INSTITUTE FOR ENERGY AND ENVIRONMENTAL RESEARCH

Washington, D.C. office:
6935 Laurel Avenue
Takoma Park, MD 20912
U.S.A.
Phone: (301) 270-5500
Telex: 6502975485

GLASS IN THE ROCKS

Some Issues Concerning the Disposal of Radioactive Borosilicate Glass in a Yucca Mountain Repository

Arjun Makhijani, Ph.D.

Prepared for the

Nevada Nuclear Waste Task Force

and the

Nevada Agency for Nuclear Projects

Nuclear Waste Project Office

State of Nevada

January 29, 1991

9102120089 910129
PDR WASTE
WM-11 PDR

102.3
WM-11
NH03

ADD: Joe Youngblood

European office: IFEU—Institut für Energie-und Umweltforschung Heidelberg e.V., Im Sand 8, 6900 Heidelberg, Federal Republic of Germany, Tel. (011-49) 6221-10101

Table of Contents

GLASS IN THE ROCKS

Some Issues Concerning the Disposal of Radioactive Borosilicate Glass in a Yucca Mountain Repository

Executive Summary

Summary of Findings

Our principal technical findings with regard to DOE's current plans to store defense high-level wastes in a repository at Yucca Mountain in the form of vitrified borosilicate glass are as follows:

1. The phenomenon of hydration aging of vitrified glass, followed by leaching can result in the rapid disintegration of the glass. *This represents a potentially serious problem for the long-term isolation of wastes in glass form in a repository.* The problem is that the glass waste, once hydrated, may be much more susceptible to leaching than the original glass form, possibly leading to relatively rapid escape of radionuclides from the repository.

2. The risks that hydration aging will pose a problem would be *especially* and *uniquely* great at a Yucca Mountain site. This is because the hydration reaction can proceed rapidly under conditions of high temperature and optimum humidity which are possible in an *unsaturated* environment such as that expected at Yucca Mountain (often cited as one of the site's strong points).

3. Increasing areal power density, that is, raising the temperature of the repository substantially above the boiling point of water, as DOE is currently considering for a Yucca Mountain repository, may increase problems due to hydration aging and subsequent rapid disintegration of glass, if the repository goes through a period of increasing humidity followed by saturation and if it results in higher glass temperatures.

4. In the event that hydration aging occurs at a Yucca Mountain repository, and that releases from hydrated glass are not contained by other barriers, such releases could exceed even the minimal environmental standards proposed by the EPA.

   Worse, under such circumstances the more reasonable standard of limiting maximum individual dose from the repository for an indefinite period, as

recommended by a 1983 National Academy report, would be exceeded by an even larger margin. As it is the situation in this regard has been estimated to be poor by the 1983 National Academy of Sciences report. That report estimated that even without hydration aging, doses to the maximally exposed individual from contaminated groundwater could range from 300 millirem per year to over 1,000 rem per year. This last figure is a huge dose and forty thousand times the current EPA maximum allowable dose from the civilian nuclear fuel cycle.

Our investigation of the technical issues has also revealed a number of findings which raise concerns about the DOE's procedural steps and management priorities in its repository development program. These findings include:

1. Although in principle waste forms exist which have far lower solubility than glass (and which would therefore be less likely than glass to allow excessive radionuclide escape to the environment), there has been no significant effort on the part of the DOE to investigate alternatives to the glass waste form for wastes at Savannah River and Hanford.

2. Despite the fact that the hydration aging issue was first raised as early as 1982, and there were indications that DOE was beginning to focus on Yucca Mountain as a likely site even at that time, DOE failed to investigate the potential problems of hydration aging as a matter of high priority until recently.

3. It appears from the decision-making process and the speed with which glass was selected over other waste forms, and available technology for manufacture glass compared other alternatives played a greater role in selecting glass than any inherently superior characteristics for long-term containment. This indicates that short-term considerations and minimizing costs may have played an unduly large role in waste form selection relative to long-term isolation of wastes from the human environment.

In sum, our survey of the question of borosilicate glass at Yucca Mountain indicates that DOE should be putting far more emphasis on the problems of waste forms and engineered barriers performance -- not that one would expect a repository to perform a lesser role in containment, but from the point of view of meeting reasonable health criteria with the greatest possible confidence.

This survey indicates one more way in which the DOE is embarked on a program which may pose risks in areas which are not yet fully recognized or incorporated in program decision-making. If such risks turn out to degrade repository performance, it is a matter of urgency to investigate and resolve the issues. If not, DOE will again have chosen a path that may result in high cost, long delays and increased risks.

Recommendations

In consideration of the above findings, we submit the following specific recommendations:

1. *That the DOE intensify research on the problem of hydration aging of glass which includes consideration of the following factors, among others:*

   - the effect of repository design temperature on the phenomenon of hydration aging of glass. Specifically, DOE's potential plans to increase repository temperature (i.e. by increasing areal power density) should be reconsidered in light of its relation to the problem of hydration aging of glass. Specifically, we recommend that the implications of high repository temperature under conditions of gradually increasing humidity and eventual saturation should be carefully evaluated.

   - the potential for rapid transport of the colloids produced by the hydration aging of radioactive borosilicate glass.

2. *That the Department vigorously research and develop alternative waste forms that have the potential for far better isolation of radionuclides under a wider variety of conditions than appears to be true of glass.*

   Desirable properties of the waste form would include relative insensitivity to both repository host rock characteristics and hydrogeological conditions.

3. *That the way in which research priorities for waste forms have been set also be carefully investigated in order to improve decision-making for choosing a waste form for high-level defense wastes.*

   The special relevance of hydration aging to the Yucca Mountain site and the fact that Yucca Mountain has long been on the list of potential sites indicates a need to reevaluate DOE's decision to rely on borosilicate glass as the waste form for highly radioactive wastes from Hanford.

   Such an evaluation is especially urgent now since the vitrification plant at Hanford has essentially been put on hold pending the testing of the Savannah River facility. This therefore appears to be an opportune time to devote more resources to investigation of alternative waste forms.

Introduction

The production of nuclear weapons in the U.S. has led to the accumulation of large amounts of highly radioactive wastes, most of them in liquid form, at the defense production facilities at Savannah River in South Carolina, Hanford Reservation in Washington state, and the Idaho Chemical Processing Plant near Idaho Falls in Idaho. As of the beginning of 1988, there was about 380,000 cubic meters of these wastes, containing about 1.3 billion curies of radioactivity.[1]

Current U.S. government plans for most of these wastes (i.e., those at Savannah River and Hanford) are to first convert them, through a process known as vitrification, into a borosilicate glass form, and then dispose of them in a repository below the surface of the earth in a mined deep geologic repository. In this same repository, according to current policy, the highly radioactive spent fuel wastes from U.S. commercial nuclear power reactors will also be stored.

