

RAPID INCREASES IN PERMEABILITY AND POROSITY OF BENTONITE-SAND MIXTURES DUE TO ALTERATION BY WATER VAPOR

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ABSTRACT

Packed columns of canister packing material containing 25% bentonite and 75% quartz or basalt sand, were exposed to water vapor at temperatures up to 260°C. The permeabilities of the columns were subsequently measured after complete saturation with liquid water in a pressurized system. Exposure to water vapor caused irreversible increases in permeability by factors of up to 10^5 . After saturation with liquid water, the permeability was nearly independent of temperature. The increases in permeability were due to a large decrease in the ability of the bentonite to swell in water. Calculations suggest that swelling of bentonite altered at 250°C was not sufficient to fill the pore spaces. If the pore spaces are filled, the mixture will form an effective barrier against flow, diffusion, and transport of colloids.

The results suggest that if bentonite-based canister packing material is exposed even briefly to water vapor at high temperatures in a high-level nuclear waste repository, its performance will be seriously impaired. The problem is less severe if the proportion of bentonite is high and the material is highly compacted. Previous results show significant degradation of bentonite by water vapor at temperatures as low as 150°C. This suggests that in some repositories, backfill in tunnels and drifts may also be affected.

INTRODUCTION

Mixtures of bentonite and crushed host rock may be used for packing around waste canisters and for filling tunnels, shafts, and rooms in high-level nuclear waste repositories. For the planned repository in basalt, a packing material consisting of 25% bentonite, and 75% crushed basalt, loosely compacted, is planned for use around the waste canisters [1]. Depending on the design of the repository and the age and type of waste, the canister packing material may be exposed to temperatures as high as 250°C or 300°C [1].

At these temperatures bentonite is degraded by heat or by hydrothermal reactions with liquid or vapor. Exposure of bentonite to moisture for a few days at temperatures of 150°C or higher has been shown to produce rapid reduction of the ability to swell in water [2]. After treatment at 250°C, severalfold reductions in swelling capacity were observed [2]. Bentonite was also found to be extensively altered by reaction with basalt and liquid groundwater at 300°C [1]. The swelling properties of the products were not tested, but the resulting smectite minerals were presumed to retain their ability to swell [1]. However, because of the compositional changes, the altered material may not retain swelling ability comparable to that of unaltered bentonite. Decreased swelling ability of bentonite due to ion exchange after hydrothermal treatment at 360°C has been observed [3]. A slight decrease in swelling ability of bentonite heated dry at 100°C to 300°C has also been observed [3-5].

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The available data, as shown in Fig. 1, suggest that moisture in limited amounts is more effective than excess groundwater or dry heat at altering the properties of bentonite. Limited moisture acts relatively rapidly and at relatively low temperatures, as shown.

The swelling ability of the bentonite is closely related to the permeability of backfill mixtures; loss of swelling ability will lead to an increase in permeability. The effect of alteration on the permeability and swelling ability can be determined directly. This paper reports measurements of the permeability of fresh and altered backfill mixtures at temperatures from 25°C to 260°C. Many of the measurements are reported elsewhere in more detail [6, 7].

