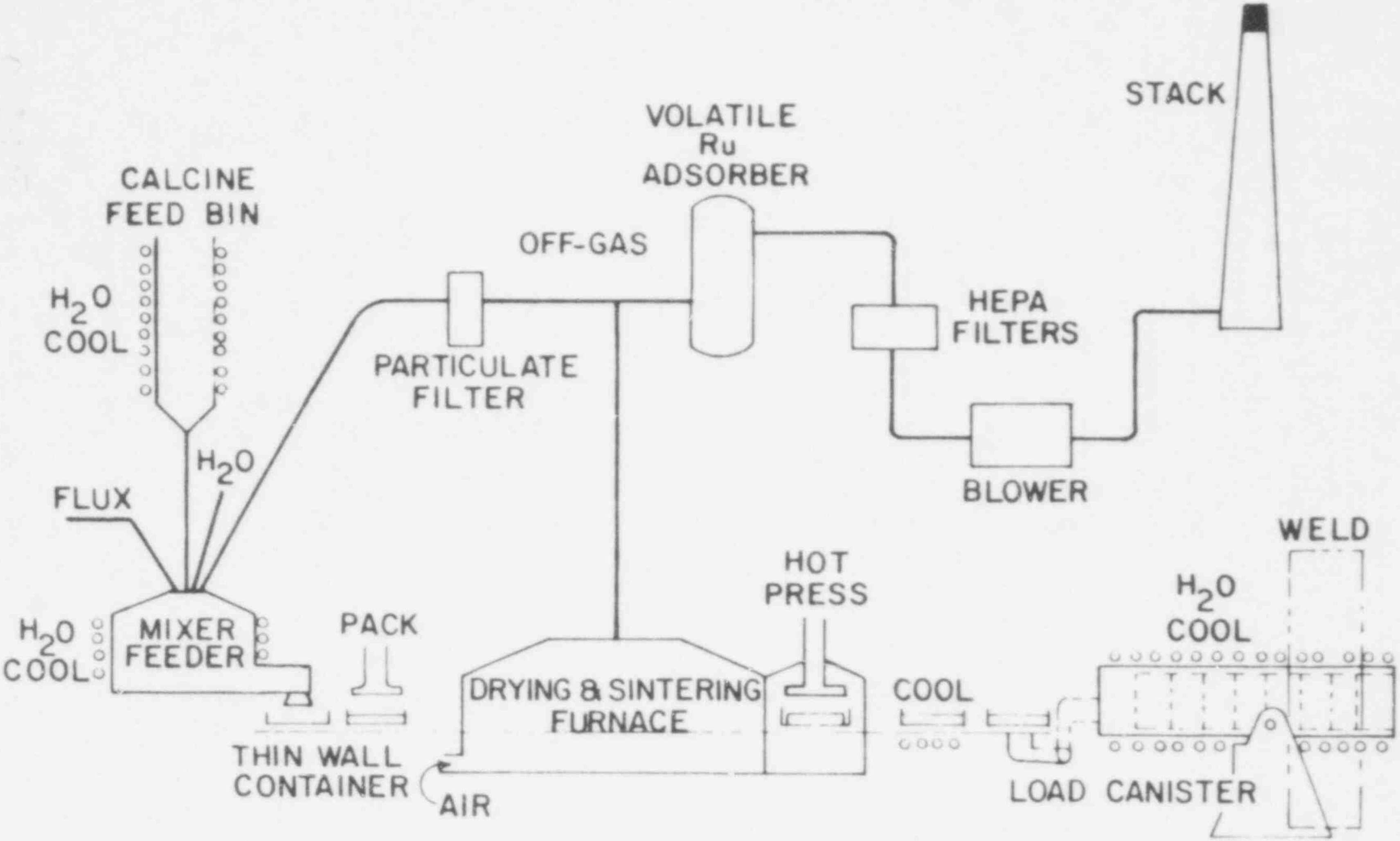
In the hot-pressed ceramic matrix product, approximately 30 wt% of HLW calcine is mixed with powdered quartz and a small amount of a low-leachability glass frit and hot pressed at 1,100 to 1,200°C, 2,000 to 4,000 psi. Compared with glass at the same level of waste loading, the product has a similar leachability but a greater thermal stability. Laboratory-scale demonstration was completed in 1975 using a cold but otherwise full-composition clean waste (PW-4b). Further work has not been scheduled, because it was believed that continuous, remote hot pressing under high radiation conditions was not feasible.

The sintered calcine-glass products are a mixture of HLW calcine (50 to 70 wt%) and either a suitable glass frit or a mixture of glass-making raw materials. The following excerpt is a process description from ERDA (1976b):

> "Calcine is mixed with a flux and a binder-lubricant, which can be water. If large disks are desired, the mixture is pressed to a low-profile, thin-walled steel container. If smaller pellets are to be formed, the powder is fed to a pelletizer. The shaped mixtures are then sintered with the large disks requiring a low-pressure pressing while still hot to conform the product to the container. After cooling, the disks could be loaded directly into the canister. The pellets would require a matrix and could be coated."

The INEL version of this process is illustrated in Figure 7.1.

Some of the crystalline phases resulting from the reactions between the calcine and glass have been reported and are listed in Table 7.2.



Source: Berreth et al. (1976).

FIGURE 7.1 Conceptual sintered glass-ceramic process.

TABLE 7.2
Crystalline Phases Resulting From Calcine-Glass Reactions

PW-4b + Zinc Borosilicate Glass (PNL)	PW-7 + Ba-Zn-Ti-Aluminosilicate (INEL)
[$(Ce,RE,Zr)O_{2\ x}$]	[$RE_2Zr_2O_7$]
[$(Sr,Ba,Ca)MoO_4$]	[Fe_3O_4]
[$(Ni,Zn,Mg,Co)(Fe,Cr)_2O_4$]	[CeO_2]
[$REBSiO_5$]	[Gd_2O_3]
	[$GdFeO_3$]

NOTE: RE refers to rare earth cations.

The INEL phases should be considered as structural types representing complex crystalline solution phases rather than as the simple compounds listed. The products are relatively dense and hard and have leachabilities approximating several times that of laboratory borosilicate glass.

The classical (i.e., PYROCERAM) glass-ceramic approach to a HLW form has not been used to any extent in the United States. It is under active investigation in West Germany, principally at the Hahn-Meitner Institute (HMI) in Berlin. U.S. ERDA (1976b) describes the processes as follows:

> "Liquid HLW is calcined and melted with the addition of glass frit. The melt is cast in small blocks or plates sized so that temperature gradients will be small. The blocks are cooled rapidly so that they remain completely vitreous and are then taken through a carefully programmed thermal treatment to promote controlled nucleation and crystallization. The blocks are stacked in a canister and the annulus filled with metal for enhanced heat transfer."

The same publication further notes that "a glass-ceramic is stronger than glass, would not be as susceptible to uncontrolled devitrification at high storage temperatures and would have leach resistance similar to glass."

Results of the HMI cold laboratory-scale HLW glass-ceramics investigations were published recently (De et al. 1976) and a few highlights are listed below.

- Process temperatures are: melting, 1,400 to 1,400°C; nucleation, 530 to 700°C; crystallization, 630 to 960°C.

- Waste composition is similar to PW-7a; glass of the alkali or alkaline earth aluminosilicate types.

- Bulk leachabilities are slightly greater in the crystallized product than in the parent glass.

- Nuclides of concern (e.g., ^{90}Sr, ^{137}Cs) are crystallized in tailor-made host phases.

The HMI group indicates that one of the first goals in tailor-making a HLW glass-ceramic was to fix Cs in pollucite, $CsAlSi_2O_6$. For this reason the group always uses aluminosilicate-based formulations. In their paper, they demonstrate pollucite crystallization (and coincident Cs depletion in the surrounding residual glass) with electron probe analysis. Pollucite is the most common host for Cs (and Rb, another HLW ion) in nature. Because it crystallizes from igneous formations that are as complicated chemically as HLW, nature has given us some indication of its great stability. It is highly resistant to water leaching of the Cs (Barrer and McCallum 1951) and has good thermal stability (Gallagher et al. 1976). (A definitive study of the crystal chemistry, phase relations, leachability, and thermal stability of pollucite is in progress at PSU.) It is no coincidence that pollucite is the Cs-fixation phase in the three tailor-made waste forms, glass-ceramic, titanate ceramic, and supercalcine.

One problem with the glass-ceramic approach is that in order to make the original glasses meltable at reasonable temperatures, fluxes such as B_2O_3 must be added to the aluminosilicate formulations. This leaves a relatively leachable borate-rich residual glass after crystallization that makes the bulk leachability slightly higher than that of the parent glass. Leachabilities of the ions (Cs, Sr, etc.) fixed in the crystalline phases are not reported, but these should be at a significantly lower level than leaching from the total glass.

The HMI glass-ceramic process has been demonstrated both cold and hot on a laboratory scale and is currently in the hot pilot scale stage of testing.

Titanate Ceramic

The titanate ceramic HLW form is the product of hot pressing consolidation in the Sandia Solidification Process, a rather complex process that may be realistic for military waste. ERDA (1976b) describes the process for commercial wastes as follows (see Figure 7.2):

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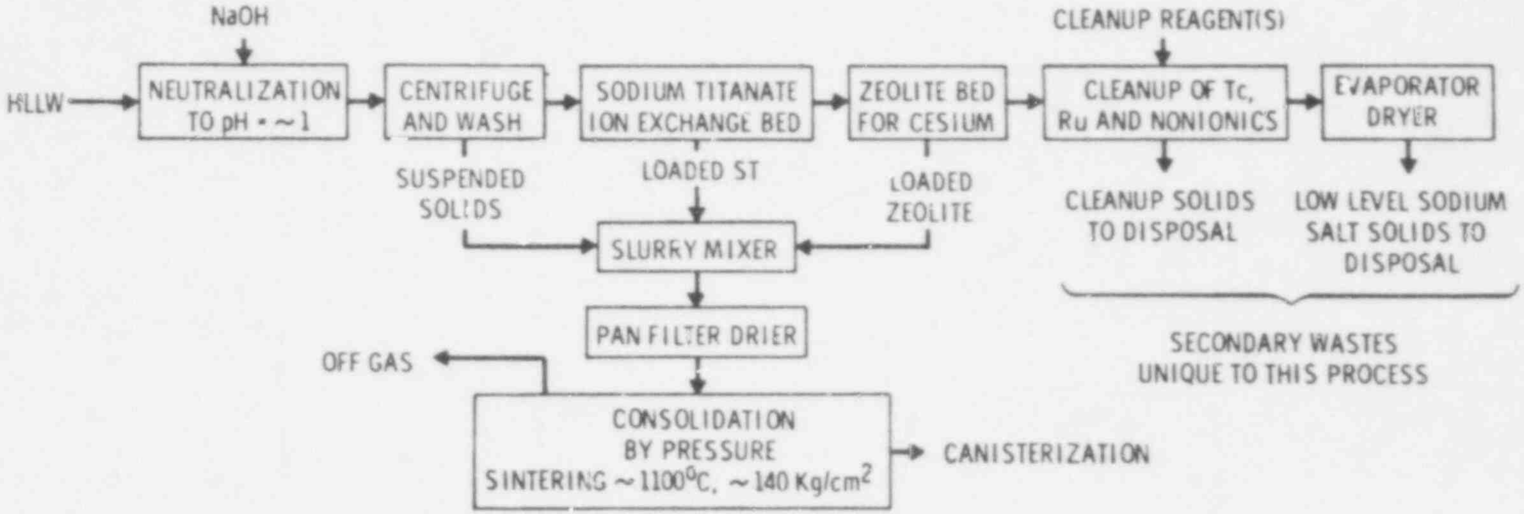


Source: U.S. ERDA (1976b).

FIGURE 7.2 Sandia solidification process.

> "HLLW is neutralized to pH = 1 with NaOH and clarified by centrifugation. The clarified waste is then almost completely decontaminated (10^{-5} Ci/ml total activity, mostly ruthenium, cesium, and technetium, and $<10^{-10}$ Ci/ml α-emitters demonstrated on a laboratory scale) by ion exchange with sodium titanate (ST). Cesium is subsequently removed by ion exchange with a zeolite, and the remaining trace wastes such as ruthenium and pertechnetate ions are removed with an anion exchange material and other reagents. The exchanged ST and zeolite are removed as slurries and combined in slurry form with the suspended solids which were removed in the clarification step. This mixture of slurries is dewatered and dried on a pan filter, then consolidated by pressure sintering, the only high-temperature step in the process."

The hot-pressed titanate ceramic products are largely crystalline. Only a small amount of alumina-silica from the zeolite and silica from the oxidation of the Si metal additive is noncrystalline. About half of the product is rutile, TiO_2. Silicon metal was added to maintain a reducing environment, so many waste constituents occur as metals (Mo, Pd, Rh, and perhaps Te and Fe). Alkaline earths and rare earths form stable and refractory titanates. In the early stages of the work it was found that alkali (Cs, Rb, Na) titanates were formed during consolidation, but these had poor leaching resistance and thermal stability. Therefore, the zeolite exchange step was added, resulting in the fixation of Cs and Rb in pollucite. Other oxides occur uncombined with titania (CeO_2, UO_{2+x}, CeO_2). The presence of each of these phases was identified or confirmed using selected area electron diffraction combined with scanning transmission electron microscopy.

On the basis of what has been learned to date, it is likely that the titanate ceramic is reasonably close to thermodynamic equilibrium under HLW storage conditions and in a closed system (such as a sealed canister). Compositional design such as that applied to supercalcine has not yet been employed to optimize the composition. Using data obtained by PSU, this modification can easily be made, and the Swedish effort is taking a step in this direction. The individual phases--TiO_2, titanates, aluminosilicates, oxides, and metals--are apparently compatible.

A program is currently under way to apply the Sandia Solidifcation Process to DOE defense wastes at Hanford.

SUMMARY AND RECOMMENDATIONS

Research and development activities have demonstrated the potential advantages of various ceramic processing methods for the solidification of HLW. Stable crystalline forms have been identified and synthesized as host structures. The complexity of the processes used varies, both in operation and in resulting properties. Table 7.3 provides an assessment of ceramic-forming processes in the form of a matrix chart.

The efforts to date, although rather limited in scope, have revealed considerable potential; yet, many of them appear to have been shelved. Although ceramics have high-quality properties, much more R&D is required to assess the feasibility of processing them. Even if this assessment should prove favorable, a process can be selected only after the cost and risk to facility operators are considered.

Special emphasis should be given to the "ceramic sponge" adsorption/densification process, since it is potentially simple and inexpensive and produces a stable product.

Improvement of processes, to make them simpler and easier to operate and to increase the longevity of containment and molding materials should also be emphasized. In addition, operating parameters with reasonable latitude, e.g., extended temperature, pressure ranges, should be established for particular compositions. In this fashion, efficiency would be enhanced, and stringent process controls would not be required. Certain borosilicate glass compositions, for example, require melting temperatures of about 1,400°C. Such compositions in particulate form, however, can be densified by hot pressing over an extended temperature range beginning as low as 700°C at about 2,000 psi with insignificant mold interaction.

NOTE

1 The metal in metal matrix composites is a secondary waste containment form (see Chapter 10).

TABLE 7.3

Process - Property Matrix

	Fusion Casting	Glass Ceramics	Sintering		Hot Pressing	Adsorption/ Reaction
			Low Temperature	High Temperature		
A. Process Parameters						
Complexity	Slurry/Particulates to Melter; composition and temperature control	Slurry/Particulates to Melter; composition and temperature control	Mix supersludge as slurry; can as blocks; sinter	Particulates to Consolidation to Sinter-Densification; composition and temperature control	Particulates to Densification; composition and temperature control	Inorganic exchange reaction relatively simple for Cs, Sr. Fluid to solid; completeness of reaction; composition and temperature control
Maximum Temperature	≈1,400°C but composition dependent	≈1,400°C	500-1,000°C	1,200°C	1,000°C	1,000°C
Characteristics of Remote Operation	Difficult: high potential for malfunction; refractories longevity	Difficult: high potential for malfunction, refractories longevity	Simple scrap potential	Difficult: numerous steps; high scrap potential	Difficult: mold longevity; equipment malfunction	Relatively less difficult process control
Contamination Potential	Considerable	Considerable	Considerable	High	High	Considerable

B. Property Characteristics

Leachability	Low if microcracks and pore clusters contained	Very low	Low	Potentially low	Extremely low	Marginally higher (because of residual porosity)
Thermal Conductivity	High	Can be high; depends on phase content	Low	High for fully dense	High	Lower because of residual porosity
Thermal Stability	Good (>1,000°C)	Good (>1,000°C)	Fair	Very good (>1,000°C)	Very good (>1,000°C)	Lower (~500°C)
Dispersibility Resistance	Potentially good	Good	Fair	Good	Good	Poorer

CHAPTER 8

GLASS

DEFINITION AND GENERAL DESCRIPTION

Glass is defined by the American Society for Testing and Materials as "...an inorganic product of fusion which has been cooled to a rigid condition without crystallization." This definition is somewhat too restrictive for scientific use, but it is adequate to characterize the waste form to be discussed in this section.

The structure of glasses is amorphous because the aperiodic structure of the liquid state has persisted essentially unchanged during the cooling into a rigid condition. The formation of a glass rather than of a crystalline solid is entirely a matter of kinetics; that is, when the temperature is reached at which a crystalline phase could form (the "liquidus" temperature) the cooling rate must be fast enough to bypass the natural crystallization tendency of the melt. If the viscosity reaches approximately 10^{14} poises (the so-called transition range) without crystallization occurring, the formation of a glass is virtually assured; that is, the amorphous structure is effectively frozen in, and the rate of further cooling is not critical.

However, it is important to realize that the glassy state remains perpetually metastable with respect to crystallization. If a glass is reheated above the transition temperature range but below the liquidus long enough, a progressive conversion to one or more crystalline phases will usually occur. This conversion is known as devitrification. In a homogeneous glass the conversion invariably begins at the surface (because nucleation sites are available there) and grows toward the interior. Interior surfaces (bubbles) do not normally initiate devitrification. In glasses that contain crystalline inclusions such as unmelted or insoluble components, crystallization begins on these internal surfaces as well. If the glass composition and thermal history are such that these internal nucleants are finely divided and evenly dispersed, crystallization may be orderly, leading to a fine-grained glass-ceramic. On the other hand, if the internal nucleating phases are coarse or unevenly distributed, volumetric changes accompanying crystallization will probably lead to internal fracturing and loss of mechanical coherence of the material.

Glass has many attractive features as a form for the solidification of nuclear wastes. Inorganic glasses are good solvents for nearly all metallic oxides, owing partly to the high temperatures at which the solutions are formed, and partly to the nonspecific nature of the amorphous, glassy structure. Furthermore, the common silicate glasses tend to be relatively insoluble, owing to the three-dimensional nature of the silicon/oxygen network. Thus, divalent and trivalent cations are also effectively made insoluble, because they are, electrostatically, a part of the network. Monovalent cations tend to remain less tightly bound, but the rate of their extraction by water is substantially restricted at ordinary temperatures by the network cages in which they are enclosed. Natural glasses such as obsidian furnish some evidence of the chemical stability of high-silica glasses over geologic time periods, though the significance of this evidence has been overrated. The surviving natural glasses are of recent geological origin, and have been favored by dry environments. (In fact, natural [mineral] glasses are unknown in any pre-Pleistocene geologic environment--even at low temperatures--when water is present.) Well-made glasses are also nonporous, which avoids wasted volume, improves thermal conductivity, and minimizes the area exposed to chemical attack. Glasses are relatively resistant to both ionizing and displacing radiation, and helium (from alpha decay) diffuses fairly rapidly within the open structure of silicate glasses.

Glasses also have some disadvantages for waste solidification. The tendency to devitrification at modest temperatures, with resultant change of properties, has been mentioned. The high temperatures needed to make glasses cause processing problems, particularly corrosion and warping of equipment. Control of gases and vapors produced in hot operations is also troublesome. The concentration of wastes that can feasibly be incorporated in glasses is limited, if chemical durability is to be retained. Commercial glasses seldom contain less than 70 percent of network-forming oxides (SiO_2, Al_2O_3, B_2O_3), of which the major part must be SiO_2. Use of glasses with a lower level of these oxides invites deterioration of chemical durability; glasses with less than 50 percent SiO_2 are usually soluble in acids. Furthermore, glasses are brittle and will crush on impact; thermal gradients can cause cracking. Thermal conductivity is about ten times poorer than that of metals.

STATE-OF-THE-ART SURVEY

Recent surveys of radioactive waste management (IAEA 1976; U.S. ERDA 1976b, 1976c) indicate something approaching a worldwide consensus that HLLW should be solidified, and that glass technology is the most advanced solification alternative. The U.S.S.R. is an exception; Soviet Union solidification studies are supplemented by a program wherein liquid wastes are pumped directly into porous underground strata (W. Bishop, U.S. Nuclear Regulatory Commission, personal communication, 1977).

France and the United Kingdom are fully committed to glass; no other HLW forms are under active consideration. A production-scale vitrification unit is scheduled to go on-stream at Marcoule late in 1977, treating active wastes. Other countries are still giving some consideration to other alternatives, but more money has been and continues to be spent on glass than on all other waste forms combined. As a consequence, the concept of waste fixation in glass has developed such momentum and acquired so many vested interests that an objective critique of its efficacy may be unwelcome.

A preliminary step in such a critique is to survey the status of existing vitrification programs. Fortunately, international communications in the area of waste management are tolerably good, and information is freely available. However, the information is chiefly at the conceptual and schematic level, and engineering details are not usually published. This omission of engineering details is understandable, in view of the constantly evolving nature of engineering design and the sheer bulk of documentation necessary for an adequate description of a working system. But it is important to be aware that competent engineering design can often turn an unpromising concept into successfully functioning hardware. By the same token, inadequate engineering can lead to poor performance in spite of a sound basic concept.

The French Program

The continuous vitrification process (AVM) that is soon to go into operation at Marcoule is the fruit of a major program begun in 1959. The plant is engineered to process 30 liters per hour of HLLW; this corresponds to the rate of liquid waste output from the reprocessing of "Natural G" fuel at the rate of 1 ton per hour.

Each day's glass product, about 430 kg, will be sealed in a metal container 50 cm in diameter and 100 cm high. Ten such containers will be stacked in each of the steel-lined vertical pits in the storage area. Enough pits (220) are installed at present to store the expected output of the first ten years of operation, by which time a national depository may exist to which the stored cylinders can be transported. If not, the storage area can be extended.

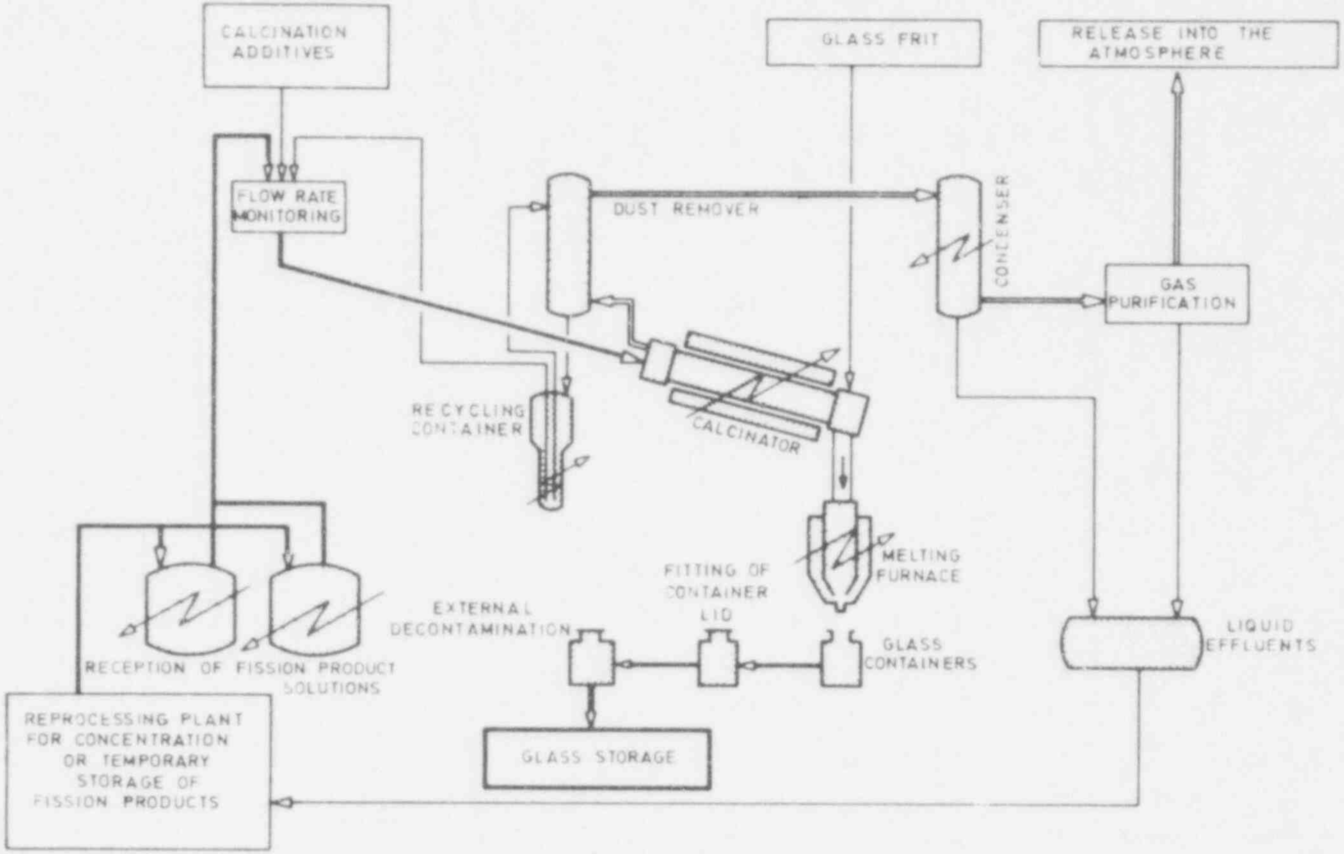
A diagram of operations in the vitrification plant is shown in Figure 8.1. Evaporation and denitration of the HLLW are accomplished in the rotating-drum calciner at about 400 to 500°C. A free-rolling internal bar keeps the solids broken free of the calciner wall. Proper granulation of the calcined solids is also aided by organic calcination additives. Glass frit of a special composition is supplied continuously in the required proportion at a location near the discharge end of the calciner. The mixture of frit flakes and calcine powder falls into the melting chamber, where denitration is completed and the fission-product oxides are dissolved by the molten frit. At eight-hour intervals the melter is tapped by heating a plug of frozen glass in the bottom of the melter. A siphon device prevents the complete discharge of the melter contents. The progress of the casting operation is monitored remotely by observation of the weight of the receiving canister. The flow of materials into the melter is not interrupted during the casting operation.

In spite of the relative simplicity of this process, the necessity of providing for remote operation and maintenance and for complete containment of radioactive materials introduces formidable complications into the equipment. Some of the critical special problems and the measures selected for dealing with them deserve mention.

The melter is a relatively thin-walled, metallic cylinder that nominally operates at 1,050°C. It is possible that this container will some day be inadvertently perforated, allowing molten glass to escape. In such an event, it is expected that the escaping glass will promptly be solidified by contact with a relatively close-fitting ceramic shroud that surrounds the melter. This shroud is shown schematically in Figure 8.1. The shroud remains relatively cool because the melter is not heated by radiation, but by induction from cooled 10 kHz coils that surround the shroud.

The calciner produces large volumes of gas (steam, NO_x, volatile fission-product compounds) and dust. The diagram indicates the provision for treating these off-gases and for recycling contaminated condensate to the reprocessing plant. Dust is recycled as a slurry to the calciner feed.

The rotating calciner cannot be completely sealed at the locations where it joins the stationary parts of the system. To prevent the escape of gases and dust, a reduced pressure is to be maintained in the calciner-furnace section of the



Source: IAEA (1977).

FIGURE 8.1 Diagram of operations at the Marcoule Vitrification Facility (AVM).

system. The idle flow of air through the system is minimized by carefully fitted graphite rotary seals.

These specially engineered provisions seem adequate, but the severest test is the lapse of time under production conditions. The success of this plant will be determined by how long equipment of this complexity can be operated, and particularly by what quantity of waste can be treated before the system reaches an inoperable condition.

The composition of the frit is critical. The permissible range is narrowed almost to vanishing point by the necessity of simultaneously satisfying several conflicting requirements:

1. The frit must melt, flow, dissolve calcine, and homogenize at 1,050°C.

2. The content of fission-product oxides must be acceptably high.

3. Chemical durability must be acceptable.

4. Segregation of an alkali molybdate phase should be prevented.

Frit composition is so critical that a special type must be provided for each of the three kinds of wastes that are to be processed at Marcoule. The composition to be used for Sicral G waste, and the composition of the glass derived from it, are shown in Table 8.1. Note that the concentrations of fission-product oxides are quite low, owing to the relatively large amount of inactive Al_2O_3, Fe_2O_3, and MgO that accompany the fission products in this particular type of HLLW. The volume reduction factor (HLLW volume/glass volume) is also low, only 5.4.

Difficulty with molybdates has been encountered in every vitrification program. Molybdenum, one of the most plentiful fission-product elements, occurs in oxidized glasses as the molybdate anion, which is reluctant to participate in network formation. Accordingly, a fused alkali molybdate phase of low viscosity frequently separates from the glass, even at melter temperatures. A high level of B_2O_3 in the glass (24 percent) will hold the molybdates in solution, but such a high level conflicts with other considerations. At the compromise B_2O_3 level (14 percent), spherical nodules of crystalline alkali molybdates will occasionally be encountered in the product glass. These nodules are water-soluble, which leads to concern as a matter of principle, but it can be argued that they have little practical importance because the vast majority will be fully encapsulated by the glassy matrix.

TABLE 8.1

Frit and Solid Waste Compositions

Chemical Component	Frit (wt%)	Solid Waste (wt%)
SiO_2	57.5	48.8
B_2O_3	25	14.2
Na_2O	17.5	15.0
Al_2O_3		8.4
Fe_2O_3		2.6
MgO		6.3
Ni/Cr		0.2
Fission products		4.5

Source: Bonniaud et al. (1976).

The capacity of the Marcoule vitrification plant is sufficient for the weapons-waste processing that is to be done there, but is too small to handle the large volume of commercial light-water reactor waste that will be generated at the reprocessing plant at La Hague. The limiting element of the AVM plant is the poor heat-transfer performance typical of a heated-wall melter, which is aggravated by the high viscosity of the melter contents. An increase in the physical size of such a melter makes the surface/volume ratio smaller, and the heat transfer performance even worse. An effective way of solving the problem is to generate the heat directly within the glass. This is done in commercial glass plants by inserting electrodes into the melt. The French, however, have chosen to work with a prototype that retains the concept of induction melting. A nonconductive ceramic container is surrounded by induction coils operating at 100 to 200 kHz; these coils are designed to induce circulating electrical currents in the molten glass.

