

July 26, 1984

SUMMARY REPORT

On

POSSIBLE EFFECTS OF GEOLOGIC ENVIRONMENT
ON THE PERFORMANCE OF CANDIDATE
WASTE PACKAGE MATERIALS

By

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INTRODUCTION

In the late summer of 1984 the Department of Energy (DOE) is expected to nominate five sites that are suitable for site characterization for selection of the first repository site. Each nomination will be accompanied by an environmental assessment which includes a detailed statement of the basis for such recommendations, the probable impacts of the site characterization activities for the site, and the means to mitigate such impacts. The DOE is using available geophysical, geologic, geochemical, and hydrologic information in evaluating sites to be nominated for characterization. The five nominated sites are expected to be located in three different geologic media: basalt, salt, and tuff.

The NRC is preparing now to evaluate the environmental assessments to be submitted by the DOE. This paper on the long-term performance of waste package materials is intended to be a part of the information base available to the NRC staff in this preparation. The DOE will not select materials for the waste package nor develop a final waste package design until site-specific data are collected during the site characterization processes, thus the environmental assessments are not expected to contain an evaluation of waste package performance. DOE has stated that engineered barriers will be considered only to the extent necessary to obtain realistic source terms for comparative site evaluations. However, the physical and chemical properties of the repository environment will have a dominant role in the performance of the waste package, and some understanding of the effects of this environment will assist in evaluating any geophysical and geochemical information produced by the DOE.

The studies of the performance of waste package materials at Battelle have been directed primarily at material performance in the environment expected in a basalt repository with some early work on the corrosion of metals in brines typical of salt repositories. A tuff repository is expected to be located in the unsaturated region above the water table as opposed to the saturated conditions of a basalt repository. However, much of the information from the study of the material performance in a basalt repository environment can also be applied to that in a tuff repository. This paper has been prepared to give a brief summary of the findings from Battelle's studies from the perspective of the effects of the geologic environment, primarily the groundwater, on the performance of candidate waste package materials. These suggestions follow the brief description of Battelle's research program for understanding the long-term performance of high-level waste package materials.

SUMMARY DESCRIPTION OF BATTELLE'S RESEARCH PROGRAM
FOR UNDERSTANDING THE LONG-TERM PERFORMANCE OF
WASTE PACKAGE MATERIALS

It is generally accepted that after repository closure the dominant mechanism to cause the release of radionuclides from the repository is groundwater transport. The approach to minimizing the release is to provide a number of different barriers to the dissolution and transport of radionuclides by the groundwater. For a deep-mined repository, the geohydrologic features of the Earth itself are expected to be a major barrier to the release of radionuclides. The repository will be selected so that radionuclides will be isolated for very long times. In addition, engineered features of the repository will act as a barrier to the release of radionuclides. The repository will be constructed in such a manner as to minimize disturbing the adjacent rock and will attempt to accommodate the thermomechanical effects of the emplaced wastes with a minimum of degradation to its geohydrologic properties. Upon closure, the underground openings and shafts to the surface will be backfilled and sealed to minimize groundwater flow paths.

The waste package--which is the center of Battelle's study--will be constructed to provide essentially complete containment of the radionuclides through the period of time in which the repository is heated significantly by decaying fission products. After the container is eventually breached by some process, the waste form must remain sufficiently resistant to groundwater attack to provide high retention of the radionuclides and, together with the repository, to control the release of radionuclides for thousands of years. The objective of our research is to provide an improved understanding of the long-term performance of the materials used for the high-level waste package. More specifically, we are identifying those processes that tend to degrade the performance of the waste-package materials, performing experiments to produce data where data are otherwise lacking on material performance, and analytically modeling the processes to utilize the data to better understand how the processes will affect the material's future performance. In addition, we are identifying areas of work that should be performed by DOE to provide missing data which are beyond the resources of the NRC.

Individual Program Tasks

The program is being conducted in three parallel efforts: waste-form studies, container studies, and waste-package studies. A more detailed summary of achievements to date can be found in the second annual report for this program.*

*NUREG/CR-3427, Volume 4, June 1984, Section 1.

Waste Forms

The waste-form studies are aimed at first describing and modeling those mechanisms that will alter or "age" the waste form during the containment period, and second, identifying and describing those processes that will influence waste-form dissolution after it is exposed to groundwater. The waste-form studies have been largely centered on borosilicate glasses for both defense and commercial high-level wastes; some effort has also been directed toward evaluating spent fuel as a waste form.