The current focus of the U.S. radioactive waste repository program is a site in the state of Nevada, at Yucca Mountain, about 100 miles northwest of Las Vegas. The U.S. government, through a program run by the Department of Energy (DOE), is currently directed by Congress to undertake an extensive characterization process to determine the suitability of the site. If the site is found suitable, the DOE plans to construct a repository there and open it by 2010. The State of Nevada has opposed this project and is currently litigating the 1987 law that singled out Yucca Mountain for characterization.

The permanent disposal of radioactive wastes has been a long-standing and controversial problem in the U.S., and indeed, throughout much of the world. The scientific, technical, managerial, and political difficulties presented by a million-plus-year disposal problem are varied and enormous. The purpose of this paper, however, is to focus on one particular set of technical concerns related to the use of a possible Yucca Mountain repository to dispose of high-level radioactive defense waste in the form of vitrified glass.

The principal issues that will be raised in this paper relate to a phenomenon known as hydration aging, a process just beginning to be understood. This phenomenon can lead to the rapid changes in the glass form, with potential subsequent disintegration by leaching. It is crucially important, therefore, that this process and its potential implications for the isolation of dangerous radionuclides over the long term be better understood.

---

1 U.S. Department of Energy, *Integrated Database for 1988: Spent Fuel and Radioactive Waste Inventories, Projections, and Characteristics*, DOE/RW-0006, pp. 55-56 (Sept. 1988).

1. Overview of Glass as a Waste Form

Borosilicate glass as a waste form

Borosilicate glass contains high levels of boron (several percent), like the familiar "Pyrex" glass from which kitchenware is made. It has long been considered as a possible medium in which to mix highly radioactive wastes from plutonium production (civilian or military), in order to immobilize the wastes and to dispose them of in a geologic repository. One reason why borosilicate glass has been thought appropriate for immobilizing high-level radioactive waste is because of its higher temperature resistance, compared to ordinary glass.

The properties of the glass, such as solubility, change with temperature, and other aspects of durability depend on its overall composition, including its boron content. The process of producing glass containing radioactive waste is known as vitrification.

In the United States, the decision was made in 1982 that spent fuel from civilian reactors would be disposed of in a repository without reprocessing and therefore without the waste being converted into a form which would be suitable for vitrification. At about the same time, the Department of Energy committed itself to building a vitrification plant at the Savannah River Site where its main military plutonium production activities (by reprocessing irradiated uranium fuel) have taken place over the last two decades. In terms of radioactivity content, high-level waste at Savannah River contains about 60% of the military high-level wastes in the entire nuclear weapons complex.

The vitrification plant at Savannah River is called the Defense Waste Processing Facility (DWPF). There is another vitrification plant being built at West Valley, New York, near Buffalo, where there was a commercial reprocessing plant in operation from 1966 to 1972. While both plants will produce borosilicate glass, the composition of the two glasses is somewhat different.

Waste Form and Repository Performance Standards

The waste form is one part of a planned system of barriers for preventing radionuclides from the waste form reaching the human environment in quantities that exceed that radionuclide release or dose criteria. The other parts of the system are: a canister in which the waste form is to be placed; an "overpack" of metal such as titanium; and backfill in the borehole where the package is to placed. This constitutes the "engineered barrier system." Finally, there is the geologic system in which the engineered system is located, which is considered the primary barrier to prevent or retard radionuclides form reaching the human environment. Figure 1 shows the conceptual design of military high-level radioactive waste package.