The British Program

The British vitrification program began almost 20 years ago at Harwell with the FINGAL pilot plant. Striving for the ultimate in simplicity, the designers limited the number of processing vessels to one, a heated cylinder that combined the functions of evaporation, denitration, vitrification, and storage. Liquid waste and a suspension of silica in sodium tetraborate solution were simultaneously metered into the cylinder. As the level of the accumulating molten glass rose, a rising zone of externally applied heat was provided to follow it. The FINGAL plant was shut down in 1966 after completing 72 runs, of which 8 involved the processing of fully active waste. Stainless steel was used for the container, and operating temperatures were about 1,050°C.

In 1972 a decision was made to install a vitrification process for routine use. This plant will use the HARVEST Process, which is a modification and enlargement of the FINGAL concept. A pilot model of the plant is being tested at Harwell.

The simplicity of the HARVEST concept is attractive, but the throughput rate will probably be low, owing to the large amount of heat consumed by evaporation of water before melting can begin. The use of exterior heaters does not provide the fail-safe feature of the French AVM process, with its cool shroud surrounding the melting chamber.

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The German Program

German R&D on vitrification has been under way for about ten years. Work is going on at three sites, and several competing concepts are under study. The VERA concept being developed at the Karlsruhe Nuclear Research Center is at an advanced stage.

The VERA process uses a spray calciner, which is heated by the injection of superheated steam at 600°C. The calciner product joins a metered stream of glass frit in a metallic melter at 1,150°C, much as in the French process, and the contents of the melter are periodically drained into a metallic storage canister.

An important feature of the VERA process is the use of formic acid to deacidify and denitrate the liquid waste before it enters the calciner. This significantly reduces the volatilization of Ru as oxide, which is a troublesome feature of processes that perform the calcination in an oxidizing atmosphere. A further virtue of pre-denitration is that it virtually eliminates the production of uncondensable off-gas in the calcination.

Recent information (IAEA 1977) indicates that the VERA concept has been modified in favor of a refractory-lined melter (Figure 8.2). Heat is supplied directly to the molten glass by immersed, renewable molybdenum electrodes. Evaporation and denitration are carried out in the same enclosure, by spraying a slurry of powdered frit and HLLW directly on to the surface of the melt. The favored frit composition is shown in Table 8.2.

TABLE 8.2
Frit Composition

Chemical Component	Frit (wt%)
SiO_2	51.87
TiO_2	8.82
Al_2O_3	1.31
B_2O_3	14.02
CaO	2.62
Na_2O	21.36

Source: Personal communication from R.E. Blanco, Oak Ridge National Laboratory, to D.E. Ferguson, 1977.

The rationale for this particular choice of composition is not available, but its principal novelty is the use of TiO_2 which, in moderate amounts, will lower the viscosity of glass melts without seriously reducing the chemical

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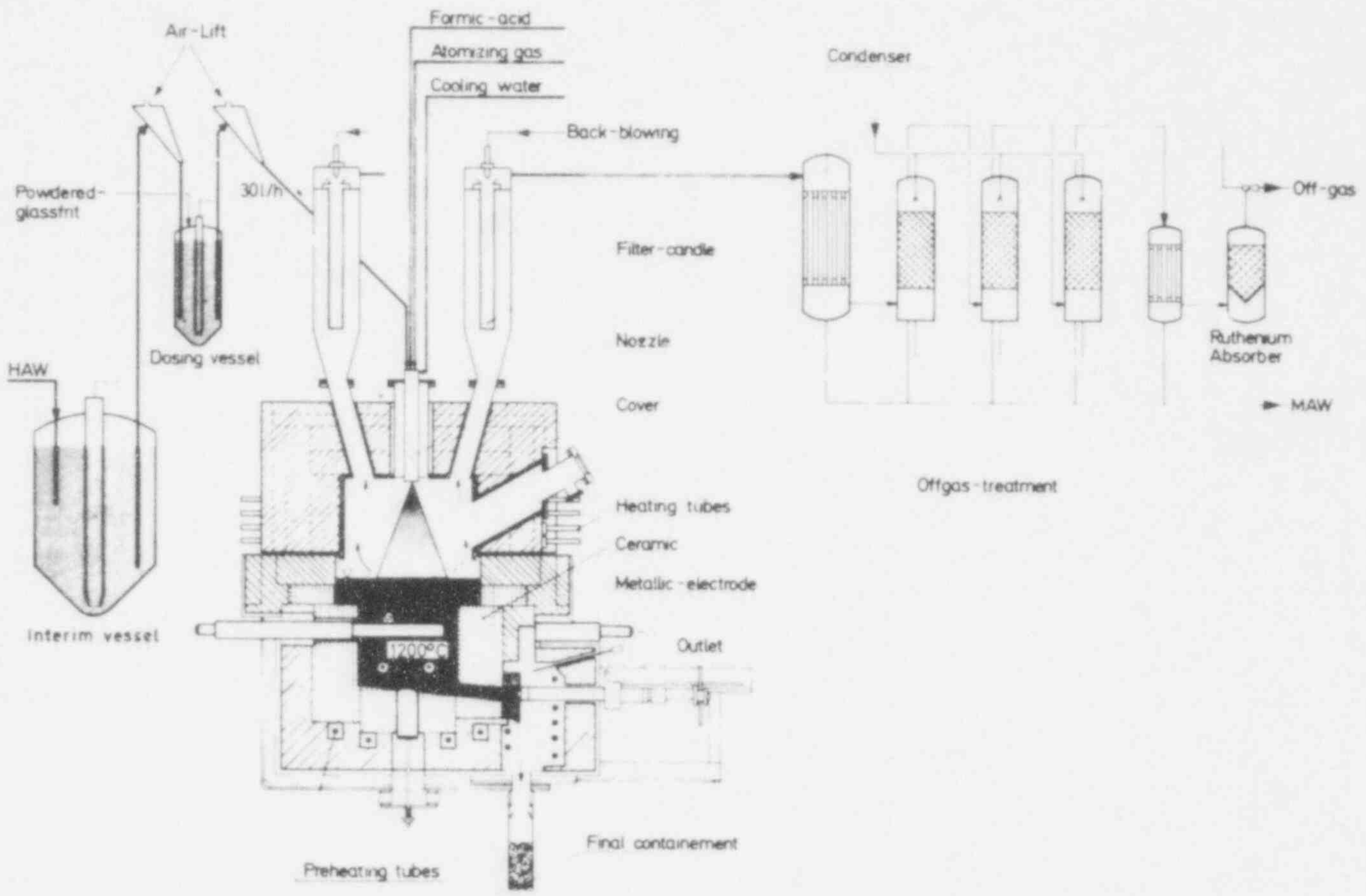


Source: IAEA (1977).

FIGURE 8.2 Simplified flowsheet and illustration of refractory-lined melter (VERA).

durability. The frit is capable of dissolving 30 percent waste solids at the processing temperature of 1,200°C.

Other German vitrification processes are: (1) a thermite reaction with MnO_2 as oxidizer, aluminum powder as fuel, and silica and calcine as glass-formers (Karlsruhe); (2) a glass-ceramic (Hahn-Meitner Institute); (3) a drum dryer fed by a slurry of denitrated fission products, silica, and lime, producing a material suitable for melting directly in a storage canister (Julich); and (4) the PAMELA process, in which denitrated waste is mixed with phosphoric acid and melted at about 1,000°C in platinum to form a low-viscosity glass that is collected as droplets (Gelsenberg and Eurochemic). These droplets are subsequently dispersed in a metal matrix for protection and for heat transfer.

The United States Program

The waste solidification problem in the United States differs in certain respects from that in Europe. Most European wastes are single-phase acidic solutions of relatively fresh fission products arising from the reprocessing of power-plant fuel elements. In the United States the reprocessing of commercial fuel would involve similar compositions and much of the work is aimed at such wastes. However, commercial reprocessing is currently deferred and, except for the short-lived operation at West Valley, New York, most of the existing liquid wastes are a by-product of the United States nuclear weapons program. Much of this waste is quite old, with a correspondingly low specific rate of heat generation. The chemical composition is variable, reflecting the successive generations of reprocessing technologies that have been used. Furthermore, except at the Idaho reprocessing plant, the military wastes have been and continue to be neutralized with sodium hydroxide. Neutralization causes essentially all fission-product elements other than Cs to be precipitated. Thus most United States wastes are a two-phase mixture consisting of sludge and supernate.

All the military reprocessing centers include vitrification among their solidification alternatives. Most of the development work on vitrification of commercial wastes has been done and continues to be done at Battelle Pacific Northwest Laboratories, although a significant program oriented to ERDA waste vitrification is now being developed at the Savannah River Plant. The PNL studies deal mostly with acidic wastes, but process modifications have been worked out for other varieties of liquid waste.

The PNL program includes parallel efforts on developing two concepts: the "in-can melter" and the "continuous ceramic melter." Like the British process, the in-can melter carries out the melting in the same canister that will encapsulate the solidified waste for storage. In the continuous ceramic melter process, a separate electrically-heated, refractory-lined melter delivers molten glass to the storage canister. Various methods for preparing the input to these melters are being considered, but spray calcination of an acid waste appears to be the favored alternative. The glass-forming ingredients are added to the calciner output as a separate metered stream of frit. The frit composition is severely constrained by the need for a relatively low processing temperature (1,050°C); a zinc borosilicate was once preferred, but the ZnO content is being substantially lowered in the newest formulations.

EVALUATION OF CURRENT R&D

The previous section has commented on some specific aspects of each of the major national programs. This section deals with elements that are for the most part common to all vitrification schemes.

Processing Technology

It is not easy to engineer a process for the converting of HLLW into glass in a totally enclosed, remotely operated, remotely maintained system. The most serious difficulties arise from the need for high temperatures. The problem in the selection of materials is compounded by the fact that molten glass is both corrosive and a liquid; leakage is accordingly an ever-present possibility. The high temperature also promotes volatilization of several radionuclides, especially Ru and Cs. The drying and denitration that must precede glassmaking produce large quantities of gases and vapors, which are more or less contaminated with radioactive dusts and vapors.

Another problem inherent in small-scale glassmaking which, unlike those already named, seems not to be explicitly recognized is that of providing adequate heat transfer. Because the glass must be melted at a viscosity of about 100 poises in small containers, convective heat transfer is almost completely ineffective; and because these glasses are opaque to near-infrared, radiative heat transfer is negligible. Thus neither of the heat transfer mechanisms that predominate in commercial glassmaking is available. Only conduction remains. As a result of inadequate heat transfer, the production rate of heated-wall melters is disappointingly small. The extra time required to process a unit of material means a low value for the true merit index of a plant; that is, the number of tons of glass produced between major overhauls.

A trend toward immersed-electrode melting is apparently well under way in both the German and the U.S. programs. This trend is to be commended. The molten glass itself becomes the heat-producing resistive element, with the result that a substantial portion of the applied electrical energy is released where it is needed. Combination of immersed electrodes with a refractory-lined melter basin can virtually eliminate restrictions on vitrification temperature, if molybdenum electrodes are used.

Another important potential advantage of this type of melter is the fact that it can be operated with a "cold top"; that is, with cold unmelted batch solids floating on the surface of the melt. It is well known in commercial practice that this configuration quite effectively controls the evaporation of volatile components of the glass. The cold material acts simultaneously as a condenser and filter, and continuously returns volatile components to the melt.

It is distressing to find, however, that both in the United States and in Germany the design of refractory-lined electric melters has apparently been done on an ad-hoc basis, in spite of the existence of a well-developed, commercial technology that corresponds very closely to the requirements for vitrifying HLLW. An example of the commercial technology is the Pochet melter (U.S. Patent numbers 3,143,328; 3,429,972; and 3,580,976) currently used by the Ferro Corporation and the Babcock & Wilcox Company, Refractories Division. The latter organization uses the Pochet furnace to melt pure kaolin clay, which illustrates the extraordinary high-temperature capabilities of this technology. The failure to draw fully upon available commercial technology has delayed to some extent the development of the refractory-lined melter for use in radioactive waste solidification.

Little reference has been made to the use of graphite as a glass-contact material, a surprising oversight. Graphite is chemically so different from the usual glass-contact materials that its use may seem unthinkable, but it has much to recommend it: its temperature limitations are minimal; it is easy to fabricate; it is electrically conductive, cheap, and nonstrategic; and it can be disposed of by oxidation. Another potentially useful characteristic is the fact that a fully reduced glass does not wet graphite (Swarts 1965). The reducing effect of graphite on transition-metal cations will have consequences that need to be examined. In the case of molybdenum and ruthenium, reduction would tend to solve existing problems of immiscibility and volatility, respectively.

The use of ferrous superalloys as glass-contact materials in a melter is a marginal technology at best. The upper service limit for these materials is about 1,100°C, yet this is approximately the minimum temperature required for melting the frit and dissolving the fission-product oxides. A process with so little latitude is not desirable.

As a general comment on processing technology, it is disappointing to find that so little effective use has been made of information and technology that already exists in the glass industry. To the Panel's knowledge, agencies and contractors have not hired experts in the science and technology of glass, nor have they effectively used consultants in the field. Even the professional societies remained essentially unaware of these activities until recently. Waste vitrification activities began in the United States in the late 1950s; the Waste Solidification Engineering Prototypes pilot-scale, in-can melting program was completed at PNL between 1966 and 1970; yet the Nuclear Division of the American Ceramic Society did not hold its first half-day session on Management of Nuclear Wastes until 1974.

Quality Control

In ordinary manufacturing operations, quality is maintained by inspection of the product. If product quality is critical, 100 percent of the product is inspected. However, all the vitrification processes for silicate glasses are designed to operate under totally enclosed conditions, including placement of the glass in its final container. Thus there is no provision for inspection of a product whose quality is usually considered to be critical.

The absence of inspection is particularly serious for the in-can type of melter, where layers of virtually unmelted material could exist without detection. Indeed, the desire of the process operator to increase throughput and minimize operating temperatures is an incentive that can be depended on to lead frequently to the production of poor-quality glass if inspection is absent.

On the other hand, processes that use a separate melting chamber inherently provide a verification that the molten state has been achieved; otherwise, the contents of the melter could not be tapped off. The viscosity can be roughly estimated from the time necessary to cast a certain mass of glass. If a viewport is provided, the presence of undissolved material or other gross inhomogeneities can be detected by observation of the luminosity and profile of the flowing stream of glass. These are only limited types of inspection, but will probably serve the purpose.

The only existing vitrification process that might be completely inspectable is the bead-forming operation that is part of the PAMELA phosphate glass process. Beading could also be done with silicate glasses if a melter were used that could deliver glass at the requisite low viscosity (about 10 poises).

A stream of glass at a higher viscosity (1,000 to 10,000 poises) can be mechanically sheared into "gobs" and rolled into spherical marbles with standard machinery, but those who have experience with this type of operation advise against attempting it in a remote operation. Constant operator attention is necessary, because the shears must constantly be lubricated in a critical way, and they must frequently be removed and resharpened (Richard Hunter, Johns Manville Corporation, personal communication, 1977; William Shuler, PPG Industries, personal communication, 1977).

The Leachability Concept

The worldwide enthusiasm for glass as a solid form for incorporating nuclear waste is puzzling, because the rationale for the preference is nowhere explicitly stated. Nonetheless, it is clear from the data reported in connection with composition studies that leachability is perceived as the performance property of paramount importance. This perception probably derives from a "worst-case" scenario in which the bare waste form is inadvertently and irretrievably exposed to flowing water. Under these conditions it is obviously desirable that the rate of dissipation of radionuclides into the water be as low as practical. A solution rate of 10^{-7} g/cm^2/day seems to be regarded as acceptable, apparently because it is comparable to the solution rate of chemical Pyrex (Corning Glass Works, Code 7740) under the same conditions.

Before making further comments on the leachability concept, some background information is needed on the nature of the interaction of glasses with aqueous solutions. The issue is not one of simple solubility. A great deal of published information is available on this subject, because the aqueous reactivity of glasses of all kinds has been a matter of intense practical concern for many years.

The interaction of water with silicate glasses is hydrolytic in character; that is, the essential reaction is the cleavage of an Si-O-Si bond by a water molecule to give a pair of SiOH groups. Composition is the principal variable that influences the rate and extent of this hydrolysis. Pure fused silica is quite resistant to hydrolysis, owing to its fully crosslinked structure. Unless the conditions of temperature and water vapor pressure are extreme, the hydrolytic reaction with pure vitreous silica is very superficial, probably only monomolecular.

When oxides of low-valency cations are dissolved in silica in the glass-making process, the crosslinking of the structure is progressively destroyed, and hydrolysis becomes easier. Sodium silicate glass in fact becomes totally soluble in water when the silica content is reduced to about 70 percent by weight.

Oxides of divalent ions (Ca, Mg, Sr) do not have such a catastrophic effect on hydrolytic susceptibility. Moderate additions of these oxides along with oxides of the monovalent cations can provide compositions that combine relatively low melting temperature with acceptable chemical durability. Commercial glasses are designed in this general way. Useful compositions in the soda-lime-silica system have the approximate formula $Na_2O \bullet CaO \bullet 6SiO_2$. Commercial compositions usually contain about 70 percent silica by weight.

The presence of these low-valency cations in a glass complicates the chemistry of the water-glass reaction. As the cations are hydrolyzed, they become water-soluble hydroxides that will be extracted and carried away by a moving aqueous environment. However, if the silica content of the glass is high enough to make the glass "durable" by commercial standards, the three-dimensional silica network remains in place. The exposed surface thus becomes covered with a thin layer of hydrated silica so impermeable that the effective rate of hydrolysis soon drops essentially to zero.

As the silica content of the glass is reduced below 70 percent, the behavior of the glass becomes increasingly complex. As the film of residual silica becomes less highly polymerized it becomes more and more soluble in water and particularly in acids. A condition may be established in which all constituents of the glass are removed at nearly the same rate, thus mimicking the relatively simple process of solution characteristic of a sparingly-soluble pure compound. Some of the fission-product glasses apparently behave in this manner. Glasses with less than 50 percent silica are usually found to be soluble in dilute acids; that is, at pH of 4.0 and below.

If the aqueous environment is stationary, the chemical attack tends to become autocatalytic, owing to the accumulation of the intensely alkaline hydrolysis products. The film of hydrated silica cannot withstand the corrosive effects of strong alkali, so leachability may increase with time under these conditions.

The use of moderate amounts of B_2O_3 in a silicate glass composition introduces still another significant consideration; namely, phase separation. Borosilicate glasses are unstable; they are known to separate into silica-rich and borate-rich glassy phases. The familiar process for making high-silica laboratory glassware is based on this fact. Not so well-known is the fact that borosilicates as a class are subject to phase separation. Even the justly renowned Pyrex is believed to be phase-separated as commercially produced (Charles 1964). If Pyrex is annealed too long or at too high a temperature, the texture of the phase separation coarsens and the chemical durability rating drops from excellent to useless (Volf 1961).

Enough has been written to demonstrate that the interaction of glasses with water and aqueous solutions is too complex to be described by a single figure unless the number of parameters is arbitrarily reduced. This reduction is accepted practice in the evaluation of solid waste forms; it is customary to use only distilled water, frequently renewed. With selected compositions, more elaborate testing is done (Mendel et al. 1977).

Little effort has been made under the current radioactive waste management program to assess the performance of glasses in the presence of steam at high pressure and temperature (i.e., under hydrothermal conditions). Nevertheless, the literature contains ample evidence that glasses even of a much stabler "basaltic" composition deteriorate rather completely at about 300°C and 1 kbar in a matter of days. Under the same conditions, crystallized glass shows no change at all (Hawkins and Roy 1963). In the actual storage environment, high-temperature, moderate-pressure conditions, rather than the presence of a cool flowing aquifer, will probably prevail. It is not unlikely that a vitrified waste will be exposed to hydrothermal conditions after geologic disposal. Sealed burial under several hundred meters of earth may provide the high pressure (approximately 1 psi per foot of depth), and nuclear self-heating may provide the high temperature, depending on the power density employed in the repository and the thermal conductivity of the surroundings. Water will be present in a shale or salt environment, and may be present even in an igneous formation, given fissures penetrated by ground water. Under hydrothermal conditions even commercial glasses are rapidly converted to a friable mass of crystalline and amorphous hydrates. Charles (1958) found that soda-lime glass rods 0.1 inch in diameter completely deteriorated after exposure to saturated steam at 250°C for seven hours. During this decomposition, much of the sodium and part of the calcium was no doubt released in a water-soluble form.

Since the typical radioactive waste glasses proposed are considerably less stable than commercial soda-lime glass, they will unquestionably undergo rapid metamorphism if exposed to hydrothermal conditions. The leachability of the resultant material will not be that projected by laboratory tests on the glass at 25ºC or 100ºC. The metamorphosed glass will be an assemblage of hydrated (and possibly anhydrous) crystalline phases with a very different leachability than the parent glass. It follows that if hydrothermal conditions are encountered, little has been gained by vitrifying wastes rather than incorporating them in cement.

The composition of waste-fixation glasses can be designed with the possibility of a future hydrothermal reaction in mind. If composition is appropriately chosen, it should be possible to ensure that hydrothermal metamorphosis will produce a mixture of phases that includes enough clays and zeolites to retain the fission-product ions in an immobile state. This dimension of the vitrification option deserves attention.

The rate of transport of ions from a solid into a solution is strongly dependent on temperature, E , pH, and whether or not the system is open or closed. Unless these parameters are specified, any measurement of leachability cannot be regarded as meaningful. Our conclusion about the term "leachability" as presently used, therefore, is that it is an ill-defined quantity that often has little relevance to conditions that will be encountered in a repository. Not only are the typical temperatures used in the tests unrealistically low, but the tests themselves do not take into account hydrothermal conversion, devitrification, and the interaction of the solid waste with the host rock, which is a major variable in the system. The release of ions from the crystalline phases formed after reaction of the waste form with water and rock is a more meaningful parameter than the leachability of the waste form alone.

It is our belief that the limited sort of leachability testing that has been done is chiefly relevant to the transportation and temporary storage steps of the waste-management system. For example, if the solid wastes were inadvertently dumped into a river during a transportation accident, the typical leachability measurements would give a good indication of the rate of dissolution of the wastes. After solidified waste has been emplaced in a properly chosen geological disposal site, leachability as currently defined has little importance. To be relevant to this step of the system, leachability studies should characterize the material that remains after hydrothermal conversion of the glass into the phase assemblage (including the solution phase) formed by the waste/rock interaction.

NOTE

1 A Canadian field test in a cool flowing aquifer was started in 1958. The glass was made of 85 percent nepheline syenite and 15 percent lime with tracer quantities of fission products. Their blocks of glass were buried in an alluvial soil, below the water table. Periodic monitoring of ^{90}Sr release showed that the release rates dropped very steeply the first few years, reaching a negligible level within ten years (Merritt 1976).

CHAPTER 9

CEMENT AND CONCRETE COMPOSITES

INTRODUCTION

Concrete, the most widely used building material, consists of sand, gravel, crushed rock, or other aggregates held together by a hardened paste made of hydraulic[1] cement and water. The thoroughly mixed ingredients, when properly proportioned, make a plastic mass that can be cast or molded into a predetermined size and shape. Once the cement is hydrated, the resulting concrete becomes comparable in strength and hardness to many types of natural rock. The most valuable engineering properties of cement paste and concrete are their workability, durability (against atmospheric weathering, chemical attack), watertightness, and dimensional stability (shrinkage and/or expansion after setting).

The relevant properties of concrete that make it useful as a material for incorporating radioactive waste are its unit weight or density, leachability, thermal stability and conductivity, and radiation stability. Strength development appears to be adequate and is of importance mainly during transportation. 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. 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. This amount is usually expressed as water-to-cement ratio (w/c). Generally, a lower w/c gives a product of higher quality.

DEFINITIONS AND BACKGROUND

Two different kinds of hydraulic cement exist, both of which can be used as matrices for incorporating primary containment forms. These are the "portland cements" and "high-alumina" cement.

Portland Cements

Portland cements are inorganic materials consisting primarily of tricalcium silicate (Ca_3SiO_5), dicalcium silicate (βCa_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_6$), and a calcium aluminoferrite solid solution. The ratio of these components, by definition, must lie within a certain range. Cement clinker, containing the above phases, is interground to higher surface areas (e.g., 3,500 cm^2/g) with a defined amount of gypsum ($CaSO_4 \cdot 2H_2O$) to form cements.

The American Society of Testing and Materials (ASTM) classifies portland cement into five types according to mineralogical composition and performance characteristics. Various additives (e.g., fly-ash, blast-furnace slags) and admixtures (e.g., water-reducing and air-entraining compounds) can be added to the mix to influence the previously identified engineering properties of the product. Table 9.1 shows typical values for the basic properties concretes with portland cement bases.

High-Alumina Cement

High-alumina cement is composed predominantly of monocalcium aluminate ($CaAl_2O_4$). Its rate of strength development at the early stages of reaction with water is much higher than that of portland cements. It has been developed mainly as a cement highly resistant to chemical attack by seawater, sulfate solutions, and high-alkali soils.

At ordinary concreting temperatures, the main products of hydration are metastable calcium aluminate hydrates. At temperatures above 25°C and high humidity, the conversion to stable hydrates results in an increase in density from less than 2.0 to more than 2.5 g/cm^3. This change may lead to increased internal porosity of the matrix, usually accompanied by increased permeability. A decrease of compressive strength and reduced resistance to sulfate waters and other media will follow. A low w/c is desirable in portland cements as well as in other mixes designed for chemical resistance.

Aggregates

Depending on structural, environmental, and economic requirements, many types of natural and artificial rocks are added to cement paste to form concrete. A dense, compact aggregate is believed desirable for any structure in which low permeability and high durability are required. In all HLSW applications, including grouting, the solidified waste will act as the "aggregate." In other waste disposal

TABLE 9.1

Typical Concrete Properties[a]

Density	2,200 - 2,300	kg/m^3
Compressive Strength	150 - 1,000	kg/cm^2
Tensile Strength	15 - 100	kg/cm^2
Modulus of Elasticity	250,000 - 400,000	kg/cm^2
Average Thermal Coefficient of Expansion		
Cement paste	0.000013	$(^{o}C)^{-1}$
Limestone aggregate	0.000006	$(^{o}C)^{-1}$
Quartz aggregate	0.000097	$(^{o}C)^{-1}$
Concrete	0.0000056-0.0000104	$(^{o}C)^{-1}$
Thermal Conductivity	1.2 - 1.6	kcal/m hr^{o}C
Drying Shrinkage	0.06 - 0.08% over 1-year period for w/c = 0.45	

[a] All values are dependent on the materials and proportions used, and upon the conditions under which concrete was made and has hardened.

applications, aggregates may be used in such products as concrete containers or silos.

STATE-OF-THE-ART REVIEW

Considering the advantages of low-temperature cement processing, experimental work on this waste form is surprisingly scarce. In the Panel's view, cement products, solely on the basis of their alleged high leachability (compared with metal matrix forms and some glasses), are often unjustifiably excluded from consideration as a medium for incorporating HLW.

United States Experience

Existing Commercial High-Level Wastes

At present, the only commercial radioactive wastes existing in the United States are being stored at a plant in West Valley, New York owned by Nuclear Fuel Service. Among the alternatives being considered (U.S. ERDA 1976b, U.S. NRC 1976) for solidifying this waste 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, a federal repository, or both.

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. Alternatively, the sludge and/or zeolite might be incorporated into a glass. This option is now being actively developed for application to DOE neutralized waste.

Shale fracturing. In this technique, a grout consisting of low-temperature ceramic 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 after injection, permanently fixing the radioactive waste in a rock-like sheet of concrete within the shale formation. Subsequent injections ideally form sheets parallel to and a few feet above the first.

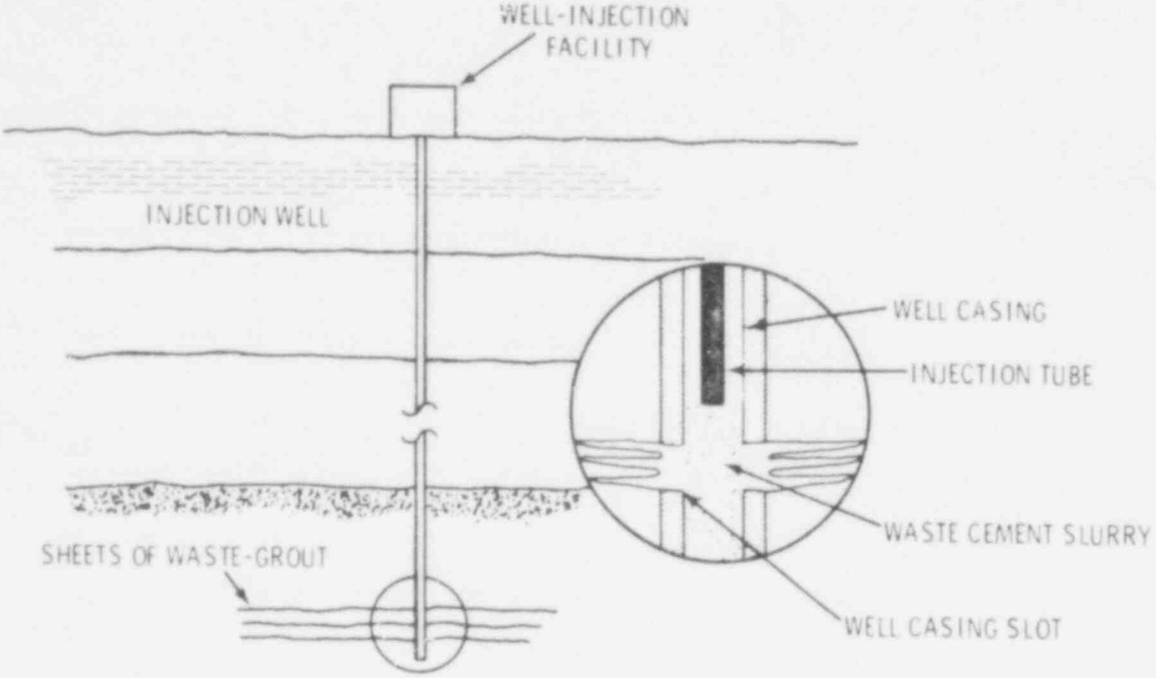
The shale fracturing technique is illustrated in Figure 9.1. The shale fracturing option is a waste disposal process that has been successfully used at Oak Ridge National Laboratory for permanent disposal of locally-generated intermediate-level waste (ILW) solutions.

Shale cement process. This process is an outgrowth of the shale fracturing alternative. The process is carried out at ambient temperature and entails combining the liquid wastes with an appropriate mixture of cement and solid mineral additives, including 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 alternatives has its advantages and disadvantages (see Table 9.2), and all require further research and development.

In a recently published report (U.S. ERDA 1977c) on the alternatives for long-term management of defense HLW at the Savannah River Plant, 9 of the 23 alternative plans discussed consider the use of concrete as a waste matrix. (The average chemical composition of fresh HLW from the Savannah River Plant is shown in Table 9.3.) 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 in diameter by 10 ft high. The welded, inspected, and decontaminated canisters will be deposited at onsite or offsite disposal localities. Each canister would consist of 200 gal of concrete containing 36.4 kCi of ^{90}Sr-^{137}Cs with a heat output of 209 watts. The conceptual waste solidification process is shown in Figure 9.2.

