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Some Characteristics of Potential Backfill Materials

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ABSTRACT

A backfill material is one of the multiple barriers that may be involved in the disposal of nuclear waste. Such backfill should be a desiccant with the hydrous product having acceptable stability; it should sorb any released radioisotopes, and it should reseal any breached site. The backfill must also have acceptable thermal conductivity.

This report presents data on the rate of hydration and the nature of the product of reaction of some candidate backfill materials with water and with brine. Thermal conductivity data is reported for both the reactants and the products.

Granular MgO at 150C completely hydrates in less than 10 hours. At 60C and 20C, such extensive hydration requires about 100 and 1000 hours, respectively. The product of the reaction is stable to more than 300C.

A doped dicalcium silicate was less reactive and the product contains less water of crystallization than the MgO. The reaction product of dicalcium silicate is cementous, but it has low thermal stability.

Bentonite readily reacts with water and expands. The hydrous product has very low thermal stability with the water lost continuously in the range of 20 to 105C. Thus, this low-temperature desiccant becomes a water source with even a slight increase in temperature. Bentonite reacts with an NBT-6a type brine. The reaction product has the properties of vermiculite, which indicates that magnesium ions have diffused into the bentonite structure and are not simply adsorbed on the surface. If bentonite is emplaced in a saline environment, the properties of vermiculite, the reaction product, should also be considered.

The thermal conductivity of MgO, dicalcium silicate, and bentonite is primarily dependent on the porosity of the sample. With a range of porosity of 36 to 56 percent, thermal conductivity values of 0.22 to 1.02×10^{-3} cal/cm. sec ° were determined. Thermal conductivity values increased with increased hydration of the samples. The samples were jacketed for the determinations. A slight increase in thermal conductivity was found with increased temperature, in contrast to most rocks. This may result from the jacketed samples getting a better grain-to-grain contact with increased temperature.

If the conductive data for the different materials is equated to the same porosity, MgO has the superior thermal conductivity compared to bentonite or dicalcium silicate. Porosity is an extrinsic variable controlled by grain size and installation techniques. In practice, the thermal conductivity can be improved by installing anhydrous material which then is subjected to a partial or complete in situ hydration. Since the hydrous product has a larger volume, such controlled hydration would reduce the porosity.

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1.0 INTRODUCTION

The disposal of nuclear waste in a geologic setting involves the multiple barrier concept. A backfill material around the waste canisters may be one of the barriers. Ideally, the backfill material should serve as a long-term desiccant for the system and have appropriate thermal conductivity. If a catastrophic or accidental breaching of the system should occur, the ideal backfill should restore the integrity of the system, seal openings, and sorb and confine the contaminants.

Earlier research was aimed at screening candidate materials for potential use as backfill for radioactive waste stored in salt beds. A number of materials were identified, and subsequent experiments showed them to be suitable and effective for such a role in a salt environment.

The chemical variants of dicalcium silicate were also studied to determine their suitability as backfill materials. Dicalcium silicate is a principal constituent of portland cement. It is known to hydrate to a compound with an enormous surface area, tobermorite, and yet have a set strength that would reestablish the integrity of a breached system. This "cementing" material was doped with CaNaPO_4 to stabilize some desirable phases and introduce phosphate into the system. CaNaPO_4 dissociates in water forming apatite and a basic solution. Apatite is the mineral of teeth, bone, and phosphorite deposits, and it is a scavenger used for filtering and ion exchange.

The sodium phosphate-bearing variant of dicalcium silicate hydrates to apatite and tobermorite. These hydration products have a large surface area, some desirable ion exchange properties, and a set strength. The research was directed at establishing the phase relations of the binary

system $\text{CaNaPO}_4\text{-Ca}_2\text{SiO}_4$ at high temperatures. From these relations the best compositions were selected for hydration studies. These hydration studies were at 20C and one atmosphere. The stability of the hydration product was established by differential thermal analysis and thermogravimetric analysis. Some feasibility experiments bearing on the hydration were conducted at elevated temperature and pressure.