In borosilicate glasses, the glass-forming agents can be expected to be tailored to optimize the waste-form properties for each type of high-level waste. After the waste forms are produced, particularly during the very long period of time after disposal while sealed in their container, they will experience processes that will cause changes. One detrimental effect is devitrification of the glass, which can lead both to new phases with increased solubility and to cracking of the glass (which is detrimental because it allows a greater surface area of the glass to be contacted by the groundwater). A model has been developed to predict the degree of devitrification that will occur from subsequent reheating in the repository after disposal. Another detrimental effect is cracking, which could be induced by the effects of radiation on glass. A study of the radiation effects on glass has revealed no new approach to evaluating this phenomenon experimentally, so we are largely dependent on the existing literature which indicates that radiation produces only a small effect on glass performance.

Container Materials

The container studies focus on processes that can degrade the metallic waste-package container. The objective is to collect data on the parameters that influence the degradation processes, to identify the controlling parameters, and ultimately to model the degradation processes that determine the long-term performance of the container. The material under study is cast low-carbon steel for use in a basalt repository, which is the material currently favored by DOE.

The dominant degradation processes that affect the outside of the container are general corrosion, stress-corrosion cracking, pitting, crevice corrosion, hydrogen attack, and mechanical stress. These processes may occur individually or in combination. The parameters that affect these processes include chemical composition and physical state of the steel, groundwater composition and flow rate, temperature, radiation intensity, availability of air, lithostatic forces, redox state, alkalinity/acidity, and availability of hydrogen. These can produce general corrosion, in which the rate of general corrosion will determine the necessary wall thickness, or localized corrosion (such as pitting or crevice corrosion), in which the rate of the localized attack and the container life must be used to establish the wall thickness.

If the steel is susceptible to cracking, failure can be so rapid relative to required container life that the corrosion-allowance approach cannot be used to achieve acceptable performance. What is important is the susceptibility of the metal to crack initiation. Cracking may result from stress-corrosion cracking or from reduction in fracture toughness from hydrogen attack. Both of these processes are under investigation.

In addition, a comprehensive mathematical model is under development for use in understanding the corrosion processes associated with the waste-container materials in a repository environment. These analytical efforts are well integrated with the experimental efforts and are being directed to providing an understanding of the long-term performance of the container materials, with emphasis on those processes that can lead to poor performance.

Integrated System Performance

The waste-package system studies interact with the waste-form studies and the container-material studies to provide an improved understanding of the performance of the total waste-package system. The current emphasis is on providing information for a better understanding of the processes involved in waste-package system degradation. One aspect of the total system under study is the production of radiolysis products in the groundwater by gamma radiation from the waste. This is of major importance in modeling the corrosion of the container and in planning experiments to determine the effects of radiolysis. Our radiolysis model is based on existing codes and sets of chemical reactions combined to provide the best description of experimental data found in the literature. The output of the radiolysis model calculations provide input to the water-chemistry model, which is a fundamental part of the glass-dissolution model and the general-corrosion model.

In-cell integral experiments have been planned which will employ high-level radioactive waste glass, simulated high-level radioactive waste glass, and spent fuel. These experiments are intended to be scoping in nature in order to provide a qualitative basis for identifying those combined-effects processes which are likely to occur and for prioritizing further research on combined effects.

A preliminary study was performed to evaluate methods for performing uncertainty analysis of physical models used to describe long-term waste package performance. Monte Carlo, Latin Hypercube Sampling, and Discrete Probability Distribution (DPD) methods were used to evaluate uncertainties in a test corrosion model. In this study, the DPD method was found to be the preferred method when a Monte Carlo analysis is not possible.

Overall Program Objectives

In all the program tasks, the ultimate objective is to develop a base of information to assist the NRC in evaluating the performance of the waste package proposed in DOE's license application. A near-term objective is to provide information to allow the NRC to prepare position papers on the information required of DOE for evaluation of DOE's proposed waste package. Of significance here is identifying sensitive parameters affecting the performance of materials and identifying data requirements.

To achieve the above objectives, the waste-form task is providing information to give a better understanding of the release of radionuclides from the waste form, beginning at the time it is first contacted by groundwater through the 10,000-year period defined in the draft EPA Standard. This includes an understanding of the probable physiochemical condition of the waste form when it is contacted by groundwater, as well as the parameters of waste-form composition and environment conditions which will cause changes from its state at the time of disposal. In addition, we are producing experimental data on the parameters that affect dissolution of the waste form, including composition of the groundwater and environmental conditions. The waste-form dissolution process is also being mathematically modeled to allow analysis of the performance of the waste form under specific input conditions.

The information on the performance of the container materials relates to the required containment period of 300 to 1000 years. The container performance is expected to be most affected by corrosion and hydrogen-attack processes. We are attempting to provide information on the parameters of container-material composition, groundwater composition, and environmental conditions that are most significant in these processes. Our studies of cast low-carbon steel in a basalt environment (the container/material currently favored by DOE) focus on the susceptibility of the metal to stress-corrosion cracking under repository conditions, because steel is known to fail by this process in some environments. We are studying the chemical species and environmental conditions that cause cracking to determine whether this mode of failure is expected under credible repository conditions. Our experimental studies on general and localized corrosion, together with our comprehensive general-corrosion model, will assist in evaluating the corrosion-allowance approach for the use of steel as a long-life container.