Oak Ridge National Laboratory

Two different processes of immobilization of radioactive waste solutions have been pursued at ORNL: (1) the shale fracturing process and (2) waste fixation in cement for drum storage (R.A. Robinson, ORNL, briefing to Panel on Waste Solidification, 1977; Weeren et al. 1976). Although developed for ILW, there is no evidence to suggest that further research could not lead to HLW applications. The shale fracturing process consists of fracturing the horizontally deposited red shale formation by water injection, subsequent injection of waste-containing cement grout, and hardening of the grout underground. No evidence has been found by ORNL to suggest that this silicate waste/rock interaction will cause any problems. A grout typically consists of portland cement, ILW solution, and various additives. In this particular case the additives are fly-ash, Attapulgite-150 (a palygorskite-type clay mineral product), Grundite (an illite-type clay mineral



Source: U.S. NRC (1976).

FIGURE 9.1 Shale fracturing and grout concept.

TABLE 9.2

Advantages, Disadvantages, and Status for NFS Waste Management Alternatives Based on U.S. ERDA Processes

Alternative	Advantages	Disadvantages	Current Technological Status
Conversion to Cement	Low-leaching solid product Good retrievability Easily transported	Difficult to change to alternative form if necessary Technology has not been demonstrated Need to store large volume of residual salt Potential for container to pressurize Salt product would contain significant quantities of water (up to 20 percent)	Process is under active laboratory development, and conceptual design of facilities for application to U.S. ERDA neutralized high-level radioactive wastes

Shale Fracturing	Low-leaching solid product No offsite shipping Immediate placement in geologic formation Process has been field tested using intermediate-level radioactive waste Not susceptible to environmental influences	Site verification required Criteria for disposal of long-lived alpha emitters not established Waste is not retrievable Not possible to change to alternative form Requires pipeline transport of liquid high-level waste for distance of about 1 mile Technology has not been demonstrated for NFS waste	Full-scale demonstration for U.S. ERDA neutralized low-level and intermediate-level radioactive wastes at ORNL
Shale Cement	Low-leaching solid product Key portions of process use state-of-the-art technology Good retrievability Easily transported	Large volume of waste-grout mixture must be stored Potential for container to pressurize Difficult to change to alternative form if necessary Technology has not been demonstrated	Process is in the conceptual stage

Source: U.S. NRC (1976).

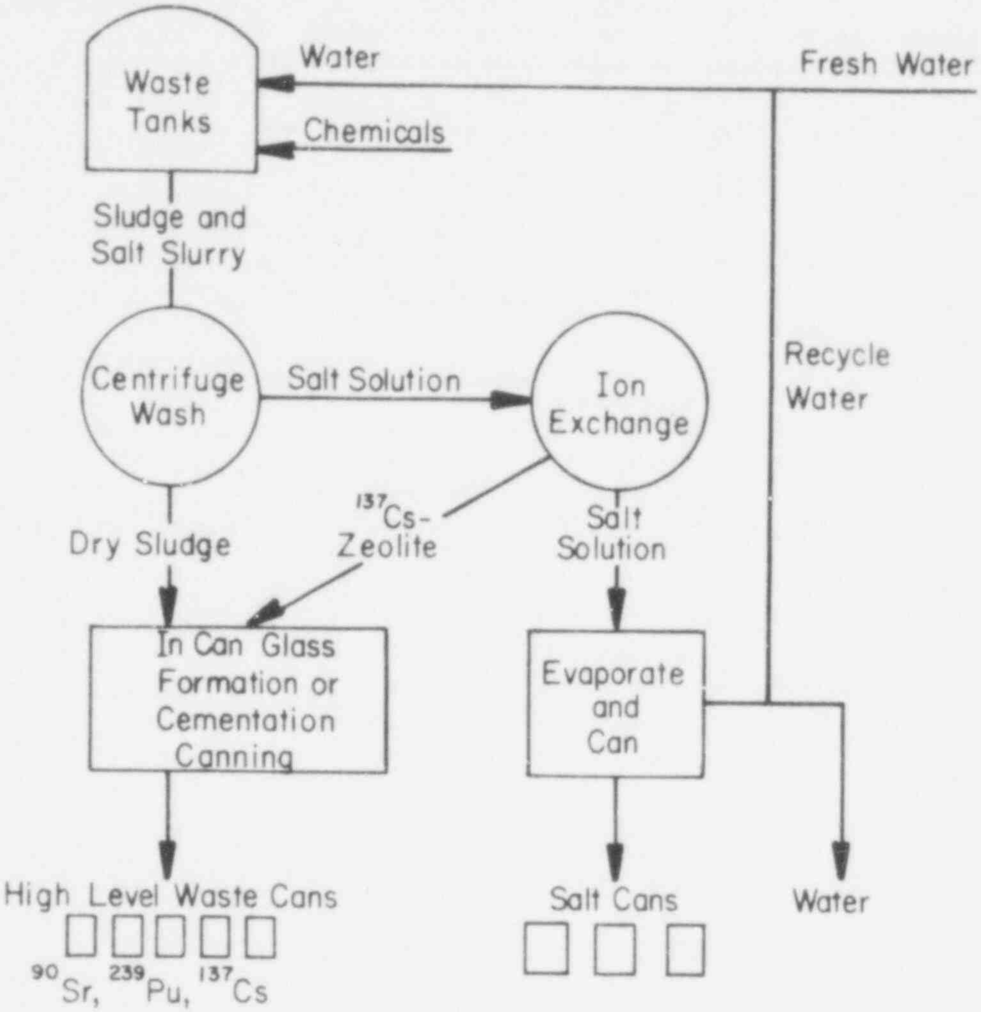
TABLE 9.3

Average Chemical Composition of Fresh SRP High-Level Waste

Constituent	Molar concentration
$NaNO_3$	3.3
$NaNO_2$	<0.2
$NaAl(OH)_4$	0.5
$NaOH$	1
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 (1977c).



Source: U.S. ERDA (1977c).

FIGURE 9.2 Conceptual waste solidification process.

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product), and chemical admixtures to modify cement setting. Other combinations are possible. In the terminology used in this report, the radionuclides are fixed in the primary containment phases provided by these open-structured silicates, which are themselves incorporated into a solid cement matrix. Using the IAEA technique, leach rate values comparable to those for wastes incorporated into borosilicate glass were obtained for the ILW grouts (Doerr et al. 1974, Moore et al. 1975). Leach rates for Cs were substantially reduced by adding Grundite, pottery clay, or Conasauga shale to the grouts. A substantial decrease in the leach rate for radioactive Sr has been achieved by adding stable Sr or Ca (e.g., in the form of chlorides) to the waste. The amounts of Cs and Sr leached out of the hydrofracture grout depend on the "quality" of curing (which is lower when grout is cured in high relative humidity) and are inversely proportional to the time of curing.[2] The leachability also depends on the composition of the leachant; distilled water gives the highest values (Moore 1976).

Similar grouts can be used for storing wastes containing radionuclides in drums. The process is technically simple; the main disadvantage is the possibility of pressurization arising from radiolysis.

Leach studies of irradiated Type I portland cement specimens containing various iodates showed that ^{60}Co irradiation has little, if any, effect on the leachability of iodine from the concrete by CO_2-free distilled water. Conversion of iodate to iodide is insignificant. Radiolysis of water and formation of gaseous products has not been studied (J.G. Moore, Oak Ridge National Laboratory, personal communication, 1977).

Idaho National Engineering Laboratory

Alternative methods of solidifying Idaho Chemical Processing Plant (ICPP) wastes from Navy reactors have been studied at INEL. One of the possibilities explored was the incorporation of ICPP calcines into calcium-aluminate-cement-based concretes. Concretes containing approximately 30 to 60 wt% of calcine exhibited adequate strength of above 3,000 psi. The ability of several additives to decrease the leach rates of Na and Cr, the two most leachable ions, was studied. The Na leach rates were significantly reduced by the addition of $CaCl_2$ or sand. Using high-alumina cement and assuming a heat source of 30 W/s/m^3 (for 50 wt% of calcine) and thermal conductivity of 0.2 J/K•m•s, the centerline temperature was calculated to be 80°C--well below the temperature (250°C) where the thermal stability of high-alumina concrete is suspect. Although suitable processing techniques remain to be developed, incorporation of ICPP wastes in concrete appears to be practical.

Brookhaven National Laboratory

The results of several procedures involving the use of concrete for incorporating radioactive waste have been reported by the Brookhaven National Laboratory (Colombo and Neilson 1977a, 1977b).

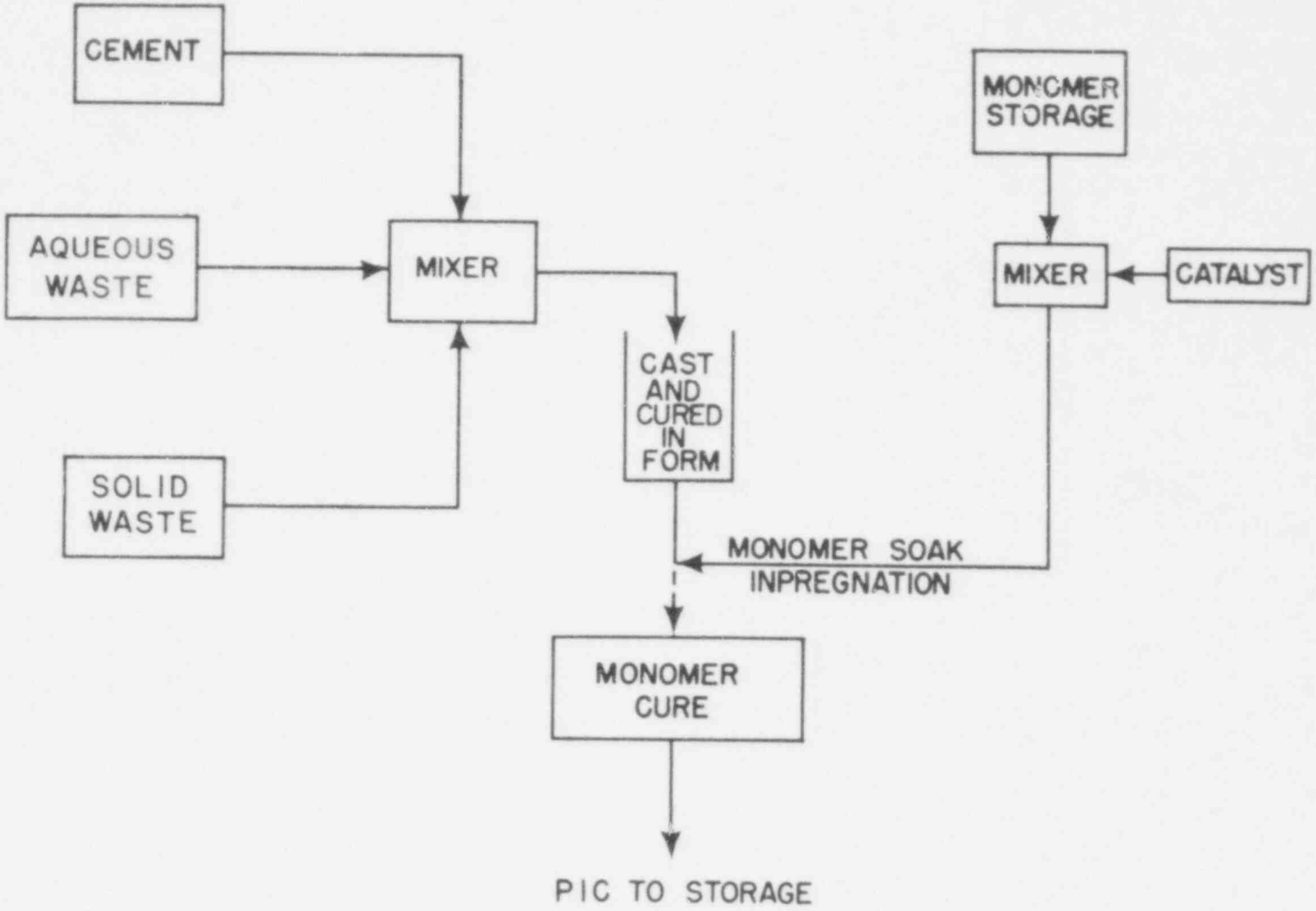
First, reinforced concrete casks were built for the deposition of low-level waste (LLW), contaminated machinery, and compressed solid combustibles. The liquid radioactive wastes, consisting mainly of beta and gamma emitters, are deposited into these reinforced concrete casks in the form of slurries consisting of portland cement, vermiculite, and the waste.

Second, the leach rates from cement-based composites of simulated SRP wastes have been studied. The composites were made from combinations of waste sludge, portland cement, high-alumina cement, and zeolite. Using a modification of the IAEA leach test method, Sr and Cs bulk leach rates ranging from 10^{-3} through 10^{-6} g/cm^2 day were obtained.

Improved leach rates could be obtained by impregnation and subsequent polymerization of cement-waste composites by organic polymers. A comprehensive review on the subject of polymer-impregnated concrete (PIC) has been published recently (Clifton and Frohnsdorff 1976). Manowitz and coworkers (1972-1975) have shown that hardened cement-waste products, impregnated by styrene monomers containing a polymerization catalyst and cured by heating at 50 to 70°C, give an essentially impermeable composite with much improved strength, durability, and resistance to chemical attack and leachability. For example, bulk leach rates for Cs and Sr can be improved by as much as two orders of magnitude to 10^{-7} to 10^{-8} g/cm^2/day. A simple flow diagram for solidification of radioactive waste in polymer-impregnated cement products is shown in Figure 9.3.

Polymer-impregnation technology for concrete products in general and for radioactive waste in particular is still not sufficiently developed. A significant amount of work is required to demonstrate and optimize the effects of monomer impregnation and subsequent polymerization (by heat or radioactive treatment) on large-scale concrete products (U.S. ERDA 1976b).

Brookhaven studies have also demonstrated that the radiation stability of cement products is excellent (Manowitz et al. 1972 to 1975). No deterioration in strength or leachability has been detected at an integrated dose of



Source: Columbo and Neilson (1977a).

FIGURE 9.3 Process flow diagram for the fixation of radioactive wastes in polymer impregnated concrete (PIC).

10^9 rads (using ^{60}Co gamma rays) for cement products containing up to 30 wt% $NaNO_3$.

Savannah River Laboratory

Neutralized HLW from the Savannah River plant consists of a solid component (sludge), containing various metal hydrous oxides, and an aqueous component (supernate), composed of various soluble salts, such as sodium nitrate. Most of the fission products, including ^{90}Sr, are incorporated in the sludge. However, ^{137}Cs is typically found in the supernate. To assess the possibility of incorporating these wastes into cement paste, studies concerning leachability, thermal stability, radiation resistance, and handling have been conducted (Stone 1975, 1977; Wallace et al. 1973). Cement products are considered attractive candidates because of their relatively low cost, expected compatibility with SRP wastes, and simple handling at low temperatures.

Testing of cement paste containing 40 percent washed wastes has shown the product's compressive strength to be 2,000 to 3,000 psi. A strength of 2,000 to 5,000 psi is considered satisfactory for most commercial applications of concrete. High-alumina cement gave consistently higher strengths than portland cement-waste composites. Heating to 100°C did not affect the strength of either of the concrete types. Prolonged heating decreased the strength of high-alumina cement, most probably as a result of the conversion mentioned earlier. Portland cement was found to be unaffected up to 300°C; a prolonged curing at 500°C, however, caused a 75 percent strength loss.

Generally, most of the concrete formulations were very resistant to gamma radiation. Reactor shields composed of portland cement showed only a 50 percent loss of compressive strength after exposure to 3×10^{18} R (Tipton 1960).

Specific leach tests on poorly specified phase compositions have shown that the Sr leachability decreases with leaching time from an initial 10^{-2}g/cm^2/day down to 10^{-5}g/cm^2/day at six weeks (Stone 1975). According to Wallace et al. (1973), the leachability of cement containing no soluble salts is much lower than that of cement containing salts. There is some indication that MnO_2 acts as a scavenger for Sr. High-alumina cement has shown lower Sr leachability than portland cement. Strontium leachability was generally lower after gamma irradiation. Cesium leachability values ranged between 10^{-1} initially and 10^{-6} g/cm^2/day; plutonium leachability was extremely low in all cases (10^{-4} initially to 10^{-8} g/cm^2/day after 12 weeks).

In general, the data obtained by SRL--which are based primarily on leachability results--seem to indicate that high-alumina cement is superior to portland cement concretes. Of the portland cement-based concretes, those containing pozzolanic additives[3] were the best because the decrease in $Ca(OH)_2$ content, due to its reaction with SiO_2 present in these additives, improves leachability. Initial leachability of concretes containing these additives was 7×10^{-4} g/cm^2/day; this value dropped to 2.6×10^{-6} g/cm^2/day after 119 days.

Gases produced by in situ radiolysis of 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-beta radiation. These forms were: cement containing simulated fission product sludges, vermiculite containing organic liquids, and cellulosics contaminated with alpha-emitting transuranic isotopes. 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. Based on limited data, it is assumed that oxygen will be completely consumed and nitrogen unaffected (Bibler 1976, Bibler and Orebaugh 1977).

It has been calculated (Bibler 1976, Bibler and Orebaugh 1977) that alpha radiolysis, which will predominate after about 200 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 high temperatures and a gamma radiation field.

Atlantic Richfield Hanford Company

Only limited experimental data have been obtained at the Atlantic Richfield Hanford Company because work on a cement immobilization process relied mostly on more extensive data obtained at the Savannah River site and at Brookhaven. The immobilization of Hanford wastes by incorporation into cement/concrete has been given low priority in the past (D.R. Gustavson and W.W. Schulz, Atlantic Richfield Hanford Co., personal communication to Panel on Waste Solidification, 1977).

Portland Cement Association

Under a contract from Battelle Pacific Northwest Laboratories, the Portland Cement Association evaluated elastic and strength properties of Hanford concrete mixes at room temperature and at 177° and 232°C. The variables studied were temperature, length of exposure to elevated temperature, and curing time before the exposure to elevated temperatures. Data were obtained for changes in the modulus of elasticity, Poisson's ratio, and strength (Abrams 1975). Because of batch-to-batch variations of the concrete mixes used and the small number of test specimens, the data are not conclusive.

The modulus of elasticity and Poisson's ratio decreased with increasing temperature. In general, the moduli of elasticity of the tested mixes decreased from approximately 0.42×10^6 kg/cm² at room temperature (21°C) to approximately 0.28×10^6 kg/cm² at 177°C, and to approximately 0.155×10^6 kg/cm² at 232°C. The length of moist curing before the high temperature exposure did not affect the results. In general, marginal increases in compressive strength with increasing temperature were found.

Pennsylvania State University

Exploratory research was conducted on the possible application of "hot pressing" (compaction at increased temperatures) to mixtures and combinations of cement and fission products (Roy and Gouda 1974). With both high-alumina and portland cements, it has been demonstrated that 10 to 50 wt% of solid simulated radioactive waste can be solidified in cement by hot pressing. The technique enables very high density specimens (2.80 to 2.94 g/cm³) to be produced, in which the waste is either (a) spread evenly in the cement matrix, (b) encapsulated in the core of a previously hot-pressed cement paste cylinder, or (c) added to the cement mixture as pelletized or sintered aggregate before pressing. Although somewhat better results were obtained with the high-alumina cement, both cement types can give products that are thermally stable (some cement-waste forms are stable up to 750°C), resistant to hot-water leaching, and very strong (1,400 to 4,200 kg/cm²).

Foreign Experience

Only very limited information on the use of cement/concrete as a possible radioactive waste matrix is available from abroad. In Europe as well as in the United States, incorporation of HLW in concrete has not been considered a high priority option. Data are available on the use of heavy concrete for shielding of radiation in nuclear power plants, but information on its use for actual waste disposal is scarce.

Cement has been used in the U.S.S.R. for disposal of LLW in the form of concrete monoliths but, because of their size and weight, their transport was considered to be uneconomical (Belitzky 1977).

Solidification of LLW and ILW in cement/concrete products is being considered in the Federal Republic of Germany (I. Odler, Technical University, Clausthal-Zellerfeld, West Germany, personal communication, 1977). It is possible that the wastes will be deposited in the form of grouts into stable salt formations, as retrievability of these wastes is not an issue.

Limited tests on the leachability and other properties of waste-cement products have been performed in Japan (Hatta et al. 1975, Matsuzuru et al. 1977), Italy (Lazzarini and Tognon 1963), Czechoslovakia (Schejbalova and Novotny 1967), France (Bonniaud and Cohen 1960) and other countries. Like the German Federal Republic, these nations are not at present planning to solidify HLW in cement and concrete.

EVALUATION OF CEMENT R&D

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. Yet, this waste form has received marginal publicity, little support, and general neglect.

The advantages of concrete as a waste form include the following: (a) it employs the lowest solidification processing temperature; (b) simple remote-control processing is possible; (c) it can be pressure-injected into selected geological formations and then solidified; (d) cement-waste mixtures can be embedded into metal or concrete containers; and (e) the cost is low.

There are some disadvantages, however. For example, if high strength is required, the temperature of the concrete must be kept below 350 to 500°C. Furthermore, under some conditions, the leachability of concrete is higher than that of other waste forms. The most serious potential disadvantage, and one that has been studied the least, is the radiolytic decomposition of water present in the concrete (see Chapter 12). The results of Burns (1971) suggest that it is not a serious problem. If additional research, which is in progress at Karlsruhe and Oak Ridge, confirms these early results, cement-based composites have a very high potential in future HLSW technology.

The leachability of cement composites should not be a problem if they are properly made, and placed in a stable and hydrologically sound geological environment. It is anticipated that the chemical reactivity of concrete with siliceous rock formations will be less than that of many other forms.

The thermal conductivity of concrete is of the same order of magnitude as that of most natural rock formations. Because of the hydrated nature of concrete, wastes that generate considerable heat may cause temperatures to rise above the dehydration temperatures of some of the hydration products. This occurrence may lead to a partial decrease of strength which, in most instances, is not critical. Because the temperatures are not expected to exceed 250°C in the surrounding rock environment, none of the common minerals in granite or shale (e.g., micas or clays) will lose their OH-water.

The strength of concrete will be critical only during transportation, when the dispersibility of the solid form in case of an accident must be considered. Concrete containing polymer-impregnated waste products has improved strength and should be considered for use when this quality is required. Thermal conductivity (and stability) of container-stored, concrete-embedded waste can be increased by the use of a honeycomb container configuration or other similar structures. It has often been assumed that the total weight of a concrete waste matrix may limit its practical transportation. If one incorporates 40 to 50 percent of sludge or calcine in concrete, however, the total weight will be similar to that of the glass or metal matrix options.

If the waste-cement composite is to be stored in metal containers, provisions for possible radiolytic gas generation should be made. Venting of the containers and its effect on the mobility of radionuclides must be studied. A systematic investigation of the effects of radiation on concrete is needed; the investigation should consider a combination of such variables as heat, pressure, dose rate, total dose, type of radiation, and decay energy spectrum, as well as w/c ratio, type of cement mixture, and curing conditions.

A simple process-properties matrix for the possible cement products is given in Table 9.4.

For each particular waste type, the chemical composition and level of radioactivity will require that a well-defined form of cement/concrete matrix be specified. The waste to

TABLE 9.4

Process-Property Matrix [a]

Parameters	Grouting	Cast Concrete	Pelletization
Process Parameters			
Complexity	Mixing-Transport/ Injection	Mixing-Transport-Curing; Possibly impregnation by polymer, etc.	Mixing-Pelletization-Transport; Possible impregnation and/or transport in metal containers
Maximum Temperature	Ambient	Ambient or Steam Curing (150-200°C)	Ambient
Ease of Remote Operation	High	High	Medium
Property Parameters			
Leachability[b] [c]	Medium	Potentially 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

---

[a] Comparisons are relative to glass.

[b] Depends on the density of cement product (w/c ratio, polymer impregnation, etc.).

[c] Some difference between portland and high-alumina cements.

be incorporated in cement should not contain water-soluble compounds that could modify the path of cement hydration and thus impede the development of necessary properties.

More research is needed to explore the possible effect of insoluble or slightly soluble waste compositions on cement matrix properties, and to develop admixtures and additives to improve the workability or "pumpability" of the freshly mixed cement-waste mass. Such improvements will enable its compact, dense, and impermeable placement (if at temperatures up to 200°C) into the desired cement-containing structure or environment. Combinations of admixtures that will improve cement paste/concrete properties and decrease the leachability of the radioactive species to be solidified should be developed.

Clearly, a major research objective is to develop cement composites with maximum waste loading and with additives that will trap waste ions in case of leaching. The compatibility of a specific waste with a particular matrix must be explored. It is likely that silicate supercalcine or ceramic will interact only minimally with a cement matrix. Possible uses of cement/concrete for radioactive waste solidification are summarized in Table 9.5.

TABLE 9.5

Possibilities of Using Concrete for Radioactive Waste Solidification

Type of Concrete Products	Examples of Possible Use
Cement Slurries, Grouts, or Gunite	Fixation of waste in fractured shale Storage in concrete and/or other vessels
Concrete Casks, Tanks or other Storage Vessels (with or without reinforcement, special radiation-shielding aggregates, and/or polymer impregnation)	Storage of cement slurry-embedded wastes Storage of solidified powdered or pelletized as-is waste Storage of waste in the form of glass, calcine, etc. Storage of spent fuel pins
Bulk Concrete (with or without metal "honeycomb" reinforcement to increase thermal conductivity)	Deposition and shielding of used equipment, spent fuel pins Retrievable or irretrievable concrete blocks for geological and/or deep-sea deposition of solidified as-is waste As above but use of other waste as "aggregate"
Pelletized Cement Paste (Cold or Hot Pressing)	Storage in concrete or other vessels (metal) Encapsulation of pellets in concrete on other media

NOTES

1 "Hydraulic" denotes the ability to develop strength under water. This strength development does not depend on drying or reaction with atmospheric CO_2.

2 "Curing" refers to a set of atmospheric conditions under which the concrete matures (hardens, ages), e.g., temperature, pressure, and relative humidity.

3 Siliceous or aluminous materials that manifest their cementing properties only when finely ground and in the presence of moisture and calcium hydroxide.

4 The generalized model for the concrete waste form consists of about 40 percent of the primary containment material in the form of supercalcine or an oxide sludge adsorbed on to network or layer silicates, and incorporated as the aggregate into a high-alumina or portland cement. This paste can be cast either into large cylinders or grouted into suitable geological formations.

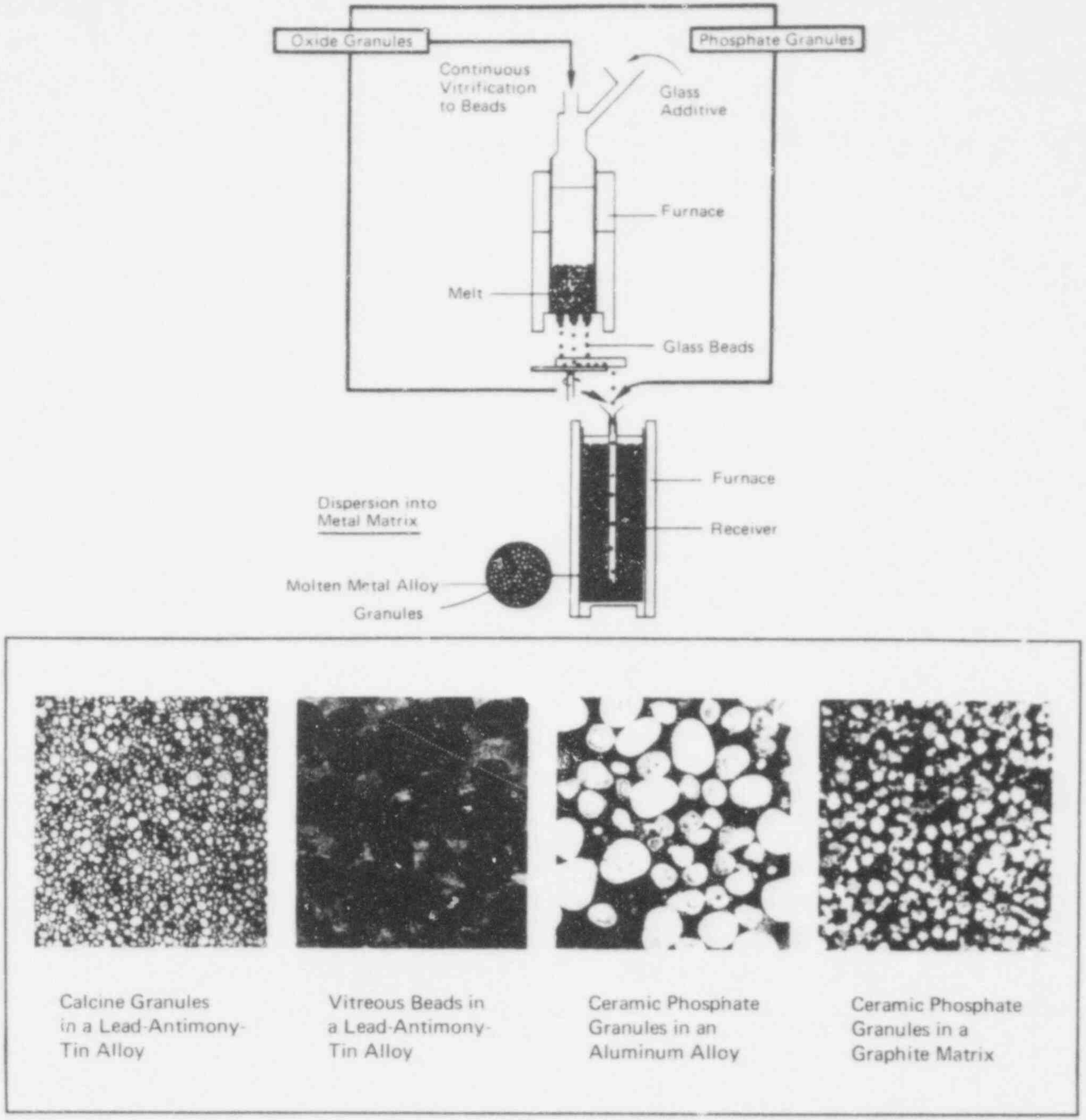
CHAPTER 10

METAL-MATRIX COMPOSITES AND METAL CONTAINERS

INTRODUCTION

One proposed solid form for HLW disposal is produced by the encapsulation of primary containment phases such as calcine or glass in a metal (or graphite or glass) matrix. Large cyclinders of the resulting composite can be placed in a metal container, which provides the potential for short-term retrievable or long-term irretrievable storage (Berreth et al. 1975, 1976; Dan and Williams 1976; Heimerl et al. 1976a; Rhodes 1969; Sump 1976; U.S. ERDA 1976b; Geel and Eschrich 1975; J.C. Malaro, U.S. NRC, personal communication, July 1976). Metal, the promising matrix material, and the one on which most work has been performed, receives the major emphasis in this chapter. The Eurochemic Corporation in Belgium has been by far the most active center for such work, and is now implementing a metal-matrix process (van Geel and Eschrich 1975, Heimerl et al. 1976b). Their process, which is in the pilot development stage, involves glass beads made by the PAMELA process or, alternatively, supercalcine made by the LOTES process (see Chapter 6). These primary containments are imbedded in lead by gravity casting, and encased in stainless steel (Dan and Williams 1976; Heimerl et al. 1976b; U.S. ERDA 1976b; van Geel and Eschrich 1975; J.C. Malaro, U.S. NRC, personal communication, July 1976). Early development work evaluated the metal matrix method using a calcine dispersoid (van Geel and Eschrich 1975, Rhodes 1969, Berreth et al. 1975). Largely because of better leaching resistance, recent work has focused on methods using a glass dispersoid (van Geel and Eschrich 1975, Berreth et al. 1976). Matrix formation mechanisms studied include both sintering (Berreth et al. 1975, 1976; Sump 1976; van Geel and Eschrich 1975) and casting (Berreth et al. 1975, 1976; Rhodes 1969; Sump 1976; van Geel and Eschrich 1975). Figure 10.1 shows a schematic diagram of the process and a cross section of the typical product.