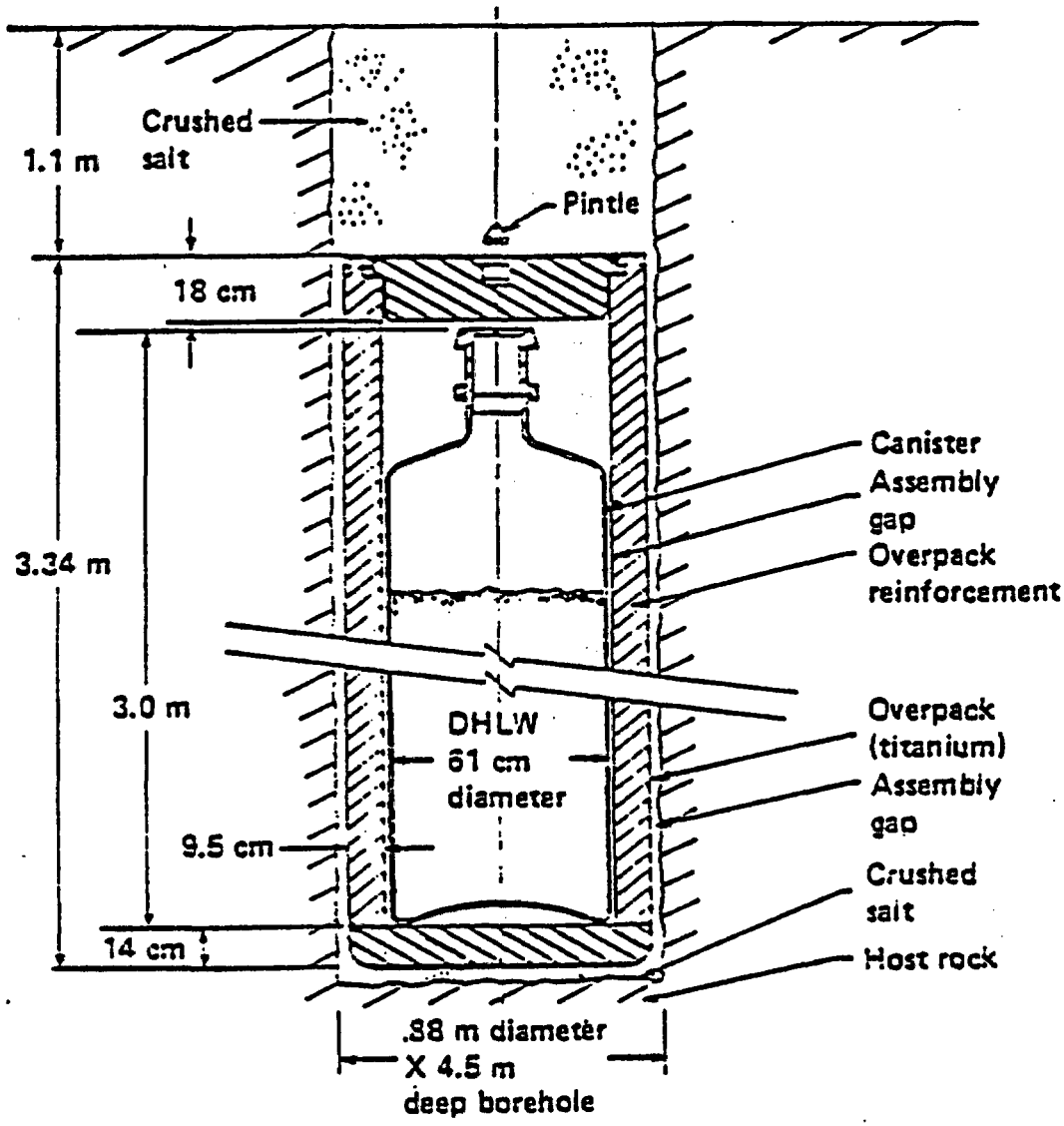

FIGURE 1. Defense high-level waste borehole waste package conceptual design.

SOURCE: National Research Council, 1983.

There are at present no legally valid Environmental Protection Agency (EPA) standards by which to judge the performance of any proposed repository. The last standards promulgated, which were voided by the courts in 1986, extended out to 10,000 years, but placed no restrictions on radiation doses after that. Present Nuclear Regulatory Commission (NRC) regulations regarding waste package performance require "substantially complete containment" for 300 to 1,000 years, and leaks limited to no more than 1 part in 100,000 per year of radionuclides remaining after 1,000 years. Thus, under NRC standards, some waste package containment of radionuclides is required for 100,000 years.

The vacated EPA standards are still used by both the NRC and the DOE as the basis for their site characterization. Research, development and design work is proceeding on the same basis. However, this vacated EPA standard is an arbitrary one, since it cuts off protection of public health at a point in time which is without reference to potential doses to the maximally exposed individual. It also does not address the question of whether that dose would exceed any present standard, such as the EPA 25 millirem per year limit for the nuclear fuel cycle, or any future more stringent standard such as the 10 millirem per year recommended by a 1983 National Academy of Sciences (NAS) report on geologic isolation systems.[2]

It is crucial to note in this context that the preliminary assessment of Yucca Mountain, Nevada tuff done by the National Academy of Sciences Waste Isolation Systems Panel concluded that the 10 millirem per year standard may not be met at Nevada, even though the vacated EPA standard may be satisfied.[3] It is important therefore to consider the performance of waste forms at Yucca Mountain not only in the context of the vacated EPA standard, but also in the context of more rigorous criteria for pubic health protection such as the NAS recommended standard, or some equivalent which limits releases into the indefinite future so as to achieve the same effect of limiting doses to the maximally exposed individual below a specified level.

Waste Form and Repository

The geologic barrier plays a central role in the conceptual design of the system by which the DOE plans to prevent releases of large quantities of radioactive materials to the environment. Repository sites that DOE has considered are highly complex and non-uniform. Each possesses its own unique physical and chemical characteristics. These characteristics interact with the chemical forms of the radioactive materials which would be

---

2 National Research Council, A Study of the Isolation system for the Geologic Disposal of Radioactive Wastes, National Academy Press, Washington, D.C., 1983; Chapter 8. Hereafter referred to as the National Academy report.. For another discussion of this issue, see Makhijani, Arjun, Reducing the Risks: Policies for the Management of Highly Radioactive Nuclear Waste, Institute for Energy and Environmental Research, Takoma Park, May 1989.

3 National Research Council; Chapter 9.

released from the waste package. Therefore, the ability of a repository to contain wastes is connected to the nature of the waste form and waste package and their potential chemical and physical interactions with the rock and water in the repository.

For this reason, it is prudent to give detailed consideration to the interactions of waste forms with a specific repository setting before selection of the waste form. However, the DOE selected glass as the waste form for military high-level wastes before the process of site selection under the Nuclear Waste Policy Act of 1982 was seriously under way, and before the issuance of final standards by which the performance of repository could be judged.

It might also be considered prudent to select waste forms whose performance can be guaranteed to be very good under a wide variety of geochemical and hydrogeological conditions. This however, may not be the case with glass. Even with the incomplete and inadequate information at hand, there are serious questions as to the performance of glass at two of the DOE's top earlier three candidate sites, both of which are currently controlled by the DOE in whole or in part -- Hanford and the Yucca Mountain site.[4]

A 1981 DOE-appointed panel ranked borosilicate glass first among candidate waste forms. However, a 1983 report by the National Academy of Sciences' Waste Isolation Systems Panel (referred to below as the NAS report in this paper) noted that the criteria which the DOE panel used to rank waste form did not relate systematically to waste form performance under repository conditions:

> It is premature to select waste form materials on the basis of such rankings. The effects of higher temperatures and the effects of realistic repository conditions could alter the rankings. Further, a number of alternative waste form materials have had little study....[F]or most of the important long-lived radionuclides the laboratory leach data that have been used in these rankings have little relevance to the releases of radionuclides in a geologic repository.[5]

Work which was published in 1982 by J.K. Bates et al. raised concerns about hydration aging of glass (see below) under conditions that might prevail at Yucca

---

4 At Hanford, the potential difficulties stemmed from rapid groundwater velocity. See Makhijani, Arjun, and Kathleen Tucker, Heat, High Water, and Rock Instability at Hanford: A Preliminary Assessment of the Suitability of the Hanford, Washington Site for a High-level Nuclear Waste Repository, Health and Energy Institute, Washington, D.C., 1985. At Yucca Mountain, they related to the potential for hydration aging, the subject of much of this paper.

5 National Research Council, 1983; p. 51.

Mountain.[6] Subsequent work done on glass and published in 1984 indicated problems with glass at high groundwater velocities, as noted above.[7]

Borosilicate glass is not the best waste form for preventing the release of radionuclides, so far as present data and theory indicate. There are waste forms which have far lower solubility than glass in principle, but what the NAS study reported in 1983 continues to be true so far as most high-level waste is concerned: these waste forms have not been developed and there "are at present no substantial development programs within the Department of Energy that are concerned primarily with alternative waste forms."[8] The one exception to this is the plan to develop of waste forms other than glass which may be suited to the reprocessing waste from naval reactor spent fuel at Idaho National Engineering Laboratory which was calcined (that is, converted from liquid to powdered form for temporary storage).