Modeling efforts in the integrated system performance task are contributing significant information to studies of general corrosion and glass dissolution. To obtain information on the amount and kind of chemical species that may be produced by radiolysis of the groundwater near the waste package as a result of gamma radiation from the enclosed waste, energy deposition and radiolysis codes are used. To determine how these radiolysis products may affect the performance of the canister and waste form, chemical activities are calculated by the groundwater-radiolysis model. The output from the water-chemistry model is the concentration

and activity of each chemical species in the groundwater near the waste package. This information is used not only as input to the general-corrosion and glass-dissolution models, but also as a point of reference in directing the experimental efforts in corrosion and dissolution.

SUMMARY OF RESULTS RELATIVE TO PRELIMINARY SITE DATA

Site-specific data are needed to design the waste package and to predict the performance of the materials making up the waste package. Much of this data will not be available until the site characterization process is in the final stages. The data available during site screening can only give some preliminary information which may allow approximating values for the data being sought. However, preliminary information on groundwater characteristics can give some insight into the performance of the waste package materials.

Groundwater Flow Rates

Our studies of container material corrosion and waste form dissolution have shown that groundwater flow rate will influence the kinetics of the chemical reactions of corrosion and dissolution. At high flow rate a continuous supply of reactive species in the groundwater and a removal of reaction products will tend to accelerate chemical reactions. At low flow rates reactive species, such as oxidizing agents, in the groundwater will be consumed (if a production source is not available) and a buildup of reaction products will tend to retard chemical reactions and permit the approach to thermodynamic equilibrium. The degree of the effects of groundwater flow rate is being analyzed in our modeling studies.

Generally, the groundwater flow rate in the repository locations is expected to be very low. Smith* reports hydraulic conductivities on the order of 10^{-12} m/sec for regions in basalt which, depending on the head, should result in very low flow rates in a basalt repository. A salt repository will have no groundwater flow unless faulted but will have some brine which will migrate toward the waste package and may accumulate at the container surface. A tuff repository is planned to be located in a dry unsaturated region above the water table and be subject to infrequent percolating water from the surface.

Preliminary site data on water flow rate will be helpful in determining whether these expected conditions will be realized. For basalt, actual flow rate data should be sought. For a salt location, site specific data on brine inclusions can indicate the quantity of brine available for migration to the waste package, and flow rate data for aquifers above or below the salt deposits can indicate the magnitude of groundwater flow that could occur from shaft seal leakage or other faults. For a tuff repository actual rates, quantities, and frequencies of percolating water should be examined.

*Smith, M. J., Engineered Barrier Development for a Nuclear Waste Repository in Basalt, RHO-BWI-ST-7, May 1980.

Groundwater Chemistry

It is generally recognized that the chemical environment created by the groundwater and the materials near the waste package will largely control the type and rate of corrosion processes that affect all of the materials of the waste package.

There is much to be learned about the chemistry of the groundwater but our research has shown some important preliminary factors. The initial (prior to construction) composition and chemical state of the groundwater can give some insight into the chemical environment that may exist as equilibrium conditions are approached in the sealed repository. The composition of the groundwater affects the corrosion of both the waste form and the container. Some groundwaters are found to be a less aggressive environment for glass waste forms than deionized water because the former contain some dissolution products of the local rock (silicates) which are common to the dissolution products of the glass, thus suppressing the reaction. On the other hand, some groundwater constituents may react with dissolved components of the glass to form insoluble species which precipitate and enhance the corrosion process by removing glass species from solution. Iron, which may be initially present or added from waste package materials, can cause precipitation of silicates and enhance glass dissolution.

Low-carbon steel is a leading candidate for the waste container material. The theory is to use a sufficient thickness of material to allow corrosion to consume a portion of the wall without causing failure during the planned life of the container. Recent results show that in some environments steel will passivate. Whereas this will reduce the rate of general corrosion, it will enhance localized corrosion such as pitting, crevice corrosion, and stress-corrosion cracking. Attack by localized corrosion is more difficult to predict than general corrosion. Again, the water chemistry controls the passivation which, in the observed case, appears to be silicates in an alkaline environment.

Minor constituents in the groundwater can have significant effects. For example, magnesium salts in brine were found to hydrolyze at a liquid-vapor interface on titanium, producing HCl, an aggressive species, in the vapor phase. Many of the minor constituents in groundwaters are known to have caused stress-corrosion cracking of steels in some environments. However, our results thus far show that stress-corrosion cracking of low-carbon steel will not occur in basalt groundwater unless some process causes significant increase in concentration of these species.