Bentonite has received considerable attention as a backfill material. It readily sorbs water and cations, and it expands with hydration. Bentonite was not considered an ideal backfill material in this study because with heating, to even less than 100C, some interlayer water is lost with partial collapse of the expanded form. With this release of the interlayer water, the fate of sorbed ions is unknown. Other problems with bentonite powder are its low density, its difficulty in packing, and its plasticity, especially when wet. For salt repositories, the behavior of bentonite in a brine is a concern. For example, some brines have a high percentage of calcium and magnesium ions that may exchange with the sodium in bentonite, yielding a calcium or magnesium-bearing bentonite. Unfortunately, the calcium bentonites lack the high expansion and sorptive capacity of the sodium bentonites. In addition, bentonites, with their extremely large surface area, may recrystallize to a more stable compound with reduced surface area. Brines are known to be potent mineralizers.

2.0 SCOPE

This report presents further research results on MgO and chemical variants of Ca_2SiO_4 . Both of these compounds have an equant form and density of 3.6 to 3.3. If these materials are screened so that grains are of one size, the resulting material will have a calculated porosity from 27 to 40 percent, depending on the packing pattern as close pack or random. With such porosity, the bulk density ranges from 2.1 to 2.6, or roughly that of salt. Ideally, poorly sized material could yield a higher bulk density, if that is desired. In this study it was found that the materials could not be packed to this ideal porosity. An advantage of equant material is that with sizing, there is some control over the porosity and therefore the bulk density. This permits modeling the backfill to be most appropriate for the geological condition and the expansion accompanying the hydration reaction. MgO and Ca_2SiO_4 are hard materials, but with a reduction in grain size, the rate of hydration increases and the possibility of damage by abrasion would be decreased.

The kinetics of the hydration reactions of MgO and variants of Ca_2SiO_4 were established by timed experiments at room temperature, 60C, and 150C. Several carefully sized fractions of the different materials were used so that the results can be related to surface area. The reaction products were established by X-ray diffraction and the extent of the reaction was determined by TGA and DTA, which showed the water loss with heating.

Another phase of the study involves the measurement of the thermal conductivity of the backfill material. Since the canistered waste is a heat source, the backfill material should have sufficient thermal conductivity to prevent excessive buildup of heat. The thermal conductivity will be a

function of the properties of the crystals, grain size, and especially packing. However, because the backfill material is a powder and there is significant porosity, it is certain that the backfill material will have poorer thermal conductivity than the surrounding rock. MgO and the variants of dicalcium silicate have a high density, crush with an equant habit and therefore pack easily, and consequently should have better thermal conductivity than bentonite, fine-grained MgO, zeolites, and other materials that have been proposed for backfill. Part of this research was to measure the thermal conductivity of MgO, bentonite, and the variants of dicalcium silicate using different packings and grain sizes. Hydrated samples were also used for the thermal conductivity measurements.

3.0 HYDRATION STUDIES

3.1 Hydration of MgO

3.1.1 Background

Periclase, MgO, or magnesia is a high capacity desiccating material that hydrates to $\text{Mg}(\text{OH})_2$, a compound called brucite. The hydrate contains about 31 percent water, and it is stable to over 300C. In an earlier study (Simpson, 1980) it was shown that MgO hydrates under a very low vapor pressure of water. For example, at 25C, MgO will hydrate under 0.027 atmospheres of water vapor pressure. At 60C with very finely divided reagent grade MgO, Simpson (1980) found that under 0.1 atmospheres of water vapor pressure the hydration of MgO proceeded rapidly for 6 days. After 10 days, the hydration reaction ceased although the sample contained much unreacted material. Apparently the reaction product $\text{Mg}(\text{OH})_2$ armors a residual core of MgO, and this armoring sharply reduces the rate of hydration. This indicates

that the grain size of the MgO is extremely important in regard to the kinetics and the extent of the reaction.

A decrease in the grain size of MgO results in an increase in the rate and extent of hydration. Reagent grade MgO is a finely divided powder, and therefore highly reactive with water, but it is also an insulating material. Some MgO is coarse grained or pelletized. Clearly, the grain size affects the rate and extent of hydration and the thermal conductivity. A high rate of hydration is desired; yet the thermal conductivity must be acceptable.

