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

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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/cm^3 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} m^2 (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 $8 \text{ cm}^3/\text{yr}$ per cm^2 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 (\leq seven days) to limited amounts of water or groundwater (water/clay

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

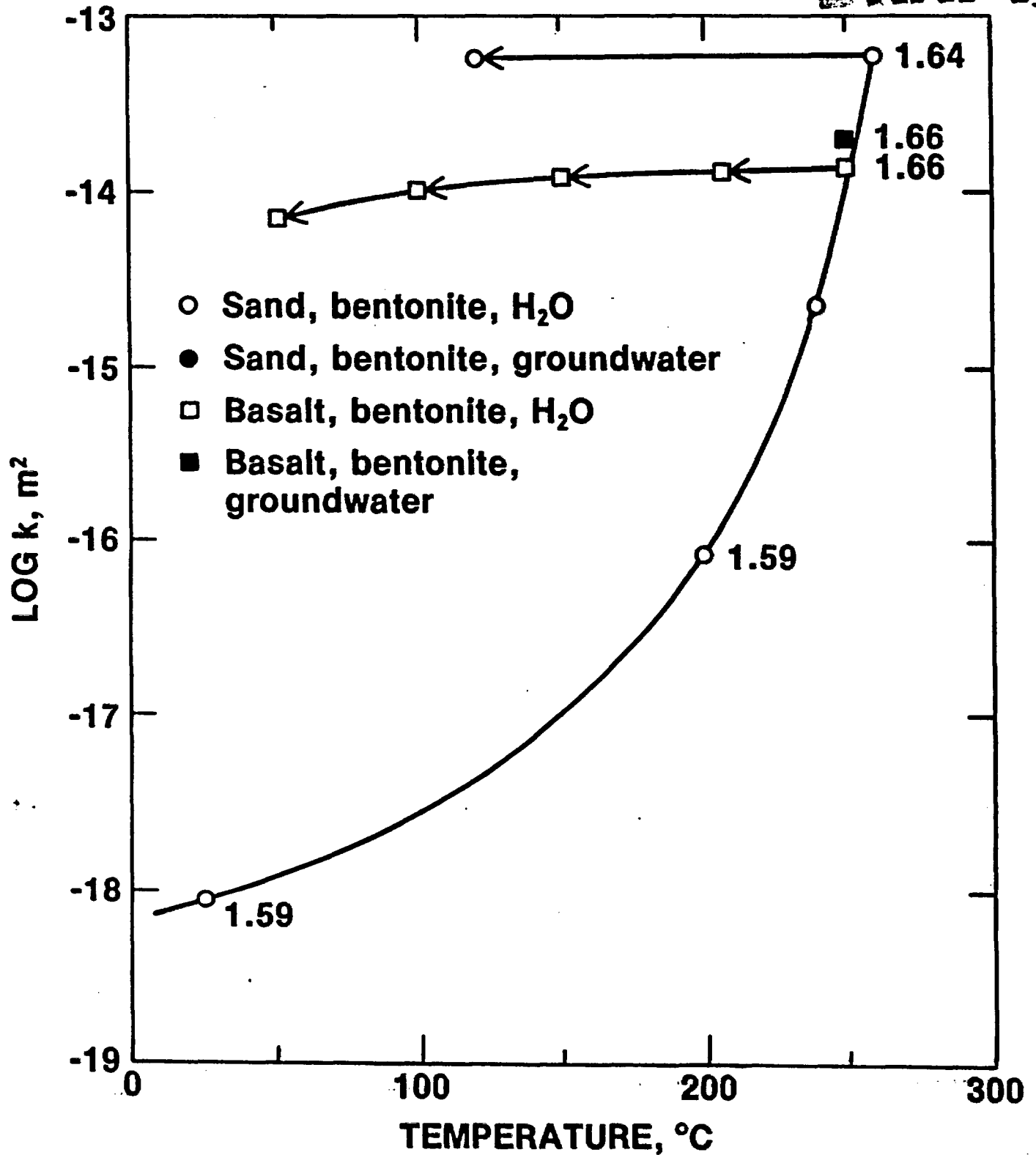


Fig. 1. Permeability of Backfill as a Function of Temperature, Plotted on a Logarithmic Scale. Arrows show reduction in temperature after saturation with liquid water. Numbers show dry bulk densities in g/cm³. Permeability is mainly a function of the temperature at which the column was saturated with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

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

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

DRAFT

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.

DRAFT

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.

DRAFTDistillation 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 (Weaver, 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

DRAFT

14

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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DRAFT

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16

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