An important advantage of metal-matrix isolation is improved thermal conductivity (about ten times better than for most glasses). This property is a primary design parameter in the transportation and retrievable storage of



Calcine Granules in a Lead-Antimony-Tin Alloy

Vitreous Beads in a Lead-Antimony-Tin Alloy

Ceramic Phosphate Granules in an Aluminum Alloy

Ceramic Phosphate Granules in a Graphite Matrix

Source: van Geel et al. (1976).

FIGURE 10.1 Eurochemic metal-matrix process and cross section of resulting products.

fresh (less than two years old) radioactive waste. Subsidiary advantages could include reduced leachability and improved impact resistance. Specific metal properties of interest are thermal conductivity, thermal expansivity, corrosion resistance, compatibility with glass (or calcine), density, ductility and thermal stability in relation to oxidation, and phase changes such as creep and melting. Process parameters of interest include volume fraction of waste, distribution of dispersed particles within the matrix, cost, strategic abundance, and transportability.

Many of these properties are also pertinent to the containment material for the metal matrix (or for other waste forms), so some discussion is devoted to this topic. Because many of the same properties would apply to direct encapsulation of spent fuel pins in a metal matrix, this process is also briefly considered. The following discussion treats the process of metal-matrix formation, properties of candidate metals, metal matrix for treated calcine or glass and for spent fuel pins (or fuel pin assembly), and the metal for containers.

METAL-MATRIX FORMATION PROCESS

Most work to date has formed the matrix-waste composite by one of three processes. One is vacuum casting with gravity feed (for lower-melting-point alloys of Al, Pb, and Zn), wherein the metal is melted in an evacuated crucible, a tube is inserted with its mouth near the bottom of the crucible, glass beads or supercalcine pellets are injected into the melt by means of an argon carrier gas, and the beads rise in the melt under gravity force to form the dispersion. A second consists of mixing the waste as powder or beads with metal powder to about the 65 percent density typical of sphere packing, cold pressing the mixture to 95 percent density, and sintering it at temperatures near the melting point. In the third method, the powders are mixed as described above, and sintered without cold pressing; the final density of the product is typically lower than that of the other two.

The goal of all work reviewed by the Panel is to incorporate 40 to 60 percent volume fraction of waste in the composite. This volume fraction is far too high if the impact strength and corrosion resistance characteristic of the metal is to be retained. Theories of connectivity (Gurland 1968) indicate that there will be continuous paths of the dispersoid when its volume fraction is greater than 20-40 percent, with the former value being more probable. The principle of the continuous phase (Rhines 1956) also indicates that mechanical properties (e.g., impact resistance) would be poor when the more brittle dispersoid is continuously distributed, although they would be incrementally better than those of the dispersoid itself. For a brittle dispersoid in a ductile matrix, mechanical properties abruptly change from those typical of the metal to those of the dispersoid at the continuous path volume fraction of about 20 percent in agreement with this principle. Also, with continuity of dispersoid, the leach rate would tend to be that of the dispersoid rather than the desired lower rate of the matrix.[1]

To gain the full benefits of impact resistance and low leachability provided by a metal matrix, the volume of fraction of dispersoid should be held to 20 percent or less. However, because these maximum benefits of the metal phase may not be necessary, a trade-off with an increased percentage of dispersoid may be possible.

So far, most work has centered on casting or sintering, supposedly because of process simplicity. However, these methods have evident drawbacks. For example, in the casting method discussed earlier, clogging of the remotely operated injection tube, reaction between the molten metal and the tube and crucible, and clumping and gravity segregation of the dispersoid are all potentially serious problems. The sintering processes have the disadvantage of requiring long times to achieve near 100 percent density (desired for isolating the dispersoid and attaining full mechanical properties), because of the slow diffusion mechanisms of densification in sintering.

Alternatives that could have advantages over these methods are cold and hot isostatic compaction (Gessinger and Bomford 1974, Johansson and Isaksson 1970). Here powders are blended into an evacuated metal container (cold or hot), which is welded shut, placed (cold or hot) into an argon-filled chamber, and stressed pneumatically by compressing the argon to 100 to 200 MPa. The hot compaction is performed at temperatures from 0.5 to 0.9 of the absolute melting temperature, depending on the time and stress employed.

One advantage of isostatic compaction processes is the rapid achievement of densification by deformation; the compacts are 100 percent dense. A second advantage is that the canned waste is isolated from the compaction device, enabling the latter to be situated in a relatively accessible portion of the remote processing facility. Another positive aspect is that the dispersoid can be uniformly blended into the charge, avoiding the possible clumping of dispersoid and gravity segregation associated with casting methods. Furthermore, since the working medium is a gas, wear of the processing equipment would be minimal relative to a conventional pressing device. It is noteworthy that direct hot isostatic compaction of a waste and alumina powder mixture has been considered in Sweden, as well as the concept of encapsulating fuel elements in hot isostatically compacted cylinders of alumina (Sweden Now 1977). Indeed, some of the risk of a domino effect, which occurs with failure of one component in a continuous process, would be avoided.

The cold isostatic compaction method, particularly, provides advantages. If supercalcine, which is produced at moderately low temperatures, was used in this method, the waste would never be exposed to high processing temperatures. Hence, problems such as volatilization of Cs and Ru, container reaction, and wear and attrition of processing materials would be minimized. Also, if only modest production were required, such batch-type compaction methods would not seriously decrease efficiency.

METAL PROPERTIES

Table 10.1 lists the properties of several candidate metals for matrix isolation. Other metals that have been suggested are not considered here because of their inadequate corrosion resistance (Fontana and Green 1977) (iron, zinc), or because of potential strategic shortages (e.g., copper-based alloys) (National Commission on Materials Policy 1973). The most frequently mentioned alloys, because of their low melting points, which permit casting without outgassing or softening of waste pellets, are those of lead or aluminum. A metal that has received relatively little attention but which is strongly supported here for reasons discussed below is titanium. Because of its high melting point, a pressing or sintering process would have to be used for titanium.

Lead

The lead-0.06 copper alloy would appear to have excellent corrosion resistance on a 10^4-year time scale[2] even if the matrix were exposed to an aquifer or a salt-moisture environment up to 100°C. It would also have adequate thermal conductivity (about ten times that of most glasses or ceramics), excellent impact resistance, low reactivity with SiO_2, and a relatively low cost per unit mass at present. However, it has some serious drawbacks.

First, the volume rather than the mass is significant in the proposed application, and lead is appreciably more expensive on a cost per unit volume basis than on a cost per unit mass basis. Second, strategic shortages of lead are projected by the year 2000; these will result in higher costs even with greater projected recycling (National Commission on Materials Policy 1973). Third, the low melting point presents the possibility of center melting

TABLE 10.1

Some Characteristics of Metals for Waste Containment

Metal	Al	Pb	Ti	Ti Sponge
Cost per kg	\$1.05	\$0.69	\$4.42	\$2.21
Cost per cc	0.28¢	0.77¢	2.00¢	1.00¢
Strategic Availability	Abundant	Limited	Abundant	
Thermal Conductivity $\frac{J}{Kms}$	220	35	79 to 99	
Corrosion Resistance	Poor	Excellent with .06 Cu	Excellent (possible problem with crevice corrosion, hydride embrittlement)	
Impact Resistance (Charpy V-notch J)	High (not standardly cited)	14 (20°C)	15 (-15°C) 34 (90°C)	
Creep Rate (min. temp. for strain rate $=10^{-6}s^{-1}$ at $=10^{-5}x$ shear modulus)	260°C	20°C	550°C	
Melting Point	660°C	327°C	1820°C	
Temperature Below Which Oxidation Rate is Logarithmic (thin film limited)	200°C	150°C (rate greatly accelerated in presence of ozone, water vapor)	300°C (film 0.44μm in 200 yr 14μm in 200,000 yr	

Source of Data:

Cost: Al, Pb, current American Metals Market; Ti, (F. Malone, Colt-Industries Crucible, personal communication, May 1977).
Strategic Availability: National Commission on Materials Policy (1973).
General Data: American Society on Metals (19)
Creep: Al, Pb, Mukherjee et al. (1969); Ti, Paton and Mahoney (1976).
Corrosion: Fontana and Green (1977).
Oxidation data: Kubaschewski and Hopkins (1962) and J. Eldridge, IBM, San Jose, Calif., personal communication, May 1977.

accompanied by reaction with the dispersoid, and the possibility of mechanical instability because of creep. If the container were breached, creep could lead to seizure of the material, causing problems in retrievability. Finally, lead's greater density would present more of a transportation problem than would other metals (though its ability to act as a gamma shield would be advantageous).

Aluminum and Titanium

Aluminum is most favorable from the standpoint of cost per unit volume, is abundant, has excellent thermal conductivity and impact resistance, has adequate creep resistance up to 200°C, and, on the basis of oxidation rate measurements (Kofstad 1966), should be relatively compatible with a glass or calcine dispersoid. A displacement reaction to form a layer of alumina surrounding the dispersoid would certainly occur, but the thickness of the layer would be limited to a few hundred angstroms.

If the metal matrix were not to be exposed to aqueous solution (aquifer) or salt-moisture (salt bed or dome), i.e., if the container itself were failsafe with respect to breaching of containment and corrosion, aluminum would clearly be the best choice of material on the basis of these advantages. However, if the container were penetrated, it would have poor corrosion resistance and would expose the dispersoid to reaction with rock and water.

Titanium would have all the advantages of aluminum, with somewhat lower thermal conductivity but with greater creep and melting resistance. Titanium has good corrosion resistance (Fink and Boyd 1970; Fontana and Green 1977; H. Bomberger, Reactive Metals Industries, Niles, Ohio, personal communication, April 1977) and would be stable over a 10^4-year time scale[2] if exposed to acidified or alkaline water or to saltwater at up to 150°C. It suffers attack, by hydride formation, only in the presence of very high partial pressures of hydrogen, most unlikely to be achieved even with radiolysis of water; it is also attacked by crevice corrosion in highly acid and reducing environments. The disadvantages of titanium are its cost and the lack of processing flexibility: it would be necessary to use compaction-sintering type processing. The reactivity of titanium with glass should be similar to that of aluminum on the basis of oxidation rate measurements. Unlike the well-established lead and aluminum prices, however, titanium prices are artificially high because of dependence on foreign sponge[3] sources and erratic tonnage sales (F. Malone, Colt Industries, Pittsburgh, Pennsylvania, personal communication, May 1977). Titanium sponge could be used directly as a compacted matrix (electrodes for consumable arc-melting are cold-pressed at room temperature to high density and moderate integrity), and would be less expensive than powder. As noted in Table 10.1, the cost per unit volume would be comparable with that of lead.

METAL MATRIX FOR TREATED CALCINE OR GLASS

On the basis of the above analysis, aluminum-based alloys in containers of commercially pure titanium are suggested as better alternatives to lead for the metal matrix material. For both materials the least certain property data are those relating to displacement reactions with the dispersoid. Studies on these reactions at temperatures of 50 to 500°C are needed. While relatively more data are available on corrosion than on displacement reactions, further studies in this area are also desirable.

METAL MATRIX FOR FUEL ELEMENTS

For the same reasons as those discussed above, isostatically compacted titanium and compacted cast or aluminum are potentially useful metal matrices for direct encapsulation of spent fuel assemblies. Once encapsulated by such methods, removing the fuel for reprocessing would be very difficult.

Metal Containers

As mentioned in Chapter 1, the outer metallic (or ceramic) waste container provides protection during transport and serves as a physical barrier during emplacement. The data just discussed are also relevant to the selection of such a container. The main suggestions for container materials are stainless steel, mild steel, and steel plated with gold or TiB_2 (G. Wranglen, Royal Institute of Technology, Stockholm, personal communication to R.L. Davies, 1977; R.L. Davies, The Gold Institute, personal communication to the Committee on Radioactive Waste Management, March 1977).

All these metals have certain disadvantages. If exposed to salt-moisture environments at 0 to 150°C, austenitic stainless steel would be highly susceptible to stress-corrosion cracking. Ferritic stainless steels* or mild steel have high enough uniform corrosion rates to be undesirable after about ten years (Fink and Boyd 1970). While gold itself is resistant to corrosion, gold plating would provide complete protection, albeit costly, only if the coating were absolutely integral and free of defect. If any fissures were present in the coating, or if the relatively soft coating were penetrated in handling (a virtual certainty), the gold plating would actually facilitate corrosion. It would act as a large-area, unpolarizable cathode, and severe, rapid pitting attack would occur in the metal acting as an anode at the break in the coating. Furthermore, gold would readily dissolve in the presence of chlorine and under oxidizing conditions, situations that could arise as a consequence of radiolysis. Gold would also provide the incentive for human intervention after emplacement.

Titanium would provide a much less costly and more effective container. Titanium would provide long-term corrosion protection along with adequate mechanical properties (impact and creep resistance) and fabricability (weldability). A composite container with titanium bonded on to steel would also be possible, but more costly. If penetrated, such a coating would not be as unfavorable as a gold coating because the thin oxide film formed on it would act as a semiconductor, polarizing the titanium to a much greater degree. Moreover, titanium would be equally protective and would be less likely to expose base metal by spalling or cracking, than titanium diboride (TiB_2) or similar ceramic coatings, which have also been suggested as alternatives.

NONMETALLIC MATRICES AND CONTAINERS

The nonmetallic matrices that have been mentioned, glass and graphite (Bunnell 1974), are inferior to metal matrices and are not recommended. Glass would have the same deficiencies as does direct formation of glass, discussed in Chapter 8, and its use in a composite would result in a process more complex than that of glass monolith production. The formation of a graphite matrix would involve depositing carbon by a chemical vapor deposition process (Bunnell 1974) and would necessitate the handling of gaseous products. The carbon matrix would be porous if produced in the glassy state by reaction at moderate temperatures (1,000 to 1,300°C), and would be graphitic and have optimum strength and density only after reaction at up to 3,000°C. Graphite's thermal conductivity and resistance to creep and corrosion would compare to those of metals, but it would be inferior in impact resistance, ductility, and oxidation resistance (Bunnell 1974).

The Swedish program is examining a hot-pressed, fully dense alumina container instead of a metal. While Al_2O_3 clearly has an advantage over any nonnoble metal with respect to corrosion, we find that the expense, and the process complexity of sealing the "cans," tip the balance toward metallic containers, especially if made of titanium.

NOTES

1 This factor has been recognized in the Eurochemic process in which a metal matrix composite heavily loaded with dispersoid (60 to 75 percent volume fraction) is surrounded by a layer of metal.

2 All corrosion resistances are based on short time exposures. Long-term corrosion tests should be initiated for all candidate materials for typical projected exposures.

3 "Sponge" is a form of titanium resulting from the standard chloride-reduction process of making titanium. The sponge is supplied as coarse particles (<6mm or <3mm in diameter, depending on the process).

4 26 Cr - 1 Mo ferritic stainless steels would be satisfactory from a stress corrosion viewpoint, have lower passive current densities than austenitic stainless steels in salt solutions at up to 100°C, and could be a possible choice (cheaper than titanium) in mild corrosion exposures (granite versus salt bed). This material would be less satisfactory than austenitic stainless steel for transportation, being susceptible to embrittlement at low temperatures and in sections thicker than 8 mm.

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CHAPTER 11

SPENT FUEL ASSEMBLIES

INTRODUCTION

The recent policy decision to defer reprocessing of spent fuel has made it necessary to consider spent fuel from nuclear power reactors as a prime solid waste form to be placed in a geologic repository or a surface storage facility. Since the physical, chemical, and radiological characteristics of spent fuel assemblies are different from those of solidified HLW, it is reasonable to expect that the problems associated with employing spent fuel assemblies as a solid waste form may also be substantially different. This chapter describes the characteristics of spent fuel assemblies that are relevant to their potential as a solid disposal form, and discusses potential problems associated with geologic emplacement of these assemblies. The surface storage of spent fuel assemblies will be considered only briefly.

DESCRIPTION OF LIGHT-WATER-REACTOR FUEL ASSEMBLIES

Physical Description

Spent fuel assemblies from light-water reactors (LWR) are composite units comprising fuel pins in a geometric cluster, held together by end pieces and a number of element spacers. Fuel assemblies from boiling-water reactors (BWR) and pressurized water-reactors (PWR) differ significantly, but the basic components of each are the fuel pins. A fuel pin of either type is a long section of metal tubing, filled with ceramic pellets of uranium dioxide or mixed uranium-plutonium dioxide and closed at both ends. Typical dimensions and other characteristics of BWR and PWR fuel assemblies are given in Table 11.1. When considering spent fuel assemblies as a waste form, two of their relevant characteristics are overall size and weight. A typical BWR assembly has a 13.9 x 13.9 cm cross section, an overall length of 447 cm, and a weight of 275 kg. Approximately 175 of these fuel assemblies are discharged each year by a 1,000-MWe BWR. A typical PWR fuel assembly (Figure 11.1) has a 21.4 x 21.4 cm cross section, an overall length of 406

TABLE 11.1

Physical Characteristics of Typical Unirradiated Light-Water Reactor Fuel Assemblies

	BWR	PWR
Overall assembly length (m)	4.470	4.059
Cross section (cm)	13.9 x 13.9	21.4 x 21.4
Fuel Pin length (m)	4.064	3.851
Active fuel height (m)	3.759	3.658
Fuel pin O.D. (cm)	1.252	0.950
Fuel pin array	8 x 8	17 x 17
Fuel pins per assembly	63	264
Assembly total weight (kg)	275.7	657.9
Uranium per assembly (kg)	183.3	461.4
Uranium dioxide per assembly (kg)	208.0	523.4
Zircaloy per assembly (kg)	56.9[a]	108.4[b]
Hardware per assembly (kg)	9.77[c]	26.1[d]
Total structural metal per assembly (kg)	67.7	134.5

[a] Includes Zircaloy fuel pin spacers.

[b] Includes Zircaloy control-rod guide thimbles.

[c] Includes Stainless Steel tie-plates and Inconel springs.

[d] Includes Stainless Steel nozzles and Inconel-718 grids.

Source: BWR, General Electric Company (1972); PWR, Westinghouse Corporation (1975).

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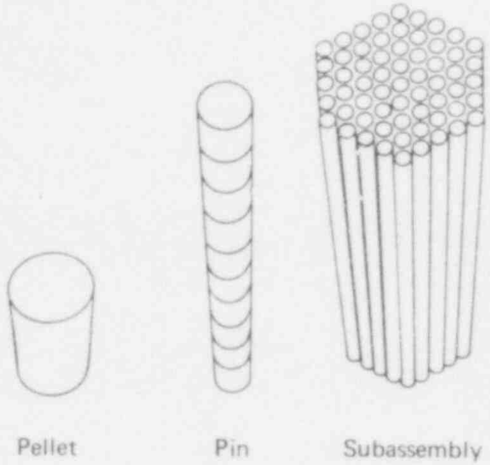

Source: U.S. ERDA (1976a)

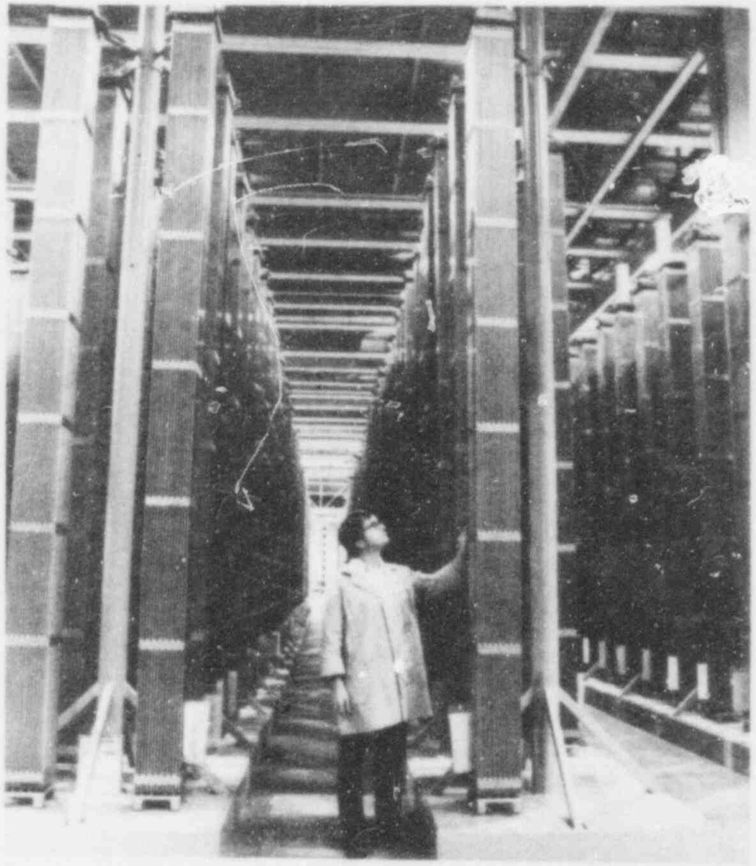

FIGURE 11.1 Structure and size of light-water reactor fuel assemblies.

The diagram shows the internal structure of the fuel assembly. It consists of a geometric cluster of fuel pins held together by end pieces and element spacers. The pins themselves are made up of small ceramic pellets stacked inside a long section of zircaloy tubing.

The photograph gives some idea of the size of typical fuel assemblies.

Source: U.S. ERDA (1976a); photograph courtesy of Westinghouse Corporation.

cm, and a weight of 658 kg. Approximately 60 of these fuel assemblies are discharged each year by a 1,000-MWe PWR.

Typical Nuclear Characteristics of LWR Fuel

Pertinent nuclear characteristics of uranium-enriched PWR and BWR fuels are summarized in Table 11.2.

The assembly is irradiated in a BWR (PWR) producing an average of 4.75 (17.3) MW of power. After the equivalent of 1,062 (880) full-power days of irradiation, the fuel assembly is discharged. At this time, it contains uranium with a ^{235}U enrichment of 0.69 (0.84) wt% and 1.57 (4.32) kg of Pu. The spent fuel also contains fission products and Np, Am, and Cm isotopes. A more detailed discussion of the composition of spent fuel is given below.

Characteristics of LWR Spent Fuel Assemblies

Calculations to predict the relevant characteristics of BWR and PWR spent fuel assemblies were performed with the ORIGEN computer code (Bell 1973) using the input data given above. The three most relevant characteristics of spent, unreprocessed LWR fuels are the thermal power, radioactivity, and potential hazard index[1] of the fuel assembly constituents as a function of decay time. The three major fuel constituent categories are structural materials (cladding, grid spacers, etc.), the actinides, and the fission products.

The variations of the thermal power and the radioactivity in both BWR and PWR spent fuel assemblies are shown in Figures 11.2 and 11.3.

The structural materials in fuel assemblies contribute little to the thermal power, radioactivity, and toxicity of the assemblies at all decay times. The fission products dominate all three characteristics at short decay times (less than 100 years decay), while the actinides dominate all parameters at long decay times (greater than 300 years decay). At decay times between 100 and 300 years, both the fission products and actinides contribute substantially to the totals.

Although Figures 11.2 and 11.3 contain information required to characterize spent fuel assemblies as a waste form, they do not show the effect that using spent fuel assemblies instead of other processed solid waste forms has on the three characteristic parameters. This effect is shown graphically in Figure 11.4, where the characteristics of a spent PWR fuel assembly are compared to those of the high-level and structural material wastes that would result

TABLE 11.2

Typical Irradiation Parameters of Light-Water Reactor Fuels, Equilibrium Core

Parameter	BWR	PWR
Uranium per assembly, kg		
Initial	183.3	461.4
Discharge	176.3	440.7
Enrichment, wt% ^{235}U		
Initial	2.75	3.20
Discharge	0.69	0.84
Plutonium per assembly at discharge, kg	1.57	4.32
Average power, MW/assembly	4.75	17.3
Average specific power, kW/kg initial uranium	25.9	37.5
Average discharge burnup, MWd/tonne initial uranium	27,500	33,000
Irradiation duration, full-power days	1,062	880

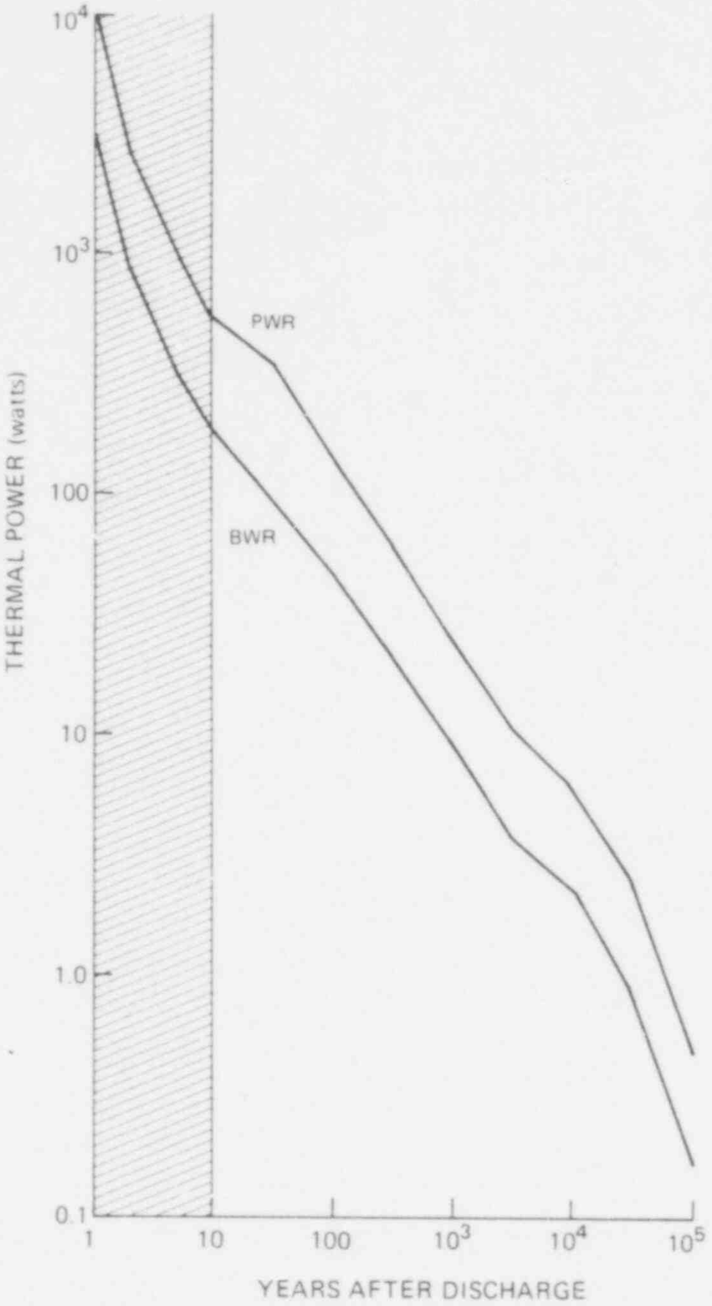

FIGURE 11.2 Thermal power of power-water reactor and boiling-water reactor spent fuel assemblies. The shaded area indicates that between the first and tenth year after discharge, the thermal power of spent light-water reactor fuel decreases by an order of magnitude.

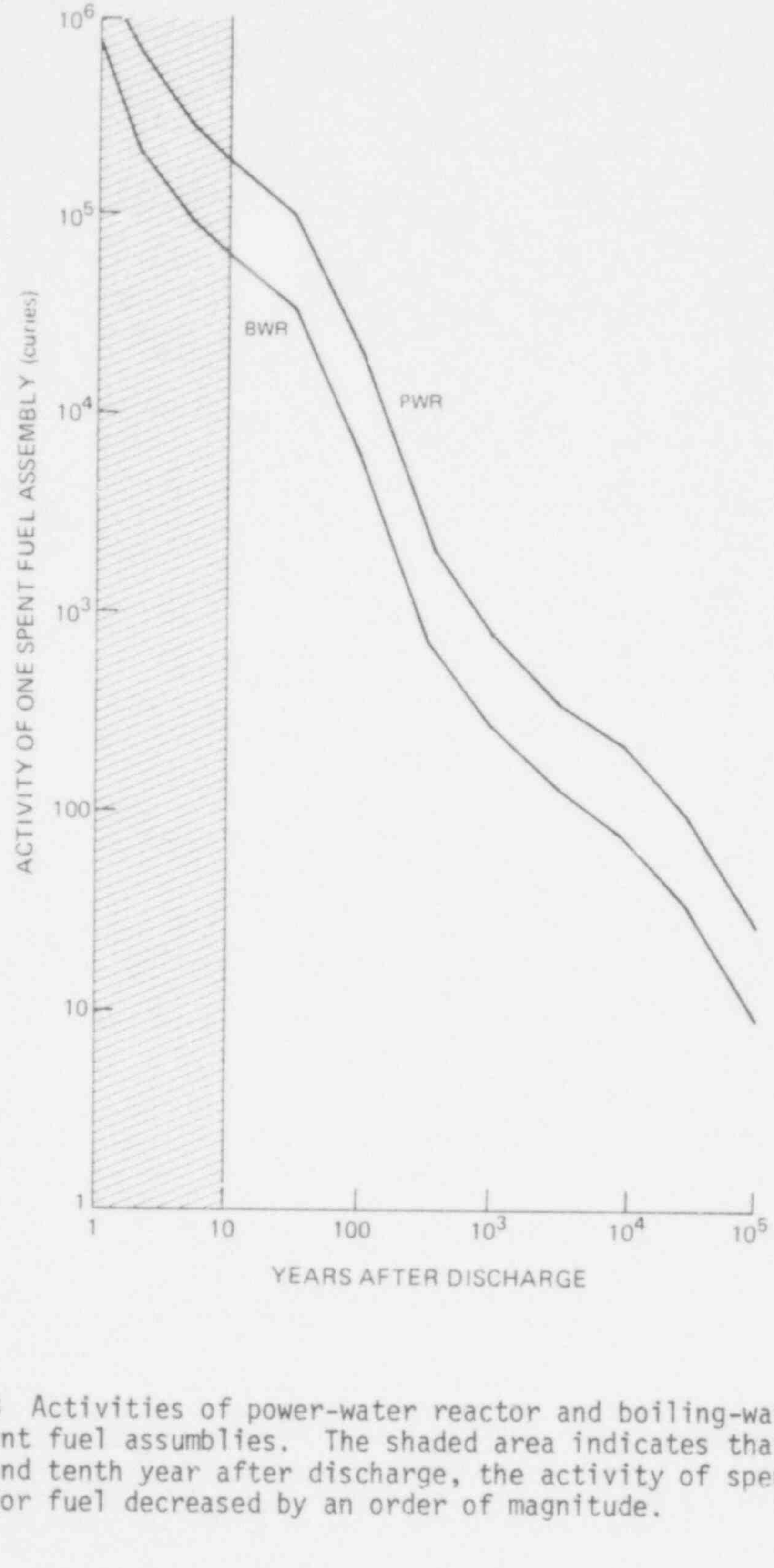

FIGURE 11.3 Activities of power-water reactor and boiling-water reactor spent fuel assumblies. The shaded area indicates that between the first and tenth year after discharge, the activity of spent light-water reactor fuel decreased by an order of magnitude.