The oxidation state and the pH of the groundwater will control many of the corrosion processes. Both of these chemical states will be changed from their initial state by the introduction of air and new materials of the waste package during construction and operation. However, information on the initial state may be indicative of the values which may be

achieved after sealing the repository and may give some insight into the performance of the waste package materials.

Environment Variability and Sensitivity Analyses

It has been reported in several references that groundwater and brine chemistry vary greatly within a geologic setting. This can lead to vastly different behavior of the waste package and the resultant release, upon waste package failure, of radionuclides to the accessible environment. Thus it would be very useful if reference groundwater and brine chemistries could be provided for each site along with information on their expected ranges. Such information on groundwater flow rates would also be very useful.

The chemistry and flow rate baseline data could be utilized by the NRC in evaluating the compliance of DOE release data to EPA and NRC requirements under expected conditions, while the range information could be used in sensitivity analyses under worse-case conditions. For the latter analysis, it is assumed that models will be available to determine the uncertainty of the output given the range of uncertainty in the input data.

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August 2, 1984

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bcc: (w/enclosures)
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RAC File

Dear Dr. Conti:

Enclosed is the requested review of the issues regarding the use of backfill materials in a basalt repository and a tuff repository. I have also enclosed a report I solicited from Prof. Donald Peacor, Dept. of Geological Sciences, University of Michigan.

There are two key points in my report. First, in short-term laboratory tests, the ability of bentonite to swell in water is severely degraded by moisture at temperatures approaching 250°C. This may place serious constraints on the design of backfill mixtures for high-temperature use in a basalt repository. Second, I believe that the use of bentonite in a tuff repository has been rejected partly for misleading or erroneous reasons, and that properly used, bentonite-based backfill may increase the margin of safety of a tuff repository.

With regard to a basalt repository, Prof. Peacor is of the opinion that a high clay/filler ratio is needed to ensure that the system remains closed, and therefore to prevent degradation of the backfill material. I agree that if bentonite does not retain its very high initial swelling capacity, 25% bentonite will not be sufficient to maintain a closed system.

If you or your staff have any questions, please do not hesitate to call me at FTS 972-4385 or -4383.

Sincerely,

Rex A. Couture

Rex A. Couture
Chemical Technology Division

RGC:rr

Enclosures: "Some Issues on the Use of Backfill Materials in
High-Level Nuclear Waste Repositories" (2)
Manuscript by Prof. Donald Peacor (2)

cc: (w/enclosures)
Dr. K. Kim, NRC
Prof. D. Peacor, U. of Mich.

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**SOME ISSUES ON THE USE OF BACKFILL MATERIALS IN HIGH-LEVEL NUCLEAR
WASTE REPOSITORIES**

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July 1984

Introduction

This manuscript describes critical issues suggested by the author regarding the use of clay backfill in repositories for high-level nuclear waste. The issues were identified from results in the NRC-sponsored research program, "Modification of Backfill Materials," FIN A2239, being conducted at Argonne National Laboratory.

Our results from laboratory testing of proposed backfill suggest that backfill is potentially very effective at limiting the flow of groundwater past the waste package, and is therefore, very important or essential to a basalt repository; it may also provide a necessary margin or safety for a tuff repository. I define backfill to mean a mineral barrier placed around the waste canisters.

Our research has suggested several issues that have not been previously identified or that have not been resolved. Recent findings suggest that alteration will place severe limits on the use of what I understand to be the current reference backfill mixture for a basalt repository. Design of the repository will have to take these phenomena into account. Many of the principal issues for a basalt repository are covered at greater length in recent reports (Couture and Seitz, 1984; Peacor et al., 1984). Those reports also cover some issues not mentioned here.

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BASALT REPOSITORY

The principal issues include (1) the time until saturation of the backfill with liquid water, and therefore, the relevant mechanisms of alteration (whether by dry heat, water vapor, or liquid water), (2) the products of backfill alteration, (3) the physical state of backfill materials after alteration (whether cemented or plastic, whether reduced in volume and permeable, or swollen and impermeable), (4) the effects on backfill of gamma radiolysis of gases, (5) the possible effects of concentration of groundwater salts by distillation, and (6) reactions of backfill in a thermal gradient. This letter covers all except number one, which is covered by Couture and Seitz (1984).

Permeability of unaltered backfill

Fresh, unaltered backfill, consisting of 25% Wyoming bentonite, 75% filler (crushed basalt, sand, or any other inactive material with similar density), compacted slightly to a dry bulk density of 1.6 g/cm³ performs very well. The bentonite component swells in groundwater to many times its dry volume. Consequently, in our experiments such mixtures were found to have very low permeabilities of about 10⁻¹⁸ m² (Couture and Seitz, 1984). The permeability is not very dependent on temperature from 25°C to 260°C. Assuming a (rather high) pressure difference of 0.1 MPa across 30 cm of this backfill, the water flow rate would be on the order of 8 cm³/yr per cm² at 200°C. This amounts to very effective control of flow.