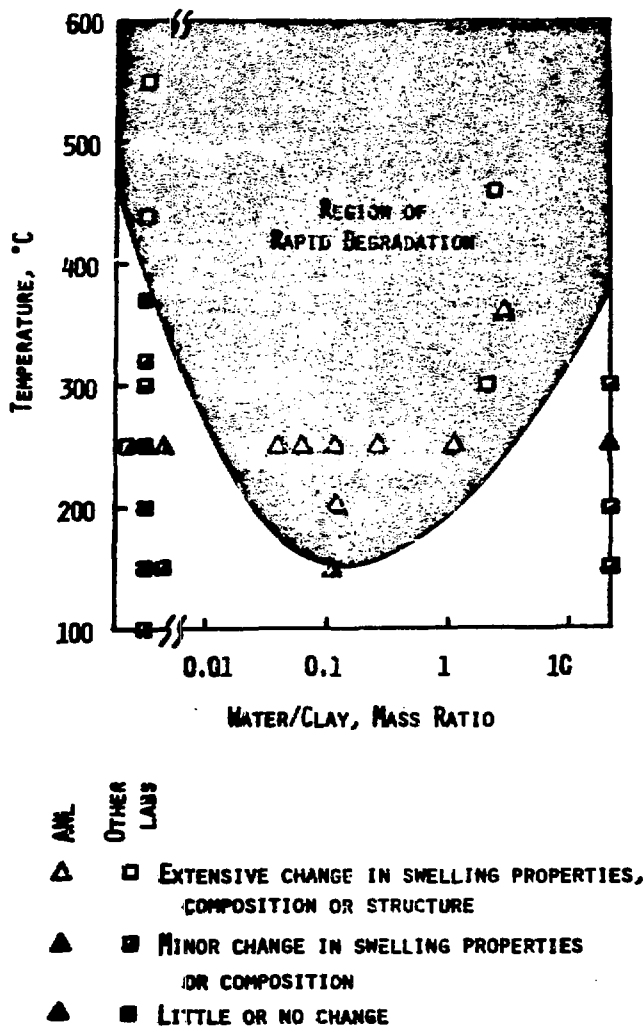


Fig. 1. Simplified Diagram Showing Hydrothermal Degradation of Bentonite as a Function of Temperature and Water/Clay Ratio. Points above the line show extensive changes in swelling properties, composition, or structure. Experiments at Argonne (triangles) show extreme loss of swelling ability in as little as seven days at intermediate water/clay ratios. Duration of experiments at other laboratories was two months to one year. References [1, 2, and 3].

METHODS

Figure 2 shows a simplified schematic of the equipment used for permeability measurements. Fresh backfill material was packed into stainless steel tubes with sintered frits of Hastelloy C ($2\ \mu\text{m}$ nominal pore size) at the ends. The columns are brought to the temperature of the test. Then water or groundwater was introduced very slowly, over periods of days, until the columns were saturated with liquid and were brought to the intended pressure. Sufficient pressure was maintained by a back-pressure regulator valve to prevent boiling. Previous experiments [2] have shown that the swelling ability of the bentonite is altered during the slow introduction of water.

The columns were then ready for permeability measurements. Water was pumped through the columns at controlled rates or controlled pressure differences, and the pressure differences across the columns were measured with a differential pressure transducer. By measuring the flow rates at both the inlet and the outlet, it was verified that there were no significant leaks.

Once the columns were filled with water, flow was brief and intermittent; and the flow rates were restricted to the minimum necessary for good measurements. It has been found that at low or zero flow rates the permeability does not vary significantly with time over the period of tests, but at high flow rates the permeability decreases with time, probably because of movement of particles within the columns [6, 7]. Such a decrease in permeability is easily detected as a time-dependent deviation from Darcy's law, and by a decrease in permeability when the direction of flow is reversed. (The equipment incorporates a valve, not shown, for reversing the direction of flow.) The measurements presented here were made at low flow rates, at which Darcy's law was found to hold.

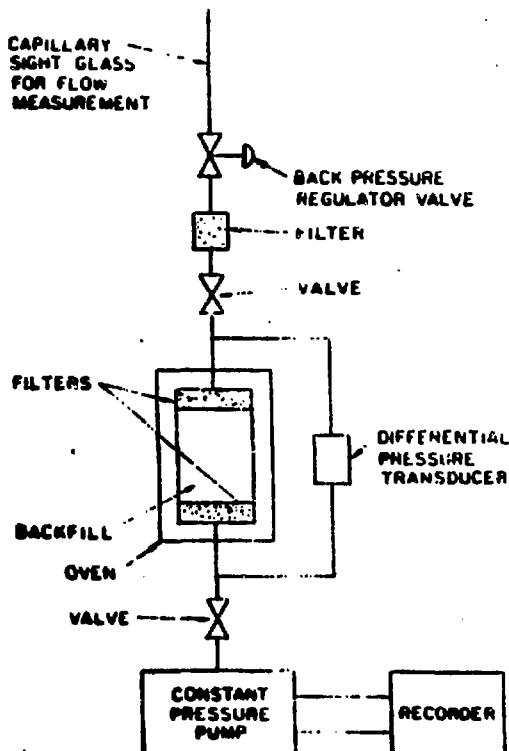


Fig. 2. Equipment Used for Permeability Measurements of Backfill Materials

The bentonite used was Envirogel, a commercial Wyoming bentonite supplied by Wyo-Ben, Inc. Except for drying, crushing and sieving by the supplier, the bentonite was not pretreated. In all experiments, 25% bentonite by weight was mixed with 75% quartz sand (180-840 μm diameter) or crushed basalt (46-850 μm). The mixtures were lightly compacted by tapping into the tubes, to a density of 1.6 g/cm^3 in most cases.