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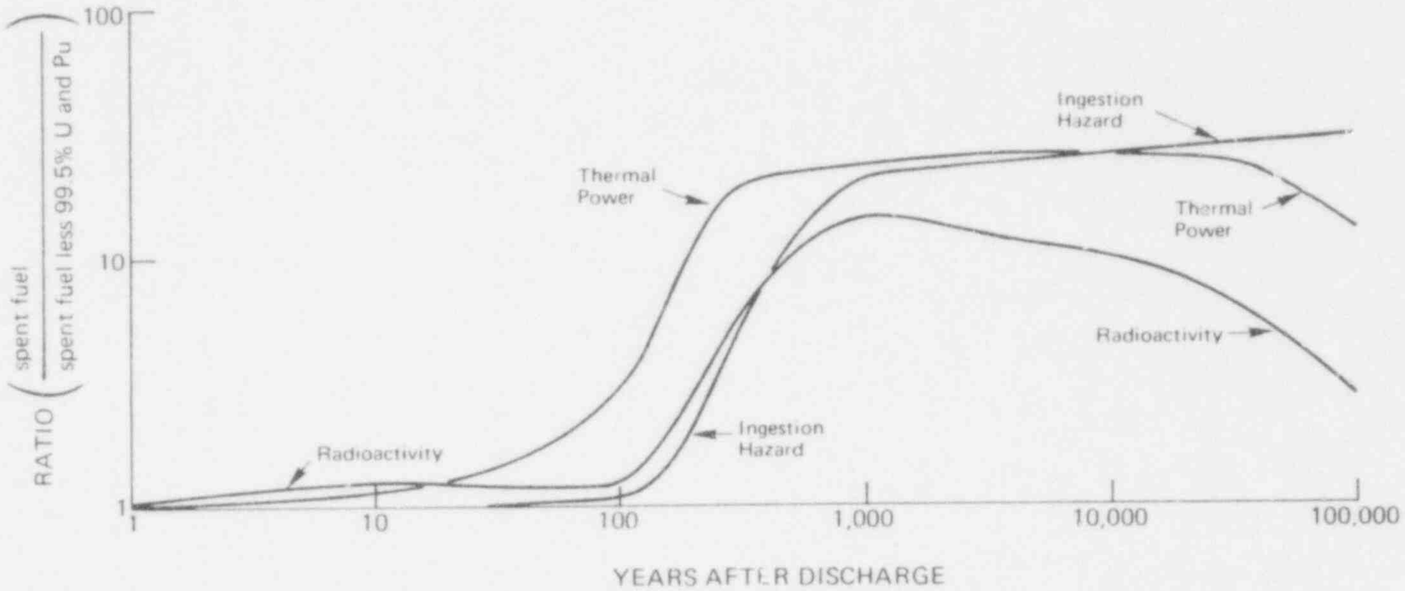

FIGURE 11.4 Comparison of the characteristic parameters of unreprocessed and reprocessed spent fuel showing that while they are essentially equal up to 100 years, thereafter the spent fuel assembilies are relatively more hazardous by a factor of about 20.

from reprocessing this assembly, assuming 99.5 percent removal of uranium and plutonium during reprocessing. The ratios for BWR spent fuel, which are omitted for the sake of clarity, would be similar to those shown in Figure 11.4 for the PWR.

The increase in the three characteristic parameters that results from not reprocessing the spent fuel is small at decay times shorter than 100 years, because the dominant fission products are present in equal amounts in both spent fuel and HLW. However, the characteristic parameters of spent fuel assemblies are greater over the long term than those of HLW by a factor of 10 to 30. Of particular interest is the greater long-term thermal power, which is the principal criterion in determining the spacing of solid waste containers in a geologic repository. This point will be discussed in more detail below.

A compilation of the numbers upon which Figures 11.2, 11.3, and 11.4 are based is given in Appendix D for both BWRs and PWRs. The physiochemical characteristics of the fuel pellets after irradiation have been well characterized (Robertson 1969) and consist of structural and dimensional changes, release of a significant fraction of fission product gases (e.g., Xe and Kr), and the segregation of other fission products (e.g., Cs) within the fuel elements.

DISCUSSION

State-of-the-Art Survey

If spent fuel assemblies are to be the final solid waste form, it is reasonable to expect that they would first be stored for a number of years in water-filled storage basins to reduce the heat generation rate before storage or disposal. In ten years, for example, this factor is reduced by more than an order of magnitude (see Figures 11.2 and 11.3). An analysis of the entire waste management system will be required to establish the optimal cooling time before shipping the spent fuel to a geologic repository or a surface storage facility. However, since short-term storage in a water-filled basin appears to be less expensive than storage in a repository, an extended cooling period would seem a reasonable measure when the heat generation rate is relatively high. This treatment would minimize the size needed for a repository or a surface storage facility, both of which have maximum thermal loading limits. Other objectives would be to keep to a minimum the processing required for the fuel assembly before geologic disposal or storage, and to avoid future difficulties of processing for U and Pu recovery should this ever become an option. For these reasons, it appears undesirable to disrupt the fuel pins, though it may be desirable to remove the end fittings to reduce the length of the assembly, making the in-repository handling of the spent fuel somewhat easier. Again, an economic and safety analysis is needed to establish the desirability of any processing at all before disposal.

Three classes of options are available for handling the spent fuel assemblies after the initial period of interim storage. The first is to continue storage in water-filled basins until a decision is made either to recover the U and Pu by reprocessing or to undertake final disposal. The second is to build and operate surface storage facilities designed for a somewhat longer term, perhaps 50 to 100 or more years. The third option is to place the assemblies, after interim storage in a water basin, in a deep geologic repository designed for retrievable storage for perhaps 25 years. This would permit a later decision on processing or permanent disposal.

The use of spent fuel assemblies as a solid waste form would pose several problems that would not be encountered if solidified HLW was used. Although the spent fuel assembly is already solid, we believe that it is too fragile to be handled without protection, and that it would therefore require a further protective solid layer, such as a metal can, for safer and easier handling at the repository. To explore the consequences of thus "canning" the fuel pins, an estimate was made of the maximum temperature a ten-year decayed fuel assembly would reach in a salt repository (W.F. Gambill, Oak Ridge National Laboratory, personal communication, May 1977). This temperature was found to be 240°C (450°F). Compared to the maximum temperature (about 425°C) that the fuel pin clad reaches in the reactor, this appears to be an acceptable clad temperature for retrievable storage. Because of its smaller size and lower burnup, the maximum temperature of a BWR fuel assembly would be expected to be less than that of the PWR assembly. Unfortunately, similar estimates are not available for other geologic formations such as granite or shale nor for retrievable surface storage facilities. On the basis of the above results for disposal in salt, it is not necessary to introduce a heat transfer medium, such as a low-melting metal, into the can containing the fuel assembly for heat dissipation purposes. If a metal such as lead were to be used, it would serve as an added barrier to the spread of contamination in the repository, but would make subsequent processing more difficult and expensive.

Other problems posed by the use of spent fuel assemblies as a solid waste form are as follows:

1. The fuel elements contain gases under pressure, which could cause rupture and the possible ejection of radioactive material.

2. The spent oxide fuel pellets are typically cracked when discharged from the reactor, and a portion of them could be accidently dispersed.

3. The spent fuel contains about 100 times more long-lived Pu than do HLW resulting from chemical processing. This greatly increases the long-term potential waste hazard index and the heat generation rate in the repository, as was noted above.

4. The presence of Pu and U make the possibility of criticality a concern if the repository were breached, water were to enter, and the fissile materials were arranged in a suitable configuration.

Spent fuel has three advantages as a disposal form: it is less costly than other forms; it requires less processing on the surface than other forms, and is therefore less hazardous in the near term; and it eliminates the need for processing and handling a variety of low- and intermediate-level wastes.

Status of Ongoing Programs

Relatively little work has been done on analyzing spent fuel assemblies as a solid waste form. There are, however, three ongoing efforts that are noteworthy: those of the DOE Office of Waste Isolation (OWI) and the Swedish firm ASEA AB concerning the geologic disposal of spent fuel assemblies, and that of the Rockwell International Corporation concerning the Spent Unreprocessed Reactor Fuel Facility (SURFF) for storage of spent fuel assemblies.

The OWI effort is investigating both the disposal and retrievable storage of spent fuel assemblies in a bedded salt repository. Preliminary results indicate that the maximum heat loading of a repository for spent fuel disposal must be reduced from the 150 kW/acre recommended for HLW to 60 kW/acre (DOE estimates that 66 to 99 kW/acre of spent fuel can be stored versus 100 to 150 kW/acre of HLW from a reprocessing plant). This reduction is necessary because more heat is released by the larger amounts of Pu in the spent fuel than in the HLW (see section on characteristics of spent LWR fuel assemblies). If the spent fuel assemblies are to be stored retrievably, the maximum heat loading must be further reduced to 30 to 36 kW/acre. This further reduction should allow the spent fuel assemblies to be retrievable for 25 years without massive structural support in the repository. Other preliminary results of OWI studies are as follows:

1. Disassembly of the spent fuel assemblies does not seem attractive.

2. Increasing the interim storage time from one year to ten years increases the allowable density of spent fuel assembly emplacement by only about 20 percent.

3. Standard 14-inch pipe, holding one PWR assembly or two BWR assemblies, with sand as a filler material is being evaluated as a container for spent fuel assembly disposal.

4. A 2,000-acre salt repository should be able to contain all the spent fuel assemblies produced through the year 2000.

The OWI program is continuing at present, and during FY 1978 will perform a systems analysis of the disposition of spent fuel assemblies, beginning at the reactor and ending with emplacement in a repository.

The Swedish company, ASEA AB, has developed a process in which the spent fuel assemblies are canned in steel containers, wound into a spring configuration and placed in a shaped aluminum oxide container about 50 cm in diameter and 3 m long. The full container is then sealed with an aluminum oxide cover that becomes an integral part of the container itself.

The program established by ERDA at Rockwell International in Richland for the development of a Spent Unreprocessed Reactor Fuel Facility, which is at an early planning stage, has the objective of providing a surface storage facility by 1985. The approach is to use only passive cooling, and an early concept is to use shallow wells spaced 25 ft apart. The wells would be cased with a corrosion-resistant material. After the spent fuel assembly or assemblies were placed in the well, the well would be sealed and shielding provided as required. One PWR assembly or three BWR assemblies would be stored per well.

The program proposes simultaneously to make a conceptual design and to do the necessary research and development. Early development will include placing electrically heated, simulated fuel assemblies in wells to determine temperature distribution. It is assumed that the assemblies will be canned on-site, and early studies will be made to establish whether some filler material is needed for temperature control, mechanical strength, or added containment.

Program planning has not yet progressed to the point that the adequacy of R&D can be assessed.

ANALYSIS OF PRESENT STATUS AND R&D POTENTIAL

Since there has been serious consideration of ultimate disposal of spent fuel pins for only a year in Sweden and less than six months in the United States, there are few R&D results. The conceptual approaches described above are the only known work.

These very preliminary analyses indicate that spent fuel assemblies are appropriate for consideration as a disposable solid waste form. However, further studies and experimental work are necessary to establish feasibility firmly and define the method of preparing the assemblies for retrievable storage or ultimate disposal.

The following studies appear necessary, as a minimum, to bring our knowledge of spent fuel as a final disposal solid form to the level reached for reprocessed solid wastes.

1. Considerably more information is needed on all phases actually present in spent fuel, i.e., the oxides that serve as the primary containment of the actinides and fission products. The gas composition pressures and condition of the cladding must be more thoroughly studied.

2. Since it appears desirable to encase the spent fuel assembly in a metal can to facilitate handling and increase safety at the repository, candidate materials for these cans must be enumerated and studied.

3. It is highly likely that some "filler" oxides will be used between the fuel pins and the can. The molecular engineering of these materials should be started at once.

4. Studies of leachability, stability, and waste/rock interaction analagous to those on other waste forms will have to be carried out on spent fuel pins.

Very preliminary calculations indicate that the thermal loading allowed in the salt repository would have to be less than that allowed for HLW because of the higher heat output after the first few hundred years of spent fuel decay.

The major disadvantages of spent fuel as a disposal form are the lower maximum allowable heat loading, the greater long-term potential hazard due to the larger quantities of Pu and U introduced into the repository, and the possibility of criticality in case the repository is breached.

The major advantages are the lower cost and increased near-term safety resulting from minimizing the surface processing of spent fuel and waste. Processing and handling of a variety of LLW and ILW are also eliminated.

The study programs initiated by OWI on geologic storage or disposal of spent fuel and the Rockwell International program on surface storage should be pursued, and experimental work initiated as indicated by these studies.

NOTE

1 Sum of the amount of water required to dilute each isotope to the point that it is acceptable for unrestricted consumption, as specified in Title 10, Part 20 of the Code of Federal Regulations.

CHAPTER 12

RADIATION EFFECTS

While there has not been any major focus on the effects of radiation on the solid forms to be used for incorporating radioactive wastes, the scientific community often expresses concern about such possibilities. It is important, therefore, to evaluate all the possible effects that the various kinds of radiation may have on the alternative solid forms we have considered here. Only those effects need be considered that will occur at the radiation levels encountered by the solids, and the effects should be viewed in the context of all the other events and changes that the waste form will experience during processing, transportation, and emplacement.

EFFECTS OF RADIATION UPON THE STABILITY OF VARIOUS SOLID FORMS

An important consideration in selecting a primary and secondary containment material for radioactive waste is its stability under continuous exposure to the radiation generated by the waste it contains. Stability means resistance to radiochemical decomposition, excessive dimensional changes, increased friability, and loss of physical integrity. A considerable body of knowledge about the effects of radiation on the physical properties of the general types of solids involved already exists (for a review see Billington and Crawford [1960]), and recent studies on glass (Hall et al. 1976, Mendel et al. 1976, Primak 1977) provide insight into the dimensions of the radiation effect problem for that particular waste form.

The period during which radiation instability is of major concern is approximately the first ten years after the wastes (in the form of spent fuel) are removed from the reactor. The rationale for placing emphasis on the first ten years is that a substantial fraction of the total radioactive decay occurs during this time.

From our knowledge of the radiation levels necessary to cause substantial structural damage, it is clear that after this first high-flux regime, structural damage will be trivial. During the first ten years, the major adverse radiation effect is on chemical reactivity, which promotes release of gaseous products; the incremental effect on such behavior is expected to be insignificant in the second time regime. Therefore, integrated exposure to radiation over the first decade is of primary importance and irradiation over the longer term is of lesser concern.

We consider first the types of radiation and the nature of the damage that they can induce in the lattice of crystals or the network of glasses. In HLW, fission products are the major early source of energetic radiation. The contribution of actinides (Pu, Am, and Cm) increases in relative importance later, as the fission products, with their generally shorter half-lives, decay. Therefore, the waste form must be able to withstand intense gamma- and beta-ray fluxes and to a lesser degree alpha particles from the actinides. The consequence of each type of radiation is considered separately.

Gamma and Beta Radiation

Gamma and beta rays interact with solids predominantly by ionizing atoms or ions. Hence, their major effect is radiochemical: covalent bond rupture (most important in glasses since it contributes to stress relaxation), OH^- and H_2O decomposition with hydrogen relocation, valence changes of metal ions, and decomposition of unstable molecular ions such as NO_3^-. In certain materials, such as the alkali halides and alkaline earth halides, ionization alone can create intrinsic lattice defects, namely vacant lattice sites (vacancies) and atoms lodged in nonequilibrium positions (interstitials). These defects, which occur in various charge states, are responsible for the familiar color centers, and can result in considerable chemical decomposition (colloidal particles of alkali, voids, or bubbles containing halogen gas). Both gamma rays, acting through the intermediary of energetic Compton or photo electrons, and beta rays are capable of directly displacing lattice atoms by momentum transfer during elastic collisions. However, the cross section for this direct "knock-on" process is quite small, and such direct displacement effects caused by gammas and betas are expected to be of little consequence.

Alpha Particles

Alpha particles lose their energy over a very short range in solids (10^{-3} cm). Although the bulk of the energy is lost in ionization, a significant portion (1 or 2 percent) goes into elastic collisions with the atoms of the surrounding solid, thereby initiating displacement cascades, i.e., displaced atoms resulting from primary, secondary, and tertiary recoils from these collisions. The result is a region of lattice damage in crystalline solids, or network damage--i.e., ruptured covalent bonds and disrupted SiO_4 tetrahedra--in glasses, in the areas surrounding the alpha particle tracks. Depending on the material, 100 to 1,000 displacement events may result from a single primary collision and, although substantial healing of the damage may occur immediately after the collision, a high concentration of lattice vacancies and interstitial atoms (or a high degree of network disruption in glasses) is expected in the wake of alpha particles. The recoiling nucleus that emits the alpha particle can also produce substantial damage.

For reprocessed nuclear fuel wastes, the cumulative dose is expected to be 2×10^{18} alpha particles per cubic centimeter during the first 100 years (Mendel 1975) and about one-fourth that for the first ten years. Therefore, in the regions affected by the alpha particle flux, substantial lattice and/or network disorder can be expected. The consequences for the various waste forms considered will be discussed in the relevant sections below.

Perhaps the most important factor in limiting the amount of alpha particle damage in the packaging matrix is the way in which the actinides are distributed. The short alpha range is scarcely larger than the calcine particle size. Therefore, if the waste is in the form of calcine particles, most displacement damage is confined to the calcine particle that contains the alpha emitters. The calcine, which is poorly crystalline to begin with, will be rendered even more so by the displacement damage. However, if the alpha emitters are atomically dispersed throughout the waste form, the entire solid will suffer some damage. The magnitude of this damage, in terms of stored energy, appears to be around a few calories per gram at most (Mendel 1975).

The above remarks apply to reprocessed commercial wastes. If unprocessed spent fuel pins are to be disposed of they will be packaged in canisters; in this case, no alpha damage will occur outside the fuel pins, since the alpha particles will be contained within them. However, within the fuel oxides this structural damage will be at a maximum. Indeed, studies of irradiated fuel might show the maximum extent of damage to be expected.

Neutrons

It has been suggested that fast neutrons could be produced by spontaneous fission of transuranics and by (α, n) reactions. However, in view of the very small spontaneous fission rates and the small (α, n) cross sections, the flux of energetic neutrons from this source is negligible.

In summary, it is evident that, except in those regions of the waste form matrix within the alpha range, the most significant radiation effects are radiochemical in nature and associated with the high fluxes of beta and gamma radiation emitted by fission products.

EFFECTS ON PROPERTIES OF SOLIDS: POTENTIALLY ADVERSE CONSEQUENCES FOR WASTE FORMS

Radiochemical Effects

As indicated above, ionizing radiation can cause radiochemical decomposition (radiolysis) of molecular species and molecular ions. The most familiar of these is the decomposition of H_2O and OH^-, which results in the release of atomic hydrogen (H) into the interstices of the solid. Because of its small size, H can diffuse readily through most materials and become attached at other locations. The most common form in which it is immobilized is as H_2 in some pocket or pore. As indicated above, alkali halides and certain alkaline earth halides can undergo radiolysis which, at a high level of exposure, can lead to a colloidal distribution of metal particles and halogen gas bubbles.

Another familiar example is the nitrate ion, which is relatively unstable chemically. In the presence of ionizing radiation, NO_3^- breaks up into oxygen gas and oxides of nitrogen. This last radiolytic process may be of some consequence in the case of military wastes, which have a high nitrate content. Such radiolytic effects can contribute to swelling and, in extreme cases, could adversely affect the physical integrity of the waste form. None of these effects has been experimentally observed. It is to be hoped that current studies on hydrogen generation in concretes will successfully resolve this matter.

Expansion and Dimensional Changes

Since extreme expansion could rupture the waste canister during the period of retrievability, it must be considered as a harmful effect of radiation. Expansion can be classified into two categories: (1) that caused by expansion of the crystal lattice or glassy network from accumulated atomic scale strains associated with lattice or network defects and (2) that caused by void or bubble formation.

Expansion resulting from defects is primarily caused by interstitial material lodged between atoms or ions on normal lattice sites. Henderson and Bowen (1971) have observed that the expansion per oxygen vacancy/oxygen interstitial pair in neutron-bombarded magnesium oxide is about nine molar volumes, a remarkably large change. These effects saturate when the separation between defects becomes a few lattice distances, so that the probability of interstitial-vacancy recombination becomes large. In network formers such as SiO_2, this simple dilatation around interstitials eventually results in lattice collapse into the disordered glassy structure, usually with large increases in specific volume. However, these are rather special cases and the fluences accumulated by the waste forms are in any case never expected to be large enough (they are 10^3 to 10^4 too low) to complete saturation.

Void formation results from coalescence of lattice vacancies. In the presence of alpha particles or protons these voids often accumulate helium or hydrogen to form bubbles; this state of affairs presents serious swelling problems in structural alloys in high flux reactors. Again, the fluences ($>10^{19}$ cm^{-2}) at which these processes occur are well in excess of those expected in the waste form matrix. It is conceivable, however, that something approaching this situation could result from accumulation of radiolytic gases (H_2, O_2, NO, etc.) in small pores or fissures in the matrix. Clearly, the degree of expansion from such accumulations would depend sensitively upon the composition of the waste, the constitution of the waste form, and the intensity of the encapsulated radiation. Only in extreme cases where each of these factors was unfavorable could expansion be expected to be a serious problem.

Possible Catastrophic Release of Stored Energy

Introduction of interstitials, trapping of electrons and holes, and rupturing of covalent bonds all increase the internal energy of crystal or glass. This increase is referred to as stored energy. Annealing at elevated temperature causes much of the lattice damage to be removed. Vacancies recombine with interstitials, and electrons and holes are released from traps and recombine. These recovery processes are accompanied by a release of stored energy, which appears as heat. If a substantial amount of stored energy is released in a narrow temperature interval, a temperature transient may result. Should other energy release stages be reached by the transient, additional stored energy may suddenly be developed, leading to a catastrophic or runaway release of energy, which can culminate in a very large temperature transient.

One material with a stored energy release spectrum favorable to a catastrophic release is graphite, which exhibits a sharp release peak at 200°C. Evidently, it was the combined effect of the large amount of energy stored in this peak and a sharp temperature excursion that resulted in the catastrophic energy release and the rupture of fuel slugs in the Windscale reactor some 20 years ago (McCullough 1959). The determinant seems to be the nature of the energy release spectrum: a sharp release peak early in the release spectrum is necessary. (The release spectrum is the incremental energy released per unit temperature rise versus temperature during a heating cycle.) The release spectra for glasses and most ceramic materials lack this feature, the energy release being more uniformly distributed over a wide temperature interval. Therefore, an uncontrolled temperature excursion as a result of stored energy release seems to be unlikely for the waste forms currently under consideration.

Enhanced Chemical Reactivity and Solubility

Since the internal energy is enhanced by radiation damage to both the lattice (network) and the electronic system, enhanced chemical reactivity and solubility (leach rate) might be expected. Although there is little clear evidence of such effects, one should be alert to this possibility in particular systems. However, from the magnitude of the energies involved (see section on possible catastrophic release of stored energy), this contribution to the ΔG of the likely waste-environment reaction is seen to be negligible.

Transmutations

Another consequence of radioactive decay of fission products is their transmutation into other elements with a different chemical behavior. These daughter products may or may not be stable in the particular phase used to contain the original nuclides. Whereas such an effect does not appear to be important for glassy matrices, it is possible to conceive of situations in which the stability or integrity of ceramic phases may be impaired. For example, ^{90}Sr decays into ^{90}Y, which is also unstable, decaying with a 64-hour half-life into ^{90}Zr, a stable nuclide. Hence in a $SrTiO_3$ phase, the ^{90}Sr would be largely replaced by ^{90}Zr in a few ^{90}Sr half-lives (28 years). Also of interest is the 30-year half-life decay of ^{137}Cs into ^{137}Ba (stable). The consequences of this decay for the stability of pollucite ($CsAlSi_2O_6$), a potential candidate for the immobilization of ^{137}Cs, has yet to be examined. Although the decay products in these two cases (^{90}Zr and ^{137}Ba) are stable nuclides and are of little concern in themselves, the structural chemical effects of their substitution may render the chosen ceramic phase unstable. Therefore, while it is not clear that such chemical effects of transmutation will have any serious consequences, this class of problems should be examined more extensively, since its effects are probably at least as significant as those of radiation damage.

CONSEQUENCES OF RADIATION EFFECTS FOR SPECIFIC WASTE FORMS

Supercalcine and Calcine

In unconsolidated calcine particles, radiation effects would be expected to have no serious consequence. Because of their relatively open, poorly crystalline structure, expansion due to alpha-particle bombardment would not be serious even though several tenths of a percent expansion might be expected before final emplacement. Expansion may lead to further fragmentation, the effect of which would be to shift the average particle size to smaller dimensions. Radiochemical effects for the most part would be confined to valence changes in certain of the metallic ions and decomposition of anion radicals, if any, with the accumulation of stored energy. These radiochemical effects would be minimized by the elevated temperature expected to exist in emplaced canisters since, in most materials, redistribution of charge and radiochemical decompositional effects can be eliminated by heating to temperatures above 300°C. Even without annealing, the energy stored would not be excessive. Assuming 5 eV for each misplaced electron, and a saturation concentration of 0.5 percent of all lattice sites affected at room temperature, a total stored energy of 2 to 3 cal/g is expected. Stored energy can also result from displaced atoms, but here again the amount is not much greater than that due to ionization. Therefore, saturation stored energy at room temperature should not exceed 10 cal/g for most materials (see, however, Roberts et al. 1976). Since, for the most part, displacement damage is accumulated at elevated temperatures, the amount of stored energy caused by it is expected to be a small fraction of this value. Therefore, even if it could be "triggered," the temperature excursion would be inconsequential.

Although not strictly a radiation effect, particle creep--i.e., physical movement caused by recoil of particles containing actinides--would be expected if the calcine particles were excessively fine, and would make them difficult to confine. For this reason alone, incorporation of calcines into some more stable form is desirable.

Cement Composite Forms

The extent of alpha-particle damage will depend upon how the actinides are dispersed in the primary containment phase. If the supercalcine or ceramic phase particles are essentially insoluble, and if their size is large compared to the alpha-particle range, relatively little damage will accumulate. Even uniform distribution of actinides in this heterogeneous, multiphase waste form would not be expected to have serious consequences. Displacement damage would be expected to result in expansion, mainly in "filler" grains such as quartz (sand) and in calcine itself, up to a maximum volume increase of 1 percent. Because of the porous structure of most concretes, this expansion could be accommodated without serious consequence, i.e., excessive fracturing. Another consequence of alpha particles is helium entrapment in the matrix, presumably as small bubbles. At the elevated storage temperatures helium would be expected to diffuse readily through the concrete matrix; serious buildup of internal stress would thereby be avoided.

Ionization effects include radiochemical decomposition of H_2O and other molecular ions, as well as trapped electrons and holes as manifested by valence changes of various ionic species. As in the case of calcine alone, no adverse consequences from these processes are anticipated, except, possibly, those from internal stresses due to bubbles of gaseous radiolytic products. Stored energy would not be expected to exceed that for calcine. Some concern, however, has been expressed by certain Soviet investigators (Sakharov et al. 1967, Spitsyn et al. 1967) that radiolytic gases generated by the decomposition of water, might present a hazard if concrete is used. Entrapment of H_2 in the canister as it diffuses from the concrete is evidently the source of their reservation. Better information on the extent of radiolysis of concrete is needed before concern about it can be laid to rest. Experiments in which hydrogen is accumulated in thin concrete slabs that are exposed to alpha particles in an accelerator beam should provide adequate information to evaluate this possibility.

It should be pointed out here that the service life of concrete in radiation environments is exceedingly good. Most of the biological shields of the earlier reactors were constructed from concrete, and many of these reactors are still in operation. It is significant that the inner surface of these shields and concrete plugs, which are still effective, have accumulated far greater doses of radiation than is anticipated for the entire service life of potential waste forms.

Since concrete is an attractive waste form for low- and intermediate-level DOE wastes, and since sodium nitrate is a major constituent of these wastes, the consequences of nitrate radiolysis in concrete also deserve attention. The NO_3^- ion is relatively unstable and readily decomposes into gaseous products (oxygen and oxides of nitrogen) when exposed to gamma radiation. Although the void space in concrete would be expected to accomodate large quantities of gas, it is obvious that an experimental evaluation of the effects of NO_3^- radiolysis as a function of the activity of waste under conditions of storage needs to be carried out.

Glasses

In the molten state, glass dissolves most radionuclides, so dispersal of actinides on the atomic scale should occur to a degree much greater than in concretes. Therefore, alpha-particle damage in the glass matrix should be appreciable. Previous studies (Hall et al. 1976, Mendel 1975, Mendel et al. 1976, Primak 1975) using a variety of energetic bombarding particles at or near room temperature show changes in a variety of physical properties. The nature of these effects is sensitive to the glass composition; both expansions and contractions have been observed. Fused silica contracts up to 4 percent when exposed to fast neutrons at room temperature.

It has been pointed out (Primak 1975) that the net effect depends upon the magnitude of several conflicting processes: ionization and disruption of the silica network produce contraction, i.e., a more ordered arrangement of the SiO_4 tetrahedra in silicate glasses. Gas retention (helium, in our case) in the form of bubbles causes expansion, as do compositional changes in certain special glass formulations. Although many glasses are permeable to helium, increasing the concentration of alkali or alkaline earth ions strongly attenuates the rate of helium diffusion. Hence, expansion predominates in calcium-containing glasses that are bombarded with alpha particles from an external source; the same effect would be expected for internal bombardment with alpha particles. The expected effect of alpha-particle irradiation resulting from actinides in waste has been simulated for certain glass formulations (Hall et al. 1976, Mendel et al. 1976) by addition of short half-life alpha emitters such as ^{244}Cm and ^{238}Pu; use of these radionuclides resulted in acceleration of the process. Both volume expansion and contraction have been observed, and stored energies of up to 25 cal/g have been recorded for irradiations equivalent to those generated in stored HLW over 2,000 years. It was found that the amount of energy stored for a given irradiation time was inversely related to the temperature at which the specimens were kept. No stored energy release was observed for samples held at or above 350°C.