Permeability of altered backfill

Our recent unpublished results show that brief exposure of backfill (< seven days) to limited amounts of water or groundwater (water/clay

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ratios on the order of 0.10, most of the water held as water of hydration) at temperatures above 200°C rapidly and severely reduces the swelling ability of the clay. A substantial effect was also observed after seven days at 150°C. We have shown that water vapor, not liquid, causes the alteration. After reaction at 250°C the clay is mineralogically very similar to the starting material (the principal component of bentonite), but no longer shows the extreme swelling of Wyoming bentonite in water. If clay is mixed with groundwater before hydrothermal treatment, there is little or no change in swelling properties. Once the clay has lost expandability, we have been unable to reverse the change by exposure to excess liquid either at 25°C or 250°C.

All Wyoming bentonite we have tested, including National Standard bentonite from Baroid Corporation, shows similar loss of swelling capacity. Thus, the results strongly suggest that water vapor at high temperatures causes rapid, apparently irreversible degradation of all Wyoming bentonite.

The reduced expandability of the clay causes a very large increase in the permeability of backfill mixtures. We have run a series of tests in which similar columns of backfill were slowly, isothermally saturated with liquid water or groundwater (Jan-Mar 1984 Quarterly Report, ANL-84-37, in press). Alteration of the clay occurred during filling. The permeability in liquid was then determined. Because of alteration, the permeability was nearly five orders of magnitude higher at 260°C than at 25°C, as shown in Fig. 1. The increase in permeability was irreversible with reduction in temperature. Injection of dye into the columns showed that the water was flowing through the backfill material, and not through cracks or around the backfill. Thus, our measurements appear to be

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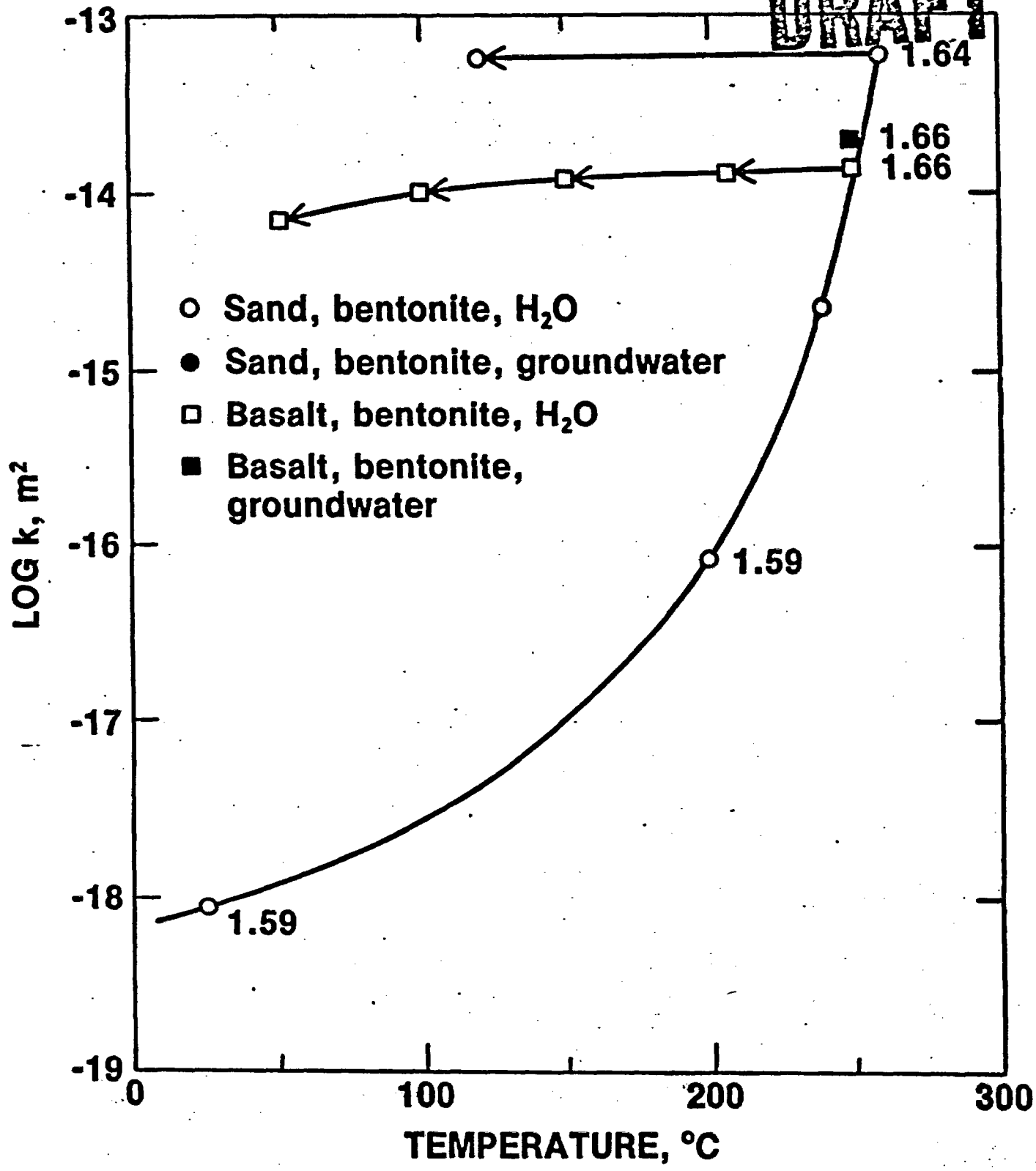