RESULTS

The results are highly reproducible. At low flow rates, Darcy's law is obeyed, as shown in Fig. 3.

Unaltered backfill mixtures have very low permeabilities. Values of $9 \times 10^{-19} \text{ m}^2$ at 25°C and $1.1 \times 10^{-18} \text{ m}^2$ at 150°C were determined, for mixtures compacted to dry bulk densities of 1.59 and 1.60 g/cm^3 , respectively. In another test, the material was saturated quickly with water at 200°C, and the permeability was measured at successively higher temperatures, up to 250°C. A pressure of 5.1 MPa prevented boiling. The permeability was $4.0 \times 10^{-18} \text{ m}^2$ at 200°C and $5.2 \times 10^{-18} \text{ m}^2$ at 250°C (dry bulk density = 1.65 g/cm^3). Reversing the flow did not change the observed permeabilities.

Altered materials have much higher permeabilities. Figure 4 shows the permeability of altered materials as a function of temperature. Alteration by water vapor introduced during saturation with liquid causes increases in permeability by factors of up to 10^5 . After saturation with liquid, the permeability was nearly independent of temperature. (Theoretically, permeability does not change because of change in viscosity with temperature.) Thus, alteration by water vapor is irreversible within the time scale of the experiments.

The effect of compaction on permeability was also determined on two columns altered at 250°C. A quartz-bentonite column had a dry bulk density of 1.93 g/cm^3 and a permeability of $1.9 \times 10^{-15} \text{ m}^2$ at 250°C. A basalt-bentonite column had a dry bulk density of 2.12 g/cm^3 and a

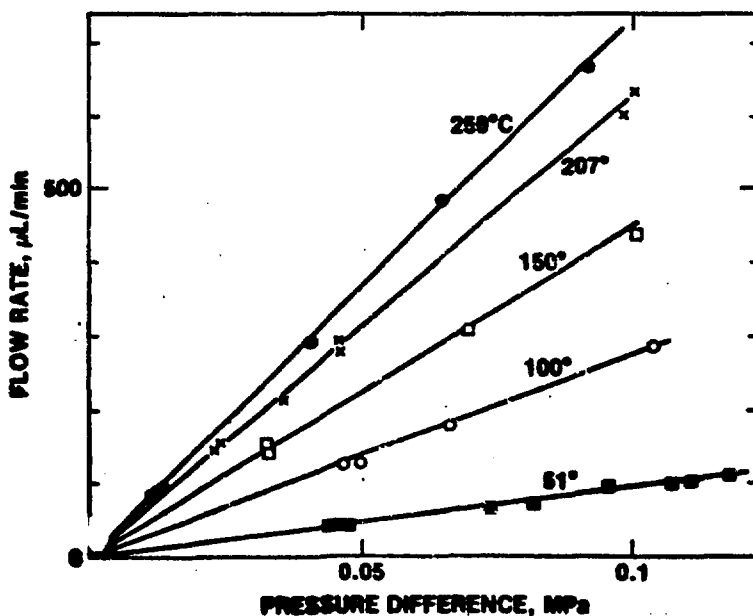


Fig. 3. Permeability Measurements in Water at Descending Temperatures. Bentonite + basalt. Column length 6.74 cm, diameter 1.00 cm, dry bulk density 1.66 g/cm^3 .