Ionization caused by beta and gamma radiation, as well as along alpha-particle tracks, can also have appreciable effects upon the properties of glasses. Again, however, most of the previous research has been devoted to fused silica, a very unusual case and a poor model for our purposes. Because of the flexibility given to the glassy network by the covalent bond rupturing accompanying ionization processes, stress relaxation and creep under load is expected. However, not much research has been devoted to these points. The electrons and holes trapped at network defects (dangling covalent bonds) and by metallic ions promote the mobility of certain types of ions, notably alkali metal ions, by reducing the density of sites that are chemically stable locations for them. An effect apparently related to this decrease in the stability of specific constituents has been reported by Primak (1975) who observed droplets of moisture on the surface of a variety of glass compositions after proton bombardment. These droplets are due to the deliquescence of Li_2O and/or Na_2O formed on the surface as a result of the outward diffusion of Li^+ and Na^+ through the radiation-affected layer. After being washed away, the droplets replenish themselves over a period of weeks. It is not yet clear whether atomic displacements in addition to ionization are necessary to produce this chemical instability.

Although it appears that glass may indeed be a suitable solid form for radioactive waste, knowledge about its chemical, mechanical, and dimensional stability in radiation fields is not complete enough to make glass a "comfortable" choice. Virtually nothing is known about glass stability at an elevated irradiation temperature comparable to the temperature reached under service conditions. Such information may be needed before the suitability of a given glass composition for waste packaging can be determined. The effect of thermal gradients similar to those anticipated under service conditions also must be evaluated; such gradients provide an additional chemical driving force for separating various constituents, and thus could influence chemical stability. Although it has long been suspected that nuclear radiation aids the devitrification process and hence affects the integrity of glasses, there is little quantitative data on this point. The extent to which these various processes that impair chemical stability would increase the rates of such crucial processes as leaching or reactivity and fragmentation cannot be stated with certainty. Therefore, from the perspective of radiation effects, the performance of glass as a waste form is somewhat uncertain. However, the magnitude of <u>all</u> these effects indicates that no major changes can be foreseen either during the first decade or two of storage, or thereafter.

Metal Matrix

As regards radiation effects, this waste form has no competitor. There are no permanent ionization effects in metals, and displacement damage would be kept to a minimum because the waste is encapsulated in a secondary phase material. Even if appreciable expansion of the second phase were to occur, the metal is expected to be sufficiently plastic to accommodate it.

Ceramics

Although a good case for specially tailored ceramic waste forms can be made on the basis of the chemical stability of a structure into which fission products and even actinides are incorporated directly, lattice damage (metamicitization) caused by alpha particles could be as extensive in ceramics as in glass. The major deleterious effect of this damage would be lattice expansion. Quartz, an extreme example, exhibits a saturation volume increase at room temperature of 15 percent, and 5 percent is typical for most perovskite, spinel, or rutile structures (Crawford and Wittels 1956). However, these expansion levels were only attained at neutron fluences $>10^{19}$ cm^{-2}. As indicated above, the total alpha-particle fluence expected in the first ten years would be only 5×10^{17} cm^{-2}. Hence, expansions of around 0.5 percent would be expected. Moreover, these values would no doubt be reduced to some degree by the annealing of lattice damage at the elevated temperatures attained by the waste package during storage, and therefore may not be a serious factor during the first decade. It should be possible to accommodate moderate expansion by providing sufficient porosity in the fabricated waste form. However, the amount of porosity required would have to be determined for the ceramic structure in question, preferably under simulated service conditions.

CHAPTER 13

INTERACTIONS BETWEEN SOLID WASTE FORMS AND ROCK

Once any solid waste form is placed in a geologic formation, the potential exists for interaction between the waste and the host rock. For some forms this interaction is a certainty; for others it is planned that such interaction be negligible during the retrievable phase. Given the conditions of time scales in the range 10^3 to 10^6 years and temperatures in the range 200 to 800°C with some water present, containers will probably be breached in virtually all cases. The result wil be direct interaction of three components: solid waste form, saturated aqueous solution, and host rock.

Since this interaction is inevitable, in selecting the solid waste form for emplacement one must consider the effects of this waste-water-rock interaction for each combination of waste form and rock type. The range of interaction between the solidified waste and the host rock is shown in Figure 13.1.

Physical Interactions

The major physical effects of the waste/rock interaction result from the thermal output of the waste (see Figure 13.1). This determines the temperature at the surface of the waste as well as in the rock itself, given the thermal diffusivity of the rock. The effects consist of thermal and mechanical stresses, which depend on the thermal and mechanical properties of the rock. The combined properties of the waste and rock will dictate the number and spacings of canisters in a particular geological formation. This problem is considered in Chapter 14.

CHEMICAL INTERACTIONS

The structural chemical effects of the interaction between the solid form and the host rock interaction are our principal concern in this chapter. Figures 13.2 and 13.3 illustrate these effects on a macroscopic and microscopic scale, respectively.

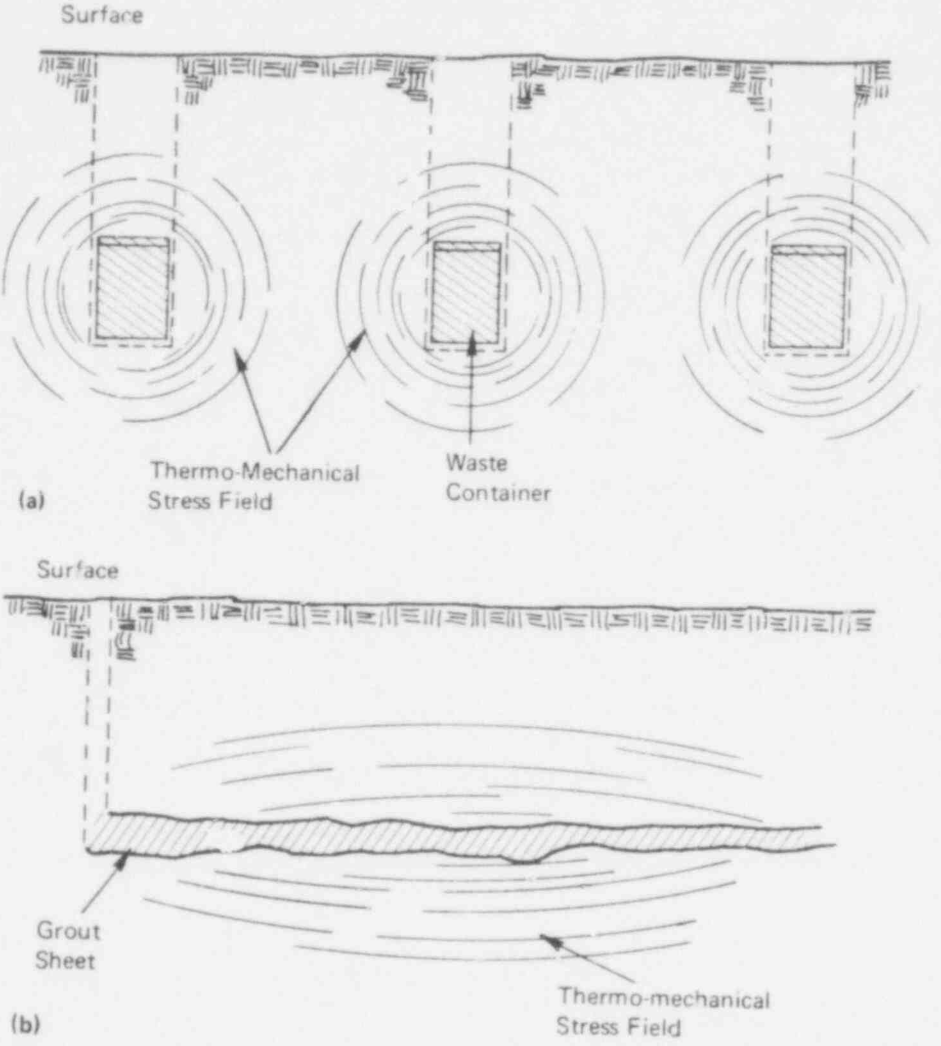

FIGURE 13.1 Thermal effects of solid waste on host rock. Emplacement of (a) waste canisters and (b) grout are shown.

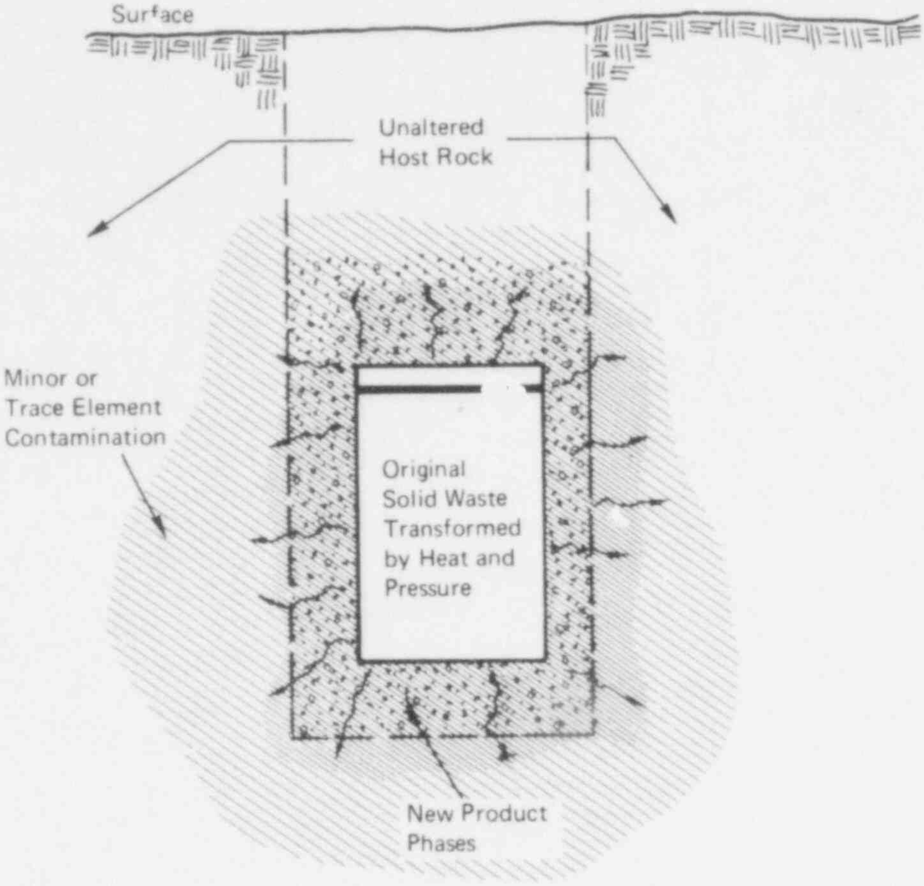

FIGURE 13.2 Chemical effects of waste-rock interaction on a macroscopic level.

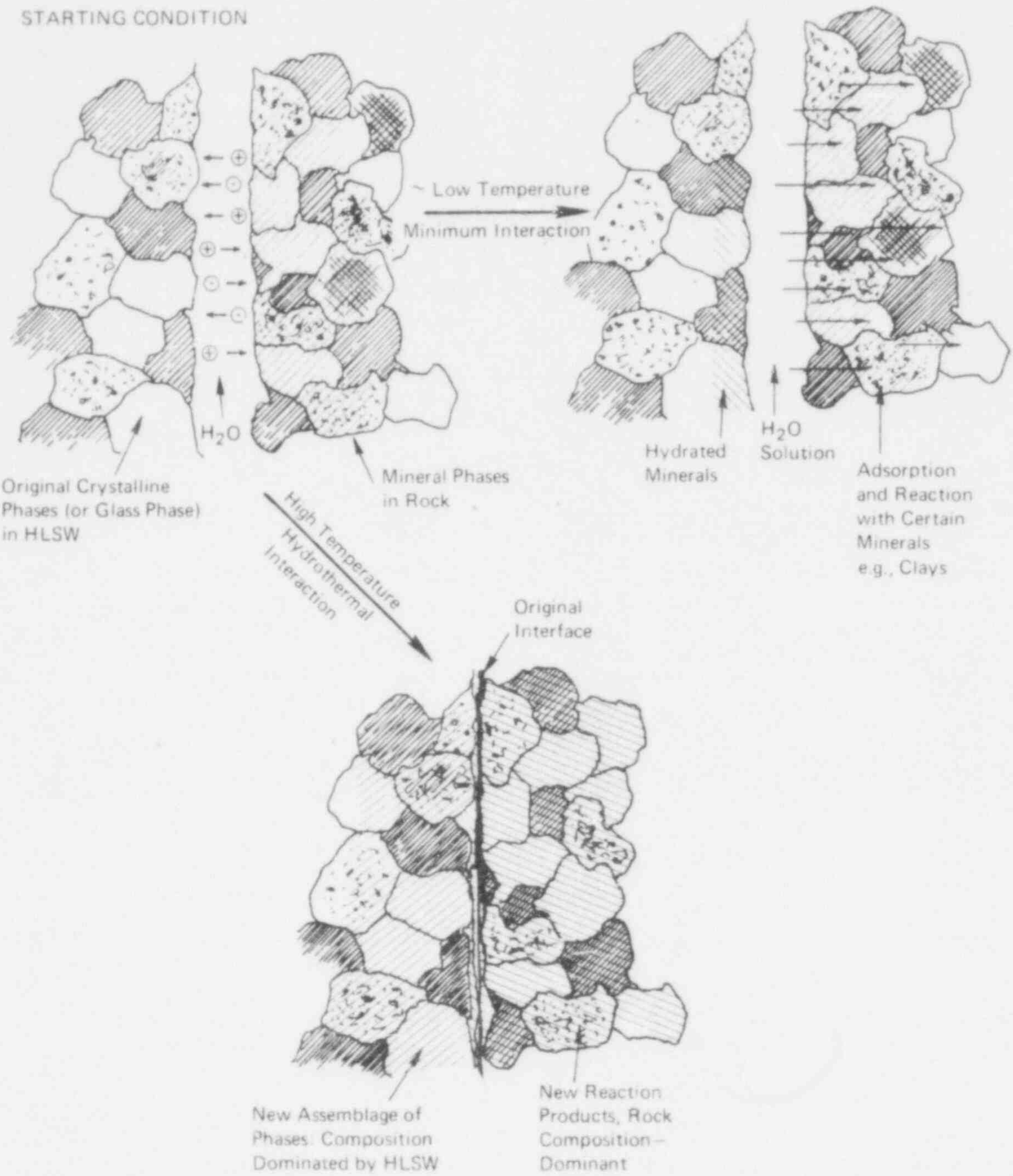

FIGURE 13.3 Chemical effects of waste-rock interaction on a microscopic level.

On a macroscopic scale, the waste will react with the rock and form a zone of reaction products. The extent and the products of the reaction will be determined by the composition of the waste and the rock, the pressure-temperature environment, and the absence or presence of water. The model of the original waste form slowly "leaching" and providing a continuous point source of ions to groundwater is both naive and incorrect. At the temperatures and pressures that will likely be encountered (between 200°C at 100 bars "dry," and 800°C at 500 bars $p[H_2O]$), and especially with water present from bubbles in salt, hydrated minerals in the rock, or groundwater, extensive reaction is certain to occur in a matter of days or weeks once the container is breached.

The redox potential, E , is also an important variable. The driving force for this reaction is no longer solubility in water, but the ΔG between equilibrium phases and the metastable assemblage: waste phases + mineral phases of the rock. Ions are leached not only from the waste, but also from the rock. The ions are not only "adsorbed" by particular minerals such as clays, but react with the clay to form new phases. The low-temperature model shown in Figure 13.3 will occur only (a) for wastes with low thermal output or (b) far from the waste canister. The higher temperature model will be the general case.

Publications on hydrothermal reactions constitute a major fraction of the postwar literature in the field of experimental petrology. In this research, various compositions are reacted under the "hydrothermal" (high temperature + high water pressure) conditions that exist in the earth. The field of metamorphic petrology, especially contact metamorphism, is concerned with conditions very similar to the ones we are now considering: intrusion of a hot body of different chemistry into a preexisting geologic formation. The results of thousands of papers establish unequivocally that in the range of conditions noted above, extensive reaction will occur rapidly. Indeed, the time scale is in terms of days to months rather than hundreds of years, although it is, of course, strongly dependent on temperature and composition. The work most directly relevant to our discussion here is that of Hawkins and Roy (1963). They compared the degree of reaction of glassy and crystalline materials of identical compositions under pressure and temperature conditions well within the present range of interest. They showed that in a matter of days, glasses of basaltic composition were rapidly attacked, while the crystallized form showed almost no change. However, experimental data on glasses and crystalline material containing fission products have not been obtained as yet.

Only during the last several months has the subject begun to be studied. The scope of the topic was outlined at an initial conference held at The Pennsylvania State University in July 1977 (Pennsylvania State University 1977), at which time preliminary data were reported by several workers from national laboratories, the U.S. Geological Survey, and the host university. These X-ray, scanning electron microscopy, and electron probe data demonstrated the rapid conversion (in a few days) of simulated waste glass in contact with salt and limited water at 250° to 300°C (Roy 1977). While all the new phases have not been identified, it is interesting to note that the Cs is converted to pollucite. In this respect, the Cs in the reaction product may be less leachable than it is the original waste form. Naturally, we must determine what happens to all the radionuclides of interest.

By considering phase equilibria and the compositions and masses of components involved, a well-designed experimental program will be able to provide good estimates of the likely final assemblages in a reasonably closed system. These entities will become, in effect, the new waste form, and interest must be directed toward them in any long-term considerations of leaching or supply of radionuclides into groundwater.

The flowing ground water model that ignores the thermodynamics of waste/rock interaction will be conservative in predicting the transport of ions, possibly by several orders of magnitude. For example, a 10-ft bed of argillaceous shale would retain almost all waste radionuclides that might be "leached" out from the waste form. The shale functions as an ion-exchange resin at low temperatures, and creates new phases at high temperature and pressure.

Table 13.1 shows the tendencies toward and degrees of interaction between various wastes and host rocks.

TABLE 13.1

Qualitative Relative Indication of Waste-Rock Interaction

	Salt	Shale	Basalt	Granite
Supercalcine	Very high	Moderate (Self-crystallization)	Moderate (Self-crystallization)	Moderate (self-crystallization)
Glass	Very high	Very high (500° C) High (300° C)	Moderate	Moderate
Ceramics	High	Very low at HT Very, very low at LT	Very low	Very low
Metal Matrix Forms	Depends on dispersed phase - Matrix nucleate effects noted above			
Cement Matrix Forms		Substantial at HT (500°C) Low - Very low (300°C)	Low - Very low	Low - Very low

HT = high temperature
LT = low temperature

CHAPTER 14

GEOLOGICAL CONSIDERATIONS

INTRODUCTION

It is generally agreed that for the immediate future the preferred option for the isolation of high-level radioactive wastes is deep continental geologic isolation. In addition, DOE continues to maintain the position that any concept of permanent storage must be tested using a prototype and that the waste must be recoverable in the event of unexpected leakage or indications of future leakage (Pittman 1972). This retrievability criterion has, in effect, specified the conventional mined cavity as the only acceptable means of emplacing the waste in a geologic formation; other suggested methods of emplacement imply permanent disposal, in that retrieval of the waste is beyond existing technology, prohibitively expensive, or appreciably more difficult than emplacement.[1]

Once radioactive waste has been emplaced in a geologic repository and the repository has been sealed for permanent isolation, radionuclides in the waste can re-enter the biosphere only by physical transfer of the rock mass containing the waste, by solid state diffusion, or by dissolution and transport of the nuclides by ground water. Either natural processes or anthropogenic activities could conceivably result in the transfer or exposure to the biosphere of radionuclides. The American Physical Society (APS) Study Group (1977) evaluated the possible occurrence and consequences of both types of disruptive event; it concluded that current knowledge and technology--if used with appropriate site selection criteria--are adequate to design and locate a suitable waste repository of the conventional mined cavity type, which would not be breached instantaneously as a consequence of either surface nuclear explosions or meteorite impact and would not be compromised by erosion. Moreover, use of appropriate criteria would make it highly unlikely that the repository would be compromised by tectonic or volcanic activity. The APS report pointed out that the most important possible hazard to be expected from radioactive waste emplaced in a geologic repository is its transport by groundwater.

This chapter is primarily concerned with the physical characteristics of proposed repository rock types and of the wastes and waste forms that can interact with rock. These interactions could conceivably affect the integrity of the repository for long-term isolation. The possible chemical interactions between the waste form and the rock were discussed in the previous chapter.

The only possible important medium for transporting deeply buried, high-level radioactive wastes is groundwater. Consequently, satisfactory isolation of such waste depends upon the choice of a repository site with suitable hydrogeology. Under favorable hydrogeologic conditions, the transport of any radionuclides, leached from the buried waste form, would be so slow and follow such long pathways that the nuclides would not reach the biosphere during the period of concern. It is therefore essential that the method of emplacement and any subsequent waste/rock interactions have no adverse effect on the hydrogeology.

Certain characteristics of the geologic disposal medium, in addition to its hydraulic transport properties, can provide additional security in isolating HLW. Shales, for example, may have such highly favorable sorption characteristics that the velocity of radionuclide transport through these rocks could be reduced several orders of magnitude below the speed of groundwater transport. Certain "chemical" effects were discussed in Chapter 12. In contrast, other properties of a disposal medium may make it susceptible to heat generated by radioactivity, with consequent changes (e.g., fracturing) that can result in more rapid transport of groundwater and any dissolved nuclides. Thus, it is important to consider the effects that the presence of high-level radioactive wastes might have on relevant properties and characteristics of these rocks, and whether these effects support or undermine the integrity of waste isolation. The emplacement and presence of radioactive waste in a deep geologic repository will result in a significant physical modification of the natural environment locally, as a consequence of thermal and stress effects induced in the rock in the immediate vicinity of the emplaced waste.

In the United States, consideration of repositories developed in conventional mined cavities has been restricted almost exclusively to rock units within regional sedimentary basins--e.g., bedded salt, domed salt, shale, and limestone. By the very nature of their origins, undisturbed sedimentary rock units are characterized by horizontal or nearly horizontal layering and high porosities saturated with fluids (principally aqueous). The layering constitutes anisotropy, which not only provides important potential pathways for interstitial fluids, but also strongly influences the deformational characteristics, such as fracturing and interlayer slip, of the individual units and of the entire sedimentary sequence. Dome salt is not, in itself, layered, but occurs within layered sedimentary sequences.

In contrast to layered sedimentary sequences, there exist igneous rock masses, such as granite, which are potentially much more homogeneous and isotropic, and which extend to great depths over large areas of the earth's crust. These may be overlain by sedimentary rocks, but they are not typically associated with sedimentary basins. Moreover, the porosity of granites (due primarily to fractures) is generally very low compared with that of sedimentary sequences, typically a few percent or less compared with more than 10 percent in most sedimentary rocks.

In either sedimentary sequences or granitic masses with fracture porosity, pore spaces tend to be filled with groundwater, which extends from the water table (the top of the saturated zone, generally a few meters to a few tens of meters below the surface) to depths of several thousand meters. Fluids associated with the formation of the rocks could be present at still greater depths. These groundwaters are the medium by which radionuclides might reach the biosphere, and it is the prediction of movements and interactions of these fluids with the rock and with contained waste that is a principal objective in planning for radioactive waste management.

Because the movement of groundwater is of primary concern in relation to "far-field" effects that have influence some distance away from the repository, it is important that potential conduits such as faults, fractures, and other discontinuities in the undisturbed rock be at a minimum. Furthermore, potential conduits produced by exploration and engineering activities must be capable of being effectively sealed once the repository is abandoned for permanent isolation. For conventional mined cavities, these engineered potential conduits are principally boreholes and shafts.

As stated above, deep continental geologic isolation is the only currently acceptable alternative for disposal of high-level radioactive wastes; in current planning this alternative is to be employed regardless of the solid waste form. The particular waste form selected and the manner of emplacement in deep geologic media can influence the security of isolation, and certain specific aspects of this influence are addressed later in this chapter.

RELEVANT WASTE CHARACTERISTICS

The important characteristics of radioactive waste with respect to deep continental geologic isolation and waste/rock interactions are the thermal power and radiation generated by the waste. Radiation effects on the waste itself have been discussed in Chapter 12. For the most part, effects of the emplaced waste will be "near-field" responses of the rock to heat, radiation, and heat-induced stress--i.e., effects that are restricted to dimensions of the repository. Certain effects, however, significantly alter the transport characteristics of the disposal medium and associated rocks, and thus can have more far-reaching influence. Of additional interest are waste/rock interactions that can potentially affect the retrievability of the emplaced waste. Retrievability here refers to the ability to remove waste from a repository with the same equipment and techniques that were used to emplace it.

Thermal Effects

Thermal power of LWR high-level wastes varies from about 200 kW/m^3 for waste less than one year old to about 0.02 kW/m^3 for 1,000-year-old waste. Ten-year-old waste generates about 10 kW/m^3, which is sufficient to melt typical silicate and halite rocks if placed in a cavity 1 m in diameter. For retrievability to be feasible, it is therefore necessary (1) to reduce the thermal loading of a waste form sufficiently that the host geologic medium is not locally brought to its melting range, and (2) to keep the thermal loading low enough that the waste form (e.g., glass) is not affected adversely or that volatile radioactive species are not driven off by the waste-generated heat. A third consideration is the influence of thermal loading on the mechanical properties of the emplacement medium (i.e., the rock in which the repository will be excavated) and the overlying geologic units. The first two considerations dictate the waste loading of the fabricated containment and the dimensions of the container; for glass, the waste loading in typical DOE designs is 25 percent waste and 75 percent glass in a cylindrical container 0.3 m in diameter by 3 m in length. These specifications would result in a maximum centerline temperature in the canister of about 600°C and a surface temperature near 400°C. The third consideration has led to the proposed emplacement of waste containers in a geometric array whose spacing is dictated by the desired thermal loading per unit (e.g., spacing of 7 to 10 m for 150 kW/acre desired thermal loading).

Other potential thermal effects of consequence for the security of waste isolation are the effect on groundwater flow of thermal gradients within and adjacent to the repository, thermally-induced cracking caused either by thermal expansion of the heated rock units or by modification of the rock stress with increased pore fluid pressure, and possible mineral or rock decomposition with attendant loss of volatiles (e.g., CO_2 and water). The development of cracks could increase by two orders of magnitude or more the hydraulic conductivity of the affected rocks; the release of volatiles would contribute carrier fluid for the potential transport of nuclides.

Specific aspects of thermo-mechanical effects on rock are discussed below in the section on relevant rock characteristics.

Radiation Effects on Rocks

Possible radiation effects fall logically into two time regimes: the period during which the waste form remains intact, and the time after its breakdown. Before the waste form breaks down, the only radiation reaching the surrounding medium will be gamma rays.

Ultimate breakdown of the waste form will result in a more intimate mixing of actinides and fission products with the minerals of the host rock. At this point displacement damage from the alpha particles might occur within the immediate vicinity of the actinides. However, unless some geologic event (e.g., breaching by groundwater) takes place to cause dispersal of the alpha activity, not much additional effect is expected. Diffusion occurs at such slow rates that the mass of rock affected would remain small even after 10^4 to 10^5 years.

Possible effects of radiation on three specific rock types--granite, shale, and salt--have been considered. The radiation fluxes affecting the rock are one to two orders of magnitude lower than those affecting the waste form. Since the phases involved are essentially similar, one can say with some confidence that radiation effects on the rocks will be negligible.

RELEVANT ROCK CHARACTERISTICS

The characteristics of rocks important for waste/rock interactions are their mechanical properties (specifically, those affected by temperature) and their potential for chemical interactions (see Chapter 13). Although both categories of characteristics can influence far-field groundwater transport, their most direct influence is in the immediate vicinity of the repository.

Thermo-mechanical Effects

Heat generated by emplaced radioactive waste can be expected to produce thermomechanical effects; the specific nature of these effects will be dictated by the physical properties and other characteristics of the repository rock and of associated geologic units. The principal physical property of rocks that affects heat distribution, and thus its effects, is thermal conductivity. Values of thermal conductivity vary among different rock types, but among the common rocks they differ by a factor of only about two or three. This property is of concern primarily with respect to thermal loading of the waste form and of the repository.

A second physical property of rocks important for thermomechanical effects is thermal expansion. In addition to possible fracturing caused by stress concentrations related to cavern geometry and engineering factors, thermal expansion of the heated rocks can lead to fracture of these or overlying units. The tensile strength of rock is generally quite low, and most rocks can sustain very limited extensional strain before fracturing. Thus, even the slightest extension of layered rock units overlying a thermally expanding rock mass can potentially lead to fracture and to enhanced permeability. The effects of displacements caused by thermal expansion will depend very much on deformational characteristics of the rock units; these, in turn, reflect the strength and ductility of individual units, and their distribution in the section. Displacements caused by thermal expansion may also alter the potential field driving the groundwater system. Because the possible effects of thermal expansion could be rather complex, depending upon specific details of the geology involved, they can perhaps be best evaluated by means of computer modeling. Preliminary modeling of thermomechanical effects is currently under way.

Fracturing can also result from fluid pressures induced by heating of the fluid or caused by pore volume reduction where thermal expansion of the rock begins to close fluid-filled voids. The compressional strength of all common rocks increases almost linearly with increasing effective confining pressure (and, incidentally, therefore with increasing depth). Increased pore fluid pressure decreases the effective confining pressure and therefore the strength of the rock, although any existing <u>differential</u> stress in the rock is not affected. Because all permanent deformation other than compaction results from applied differential stress, increased pore pressure frequently results in fracture of the rock. It should be noted, further, that the orientation of fractures thus produced will be perpendicular to the direction of minimum principal stress. If the overburden pressure is the least principal stress, the fractures will be horizontal (the only acceptable orientation for grout sheets containing radioactive waste); if the least principal stress is horizontal, the fractures will be vertical (highly undesirable with regard to waste management problems).

Most rocks are brittle at temperatures less than 100°C and at confining pressures less than 100 bars, with the degree of brittle response depending partly upon the rate of deformation. Increased confining pressure and/or temperature increases the ductility of rock, and thus promotes the transition from the fracture mode of deformation (involving loss of cohesion) to flow (deformation without loss of cohesion). For most typical rocks, the increased confining pressure that might be realized by increasing the depth of the repository from, say, 500 m, which is the equivalent of about 125 bar pressure, to 1,000 m or 250 bar would not significantly suppress the tendency of these rocks to deform by fracture at those pressures, particularly if the decreased ductility caused by pore pressure is considered. Thus, increases in depth of this order give little advantage with regard to the fracture properties of most rocks, although the increased pressure may contribute to closure of existing cracks. One might expect that thermal expansion caused by heat from emplaced radioactive waste could also contribute to crack closure. The reduction of porosity and of permeability that would result from closing of pore spaces and cracks is, of course, of considerable importance with regard to groundwater transport.

A thermomechanical effect of great concern for engineering design and for maintaining access to the mined cavity (for the purpose of retrievability) is the possible loss of strength and increased creep in the rock caused by increased temperature. This effect is most pronounced in rocks composed of minerals (e.g., halite or calcite), in which intracrystalline slip is an important mechanism of deformation. Increased temperature reduces the critical resolved shear stress needed for intracrystalline slip to occur. For the temperatures (200° to 300°C) and pressures (125 to 250 bar) that can be expected, no significant reduction in strength with increased temperature is likely to occur for granite: in contrast, limestone, shale, and salt could be affected, but the expected reduction in strength would probably lead to serious engineering redesign only for a repository in salt.