Fig. 1. Permeability of Backfill as a Function of Temperature, Plotted on a Logarithmic Scale. Arrows show reduction in temperature after saturation with liquid water. Numbers show dry bulk densities in g/cm³. Permeability is mainly a function of the temperature at which the column was saturated with liquid water.

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accurate and representative. The cause of the increased permeability was confirmed to be greatly reduced swelling capacity of the bentonite.

The same phenomenon can be expected in a repository. If the repository is subjected to high humidity at temperatures of 150°C or higher, damage to the clay may result. At temperatures approaching 250°C, the damage would be immediate and severe. Loosely compacted backfill (dry bulk density $\sim 1.6 \text{ g/cm}^3$) consisting of 25% bentonite would not be effective at retarding flow of groundwater if exposed to such conditions.

It may be possible to design a bentonite-based backfill which would be effective under such severe conditions. A high proportion of bentonite ($>25\%$), and/or much greater compaction would probably be required.

Bentonite-based backfill may also be suitable for use at temperatures much lower than 200°C. In this case the long-term effects of dry and moist heat (water vapor) need to be determined. We have observed a significant effect at 150°C; the time dependence at this temperature is undetermined.

As a general rule, the use of bentonite in any repository at elevated temperatures calls for further investigation of the effects of prolonged exposure to water vapor. In order to make a valid extrapolation to long time periods, a good understanding of the alteration mechanisms will be required.

Hydrothermal alteration products

There is seemingly ample opportunity for hydrothermal alteration of bentonite if it is mixed with basalt. It is encouraging that neither our experiments nor experiments reported by DOE contractors have convincingly demonstrated large-scale mineralogical alteration of bentonite in hydrothermal

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experiments. Still, at this point we are not able to completely rule out reaction of the bentonite with glass or with other reactive components of the basalt. Grande Ronde basalts are typically somewhat glassy. In many flows the glass contains rather high concentrations of potassium (Couture and Seitz, 1984; Peacor et al., 1984). We have found that the glass is highly reactive in a hydrothermal system. Several possible changes in the bentonite have been suggested, such as increase in calcium content (Peacor et al., 1984), partial conversion to illite or mixed layer illite-smectite (Steindler, 1984; Couture and Seitz, 1984), and conversion to paragonite plus quartz (Steindler, 1984).

I question whether current experimental procedures are adequate to detect changes in experimentally altered clays, that would be significant over the thermal period of the repository. I would suggest that a license applicant address the question of detectability of small mineralogical changes in a complex mixture such as bentonite.

Some experimental results show increase in calcium content of montmorillonite during reaction with basaltic groundwater, (Peacor et al., 1984). The calcium form swells much less than the sodium form, and mixtures containing the calcium form are, therefore, more permeable at moderate degrees of compaction. The obvious question is whether DOE laboratories have carefully determined the exchangeable ions of clay after hydrothermal alteration tests. In reports I have seen, they have not. It will also be interesting to see if they have tested the physical properties of the altered materials, or just of the fresh materials.

Other effects that obviously need to be considered are the effect of the canister on the backfill, the effect of the backfill on the canister and waste form, and the effect of a thermal gradient on alteration of the

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backfill. Assessment of these interactions is not part of my research task, so I cannot comment extensively. I wish only to say that the effects are, to my knowledge, undetermined, and could be either positive or negative. Backfill material may either promote or degrade the passivity of a metallic container. It may also tend to promote corrosion of a container or dissolution of waste glass by ion-exchange absorption of reaction by-products. However, it may also protect the container and waste form by forming a substantial diffusive barrier to the by-products. The importance of a thermal gradient in the backfill is that mass transport may cause alteration of the backfill. For example, outward transport of silica could destabilize montmorillonite. It has also been suggested that calcium minerals may be deposited in the hot inner region. I do not wish to argue that these will necessarily be major effects, but they should be resolved.