Most reprocessing wastes, however, are not calcined, but are in liquid, sludge, and salt forms in tanks at Hanford, Savannah River and West Valley, New York. The lack of research for these wastes has prevented any realistic evaluation of waste forms so far of alternative waste forms which may "offer the possibility of releasing contained radionuclides at the qualitatively lower rates that are predicted when release is controlled by diffusion with a solid."[9]

The existence of the technology for the manufacture of non-borosilicate glass, some experience of an operating plant for radioactive glass in France and experimental work far more advanced than that for other waste forms played big roles in the selection of glass as a waste form.

2. Glass in Tuff at Yucca Mountain

The Yucca Mountain volcanic tuff site for a repository is an igneous rock site, as are the basalt site that was proposed for Hanford, and the granite sites that were named as possible candidates in the eastern portion of the country in 1986. In 1987, Congress named Yucca Mountain as the only candidate repository site in the United States. The Yucca

---

6 Bates, J.K., et al., "Hydration Aging of Nuclear Wastes," Science, vol. 218, October 1, 1982; pp. 51-53.

7 Mendel, J.E., (compiler) Final report of the Defense High-level Waste Leaching Mechanisms Program, PNL-5157, prepared for the U.S. Department of Energy by Pacific Northwest Laboratory, Richland, Washington, August 1984. The report noted that at "high [water] flow rates...a dealkalized silica-rich protective layer [which slows down radionuclide releases] is not built up." p. 1.25.

8 National Research Council, 1983; p. 82.

9 National Research Council, 1983; p. 83.

Mountain rock consists of ash-flow tuffs, which are the result of volcanic and subsequent geologic alteration processes. It is the only one of the proposed sites in the United States which lies above the water table. The principal horizon proposed for the repository, in the Topopah Springs member, lies more than 100 meters above the present water table.

When repositories are below the water table, one can expect them to become saturated with water within a decade or so of closure. In the case of Yucca Mountain, where the proposed repository would be above the water table, the repository would not become saturated unless some event, such as climatic or geologic changes result in changing conditions that produce increased flows of water into the repository area. This unsaturated condition has been claimed as one of the great advantages of a Yucca Mountain repository, since water is generally accepted to be the primary way in which radionuclides in a repository would reach the human environment. Some gaseous releases are also expected, but their source would be the spent fuel and not the glassified waste form.

There are some disadvantages to a repository above the water table, however. If the repository is planned and designed to be unsaturated and subsequently becomes saturated, then the design conditions will no longer prevail and releases of radionuclides may be more rapid than predicted. This paper discusses a process, called hydration aging of glass. This phenomenon, by its nature would occur in a repository which was unsaturated for a period. It could lead to rapid radionuclide releases if hydration in the unsaturated period was followed by repository saturation which would allow water to carry away the radionuclides. This phenomenon is linked to another feature of Yucca Mountain tuff: the rock is porous and at about atmospheric pressure and would therefore have a lower boiling point that at many other locations (such as Hanford) where the groundwater is under pressure. The boiling point of water in Yucca Mountain tuff is about 96 degrees Celsius.

A shortage of water in Nevada is another disadvantage that is relevant tothis report. This has two crucial implications for public health. First, the amount of water available for dilution of radionuclides is relatively small, so that the concentration of radionuclides in the groundwater could be correspondingly large in case it does become contaminated. Second, since groundwater is scarce, the likelihood that contaminated groundwater would be used, inadvertently or under duress, is greater than in areas where groundwater supplies are more plentiful. As the National Academy study noted in 1983:

> The [Nevada] tuff site is difficult to evaluate in terms of calculated doses from use of groundwater by humans. Although our later calculations will reduce the estimated doses in groundwater [compared with the pessimistic ones under discussion], it seems that any normal, and continuing use of the potentially contaminated groundwater from a site in saturated or unsaturated tuff could present a problem, if the flow rates of contaminated groundwater are anywhere near those adopted in this study. The absence of flowing surface water in this region presents a greater incentive to use groundwater than for sites in less arid regions....Therefore we attach

> greater significance to the calculated groundwater doses for the tuff sites than for sites in less arid regions.[10]

The doses from groundwater in the pessimistic calculations due to neptunium-237 would be over 1,000 rems per year per person, or over 100,000 times the suggested maximum dose of 10 millirem recommended by the National Academy study, at groundwater travel times of 25,000 years. The doses, in the more optimistic calculations, would be about 300 millirem, still 30 times the suggested limit.

It is sometimes assumed that the doses would correspond to the more optimistic calculations, because the radionuclides will not dissolve simultaneously. That may not be the case even without complicating phenomena. It is therefore important to understand the various postulates about the dissolution of radionuclides. Moreover, the phenomenon of hydration aging may cause the rate of radionuclides releases from the glassified waste form to approach worst case postulates. Hydration aging and its significance is discussed further below.

The two mechanisms for radionuclides releases from the wastes form which were considered by the National Academy study are termed "congruent dissolution" (the pessimistic case) and "solubility-limited dissolution" (the optimistic case, considered by the National Academy study to be the more realistic case). Congruent dissolution occurs when the waste form and the radionuclides dissolve simultaneously and at the same rate. Solubility-limited dissolution is when the rates of dissolution of different components of the waste form and for various radionuclides are different depending upon the solubility of the substance, the chemical composition of the groundwater and the rate of water flow past the waste form.

The National Academy study assumed that solubility limited dissolution and subsequent dispersion of radionuclides represented the "the best estimate of geologic repositories," including the Nevada tuff repository at the time of the report.[11] The importance of the assumption of solubility limitation is illustrated by the following statement in the NAS report:

> ...long-term limiting of radionuclide release, after 1,000 years, and retrievability are desirable but not necessary waste-package features *if we can depend on geologic isolation, low solubility, and limited transport for long-term containment.*[12]

---

10 National Research Council, 1983; p. 265.

11 National Research Council, 1983; p. 255.

12 National Research Council, 1983; p. 45, emphasis added.

However, some current assessments of glass do not favor the hypothesis that dissolution will be solubility-limited.[13] Release rates for congruent dissolution can be many orders of magnitude greater than for solubility-limited dissolution. For instance, the NAS report estimated that the doses from groundwater for congruent dissolution in tuff for reprocessed spent fuel would be more than a thousand times higher than for solubility-limited dissolution for water travel times of 10,000 years. The differences are even greater for longer water travel times, since doses from congruent dissolution would remain high for millions of years.[14] For short water travel times, the doses would be high in both cases, though still considerably higher for congruent than for solubility-limited dissolution.