The reduced strength and enhanced ductility of salt caused by elevated temperatures can potentially create serious problems not only for the stability of the mined cavern during the period of retrievability and occupation by personnel, but also for the removal of waste canisters from emplacement holes in the floor of the repository. The problems may be exacerbated if unreprocessed spent fuel pins are emplaced in the repository, as this would create a more extensive and longer-lasting thermal field in the vicinity of the repository. Computer codes exist and active research is currently being carried out to model both the thermal distributions in space and time and the consequent effects of these distributions on the stability of different cavern geometries for different thermal loadings within the repository.

Two final comments on thermomechanical effects are that these are likely to be of a near-field nature (although they may influence groundwater transport in the far-field) and that the period during which they may be produced is restricted--i.e., the high temperatures, due principally to the fission products, will largely disappear after a few hundred years.

Other Effects on Rocks

Evolution of Volatiles

Many shales have porosities of around 20 percent, and the pore spaces are filled with aqueous solutions. In addition, certain mineral components of these rocks may break down at high temperatures and release gaseous effluents. Fluids thus released can be expected to interact with the waste form and, depending upon their respective compositions, form substances that could lead to ready availability of radionuclides for transport. It is unlikely that temperatures in the vicinity of a repository would reach levels sufficient to cause dissociation of limestone (approximately 700°C), but clay minerals or other impurities present in the carbonate rocks may be subject to mineralogic change or chemical breakdown. Under conditions likely to exist in a repository where either HLW or spent fuel pins were emplaced, no significant mineralogic or chemical changes would be expected to occur in a crystalline silicate rock such as granite.

In the particular case of rock salt--the geologic medium currently favored in DOE plans--two possible effects are of principal concern: (1) the migration of brine inclusions in salt toward a heat source and (2) accelerated creep deformation of salt at higher temperature. Estimates by Jenks (1972), based on an assumed brine content of 0.5 percent by volume and on a well-developed theory of brine migration, suggest that approximately 30 l of brine will accumulate at an individual canister of HLW emplaced in bedded salt within a 50-year period. This volume amounts to about one cm^3 of brine per cm^2 of canister surface area. Two possible results of this brine accumulation are corrosion of the canister, which could seriously affect its integrity for retrievability, and evolution of H_2 and other gases. Jenks (1972) estimates that normal ventilation in the repository would prevent the buildup of an explosive mixture of H_2 in air during the period of retrievability. Although the effects of gaseous buildup after conversion to terminal storage are unlikely to be important, they require further study. Current plans to counteract corrosion call for the use of a carbon-steel liner to isolate the waste canister from contact with the salt and to provide for easy removal and inspection of the canister during the period of retrievability. Such a liner could also help protect the waste canister from entrapment caused by creep of the salt.

Radionuclide Migration

Once released from fabricated containment, following the breakdown of the waste form, any movement of radionuclides through the geologic environment would be primarily through convective transfer by groundwater. If no interactions occur between the contaminant and the porous medium, the contaminants will travel at the same rate of flow and in the same direction as the carrier fluid. Typically, however, sorption will take place, with the effect of reducing the flow velocity of contaminants relative to that of the groundwater.

Exchange reactions couple contaminant ions with the solid phase of the porous medium, causing a reduction of ion concentrations in solution. If the solution is sufficiently dilute that ion exchange sites are far from being saturated, the average velocity of the contaminant ion is reduced to the product of pore solution velocity times the fraction of the ion in solution. The fraction in solution is $1/(1 + K \rho)$ where ρ is equal to the bulk density of the solid divided by its effective porosity and K is the distribution coefficient. Since K values for rocks are not uncommonly 10^3 or even larger (e.g., in shales), it is clear that favorable sorption characteristics in the disposal medium can reduce the average contaminant velocity by several orders of magnitude.

Although extensive research is currently under way to evaluate the sorption and fixation characteristics of rocks, considerable uncertainty exists regarding K values obtained and the methods of measuring them, especially as to how they relate to conditions that might exist in the natural environment. Some insight with regard to radionuclide migration in geologic media has been provided by the OKLO phenomenon in the Gabon Republic of West Africa (IAEA 1975), where convincing and quantitative evidence exists that a natural reactor operated approximately 1.8 billion years ago. Information on ion mobility at OKLO may be particularly relevant to problems of radioactive waste management. At least half of the approximately 30 fission-product elements have remained immobilized; Rb, Cs, Sr, and Ba, and probably Cd, all made in the reactor, have mostly disappeared, presumably by radioactive decay. ^{90}Zr, produced by the decay of ^{90}Sr, is accounted for, indicating that little of the ^{90}Sr was transported from the vicinity of the reactor. Walton and Cowan (1975) concluded that the principal radioactive products that were released into the biosphere in measurable amounts at the time of the reaction were ^{85}Kr and possibly a little ^{137}Cs and ^{90}Sr. Plutonium was efficiently confined.

Waste Form Stability and Chemical Considerations

Current waste management philosophy favors developing as stable a waste form as possible, so that, should groundwater come into contact with it, the radionuclides it contains would not be released at an unacceptable rate during the period of desired isolation. By far the major effort in waste form technology has been devoted to the development of a suitable glass. As indicated above, we have great reservations about the stability of glass subjected to conditions that are likely to exist in a repository. Moreover, we consider the results of standard leaching tests to be inappropriate for extrapolation to such conditions. If glass is to be the preferred waste form, compositions designed for deliberate breakdown either into stable crystalline solids (see Chapter 7) or into clay minerals and material with very low permeability and high sorption characteristics would appear to be more promising than glass of questionable quality and stability (see Chapter 8).

If sufficient confidence in radioactive waste management could be developed to the point that permanent disposal techniques were to be employed, the ultimate in waste form technology might be the direct incorporation of radionuclides into stable crystalline phases of the host rock itself. This could be effected by incorporating the radioactive waste and appropriate additives into a melt of the host rock. Thermal power in both liquid and solid waste forms can be high enough to melt the host geologic medium locally. As mentioned earlier in this chapter, waste with a thermal power of 10 kW/m^3 would melt most typical rocks if placed in a cavity 1 m in diameter, and some HLW can generate up to 200 kW/m^3. Research would be required to understand adequately the melting relations and to predict accurately the heating and cooling histories. If the crystallization process during cooling were to produce a well-defined selvage of uniformly fine-grained rock of low permeability, an additional significant barrier would be provided between the waste and any groundwater that might subsequently reach the emplacement location. Although deep hole drilling would appear to be a highly appropriate method of emplacement in conjunction with the rock-melting concept, initial experiments to develop the concept could be undertaken in conventional mined cavities. Certain rock types, including salt, shale, and limestone, would probably not be appropriate because of release and possible movement of gaseous effluents from these rocks. Crystalline rock masses such as granite would appear to be ideally suited. The concept is sufficiently promising that we would strongly encourage research in this area.

NOTE

1 The reader is referred to the Technical Alternatives Document (U.S. ERDA 1976b) for a description of waste isolation concepts and emplacement techniques and to the American Physical Society report (1977) for a general assessment of these.

APPENDIX A

SUMMARY OF COST AND RISK ESTIMATES FOR ALTERNATIVE WASTE DISPOSAL STRATEGIES AT THE HANFORD RESERVATION, THE SAVANNAH RIVER PLANT, AND THE IDAHO NATIONAL ENGINEERING LABORATORY

To provide information on possible alternatives for the long-term management of the radioactive wastes stored at the Hanford Reservation, the Idaho National Engineering Laboratory, and the Savannah River Plant, three documents (one for each site) were prepared and released to the public in September 1977 (U.S. ERDA 1977a, 1977b, 1977c). Each document describes the various alternatives that will be considered for treating, storing, and disposing of the high-level wastes, including the technology required for implementation. Also included in these descriptions are analyses of the risk to the public and preliminary cost estimates. No particular plan is selected, nor do the analyses take into account social and public policy issues.

HANFORD RESERVATION

Approximately 173,000 m^3 of HLW in the form of sludge, salt cake, and residual liquids are now being stored in underground tanks at the Hanford Reservation (DOE 1978). Twenty-seven alternative plans for the long-term management of these wastes have been considered by ERDA (1977a). All are variations on four major alternatives that are based on the location of the final disposal site:

1. existing waste tanks,
2. onsite engineered surface facility,
3. onsight geologic repository,
4. offsite geologic repository.

The four major alternatives have been expanded into 27 alternative plans through applying several additional options, including whether radionuclide removal is used to separate the wastes into two parts: a small volume high-activity fraction and decontaminated salt containing less than 6 nanocuries per gram. Other options include the type of solid waste form used and the treatment and handling of encapsulated waste. Table A.1 lists the costs and risks of the 27 alternative plans considered in the Hanford document. According to ERDA (1977a):

> "The total actual dollar amount that must be budgeted over the years to implement any alternative plan is about two to five times the constant 1976 dollar amount."

Thus, implementation costs for disposing of the Hanford Wastes could range as high as $27.2 billion (U.S. ERDA 1977a).

SAVANNAH RIVER PLANT

Approximately 82,000 m^3 of HLW in the form of sludge, salt cake, and residual liquids are now being stored in underground steel tanks at the Savannah River Plant (DOE 1978). Assuming that reactor operations cease in 1985, about 230,000 m^3 of reconstituted[1] wastes with an activity level of 1,300 curies per cubic meter will need to be disposed of. Twenty-three alternative plans for long-term management and disposal of these wastes have been considered in the SRP document (U.S. ERDA 1977c). As in the Hanford document, these alternatives are variations on four major alternatives that are based primarily on the location of the final disposal site:

1. continued storage in tanks,

2. disposal of reconstituted waste slurry in a bedrock cavern under the SRP site,

3. disposal of solidified waste in an engineered surface facility at SRP,

4. disposal of solidified waste offsite at a federal repository.

The additional options that have expanded these four major alternatives into 23 alternative plans include whether or not radionuclide removal will be used to separate the wastes into a high-activity fraction and decontaminated salt, the nature of the final waste form (glass, concrete, dry powder, or fused salt), and the final storage and disposal mode--for instance, disposal of HLSW in an SRP bedrock cavern. Table A.2 lists the estimated costs and risks for the 23 alternative plans considered.

TABLE A.1

Summary of Cost and Risk for 27 Alternative Radioactive Waste Disposal Plans at Hanford with Numerical Ranking[a]

Plan Number	Plan Description	Total Cost, million 1976 dollars		Discounted Cost, million dollars		Integrated Population Dose Risk, man-rem	
1	Storage and Disposal of Salt Cake, Sludge, and Residual Liquor in Existing Waste Tanks.	500	(1)[b]	60	(1)	1×10^{-3}	(1)
2	Glass w/RR in Canisters Disposed of in Onsite Engineered Surface Facility and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,300	(6)	260	(10)	7×10^{-2}	(10)
3	Glass w/RR in Canisters Disposed of in Onsite Geologic Repository and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,400	(8)	250	(7)	7×10^{-2}	(10)
4	Glass w/RR in Canisters Disposed of in Offsite Geologic Repository and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,500	(11)	260	(10)	2×10^{2}	(17)

5	Concrete w/RR in Canisters Disposed of in Onsite Engineered Surface Facility and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,300	(6)	250	(7)	2×10^{-2}	(8)
6	Concrete w/RR in Canisters Disposed of in Onsite Geologic Repository and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,400	(8)	240	(6)	2×10^{-2}	(8)
7	Concrete w/RR in Canisters Disposed of in Offsite Geologic Repository and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,500	(11)	250	(7)	3×10^{2}	(18)
8	Powder w/RR in Canisters Disposed of in Onsite Engineered Surface Facility and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,000	(2)	200	(3)	1×10^{-2}	(2)
9	Powder w/RR in Canisters Disposed of in Onsite Geologic Repository and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,100	(4)	200	(3)	1×10^{-2}	(2)
10	Powder w/RR in Canisters Disposed of in Offsite Geologic Repository and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,100	(4)	200	(3)	9×10^{1}	(16)
11	Powder w/RR in Bulk Containers Disposed of in Onsite Geologic Repository and Bulk Decontaminated Salt Disposed of in Onsite Surface Trench.	1,000	(2)	190	(2)	1×10^{-2}	(2)

TABLE A.1 (continued)

Plan Number	Plan Description	Total Cost, million 1976 dollars	Discounted Cost, million dollars	Integrated Population Dose Risk, man-rem
12	Glass wo/RR in Canisters Disposed of in Onsite Engineered Surface Facility.	2,700 (12)	490 (15)	7×10^{-2} (10)
13	Glass wo/RR in Canisters Disposed of in Onsite Geologic Repository.	2,900 (14)	400 (13)	7×10^{-2} (10)
14	Glass wo/RR in Canisters Disposed of in Offsite Geologic Repository.	3,700 (16)	490 (15)	1×10^{3} (19)
15	Clay wo/RR in Canisters Disposed of in Onsite Engineered Surface Facility.	3,900 (18)	730 (20)	7×10^{-2} (10)
16	Clay wo/RR in Canisters Disposed of in Onsite Geologic Repository.	4,200 (19)	540 (17)	7×10^{-2} (10)
17	Clay wo/RR in Canisters Disposed of in Offsite Geologic Repository.	6,000 (21)	730 (21)	3×10^{3} (21)
18	Powder wo/RR in Canisters Disposed of in Onsite Engineered Surface Facility.	3,500 (15)	660 (18)	1×10^{-2} (2)
19	Powder wo/RR in Canisters Disposed of in Onsite Geologic Repository.	3,800 (17)	480 (14)	1×10^{-2} (2)

20	Powder wo/RR in Canisters Disposed of in Offsite Geologic Repository.	5,500	(20)	660	(18)	3×10^{-2}	(20)
21	Powder wo/RR in Bulk Containers Disposed of in Onsite Geologic Repository.	2,800	(13)	260	(10)	1×10^{-2}	(2)
22	Capsules Packaged in Overpacked Canisters Disposed of in Onsite Engineered Surface Facility.	43	(b)	5	(a)	7×10^{-5}	(b)
23	Capsules Packaged in Canisters Disposed of in Onsite Geologic Repository.	26	(a)	5	(a)	2×10^{-9}	(a)
24	Capsules Packaged in Canisters Disposed of in Offsite Geologic Repository.	47	(c)	10	(c)	1×10^{1}	(e)
25	Capsules Converted to Glass in Overpacked Canisters Disposed of in Onsite Engineered Surface Facility.	76	(e)	10	(c)	1×10^{-3}	(c)
26	Capsules Converted to Glass in Canisters Disposed of in Onsite Geologic Repository.	59	(d)	15	(e)	1×10^{-3}	(c)
27	Capsules Converted to Glass in Canisters Disposed of in Offsite Geologic Repository.	79	(f)	20	(f)	1×10^{1}	(f)

[a] Totals have been rounded.

[b] Parentheses indicate numerical ranking.

Source: U.S. ERDA (1977a).

TABLE A.2

Summary of Costs and Risks for 23 Alternative Radioactive Waste Disposal Plans at the Savannah River Plant

Plan Number	*Description*	*Budgetary Cost, billion 1976 dollars*[a]	*Population Dose Risk, thousand man-rem*[b]	*Total Effective Cost, billion 1976 dollars*[c]	*Incremental Cost/Risk, $/man-rem*[d]
1	Glass Disposed of in Offsite Geologic Storage and Canned Decontaminated Salt Cake Stored in Outside Surface Storage Facility	2.7	.90	2.7	41,000
2	Concrete Disposed of in Offsite Geologic Storage and Canned Decontaminated Salt Cake Stored in Onsite Surface Storage Facility	2.4	.90	2.4	36,000
3	Concrete Disposed of in Offsite Geologic Storage and Decontaminated Salt Cake Stored in Onsite Underground Waste Tanks	1.2	.90	1.2	17,000
4	Concrete and Canned Decontaminated Salt Cake Disposed of in Offsite Geologic Storage	1.9	.90	1.9	28,000
5	Glass and Canned Decontaminated Salt Cake Stored in Onsite Surface Storage Facility	2.9	.22	2.9	44,000

6	Concrete and Canned Decontaminated Salt Cake Stored in Onsite Surface Storage Facility	2.8	.22	2.8	42,000
7	Concrete Stored in Onsite Surface Storage Facility and Decontaminated Salt Cake Returned to Onsite Waste Tanks	1.7	.22	1.7	25,000
8	Glass and Canned Decontaminated Salt Cake Disposed of in SRP Bedrock	2.0	.34	2.0	30,000
9	Concrete and Canned Decontaminated Salt Cake Disposed of in SRP Bedrock	1.8	.34	1.8	26,000
10	Concrete and Decontaminated Salt Solution Disposed of in SRP Bedrock	1.3	.34	1.3	18,000
11	Glass Stored in Offsite Surface Storage Facility and Decontaminated Canned Salt Cake Stored in Onsite Surface Storage Facility	3.0	.53	3.0	46,000
12	Concrete Stored in Offsite Surface Storage Facility and Canned Decontaminated Salt Cake Stored in Onsite Surface Storage Facility	3.0	.73	3.0	46,000
13	Concrete and Decontaminated Salt Cake Stored in Offsite Surface Storage Facility	3.4	.73	3.4	53,000

TABLE A.2 (continued)

Plan Number	*Description*	*Budgetary Cost, billion 1976 dollars*[a]	*Population Dose Risk, thousand man-rem*[b]	*Total Effective Cost, billion 1976 dollars*[c]	*Incremental Cost/Risk, $/man-rem*[d]
14	Dry Powder Disposed of in Offsite Geologic Storage and Canned Decontaminated Salt Cake Stored in Onsite Surface Storage Facility	2.3	.93	2.3	35,000
15	Dry Powder and Canned Decontaminated Salt Cake Stored in Onsite Surface Storage Facility	2.5	.38	2.5	38,000
16	Dry Powder and Canned Decontaminated Salt Cake Disposed of in SRP Bedrock	1.8	8.6	1.8	30,000
17	Dry Powder Stored in Offsite Surface Storage Facility and Canned Decontaminated Salt Cake Stored in Onsite Storage Facility	2.6	.89	2.6	40,000
18	Fused Salt Disposed of in Offsite Geologic Storage - No Separation of Radioactivity	1.1	1.0	1.1	15,000

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19	Fused Salt Stored in Onsite Surface Storage Facility - No Separation of Radioactivity	3.0	.22	3.0	46,000
20	Fused Salt Disposed of in Bedrock - No Separation of Radioactivity	.90	8.6	.91	14,000
21	Fused Salt Stored in Offsite Surface Storage Facility - No Separation of Radioactivity	3.5	1.0	3.5	54,000
22	Unprocessed Waste Slurry Disposed of in SRP Bedrock	.18	62	.24	Base
23	Storage of Waste as Sludge and Damp Salt Cake in Onsite Waste Tanks (Present SRP Waste Management Technique)	.24[e]	1.4	.24	1,000

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a. Undiscounted.

b. Integrated for 300 years. Assumes population grows by a factor of 5 by 2140, then remains constant. No corrective action.

c. Radiation doses were evaluated at $1000/man-rem.

d. Cost per man-rem reduction in risk, using the least expensive alternative plan as a base (Plan 22, Unprocessed Waste Slurry Stored in Bedrock).

e. Includes undiscounted costs for one generation of new tanks, starting about year 2040. This investment is more than that required to create a trust fund to rebuild tanks into the indefinite future. Such a trust fund would require new legislation for its creation.

Source: U.S. ERDA (1977c).

IDAHO NATIONAL ENGINEERING LABORATORY

Unlike the high-level wastes stored at the Hanford Reservation and the Savannah River Plant, the wastes at INEL are routinely converted to calcine and stored underground in stainless steel bins. Thirteen alternative plans have been considered in the INEL document for the long-term management of these wastes (U.S. ERDA 1977b) and are divided according to the waste form (calcine pellets, metal matrix, sintered glass ceramics) and the disposal location (retrievable surface storage facility, federal repository). An additional option is to remove the actinides and ship them to a federal repository; the remaining wastes would be stored onsite. Table A.3 lists the estimated costs and risks for the 13 plans considered.

NOTE

1 Before solidification of the wastes begins, it is assumed that they are reconstituted by dissolving the damp salt cake and using the solution to slurry the sludge from the waste tanks.

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TABLE A.3

Summary of Costs and Risks for Alternative Radioactive Waste Disposal Plans at INEL (1977 dollars)

Alternative	Total Budgetary[a] Cost Above Base, $ million	Total Population[c] Dose Risk, man-rem	Risk Value, $ million	Total Effective Cost, $ million
Calcine at ICPP	Base	0.01	Negligible	Negligible
Pellet, SGC, MM--at INEL	140[d] 190[e] 375[f]	140	0.15	140[d] 190[e] 375[f]
Remove Actinides[b] Pellet, SGC, MM--at INEL	290[d] 340[e] 525[f]	780	0.8	290[d] 340[e] 525[f]

Pellets, SGC, MM--Ship By Rail to Federal Repository	315(d) 335(e) 550(f)	820	0.8	315(d) 335(e) 550(f)
Pellets, SGC, MM--Ship By Truck to Federal Repository	315(d) 335(e) 550(f)	4,900	4.9	320(d) 340(e) 555(f)

(a) Capital plus 10-yr operating costs.

(b) Costs for shipment of actinides to and deposition at a federal repository are included.

(c) Comparable 10-yr dose, from natural background, is 200,000 man-rem for 120,000 population within 80 km (50 mi) of INEL.

(d) Pellets.

(e) SGC-sintered glass ceramic.

(f) MM-metal matrix.

Source: U.S. ERDA (1977b).

APPENDIX B

SUMMARY OF EUROPEAN R&D ON WASTE SOLIDIFICATION

Any United States waste management system will eventually be part of a worldwide system. It is therefore essential that foreign experience in waste management be considered in designing the American system. Furthermore, because most radioactive waste management systems are nationalized, and commercial interests and conflicts are consequently reduced, a sharing of waste-handling technology should be possible, and would benefit every country involved. In the following section we highlight special aspects of the work in several foreign countries that are relevant to our task. The work in France has already been discussed in Chapter 8.

COMMISSION OF THE EUROPEAN COMMUNITIES

This program, administered from Brussels, is a well-known joint international research program dealing with the management and isolation of radioactive wastes. It consists of a well-integrated R&D program on the different subsidiary tasks in radioactive waste management, such as "conditioning" of fuel pin cladding, waste solidification, storage, and isolation. Projects are assigned to various national laboratories; results are shared and future strategies planned. Virtually the only solid form being studied is glass. Special attention is focused on evaluating such glass properties as leach rate, crystallization effects, and irradiation effects with ^{238}Pu-doped specimens. The research on cladding wastes and high-temperature incineration of alpha-wastes is peripherally related to the present task, but appears to have made some novel contributions to the technology.

ROCHEMIC

This is another multinationally funded European organization--in this case an R&D center in Mol, Belgium. The solidificaton research here is as diversified and advanced as any in the world.

The laboratories have made three substantial contributions to solidification technology:

1. Their stirred-bed reactor appears to function effectively to produce calcine granules (1 to 10 mm in size) directly from HLLW, thus avoiding some of the problems of handling fine particles.

2. Their pilot plant for incorporating phosphate glass into a lead metal matrix is working in a routine manner. It is capable of handling ceramics or calcine granules, and will be of special interest for fresh wastes.

3. The underwater SiO_2-Al_2O_3-polymer "concrete" developed for incorporating cladding hulls may well be generalized to other waste forms.

THE FEDERAL REPUBLIC OF GERMANY

The program in the Federal Republic of Germany is large, centrally managed, and well articulated. Of special significance to the U.S. program is their evaluation of the total system. A report, "Systems Studies, Radioactive Waste in the Federal Republic of Germany" is being completed in six volumes concurrently with the Panel's own work. The study, managed for the Federal Republic by the Nukem Corporation, coordinates the work of all major nuclear institutions in the country and is especially strong on the risk analysis of the radioactive waste management system. One of the most significant results of these studies is the finding that the major risks from radioactive waste occur in transport. Consequently, Nukem has recommended a system where reprocessing, solidification, and isolation in a deep geological formation occur at the same site.

The German solidification studies have encompassed a great variety of solid forms. Not only glass, but glass-ceramics and concrete (for ILW), have received considerable attention. The work done jointly by the Gelsenburg Company and the Eurochemic Company, Belgium on metal-matrix composites is more advanced than similar work in any other country.

SWEDEN

The Swedish program is in some ways operating under constraints very similar to those of the United States, especially in regard to public acceptance. Because of new laws enacted in Sweden, there has been a crash development of a system to store spent fuel pins, which is much further along than any United States work. The system consists of inserting sets of the <u>uncut</u> rods in sealed, mild-steel canisters with cross-sectional areas of about 100 cm² range.

These canisters are then coiled into flat, watch-spring configurations and stacked into thick-walled containers made of isostatically pressed Al_2O_3. The container is sealed by mating two Al_2O_3 surfaces and welding the outer thin cladding steel sheet. The alumina container is designed for emplacement in granite with a surrounding overpack of clays. This is clearly a cumbersome first-generation solution, but indicates rather clearly the development of a radically different technology for waste solidification in a very short time (less than one year).

The longer range Swedish program is also well coordinated and is noteworthy in two other respects. The Swedes have paid more attention to the materials science aspects of solidification, and have involved the university community in the research to a greater extent than any other country. Novel technological suggestions include the use of a heavy copper canister for the wastes to keep E low, and the use of an overpack of reactive clays and sand around the canister as a first-level barrier for radionuclide adsorption. The basic research on inorganic materials, ranging from adsorption on zeolites to tailor-made gels for converting to stable ceramic solids, appears to have a much more prominent place in their strategy than in the corresponding U.S. program.

THE UNITED KINGDOM

The United Kingdom solidification program at Harwell goes back as far as any, and indeed the Fingal process probably was the first to solidify significant amounts of fully radioactive wastes into glass. These samples, now over a decade old, are an invaluable research resource. Current research in Britain is focused on the Harvest glass process which, from an engineering viewpoint, is probably the simplest of all processes devised so far.

U.S.S.R.

Soviet work in waste solidification is unique, and detailed exchange of data could have a profound impact on U.S R&D efforts, even though national policies on radioactive waste management may be very different. A token research effort is being made on glasses containing <u>low</u> concentrations of waste ions. For 15 years, Soviet scientists have reported on their work on pumping radionuclides into carefully-selected geological strata (Kondrat'ev et al. 1976). Data have been provided only on low and intermediate level wastes. During the last few months, information has been released (W. Bishop, U.S. Nuclear Regulatory Commission, personal communication, 1977) indicating that they have pumped HLW (one report describes tens of curies per liter) in the same way.

The waste/rock interaction has been used to solidify this waste. The minerals of the formation--principally quartz and clays--react under mild hydrothermal conditions with the liquid wastes to form new, relatively insoluble phases. The guiding principle in selecting the amounts and concentration of radionuclides for disposal appears to be that the resulting temperature should not exceed the boiling point of water at the chosen depth. In situ solidification in a formation some 1,000 m below the surface with protective argillaceous layers both above and below appears to have provided protection against the movement of any radionuclide ions, as monitored by a series of wells. The nearest approach to this process is the Oak Ridge experience with "grouting" a clay-cement-radionuclide mix some 600 m below the surface.

The absence of any in situ "solidification" approach in the United States program--e.g., studying the reactions of HLLW with typically sandy shales or argillaceous sandstones even in the laboratory--is strange, in light of the apparently successful disposal of megacuries of HLW by this method in the U.S.S.R. Since, at present, it would be extremely difficult to obtain permission to conduct full-scale experiments in the United States, efforts to exchange detailed data with the U.S.S.R. are very important.

APPENDIX C

THE PRIMARY CONTAINMENT FORM

Crystalline

As Table 1.2 indicates, there are four different crystalline or partly crystalline sets of primary ceramic hosts to contain the radionuclides of interest: supercalcine, low-temperature ceramics, high-temperature ceramics, and fuel pellets. Except for the SrF_2 and CsCl in storage at the Hanford Reservation, all forms are mixtures of oxide phases that have well known crystal structures. For example, ^{137}Cs may be incorporated into $^{137}CsAl_2Si_2O_6$– [pollucite].[1] ^{90}Sr may be in $^{90}SrMoO_4$– [scheelite][1] or $^{90}SrTiO_3$– [perovskite][1] and Ru in RuO_2– [rutile].[1]

The actinides and many of the lanthanide fission product ions end up in a (U, Pu) O_2– [fluorite] phase in the spent fuel pellets. In some of the lower temperature ceramics the ions may be bound relatively loosely on "exchange" sites on the layer silicates (clays) or network silicates (zeolites). Fortunately, most of these crystalline oxides are high melting, very insoluble phases with very high bond energies. The 30 to 40 elements in the typical waste compositions when solidified require a mixture of 6 to 7 such crystalline phases for containment. The system is quite tolerant to changes in composition, since the proportion of each crystalline phase in the solid form can be altered without altering the thermodynamics; in addition, most of the phases themselves also permit a wide range of compositional variation. A pertinent and well-known analogy is to be found in crystalline rocks, e.g. granite where two dozen elements are accommodated in the three or four major mineral phases which make up the rock.

NonCrystalline

An oxide glass is merely a variant of the theme described above, wherein <u>ideally</u> the single phase host can accommodate all the ions since the requirement of long range periodicity is removed. In practice, glasses with high loadings of waste often have small percentages of crystalline phases and/or are phase-separated into two glassy phases.