Radiolysis

I have identified gamma radiolysis of gases in the repository as a potential trouble spot. Radiolysis of moist air and nitrogen is covered in detail in our Jan-Mar and Oct-Dec 1983 quarterly reports (Steindler et al., 1984; in press). Radiolysis of gas yields products which may be quite different from those of radiolysis of liquid. It seems quite plausible that the backfill will not be saturated with liquid for the first one or two half lives of Cs^{137} (Couture and Seitz, 1984). Radiolysis of residual air in the repository is expected to yield acidic oxides of nitrogen, or possibly ammonia if the system becomes sufficiently reducing. The amount of nitrogen initially in the backfill will be quite small. However, if air or nitrogen is free to diffuse from adjacent rooms of the repository, large quantities of nitrogen could be produced.

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Hopefully, the product gases will diffuse away from the waste package. However, montmorillonite has an extremely large accessible internal surface area, compared to a small surface area for crushed basalt, and has mobile water of hydration which may be quite reactive with gases. It is known to be reactive to acids and may be reactive to ammonia as well. Radiolytically produced gases may react preferentially with montmorillonite rather than basalt. In a mixed vapor-liquid (water) system, the gases would be partitioned into the liquid phase. The obvious question is whether the applicants have considered the effects of radiolytically produced gases.

Other known alteration mechanisms

Significant reduction in swelling capacity in response to dry heating (Bradley et al., 1983; Krumshansl, in press) and in response to gamma irradiation (Bradley et al., 1983) has also been observed. Although the effects are smaller than the effect of steam, which I have just described, the changes evidently continue for at least the several months of testing (Bradley et al., 1983). Thus, the long-term response to heat or gamma irradiation is questionable, and even if the backfill remains dry for the duration of the thermal period, there is some doubt whether it will retain its expandability after prolonged heating and gamma irradiation.

In my opinion, qualification of bentonite-based backfill material for use at high temperatures in a basalt repository will require further testing for its response to dry heat, steam, and liquid groundwater. Furthermore, the material should be altered sequentially in laboratory tests. The clay which is first altered by steam may react differently with groundwater at high temperatures than clay which is not first altered by steam.

Distillation of groundwater salts

Either before or after backfilling, drying or distillation of groundwater may lead to substantial concentration of dissolved salts (Couture and Seitz, 1984). Any water flowing through fractures toward the canisters would likely evaporate and either escape altogether or be distilled into cooler parts of the repository, leaving dissolved salts behind. Deposition of silica or other dissolved materials may or may not clog the fracture and cause the process to be self-limiting. When the repository finally does fill completely with water, the soluble salts would be washed into the last area to fill, which is likely to be the hot area around the canisters.

The effect of increased concentration of groundwater salts on the mineralogical stability of the backfill has not been determined. However, it is known that bentonite does not expand in saline solutions nearly as much as in dilute solutions. Thus, the effect of concentration of groundwater may be to limit expandability of the backfill, at least temporarily.

I suggest that prudent repository design would either necessitate an allowance for this effect or a demonstration that the effect will not be important. One possible design feature that might prevent the effect, would be a metal container placed around the backfill.

Methods for permeability measurements

We have identified no pitfalls in making permeability or swelling measurements on backfill materials that are especially likely to cause serious errors, except possibly for the problems of measuring permeability of backfill that contains coarse chips of rock. I understand that using

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coarsely crushed basalt, BWIP personnel have had some problems with water leaking between the backfill and the container wall. That would cause erroneously high permeability measurements and is, therefore, not a serious concern for licensing. Dye injection tests can be used to identify such problems.

Leaks in equipment can cause positive or negative errors, depending on the location of the leak and the method of measurement. Although we have not had much of a problem with leaks and do not expect that other workers will either, I recommend that the applicant demonstrate some method for assessing the effect of leaks on permeability measurements.

We have demonstrated that competing reversible and irreversible effects change the permeability of backfill material at high flow rates. High flow rates can cause reduction in permeability because of movement of particles (Couture and Seitz, 1984). Therefore, we have suggested that extrapolations of permeability to realistically low flow rates be made with care (Couture and Seitz, 1984). We have also suggested reversal of flow as a useful diagnostic tool. With appropriate precautions, the effects we have observed using increased flow rates are demonstrably minor.