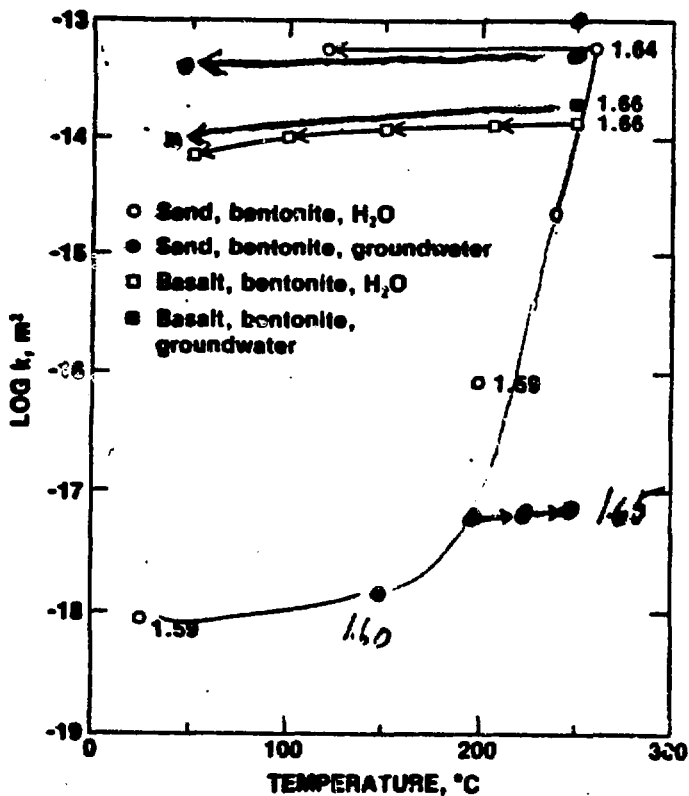


Fig. 4. Log Permeability (k) of Basalt-Bentonite Backfill Mixtures as a Function of Alteration Temperature. Arrows show measurements at different temperatures after alteration. Permeability increases with increasing alteration temperature but is nearly independent of temperature of measurement. Numbers show dry bulk densities in g/cm^3 .

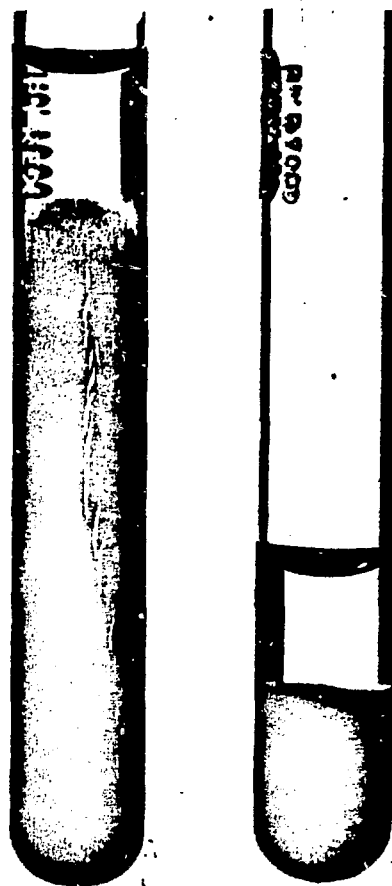


Fig. 5. Expansion of Equal Amounts of Fresh and Altered Sand-Bentonite Mixtures in Water. Left: unaltered. Right: after alteration at 260°C . The materials have been mixed with water and allowed to settle.

permeability of $1.2 \times 10^{-16} \text{ m}^2$ at 250°C . These permeabilities are intermediate between those of less compacted, altered materials and of unaltered materials.

The increase in permeability of altered materials was found to be due to a decrease in the ability of the clay to swell in liquid water. The unaltered clay forms a sticky, gummy paste when mixed with water, but the altered clay is not cohesive. Figure 5 shows the difference in the ability of the altered and unaltered materials to swell in water. These results agree with previous observations on reduced swelling capacity of bentonite altered by steam [2]. The difference in swelling capacity is also observable by x-ray diffraction. By absorbing water in hydration layers, the lattice of unaltered montmorillonite expands from a basal spacing of 10 Å in the dry state to over 100 Å in liquid water [6, 8], while after alteration at 250°C , the basal spacing expands to no more than 19 Å.

After the permeability tests, the columns were examined carefully for defects that might have caused artifacts of measurement. None was found. In two columns a volume of fluorescent dye solution equal to the pore space of the column was injected into the columns. A breakthrough volume equal to the pore space indicated essentially uniform flow velocity (plug flow). Dissection of the dyed columns showed no evidence of selective

flow through cracks or between the backfill and the walls. No clogging of filter frits was ever observed, and reversal of flow generally did not change the observed permeability significantly. Therefore, I consider the measurements to be very reliable and representative of the condition of the backfill.