NOTE

1 These are idealized and simplified formulae, see Chapter 6 for real examples.

APPENDIX D

TABULATED DECAY CHARACTERISTICS OF SPENT BWR AND PWR FUEL

[illegible]
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TABLE D.1

Decay Characteristics of Spent BWR Fuel

Parameter	Time elapsed after spent fuel discharge							
	2Y	5Y	10Y	30Y	100Y	1000Y	10^4Y	10^5Y
Thermal power, watts/assembly								
Structural materials	1.79E+01[a]	1.12E+01	5.56E+00	4.02E-01	1.46E-02	2.51E-03	2.31E-03	1.07E-03
Actinides								
Spent fuel	3.52E+01	3.11E+01	3.28E+01	3.54E+01	3.11E+01	9.19E+00	2.36E+00	1.72E-01
Less (U + Pu)[b]	1.66E+01	1.01E+01	8.66E+00	5.00E+00	1.83E+00	4.41E-01	7.81E-02	9.19E-03
Fission products	8.22E+02	2.70E+02	1.47E+02	7.48E+01	1.45E+01	3.06E-03	2.91E-03	1.93E-03
Total								
Spent fuel	8.75E+02	3.12E+02	1.85E+02	1.11E+02	4.56E+01	9.20E+00	2.37E+00	1.75E-01
Spent fuel less (U + Pu)[b]	8.57E+02	2.91E+02	1.61E+02	8.02E+01	1.63E+01	4.47E-01	8.33E-02	1.22E-02
Activity, curies/assembly								
Structural materials	2.50E+03	1.23E+03	5.18E+02	7.45E+01	3.04E+01	4.69E-01	4.06E-01	2.08E-01
Actinides								
Spent fuel	1.94E+04	1.69E+04	1.36E+04	5.94E+03	1.12E+03	2.87E+02	7.71E+01	6.40E+00
Less U + Pu[b]	5.67E+02	3.78E+02	3.19E+02	1.75E+02	6.01E+01	1.56E+01	3.44E+00	3.89E-01

Fission products	1.88E+05	7.37E+04	4.87E+04	2.79E+04	5.34E+03	3.51E+00	3.32E+00	2.60E+00
Total								
Spent fuel	2.10E+05	9.18E+04	6.28E+04	3.39E+04	6.49E+03	2.91E+02	8.08E+01	9.21E+00
Spent fuel less (U + Pu)[b]	1.91E+05	7.53E+04	4.95E+04	2.81E+04	5.43E+03	1.96E+01	7.17E+00	3.20E+00
Potential Hazard Index[c] m^3 water/assembly								
Structural materials	1.33E+08	2.86E+07	1.30E+07	2.48E+06	1.0[illegible]E+06	3.17E+03	1.89E+03	9.07E+02
Actinides								
Spent fuel	2.62E+08	2.58E+08	2.60E+08	2.58E+08	2.20E+08	6.43E+07	1.59E+07	7.57E+06
Less (U + Pu)[b]	5.91E+07	4.76E+07	4.17E+07	2.64E+07	1.27E+07	3.21E+06	5.51E+05	2.45E+05
Fission products	4.57E+10	3.67E+10	3.15E+10	1.91E+10	3.41E+09	1.88E+04	1.82E+04	1.53E+04
Total								
Spent fuel	4.61E+10	3.70E+10	3.18E+10	1.94E+10	3.63E+09	6.43E+07	1.59E+07	7.59E+06
Spent fuel less (U + Pu)[b]	4.59E+10	3.68E+10	3.16E+10	1.91E+10	3.42E+09	3.23E+06	5.71E+05	2.61E+05

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[a] Read as 1.79×10^1

[b] 99.5% removal of uranium and plutonium assumed.

[c] Sum of the amount of water required to dilute each isotope to the point that it is acceptable for unrestricted consumption as specified in Title 10, Part 20 of the Code of Federal Regulations.

TABLE D.2

Decay Characteristics of Spent PWR Fuel

Parameter	Time elapsed after spent fuel discharge							
	2Y	5Y	10Y	30Y	100Y	1000Y	10^4Y	10^5Y
Thermal power, watts/assembly								
Structural materials	1.00E+01[a]	4.86E+00	1.98E+00	2.06E-01	7.44E-02	1.88E-02	1.59E-02	5.08E-03
Actinides								
Spent fuel	1.06E+02	9.14E+01	9.57E+01	1.02E+02	8.89E+01	2.56E+01	6.37E+00	4.89E-01
Less (U + Pu)[b]	5.30E+01	3.15E+01	2.67E+01	1.49E+01	4.74E+00	1.12E+00	2.26E-01	2.80E-02
Fission products	2.47E+03	8.65E+02	4.54E+02	2.39E+02	4.44E+01	9.10E-03	8.68E-03	5.73E-03
Total								
Spent fuel	2.59E+03	9.61E+02	5.52E+02	3.41E+02	1.33E+02	2.56E+01	6.39E+00	5.00E-01
Spent fuel less (U + Pu)[b]	2.53E+03	9.01E+02	4.83E+02	2.54E+02	4.92E+01	1.15E+00	2.51E-01	3.88E-02
Activity, curies/assembly								
Structural materials	4.08E+03	1.72E+03	6.82E+02	2.44E+02	1.41E+02	2.72E+00	2.20E+00	8.66E-01
Actinides								
Spent fuel	5.66E+04	4.91E+04	3.95E+04	1.72E+04	3.21E+03	7.98E+02	2.08E+02	1.83E+01
Less (U + Pu)[b]	1.77E+03	1.15E+03	9.66E+02	5.15E+02	1.54E+02	4.04E+01	9.98E+00	1.18E+00

Fission products	6.11E+05	2.27E+05	1.47E+05	8.45E+04	1.62E+04	1.05E+01	9.94E+00	7.77E+00
Total								
Spent fuel	6.72E+05	2.78E+05	1.87E+05	1.02E+05	1.96E+04	8.11E+02	2.20E+02	2.69E+01
Spent fuel less (U + Pu)[b]	6.17E+05	2.30E+05	1.49E+05	8.53E+04	1.65E+04	5.36E+01	2.21E+01	9.82E+00
Potential Hazard Index[c] m^3 water/assembly								
Structural materials	2.46E+08	2.85E+07	1.29E+07	8.30E+06	4.87E+06	2.17E+05	1.53E+05	1.03E+04
Actinides								
Spent fuel	7.66E+08	7.48E+08	7.53E+08	7.43E+08	6.29E+08	1.80E+08	4.33E+07	2.27E+07
Less (U + Pu)[b]	1.82E+08	1.44E+08	1.25E+08	7.56E+07	3.21E+07	8.10E+06	1.58E+06	7.36E+05
Fission products	1.44E+11	1.14E+11	9.73E+10	5.91E+10	1.05E+10	4.40E+04	3.86E+04	3.00E+04
Total								
Spent fuel	1.45E+11	1.15E+11	9.81E+10	5.99E+10	1.11E+10	1.80E+08	4.35E+07	2.27E+07
Spent fuel less (U + Pu)[b]	1.44E+11	1.14E+11	9.74E+10	5.92E+10	1.05E+10	8.36E+06	1.77E+06	7.76E+05

[a] Read 1.0×10^1

[b] 99.5% removal of uranium and plutonium assumed.

[c] Sum of the amount of waste required to dilute each isotope to the point that it is acceptable for unrestricted consumption as specified in Title 10, Part 20 of the Code of Federal Regulation.

APPENDIX E

NATIONAL ACADEMY OF SCIENCES CORRESPONDENCE

NATIONAL ACADEMY OF SCIENCES

OFFICE OF THE PRESIDENT
2101 CONSTITUTION AVENUE
WASHINGTON, D.C. 20418

July 26, 1978

Mr. Joseph M. Hendrie
Chairman
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

Dear Mr. Hendrie:

In response to a request from the U.S. Nuclear Regulatory Commission, the National Research Council has conducted a study of the scientific and technological problems associated with the conversion of liquid and semi-liquid high-level radioactive wastes into a stable form for transportation and disposition. A summary of the principal conclusions and recommendations will be found on pages 1 to 5 of the report.

The study concluded that many solid forms are likely to be satisfactory for use in an appropriately designed system. At least one form, glass, because of an extensive developmental effort, is currently adequate in the opinion of the Committee 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 the study's analysis it cannot be recommended as the best choice, especially for the older DOE wastes. 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.

I hope that the findings and recommendations of this report will be helpful to you and your associates in your consideration of these problems.

Sincerely yours,

Original signed by
Philip Handler

Philip Handler
President

NATIONAL ACADEMY OF SCIENCES

OFFICE OF THE PRESIDENT
2101 CONSTITUTION AVENUE
WASHINGTON, D.C. 20418

October 30, 1978

Mr. Joseph M. Hendrie
Chairman
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

Dear Mr. Hendrie:

With my letter of July 26, 1978, I forwarded to you a prepublication manuscript copy of the report on our study of the scientific and technological problems associated with the conversion of liquid and semiliquid, high-level radioactive wastes into a stable form for transportation and disposition.

While that manuscript was being prepared for publication it came to our attention that some aspects of the data base used in the report were being questioned. Because of the importance of the substance of this study and its recommendations, we have stopped distributing the prepublication version; printing of the report has been delayed until this matter can be resolved by our Committee on Radioactive Waste Management and its Panel on Radioactive Waste Solidification. Since a number of copies of the prepublication report had already been distributed, we plan to furnish you with a supplemental statement as soon as the data base has been rechecked. At this writing, I am unable to ascertain how seriously these additional considerations may affect the principal conclusions and recommendations of the report.

I regret this delay in the availability of the final printed report. The national interest, however, will best be served by this additional assurance that the study is based on adequate consideration of all relevant technical information.

I understand that under the circumstances, you will probably consider it necessary to distribute the prepublication version for public comment. I have therefore directed my staff to make available to you a camera-ready manuscript of the prepublication version for your use, should you so require.

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I trust that this letter will be attached to all copies of the prepublication version of the report.

Sincerely yours,

P Handler

Philip Handler
President

NATIONAL ACADEMY OF SCIENCES

OFFICE OF THE PRESIDENT
2101 CONSTITUTION AVENUE
WASHINGTON, D.C. 20418

April 10, 1979

The Honorable Joseph M. Hendrie
Chairman
U.S. Nuclear Regulatory Commission
1717 H Street, N.W.
Washington, D.C. 20555

Dear Mr. Hendrie:

On October 30, 1978, I wrote to you about our study for the U.S. Nuclear Regulatory Commission of the scientific and technological problems associated with conversion of liquid and semi-liquid, high-level radioactive wastes into a stable form for transportation and disposition.

A prepublication copy of the manuscript of the report "Solidification of High-Level Radioactive Wastes" was sent to you earlier. There is enclosed a statement from the Commission on Natural Resources which refers to certain questions about the study report. The Nuclear Regulatory Commission should be aware of our reservations concerning the original study report. The National Research Council remains intensely interested in this extremely important aspect of nuclear technology and we stand in readiness to undertake further studies of these critical problems.

Sincerely yours,

P Handler

Philip Handler
President

Attachment

566239

NATIONAL RESEARCH COUNCIL
COMMISSION ON NATURAL RESOURCES

2101 Constitution Avenue   Washington, D. C. 20418

OFFICE OF THE CHAIRMAN
Institute of Behavioral Science
University of Colorado
Boulder, Colorado 80309

April 5, 1979

MEMORANDUM

To: Philip Handler

From: Gilbert F. White CB Myers FOR G.F.W.

Subject: Radioactive Waste Solidification Report

NATIONAL ACADEMY OF SCIENCES
APR 0 6 1979
OFFICE OF THE PRESIDENT

At its most recent meeting the Commission considered certain reservations that have come to its attention concerning the report, Solidification of High-Level Radioactive Wastes, by the Panel on Waste Solidification established by the Committee on Radioactive Waste Management of the Commission on Natural Resources. This report was forwarded through you to the Nuclear Regulatory Commission on July 26, 1978. In the intervening months, the National Research Council has received a number of comments from invited reviewers. Those comments are on file but have not been subjected to Academy review. Much of the report has not been questioned; however, some of the comments raise questions about part of the data base used to reach the conclusions in the Panel report.

In view of those questions, the Commission feels it desirable to initiate a further assessment of technology with respect to alternative means of solidifying wastes. Its decision is based on a broad set of reservations which the Panel on Waste Solidification has not addressed fully. Supplemental statements illustrative of such reservations by two members of the Commission on Natural Resources are attached.

Encs.

The National Research Council is the principal operating agency of the National Academy of Sciences and the National Academy of Engineering to serve government and other organizations

Oak Ridge
Associated
Universities

Post Office Box 117
Oak Ridge, Tennessee 37830
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Institute
for Energy
Analysis

March 23, 1979

Dr. Philip Handler
President
National Academy of Sciences
2101 Constitution Avenue, N. W.
Washington, D. C. 20418

Dear Phil:

I have reviewed the report on "Solidification of High-Level Radioactive Wastes" at the request of Dr. Gilbert White, Chairman of the Commission on Natural Resources. Although there are many parts of the report with which I disagree, I shall deal only with certain matters related to glass. The report states (page 61),

> "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."
>
> "Nevertheless the Panel cannot recommend glass as the best choice (page 2, [3]).

This relatively weak endorsement of glass by the Panel rests mainly on the observation (which has been contested) that glass can interact with certain host rocks at temperatures above 200°C.

What the report failed to take explicitly into account, however, was that the temperature at the interface between rock and glass in a repository is a design variable. Within large limits this temperature can be set by engineering design of the system. For example, this temperature can be maintained considerably below 200°C if the wastes are allowed to decay above ground more than the originally planned 10 years or if they are diluted to a lower concentration than envisaged in designs of depositories carried out before such possible temperature mediated interactions were recognized.

I offer these personal observations in clarification of the phrase "in an appropriately designed system." I believe it is very important to understand why, though it may not be the best solid, glass is an adequate vehicle for containing radioactive wastes.

Sincerely,

Alvin

Alvin M. Weinberg
Director
Institute for Energy Analysis

AMW:bc

UNIVERSITY OF CALIFORNIA

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INSTITUTE OF MARINE RESOURCES
OFFICE OF THE DIRECTOR

MAIL CODE A-027
LA JOLLA, CALIFORNIA 92093

28 March 1979

Dr. Gilbert F. White
Institute of Behavioral Science
University of Colorado
Boulder, CO 80302

Dear Gil,

I have reviewed the prepublication report of the Panel on Waste Solidification entitled "Solidification of High-Level Radioactive Wastes," along with comments by reviewers and the responses of the Panel to those comments.

The Panel has undertaken to advise broadly and pivotally on one vital component of any future integrated system of handling, transporting and sequestering the high level radioactive materials resulting from nuclear reactor operation — the solidification of these perilous substances.

The central undertaking of this report is, of course, to appraise and advise on the relative advantages of various present and potential forms of solidification of these materials--glass, cement, ceramics, etc. I will not attempt to comment on the discussion directly relating to the solidification, for there are many comments from reviewers who are much better qualified than I in that area. However, many of their criticisms of the report appear to me to be substantial and seriously to question a number of the findings of the Panel.

The solidification of radioactive materials is only an early probable step of any eventual disposal system. The report, however, ventures outside of the single matter of solidification, and, I believe, outside the Panel's interest and competency, and it is in these adventures into further peripheral areas that I find the most serious faults.

Any eventually acceptable solution to the crucial problem of the disposal of nuclear wastes will be made up of a series of interrelated steps, which must be viewed as a system. It is clear that each component of the system (e.g.: solidification) cannot be optimized *in vacuo*, but rather only in the context of the entire system. Indeed, it is generally manifest that in such sequential interdependent systems, optimization of each component on its own internal and limited criteria will rarely, if ever, lead to optimization of the entire system. The Panel has attempted to place its specific component (e.g.: solidification) into an imagined broader system. To reiterate, it is this venture that I fault, not particularly because of what is envisioned, but what is not. The result is a highly constrained view of those parameters of solidification which the Panel deems to be of importance to its particular and limited view of the potential holistic systems.

Given their constraints, the Panel would, perhaps, have done better to have considered the properties of various solidification and packaging possibilities related only to a well-thought-out series of physical-chemical conditions (e.g.: temperature, hydrostatic pressure, Eh, pH, conductivity, etc.) without reference to other system components, other than to include the conditions of potential repositories within the considered range of parameters. Such an approach would have allowed the Panel's findings to be meaningfully considered in a wide range of potential systems.

Let me more specifically, albeit briefly, address the above points. The Panel's ventures into areas outside its interests and competency have lead to constraints of presumption which seriously and fundamentally impair the usefullness of the report. The report acknowledges that the ultimate aim of solidification and containment is "protection of the biosphere." Yet, in the face of a problem that is ultimately and fundamentally biological, the report is inorganic throughout. Broader views would have lead to a consideration of the chemical richness (i.e., the range of critical chemical species present) of the host material, since isotopic dilution is the only irreversable dilution in any eventual release.

To continue, the Panel is concerned with host rock fractures, ground water transport, contamination of freshwater, internal pressure of containers, thermal transients, gas, devitrification bubbles, etc., none of which are important (or in some cases, necessary) conditions in some potential disposal systems. For example, for deep-sea subsediment disposal, internal gas pressure buildup, fissures of the host material, ground water transport, freshwater contamination, etc., are nonexistant or unimportant considerations.

In summary, I recommend that the Panel revise their report, confining it only to the steps of solidification and containment, and relate the properties of the potential candidates for those steps solely to a well-considered set of physical and chemical parameters that cover a wide range of potential repositories.

My detailed and general comments on the report are contained in a memorandum to the Chairman of the Commission on Natural Resources, dated 15 January, 1979.

Sincerely,

JOHN D. ISAACS
Professor of Oceanography

by: Nance North
Secretary

JDI:rh

GLOSSARY

absorption: See sorption.

actinide series: The series of elements beginning with actinium, element No. 89, and continuing through lawrencium, element No. 103, which together occupy one position in the periodic table. The series includes uranium, element No. 92, and all the manmade transuranium elements. The group is also referred to as the "actinides."

activity: A measure of the rate at which a material is emitting nuclear radiations; usually given in terms of the number of nuclear disintegrations occurring in a given quantity of material over a unit of time; the standard unit of activity is the curie (Ci), which is equal to 3.7×10^{10} (37 billion) disintegrations per second.

adsorption: See sorption.

alpha-radiation: See radiation.

barrier: One component in a multicomponent repository system for radioactive waste containment and isolation that retards the movement of one or more radionuclides. (See multiple barrier concept.)

beta-radiation: See radiation.

biosphere: That part of the earth that contains life.

calcine: A powder or granular form of high-level solid waste produced by evaporating and decomposing HLLW at temperatures above 500°C.

cement/concrete composites: A waste form that uses cement (primarily calcium silicate and aluminates) as a material for incorporating primary solid forms such as supercalcine or supersludge.

ceramic: A highly insoluble inorganic nonmetallic material. As a solid waste form, it is composed primarily of crystalline oxides and has the ability to contain all hazardous radionuclides such as ^{137}Cs and ^{90}Sr, in thermodynamically stable phases.

chromatographic separation: Separation of chemical compounds by selective adsorption on surfaces of adsorbent materials such as clay.

commercial wastes: Radioactive wastes produced by commercial nuclear power reactors. At present, most of these wastes are contained in spent fuel stored at the reactor sites. Should a decision eventually be made to reprocess commercial spent fuel, the radioactive wastes would probably be stored as acid solutions until solidified.

criticality: A set of physical conditions in which a nuclear chain reaction is self-sustaining. The principal variables influencing criticality include the amount (critical mass) of fissionable material, its distribution in space, the presence or absence of neutron absorbers and of moderators (materials that slow down fast neutrons).

curie (Ci): A unit of radioactivity defined as the amount of a radioactive material that has an activity of 3.7×10^{10} (37 billion) disintegrations per second (d/s); millicurie (mCi) = 10^{-3} curie; microcurie (μCi) = 10^{-6} curie; nanocurie (nCi) = 10^{-9} curie; picocurie (pCi) = 10^{-12} curie; femtocurie (fCi) = 10^{-15} curie; megacurie = 10^{6} curies.

DOE wastes: Radioactive wastes produced by the U.S. military program. The majority of these wastes have been neutralized with sodium hydroxide and are stored as a mixture of liquid salt cake and sludge.

disposal: Confinement of radioactive waste in such a way that its separation from the biosphere is expected to be permanent.

first generation: In this report, refers to the first or prototype system used to solidify and dispose of high-level radioactive wastes. See second generation.

first-generation solid form: A solid form used in a first-generation solidification and disposal system.

fissile material: While sometimes used as a synonym for fissionable material, this term has also acquired a more restricted meaning, namely, any material fissionable by neutrons of all energies, including (and especially) thermal (slow) neutrons as well as fast neutrons; for example, uranium-235 and plutonium-239.

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fission: The splitting of a heavy nucleus into two approximately equal parts (which are nuclei of lighter elements), accompanied by the release of a relatively large amount of energy and generally one or more neutrons. Fission can occur spontaneously, but usually is caused by nuclear absorption of gamma-rays, neutrons, or other particles.

fission products: The nuclei (fission fragments) formed by the fission of heavy elements, plus the nuclides formed by the radioactive decay of fission fragments.

fissionable material: Commonly used as a synonym for fissile material. The meaning of this term also has been extended to include material that can be fissioned by fast neutrons only, such as uranium-238. Sometimes used in nuclear reactor operations to mean fuel.

fuel (nuclear, reactor): Fissionable material used as the source of power when placed in a critical arrangement in a nuclear reactor.

fuel assembly: A grouping of fuel pins that is not taken apart during the charging and discharging of a reactor core.

fuel cycle: The complete series of steps involved in supplying fuel for nuclear reactors. It includes mining, refining, the original fabrication of fuel elements, their use in a reactor, chemical processing to recover the fissionable material remaining in the spent fuel, reenrichment of the fuel material, refabrication into new fuel pins, and management of radioactive waste.

fuel pin: The smallest structurally discrete part of a reactor fuel assembly that has nuclear fuel as its principal constituent (United States of America Standards Institute 1967).

fuel reprocessing: Processing of irradiated (spent) nuclear reactor fuel to recover useful materials as separate products, usually by separation into plutonium, uranium, and fission products.

gamma-radiation: See <u>radiation</u>.

glass: An inorganic product of fusion which has been cooled to a rigid condition without crystallization. As a waste form it is usually based on a silicate or phosphate network which has the ability to contain high percentages of waste ions.

grout: A mixture of waste, cement, and other additives used in the grouting process.

grouting: A process developed by the Oak Ridge National Laboratory to solidify and dispose of intermediate level wastes. It consists of injecting a thin horizontal sheet of cement-waste composite (grout) into the host geologic formation, which has first been fractured by pressure from a small volume of water.

half-life: The time in which half the atoms of a particular radioactive substance disintegrate to another nuclear form. Measured half-lives vary from millionths of a second to billions of years. After a period of time equal to 10 half-lives, the radioactivity of a radionuclide has decreased to about 0.1 percent of its original level. After 20 half-lives, it has decreased to less than one millionth (10^{-6}) of its original value.

high-level liquid waste: The aqueous waste resulting from the operation of the first-cycle extraction system, equivalent concentrated wastes from subsequent extraction cycles, or equivalent wastes from a process not using solvent extraction, in a facility for processing irradiated reactor fuels. This is the legal definition used by DOE.

high-level solid waste: High-level waste that has been converted to solid form. For purposes of this report spent fuel pins are considered a potential solid waste form.

hydrology, hydrogeology: The science of the phenomena and distribution of the waters of the earth.

ion exchange: A chemical process involving the reversible interchange of various ions between a solution and a solid material, usually a plastic or a resin. It is used to separate and purify chemicals, such as fission products or rare earths in solution. This process also takes place with many minerals found in nature and ions in solution, such as in groundwater.

ionizing radiation: Any radiation displacing electrons from atoms or molecules, thereby producing ions. Examples: alpha-, beta-, and gamma-radiation, or short-wave ultraviolet light. Ionizing radiation may produce severe skin or tissue damage.

isolation: The management of radioactive wastes in such a way as to minimize their migration to the biosphere.

isotope: One of two or more atoms with the same atomic number (the same chemical element) but with different atomic weights. An equivalent statement is that the nuclei of the isotopes of a given element have the same number of protons but different numbers of neutrons.

Isotopes usually have very nearly the same chemical properties, and most of the same physical properties, but may differ greatly in radioactive behavior.

long-lived isotope: A radioactive nuclide that decays so slowly that a quantity of it will exist for an extended period; usually a radionuclide whose half-life is greater than three years.

man-rem (or person-rem): A unit used in health physics to compare the effects of different amounts of radiation on groups of people. It is obtained by multiplying the average dose equivalent to a given organ or tissue (measured in rems) by the number of persons in that population.

megacurie: One million (10^6) curies. Symbol: MCi.

metal matrix: A waste form that uses a metal, such as lead, aluminum, or titanium as a material for incorporating primary solid forms such as glass or supercalcine pellets.

metamictization: Structural damage in minerals caused by radiation or particle bombardment.

multiple barrier concept: A concept of radioactive waste disposal whereby the movement of radionuclides to the biosphere is retarded by the combined action of several independent barriers. These include the geologic medium, the waste container, and the solid waste form itself.

neutron: A subatomic particle with zero electric charge, and with a mass nearly that of a hydrogen atom.

nuclide: A species of atom having a specific mass, atomic number, and nuclear energy state. These factors determine the other properties of the element, including its radioactivity.

permeability: In hydrology, the capacity of a rock, sediment, or soil for transmitting groundwater. Permeability depends on the size and shape of the pores, and how they are interconnected.

pH: A measure of the relative acidity or alkalinity of a solution; neutral solution has a pH of 7; an acid has a pH of less than 7; a base has a pH of greater than 7.

plutonium: A heavy, radioactive, man-made, metallic element with atomic number 94. Its most important isotope is fissionable plutonium-239, produced by neutron irradiation of uranium-238. It is used in weapons and for reactor fuel.

porosity: The ratio of the total volume of interstices in a rock or soil to its total volume, usually expressed in a percentage.

primary containment: Containment of hazardous radionuclides at the atomic or molecular level. For example, ceramics and glasses provide primary containment. (See secondary containment.)

rad (acronym for radiation absorbed dose): The basic unit of absorbed dose of ionizing radiation. A dose of 1 rad means the absorption of 100 ergs of radiation energy per gram of absorbing material.

radiation: The emission and propagation of energy through material or space by means of electromagnetic disturbances, which display both wave-like and particle-like behavior; in this context the "particles" are known as photons. Also, the energy so propagated. The term has been extended to include streams of fast-moving particles (alpha- and beta-particles, free neutrons, cosmic radiation, etc.). Nuclear radiation is that emitted from atomic nuclei in various nuclear reactions, including neutrons and alpha-, beta-, and gamma-radiation. Alpha-particles are the nuclei of helium atoms (mass 4, charge +2) produced by radioactive alpha decay of certain radionuclides. Beta-particles are electrons emitted in the process of radioactive beta-decay by certain radionuclides. Gamma-radiation is a kind of high-frequency electromagnetic radiation similar to X rays, produced by certain energetic radioactive reactions.

radioactive waste: Waste materials that are contaminated with radioactive material.

radioactivity (often shortened to "activity"): The spontaneous decay or disintegration of an unstable atomic nucleus, usually accompanied by the emission of ionizing radiation. The word "radioactivity" is often used to refer to radioactive materials or radioactive nuclides, but strictly speaking, this usage is not correct. Radioactivity is a process, not a material substance. The unit of radioactivity is the curie (see also curie).

radioisotope: A radioactive isotope. An unstable isotope of an element that decays or disintegrates spontaneously, emitting radiation. More than 1,300 natural and artificial radioisotopes have been identified.

radiolysis: The radiation induced decomposition of various chemical constituents in radioactive waste. Of particular importance are the decomposition of nitrates to form nitrogen oxides and the decomposition of water to form oxygen and hydrogen.

radionuclide: A nuclide that is radioactive (see also nuclide).

rem: An unofficial, but widely used unit of measure for the dose of ionizing radiation that gives the same biological effect as 1 roentgen of X rays; 1 rem equals approximately 1 rad for X, gamma-, or beta-radiation.

roentgen (abbreviation r): A unit of exposure to ionizing radiation. It is that amount of gamma- or X rays required to produce ions carrying 1 electrostatic unit of electrical charge (either positive or negative) in 1 cubic centimeter of dry air under standard conditions. Named after Wilhelm Roentgen, German scientist who discovered X-rays in 1895.

second generation: In this report, refers to an advanced or improved system used to solidify and dispose of high-level radioactive wastes.

second generation solid form: A solid waste form used in a second generation solidification and disposal system.

secondary containment: Containment of hazardous radionuclides by materials that serve as a matrix for incorporating various primary solid waste forms. An example is supercalcine embedded in lead. (See primary containment.)

short-lived isotope: A radioactive nuclide that decays so rapidly that a given quantity is transformed almost completely into its daughter products within a short period (usually those with a half-life of days or less).

solidification: see waste solidification.

sorption: In chemistry and geochemistry, the general term for the retention of one substance by another by close-range chemical or physical forces. Absorption takes place within the pores of a granular or fibrous material. Adsorption takes place largely at the surface of a material or its particles.

spent fuel: Nuclear fuel that has been irradiated and subsequently removed from the reactor. It contains uranium, plutonium, other actinides, and radioactive fission products. Because of current U.S. policy to defer indefinitely the reprocessing of commercial spent fuel, it is necessary to consider spent fuel as a potential solid waste form.

storage: Temporary isolation and retention of radioactive waste material in a manner designed to facilitate removal at a future time without significantly increasing the risk of radioactive contamination due to handling and/or retrieval.

supercalcine: A form of high-level solid waste produced by evaporating and decomposing HLLW to which selected materials have been added. The solubility of supercalcine can be 5 to 6 orders of magnitude lower than that of calcine.

supergrout: A mixture of supersludge and cement for use in a grouting process.

supernate: Alkaline liquid fraction of DOE wastes produced by neutralizaion of acid HLLW.

supersludge: A mixture of sludge (from neutralized wastes) and slurries of materials such as clays and other aluminosilicates to form a product with improved properties. It can be further treated to form a ceramic or incorporated into a cement/concrete matrix.

tonne: A metric ton, or 1,000 kilograms (2,204.6 pounds).

transuranium nuclide: A nuclide having an atomic number greater than that of uranium (i.e., greater than 92). The transuranium nuclide produced in largest amounts is plutonium-239 (half-life = 24,390 years); americium-241 (half-life = 458 years)is also produced in significant amounts.

uranium: A radioactive element with the atomic number 92 and, as found in natural ores, an average atomic weight of approximately 238. The two principal natural isotopes are uranium-235 (0.7 percent of natural uranium), which is fissile, and uranium-238 (99.3 percent of natural uranium), which is fertile. Natural uranium also includes a minute amount of uranium-234. Uranium is the basic raw material of nuclear energy used by man.

waste/rock interaction: The physical and chemical interaction between the waste form and the geologic medium in which it is placed.

waste solidification: The conversion of waste to an essentially dry and chemically, thermally, biologically, and radiolytically stable solid having the capability of restricting the mobility of radionuclides both within and from the solid matrix.

LIST OF ACRONYMS

BWR	Boiling-Water Reactor
ERDA	Energy Research and Development Administration
HLW	High-Level Wastes
HLLW	High-Level Liquid Wastes
HLSW	High-Level Solid Wastes
HMI	Hans Meitner Institute
IAEA	International Atomic Energy Agency
ICPP	Idaho Chemical Processing Plant
ILLW	Intermediate Level Liquid Wastes
ILW	Intermediate Level Wastes
INEL	Idaho National Engineering Laboratory
kW	Kilowatt
LASL	Los Alamos Scientific Laboratory
LLLW	Low-Level Liquid Wastes
LLW	Low-Level Wastes
LOTES	Low-Temperature Solidification
LWR	Light-Water Reactor
MCi	Million Curies
MW	Megawatt
MWd	Megawatt-days
NFS	Nuclear Fuel Services
PNL	Battelle Pacific Northwest Laboratories
PSU	Pennsylvania State University
PWR	Pressurized-Water Reactor
R&D	Research and Development
SFA	Spent Fuel Assembly
SFP	Spent Fuel Pin
SRL	Savannah River Laboratory
SRP	Savannah River Plant
SSP	Sandia Solidification Process
WSEP	Waste Solidification Engineering Prototypes

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This report presents the results of a study of the scientific and technological problems associated with the conversion of liquide and semiliquid high-level radioactive wastes into a stable form suitable for transportation and disposition and includes consideration of spent unreprocessed fuel as a potential solid waste form. The report was prepared by the Panel on Waste Solidification under the Committee on Radioactive Waste Management of the National Research Council/National Academy of Sciences.

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