Conclusions

Wyoming bentonite will suffer severe loss of swelling capacity if it is exposed to high humidity at temperatures above 200°C. The loss of swelling capacity may be less severe at lower temperatures, although the time dependence of alteration is not well known. The bentonite will also lose an undetermined portion of its swelling capacity even if the backfill remains dry during the thermal period of repository. Loss of swelling

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capacity will increase the permeability of backfill mixtures and reduce the ability to swell into fractures in the rock. We have not been able to reverse the change, so it appears that the tested mixture will probably not be suitable for high-temperature use in a repository below the water table.

Bentonite-based backfill may be suitable for use in a repository if the bentonite comprises much more than 25% of a highly compacted mixture, if the maximum temperature is limited by low thermal loading to much less than 200°C, or if it is used at depths near to or above the water table. Since Wyoming bentonite is unlikely to retain its excellent swelling properties at high temperatures, the applicant may want to plan the use of a type of bentonite which does not swell as much, such as calcium-bentonite.

A realistic evaluation of backfill performance should include consideration of the effects of dry heat, alteration by vapor, alteration by liquid groundwater, gamma radiolysis of both liquid and gas phases, radiation damage to the backfill, concentration of dissolved salts by distillation, and a thermal gradient. Evaluation should include sequential testing. Important questions have been raised about all of these effects.

The physical properties of altered materials should be tested. There is evidence that the exchangeable cation composition of bentonite may change during hydrothermal alteration, and thereby degrade its physical properties.

It is important to say that I consider the needed research to be manageable.

BACKFILL IN A WATER-UNSATURATED TUFF REPOSITORY

The principal issue is whether a swelling backfill, a non-swelling backfill, such as cobbles of tuff, or no backfill should be used in a

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tuff repository. Regarding the use of tuff as a backfill material, I tentatively advocate its use in preference to no backfill, because of its ability to provide mechanical protection and improve drainage. However, with regard to swelling backfill materials such as bentonite, I believe some important potential benefits are being ignored and potential problems exaggerated.

Swelling backfill materials have been essentially rejected for use in a tuff repository, except as an alternate material for use with spent fuel. It has been rejected for several reasons, mainly the following.

1. It is thought to attract water to the waste package.
2. The waste package will be dry during the thermal period, without the use of backfill. Good drainage, the use of capillary barriers, and the temperature gradient may keep the waste package fairly dry indefinitely.
3. Bentonite is a heat-sensitive insulator, which may require low thermal loading.
4. Montmorillonite in tuff is believed to be unstable with respect to illite or mixed-layer clays, which have very much lower swelling capacity.
5. Backfill may lead to pitting or crevice corrosion of the canister and may cause degradation of waste glass.
6. Elimination of backfill is thought to simplify the scientific problems.

Many of these reasons are erroneous or misleading. My objections will be described in the following paragraphs.

No one has suggested that montmorillonite (the active component of bentonite) will be transformed to illite in a dry system. It is expected

that the repository will remain dry until the temperature drops below 100°C, probably well below 100°C. Below 100°C transformation is exceedingly slow (Heaver, 1979; Steindler et al., in press).

It is possible that dry heating, heating in the presence of moisture, or gamma irradiation may degrade bentonite somewhat over the thermal period of the repository, as I have mentioned previously. However, in any case, it seems to me that bentonite is quite promising for use after the mandatory retrieval period. After only 50 to 60 years heat production will be reduced by 75%. An excellent time to emplace backfill around the canisters might be just before moisture begins to appear in the repository, when near-field temperatures approach 100°C or lower. Proper use of backfill at this time would absolutely prevent flow of groundwater past the waste canisters.

It has been suggested that bentonite-based backfill will attract water to the waste canisters and, therefore, should not be used. If it is certain that the waste package will stay dry, without a swelling backfill, there is indeed no merit in using swelling backfill. However, even advocates of disposal in the unsaturated zone do not foresee dryness forever (Roseboom, 1983). It is difficult to imagine a drainage system so perfect as to prevent contact of groundwater with the canisters after cooling. It seems more probable to me that water will eventually drip or flow over the canisters. On the other hand, swelling backfill material would prevent flow of water over the canisters, even if the repository is eventually flooded. Thus, although bentonite would attract water just as a desiccant would, its purpose would be to prevent flow of liquid water past the container.

Since swollen montmorillonite forms a gel with a highly expanded crystal lattice, bentonite could be used to form a semi-permeable membrane, with

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near-zero porosity. This would minimize or effectively prevent contact with liquid water, and would form a very substantial diffusive barrier.

Backfill may in fact, increase the corrosion rate of the canisters by pitting or crevice corrosion. I assume that this is true of virtually anything in contact with the canister, including metal supports, host rock, or deposits of groundwater salts. The backfill should be designed to protect the waste package.

It is true that the use of swelling backfill may add to degree of complexity to the system. However, the complexity can be reduced considerably by limiting the peak temperature.

I would strongly advocate that bentonite-based backfill be considered for use in a tuff repository, especially after a period of retrievability and cooling.

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