DISCUSSION

The effect of swelling of bentonite on permeability and swelling behavior of backfill can be estimated qualitatively. The unaltered mixtures are impermeable and exert a swelling pressure because the clay expands to fill the pores completely. The porosity of the backfill should, therefore, be a good index for estimating permeability. If the porosity is low enough so the clay can expand to fill the pores, then the mixture will be impermeable. The grain size distribution of the silt and sand fractions is expected to have much less effect on permeability and swelling, because any mixture of sand and silt will be quite permeable, and because only clay particles can completely fill the pores spaces and are fine enough to effectively block the flow of water.

The porosity of altered dry and wet backfill mixtures can be approximated from the densities of the materials if it is assumed that the basal spacing of the altered montmorillonite expands in water to 19 Å, as observed for bentonite altered at 250°C.

The estimated porosities for various altered backfill mixtures are shown in Table I as functions of dry bulk density and bentonite content. It is apparent that zero porosity is attained only for highly compacted mixtures with high proportions of bentonite.

Table I. Estimated Porosities of Dry and Wet Altered Bentonite-Basalt Mixtures^a

Bentonite Concentration (%)	Dry Bulk Density (g/cm ³)	Porosity (%) ^b	
		Dry	Wet
25	1.6	42	33
25	1.8	35	25
25	2.0	27	17
25	2.2	20	8
45	1.6	40	24
45	1.8	33	15
45	2.0	25	6
45	2.2	18	0

^aAssuming bentonite containing 100% montmorillonite, with a basal spacing of 12.4 Å when dried in air, 19 Å when wet.

^bAssumed densities: 2.47 g/cm³ for air-dried bentonite containing pure montmorillonite expanded to a basal spacing of 12.0 Å, based on 2.80 g/cm³, 10.1 Å for pyrophyllite, apparent density of water of hydration = 1 g/cm³; 2.87 g/cm³ for basalt. Bentonite containing 80% montmorillonite, 20% quartz would give porosities in wet mixtures up to 4% higher than shown.

This model seems to be in accord with data on porosity, swelling behavior, and permeability. The porosity was estimated as 23% and 26% for two dry, compacted mixtures (with dry bulk densities of 2.12 and 1.93 g/cm³, respectively). The measured porosities, as determined by water uptake, agree with these estimates to within 1 volume %. After alteration of one mixture (with a dry bulk density of 2.12 g/cm³), one end of the column was opened and immersed in water for two weeks at room temperature, but showed no evidence of swelling. This is expected from the model, since about 12% porosity is estimated for the wet column. Finally, the two columns had estimated wet porosities of 12% and 15%; accordingly, they had permeabilities two to three orders of magnitude higher than those of unaltered backfill.

Although some porosity may be allowable in the design of backfill or packing material, it is suggested that, for several reasons, the most effective mixtures would have zero porosity when wet. First, permeability is directly related to porosity, as shown above. Second, diffusive fluxes through the material will be minimized by low porosity [9]. If water flows around the material but not through it, diffusion will be the most important mode of transport from the repository. Finally, backfill or packing material with zero porosity will form an effective barrier against transport of colloids.

The results strongly indicate that if bentonite is exposed to moisture in a repository at temperatures of 250°C or above, it will probably lose a considerable fraction of its swelling ability; for backfill mixtures containing 25% bentonite or less, the permeability will be quite high. To the extent that degradation of swelling ability may have been incomplete in the experiments, the permeability in a repository could be even higher than in these experiments. Since reduction of swelling capacity has been observed at 150°C [2], it is also possible that, in time, increases in permeability may occur as a result of alteration at temperatures of 150°C or even lower. Consequently, in some repositories, degradation of bentonite-based backfill in tunnels and drifts by alteration with heated vapor cannot be ruled out.

In the long run, a possible decrease in volume due to mineralogical transformation of the clay and an increase in volume due to alteration of basalt will probably change the permeability further. Ion exchange with flowing groundwater will also have an effect on the properties of the clay. The net effect is difficult to predict from available data.

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