Figures 2 and 3 show the congruent dissolution and solubility-limited dissolution graphs for reprocessing waste, as reported by the NAS study. The study did not report similar calculations for unreprocessed spent fuel in Nevada tuff, but the general effect would be the same, though the specific ratio would be different due to different radionuclide composition of spent fuel. The radionuclides released, as shown in Figures 2 and 3 would be broadly similar to those from glass containing military high-level wastes, because the figures assume that civilian fuel has been reprocessed, with most plutonium and uranium removed prior to vitrification.

The principal reason for concern about the phenomenon of hydration aging is that whatever the assumptions about solubility, it could cause radionuclide releases from hydrated surfaces to approach those for congruent dissolution.

Hydration Aging of Glass

Hydration aging of glass is a phenomenon which causes the surface layers of glass to change chemically under the action of water vapor into secondary phases much more rapidly than would be the case if the glass were simply immersed in water or if it stayed dry. The rate at which these secondary phases of glass are formed is dependent on temperature and humidity, with the reactions proceeding more rapidly as temperature and humidity increase. These secondary phases could cause the surface layers of the glass to disintegrate rather rapidly if the repository subsequently becomes saturated.

---

13 Bates, J.K., "The Role of Surface Layers in Glass Leaching Performance," presentation at the Materials Research Society Conference, Boston, November 26-29, 1990.

14 National Research Council, 1983; figures 9-6 and 9-12.

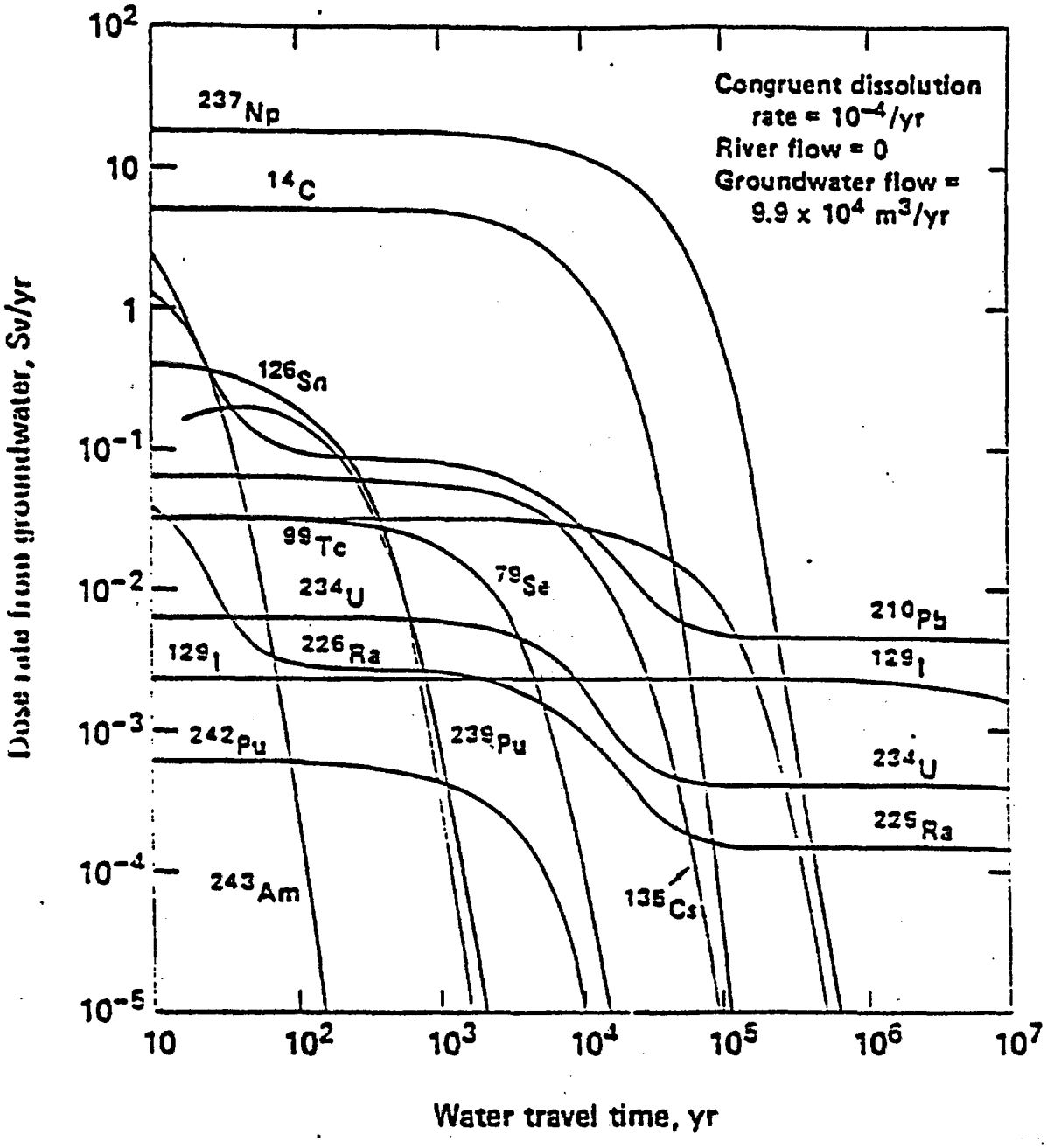

FIGURE 2. Individual radiation dose as a function of water travel time in tuff: reprocessing waste from 10^5 Mg uranium fuel, congruent dissolution, no dispersion.

SOURCE: National Research Council, 1983.

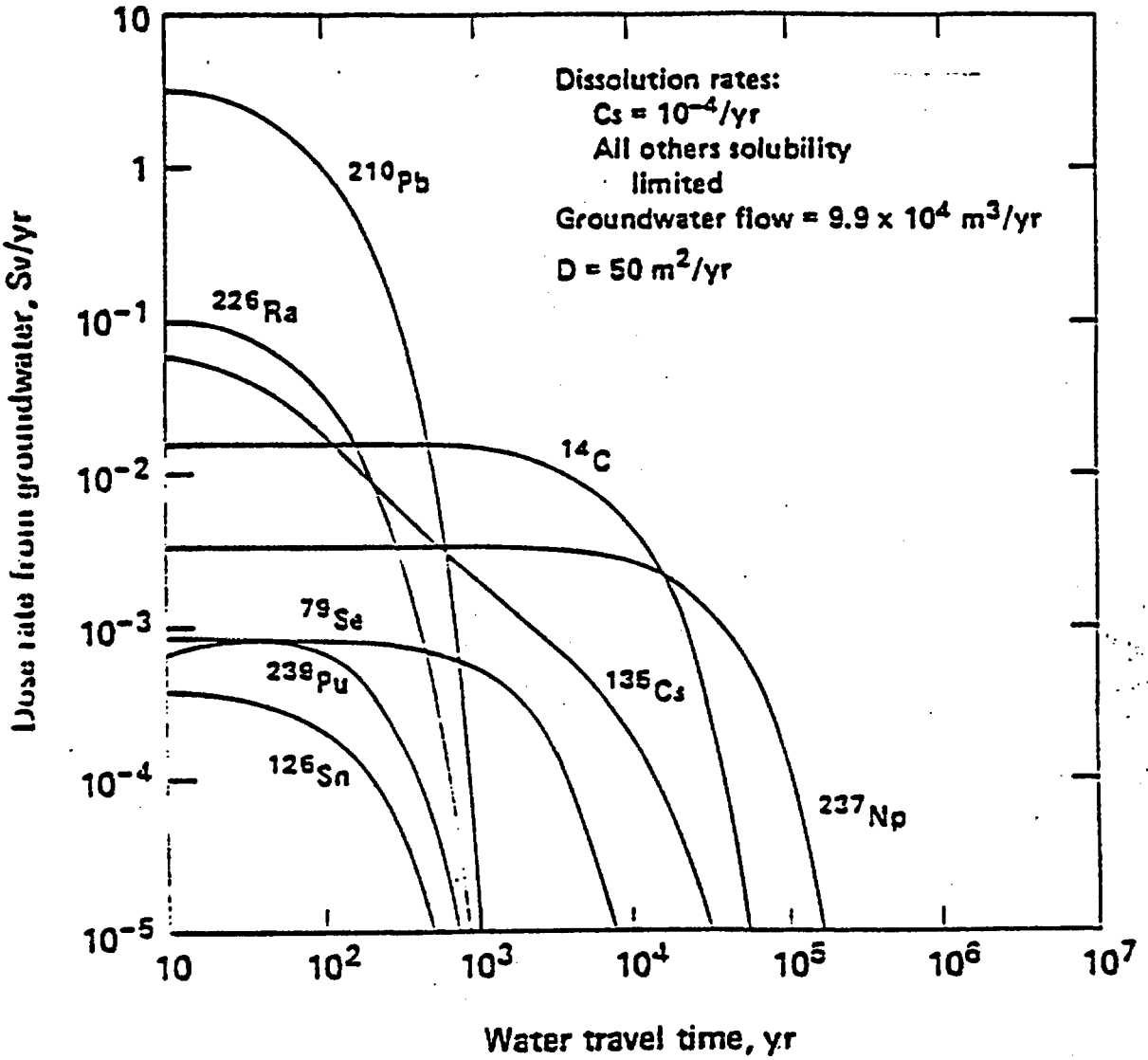

FIGURE 3. Individual radiation dose as a function of water travel time in tuff: reprocessing waste from 10^5 Mg uranium fuel, solubility-limited dissolution.

SOURCE: National Research Council, 1983.

Bates et al. have described the details of the hydration aging process as follows:

> The vapor phase hydration process occurs in a thin film of water that sorbs on the glass surface. This thin film of water rapidly becomes concentrated with components from the glass. If the film becomes saturated with respect to secondary mineral phases, mineral nucleation, precipitation, and growth may occur. As the reaction proceeds, the elements released from the glass are continually incorporated into the secondary phases while the original glass is transformed into a hydrous reaction layer overlain by a mineral mat. The hydration reaction is an aging process that changes the original properties of the glass.[15]

This aging process occurs under unsaturated conditions -- such as those expected at Yucca Mountain. Under such conditions, varying amounts of water vapor would be expected to present in the repository, depending on a host of conditions, such as temperature of the repository, extent of rock fractures, and changes in water infiltration. It must be noted that even at present the description of the Yucca Mountain site as "unsaturated" does not mean that there is no water vapor in it. In fact, rock pores can be as much as 70 to 80% saturated with water, with some fully saturated perched zones. The number of rock pores per unit volume in Yucca Mountain varies according to the amount of natural welding that the tuff has undergone. It is lower in welded tuffs, such as those in the reference repository horizon.

The rate of hydration aging of glass depends on the temperature and the amount of water vapor. The higher the temperature, the higher the rate of hydration aging for a given water vapor content. However, hydration aging seems to occur only at relatively high temperatures (well above 100 degrees Celsius). At lower temperatures, it is very slow to non-existent.

There is an optimum amount of humidity for rapid reactions (provided the temperature is high enough). Below this optimum, the humidity is too low and reaction slows down, above it, condensation on the surface of the glass slows down the hydration reaction. Of course, condensation cannot occur if the repository is above the boiling point of water, which in tuff at Yucca Mountain is about 96 degrees Celsius (about 205 degrees Fahrenheit).

The possible sequence of events for such aging is that the canister would gradually corrode in a hot humid environment, developing leaks, though which water vapor, or drops of water could enter. (The water vapor already present in the canister at the time of sealing is not expected to cause a large amount of hydration aging.)

---

15. Bates, J.K., W.L. Ebert and T. J. Gerding, "Vapor Hydration and Subsequent Leaching of Transuranic-Containing SRL and WV Glasses," in the Proceedings of the Conference on High Level Radioactive Waste Management held at Las Vegas April 8-12, 1990, American Nuclear Society, La Grange Park, Illinois, 1990; p. 1095.

If a repository becomes saturated with water after hydration reactions have proceeded on the glass surface, then the conditions of leaching are quite different from those prevailing before such aging had occurred:

> As the near-field package environment cools, it may be possible that the hydrated glass will be contacted by small amounts of liquid water and the potential for glass leaching and subsequent radionuclide transport will exist. Under such a scenario, the glass exposed to leaching action would not be "fresh" glass as is commonly used in testing to evaluate glass performance, but would be glass that had been aged via the hydration process.[16]

A rapid disintegration of the hydrated glass surface can then occur. New evidence of high leaching in hydrated glass and its consequences for actinide releases, including plutonium releases, has recently been reported by Bates et al. (1990). The rates at which actinides like plutonium are released from hydrated glass are hundreds of times greater than for non-hydrated glass. Thus, the differences on this score appear to be qualitatively the same as those between congruent and solubility-limited dissolution, as discussed above. Some of the specific findings of Bates et al. are as follows

> For SRL [Savannah River Laboratory] glass, the release of major glass components results in significantly different solution compositions for hydrated and nonhydrated experiments....Significant differences were also seen for actinide releases from hydrated and non-hydrated glasses. For example, leaching of a hydrated sample gave an unfiltered Pu [plutonium] concentration 500 [times] greater than that of less reacted or fresh sample and Am [americium] concentrations 1000 [times] greater. For total release...the Pu and Am differences are 200 and 225 [times].[17]

Qualitatively similar results were found for West Valley glass, in terms of the finely divided hydrated particles, but "[u]nlike SRL glass, however, the WV [West Valley] glasses showed no evidence that large segments of the hydrated layer had disintegrated into solution."[18]

Bates et al. reported further as follows:

> In the current experiments, most of the transuranic elements remained in the hydrated layer. As this hydrated layer disintegrated into very fine dispersible fragments, larger amounts of actinides were released into solution than would be predicted by solubility.[19]

---

16 ibid.; p. 1095.

17 ibid.; p. 1101.

18 ibid.; p. 1100.

19 ibid.; p. 1102.

Consequences of Leaching After Hydration

Rapid leaching after hydration may or may not entail more rapid escape of radionuclides out of the repository. Hydration creates secondary phases (new chemical forms). If the secondary phases are adsorbed better onto tuff or associated zeolite minerals, for instance, then radionuclides may not be released faster than otherwise and may even be retarded compared to leaching of fresh, non-hydrated glass. The fine particles may also seal the leaks in the canister through which water penetrated in the first place, preventing further leaching for an extended period. However, the colloids which result from the disintegration of a hydrated layer have the potential to be transported rapidly into the human environment, if they are not held back by other engineered barriers or by the below ground geologic environment. The needed scientific investigations to resolve these issues have yet to be carried out. We have not investigated, for the purposes of this paper, the specific nature of the releases of radionuclides and their rates of transport into the human environment subsequent to leaching of hydrated glass.

There may also be alternative period of high and lower humidity during the period when the repository is becoming saturated. The consequences of this on performance of glass need to be investigated.

3. "Hot" Repository and Consequences

When spent fuel is discharged from a reactor, it is generating heat at a large rate and must be cooled under water. The heat generation comes from the radioactive decay of the fission products in the spent fuel. Only a minor and essentially negligible portion of the heat comes from the uranium and plutonium in the fuel rods. Since the fission products are decaying constantly, the amount of heat generated per unit of time decreases as time goes on. The approximate figures for U.S. spent fuel from civilian reactors are as follows: after 1 year, the heat generation is on the order of 10 kilowatts per metric ton of spent fuel (original uranium content); after ten years this reduces to roughly one to two kilowatts; and after 100 years to about 200 to 300 watts.[20]

Disposing of spent fuel in a repository will produce high temperatures in and around the spent fuel canisters (or containers) and, depending on the age of the spent fuel and the density of its emplacement, also in the rest of the repository. The temperature which is to be expected in the repository depends on geological conditions, such as on the heat transfer properties of the rock, and whether the repository is saturated or not. It also depends on the amount and burn-up of the fuel that is placed in the repository (that is the amount of

---

20 DOE/RW-006.

energy which has been generated from the fissionable material in the fuel). Finally, the age of the fuel is a critical variable.

When fuel of a given age (a proxy for heat generation) is placed in a repository, the temperature around the waste packages will be determined largely by the spacing of the fuel -- that is by the "areal power density." Since heat generation per unit area of the repository is a critical variable, it is used in repository design as a fundamental determinant of the amount of area required in a repository. The areal power density for reference or generic repositories, for purposes of studies has been around 12 to 14 watts per square meter.

The Yucca Mountain Site Characterization Plan assumes an areal loading of 57 kilowatts per acre, or about 14 watts per square meter in the reference repository horizon. This value was not chosen by an optimization process, but by what "was judged to be typical of what might be selected for the final design."[21]

In order to provide for contingencies, such as increased waste disposal, to reduce repository costs, and possibly other reasons, the DOE has been considering significantly increasing the areal power density in the repository, possibly by as much as fifty percent.[22] This would increase the temperature of the repository.

We will not consider the subject of repository temperature in detail here, since there is not yet sufficient DOE documentation of the proposed higher areal power densities and resultant higher temperatures at Yucca Mountain and their effects upon which to base any conclusions. It is, however, important to consider in this context the known risks of decreasing repository performance by increasing repository temperature. There may also be an aggravation of the problem of hydration aging due to higher temperatures.

There are many potential disadvantages that offset the economic advantage of increasing areal power density in the repository. These disadvantages would apply generally to any hard rock repository. Higher temperatures can result in "increases in the corrosion of the waste-package container and the waste form, increases in the flow velocity [of water] near the waste, and changes in the geochemical conditions of the groundwater. Nearer-term temperature effects of practical importance are thermally induced stresses in the rock, thermal stresses in the waste package during resaturation [see below], and possible retrievability of the waste."[23] Thermally induced stresses can produce fracturing of

---

21 Mansure, Arthur, J. Underground Facility Area Requirements for a Radioactive Waste Repository at Yucca Mountain," SAN84-1153, Sandia National Laboratories, Albuquerque, New Mexico, November 1985; p. 27.

22 Blejwas, Thomas, "Alternative Designs and Contingency Plan," Presentation to the Nuclear Waste Technical Review Board, U.S. Department of Energy Office of Civilian Radioactive Waste Management, March 19-20, 1990.

23 National Research Council, 1983; p. 289.

the rock which can drastically increase the permeability of the rock mass -- increasing the rate of flow of water through the rock.

Thermal effects in tuff are even more complex. According to the NAS report, preliminary findings indicate that the performance of both welded and nonwelded tuffs could deteriorate in the cooling phase that would follow and expansion due to heating.[24]

Military Waste and Areal Power Density

Currently the DOE plants to intersperse military wastes with civilian spent fuel in the repository. This has the effect of reducing the areal power density below what it would if civilian spent fuel were put in every borehole at the same spacing, because military waste is considerably cooler than spent fuel. Thus, interspersing military and civilian waste can keep the temperatures lower for a given borehole configuration and tonnage of wastes per unit area in the repository.

The disadvantage of interspersing military wastes with spent fuel is that the heat release from the spent fuel may become an external heating source for the glass, if the areal power density is high enough and the age of the spent fuel is low enough. In that case the glass would be more vulnerable to the problems arising from higher temperatures, such as increases in cracks in the cooling phase. The glass would already have gone through one phase of cooling and cracking during its production. The cracking during this phase is important in that it increases the surface area of the glass that would be exposed to any water or humidity in the repository. Increasing power density may therefore have adverse implications for the problem of hydration aging.

An increase in temperature of the repository would under normal circumstances of an unsaturated repository reduce the humidity. Thus, the deleterious effects of higher temperature would be offset to some extent by lower humidity. However, any advantage from higher temperature may rapidly give way to serious problems if for any reason there were an increase in humidity in the repository, due to changing ground water conditions or surface conditions such as climate, or both. Thus, the repository may go through a phase of increasing humidity as it slowly cools, but when it is still at a high enough temperature that rapid hydration aging could be expected to occur (in the 150 to 200 degrees Celsius range according to the experimental results of Bates et al.)[25]

There may also be alternating periods of higher and lower subsurface humidity during the period when the repository is becoming saturated. The consequences of this on performance of glass, including its effects on hydration aging, need to be investigated.

---

24 National Research Council, 1983; p. 128.

25 Mansure, 1985.

The above discussion is framed in terms of hypotheses rather than assertions because we have not yet investigated the effects of higher areal density on hydration aging phenomena. Whether these phenomena would be aggravated or not may depend on the manner and speed of resaturation of the repository, and the time at which the resaturation occurs. This is an issue which needs to be addressed in the context of considering higher areal power density. It is important to note here that borosilicate glass is deteriorates faster with hot groundwater even in the absence of hydration aging. Thus, an important aspect of considering higher areal density would be the various deleterious effects which that may potentially have on borosilicate glass.

4. Conclusions

The National Academy of Sciences Panel in a 1983 report acknowledged the significance of the experiments of Bates et al. described in their 1982 publication in Science. Noting the formation of a hydration layer in the experiments of Bates et al, it said:

> This rapid hydration suggests that over a long time and especially at high temperatures, glass may become completely altered structurally, even though it has not dissolved. If so, present laboratory leach data that include only a relatively small degree of such alteration at the sample surface may not be indicative of longer-term releases.[26]

As it stands, the hydration aging issue appears important enough as a problem at Yucca Mountain to merit much more serious and high priority research and attention than the DOE has been giving it. The problem increases the risks that a Yucca Mountain repository may not meet performance criteria, if the releases from hydrated glass are not adequately contained by other barriers. Worse, it indicates that the site may fail to meet, by an even larger margin, the more reasonable standard of limiting maximum individual dose from the repository for an indefinite period, as recommended by the National Academy report in 1983 (or some equivalent standard such as limiting maximum radionuclides releases so as to achieve the effect of limiting maximum individual dose).

The special relevance of hydration aging to the Yucca Mountain site and the fact that Yucca Mountain has long been on the list of potential sites indicates a need to reevaluate DOE's decision to put into borosilicate glass essentially all of its resources for long-term isolation of high-level wastes at Hanford and Savannah River. We recommend that the way in which these research priorities for waste forms have been set be thoroughly

---

26 National Research Council, 1983; p. 64.

investigated in order to improve decision-making for choosing a waste form for Hanford high-level wastes.

Such an evaluation is urgent now since the vitrification plant at Hanford has essentially been put on hold pending the testing of the Savannah River facility. This therefore appears to be an opportune time to devote more resources to alternative waste forms which are both relatively insensitive to repository host rock characteristics and hydrogeological conditions. Such research should also consider waste forms with far better isolation characteristics than borosilicate glass.

Therefore we recommend that the Department begin the process of researching and developing alternative waste forms that have the potential of far better isolation of radionuclides under a wider variety of conditions than appears to be true of glass.

Increasing areal power density may increase problems due to hydration aging and subsequent rapid disintegration of glass, if the repository goes through a period of increasing humidity followed by saturation, and if the increase in areal power density is configured in a way which increases the temperature of the borosilicate glass waste forms. We recommend that the question of increasing repository temperature be looked at with some attention to its relation to the problem of hydration aging of glass. Specifically, we recommend that the implications of high repository temperature under conditions of increasing humidity and eventual saturation should be carefully evaluated.

Given the potential negative consequences of higher repository temperature, DOE should also investigate anew the benefits of extended storage of spent fuel at reactor sites so that the fuel would be much cooler before transport and emplacement in a repository.

In sum, our survey of the question of borosilicate glass at Yucca Mountain indicates again that DOE is embarked on a program which may pose risks in areas which are not yet fully recognized or incorporated in program decision-making. If such risks turn out to degrade repository performance, it is a matter of urgency to investigate them and settle the issues. If not, DOE will again have chosen a path that may result in high cost, long delays and increased risks.

And finally, the author of the present paper has repeatedly pointed out this problem since early 1985. Yet, it was not until a couple of years ago that DOE funded experiments on hydration aging of glass. DOE has funded research on the characteristics of glass at so that only a few problems are addressed in any particular period. Therefore the pace of research has been much slower than needed for sensible decisions on a repository.

Surely, this delay cannot contribute to an improvement in public confidence in the waste isolation program. An evaluation of past spending should address why the priorities of DOE were so inappropriate that hundreds of millions have been spent on design work for a repository, when so much basic work on waste forms remains to be done. For

instance, there is as yet no substantial research on the transport of radioactive colloids of the type that would be produced by hydration aging through engineered barriers and through tuff.

The failure to investigate the potential problems of hydration aging as a matter of high priority after publication of results which should have been of fundamental interest at least as far back as 1982, is a serious lapse on the part of DOE. It is even more serious in the context of indications at that time that DOE was beginning to focus on Yucca Mountain as the likely site even then. According to the National Academy report:

> We have been informed by L.D. Tyler (Sandia National Laboratories, personal communication to T.H. Pigford, 1982) that emphasis has shifted to unsaturated tuff for a possible repository location.[27]

It would appear from the decision-making process and the speed with which glass was selected over other waste forms that the ability to manufacture glass compared to the state of manufacturing for any alternative, as well as greater data on glass characteristics played a greater role than any inherently superior characteristics of borosilicate glass for long-term containment compared to potential alternatives. This indicates that short-term considerations prevailed, such as the need to solidify military high-level wastes currently in tanks, a manner that would allow for repository disposal. There were other options for this, such as calcining for solidification of military wastes, which would have left long-term options for safe disposal more open, but the DOE dismissed these early on. Minimizing short-term costs may have played an unduly large role in selection of borosilicate glass relative to long-term safe isolation of wastes from the human environment.

---

27 National Research Council, 1983; p. 265.