3.1.2 Procedure

Some pelletized, commercially available magnesia was found to be coarse grained. This material was crushed in a plate mill and mechanically sized using stainless steel sieves, with the mesh based on the ASTM scale. The different size fractions were quickly washed in water, rinsed with ethyl alcohol, and dried.

Samples from each size fraction were exposed to water or water vapor for the desired time and temperature under one atmosphere total pressure. Samples at 150C were sealed in Teflon reaction vessels with water; consequently, the pressure for the reaction is very nearly the vapor pressure of water at 150C. This vapor pressure is about 4.7 atmospheres.

After the desired period of hydration, the partially hydrated material was dried at 150C to remove interstitial water, the dried sample weighed, reheated to 630C to liberate all water of crystallization, and then reweighed. This establishes sample weight and the water of crystallization from which the percentage of hydration is calculated.

3.1.3 Results

The extent of hydration of MgO as a function of grain size is shown in Figure 1. Also shown is the ideal water content of fully hydrated MgO, which is $\text{Mg}(\text{OH})_2$ and contains 31 percent water.

At 150°C under a water vapor pressure of about 4.7 atmospheres, MgO completely hydrates in approximately 10 hours. The hydration of the finest grained sample, less than 62.5 and greater than 31 μm , was complete in less than two hours.

At 60C, the finest grained sample completely hydrated in 100 hours, but the reaction for the coarsest material was only 20 percent complete. At 20C, all size fractions required more than 1000 hours for extensive hydration.

In summary, a decrease in temperature of reaction from 150 to 60 requires about a 10-fold increase in time for the same degree of hydration. Similarly, a decrease from 60 to 20C requires about a 10-fold increase in time for the same degree of hydration. The effect of grain size, and therefore surface area, on rate of hydration is most pronounced at 60C.

Surface area was calculated for the sized fractions used for the hydration experiments. For this calculation, the fragments were considered spherical, with the diameter of the sphere taken as the mesh opening of the screen on which the sample was retained during sizing. A plot of the calculated surface area versus water of crystallization under a given time and temperature is shown in Figure 2. A fully hydrated product contains 31 percent water of crystallization. For example, a sample with uniform particles with a surface area of $2 \times 10^4 \text{ mm}^2/\text{gram}$ would have about 20 percent water of crystallization after 200 hours at 60C. Since a fully hydrated sample contains 31 percent water of crystallization, the sample containing 20

Figure 1. Hydration of MgO as a function of grain size.

Note: Completely hydrated MgO contains 31% water, as indicated by the arrow on the abscissa.

Figure 2. Hydration of MgO as a function of surface area for different times (H = hours) and temperatures ($^{\circ}\text{C}$).

percent water of crystallization indicates that 65 percent of the hydration reaction is completed. With the same temperature and time a sample with a surface area of $6 \times 10^3 \text{ mm}^2/\text{gram}$ would be 50 percent hydrated, and a sample with a surface area of $6 \times 10^4 \text{ mm}^2/\text{gram}$ would be completely hydrated under the same conditions. Given a surface area of $2 \times 10^4 \text{ mm}^2/\text{gram}$, Figure 2 shows that approximately the same degree of hydration is achieved in 1600 hours at 20C, 100 hours at 60C, or 6 hours at 150C. This degree of hydration is about 40 percent of a fully hydrated material. With interpolation, this diagram can be used to estimate the rate of hydration of MgO as a function of surface area, time, and temperature.

3.2 Hydration of Variants of Ca_2SiO_4

3.2.1 Background

Dicalcium silicate (Ca_2SiO_4) is a major phase in portland cement. This compound has many polymorphs, but it is the high-temperature polymorphs which hydrate to tobermorite, that is the cement bonding material. The high temperature compounds are unstable thermodynamically, and they invert over a long period to a low temperature polymorph that has poor cementing properties. If the high temperature polymorphs can be preserved, dicalcium silicate has potential as a backfill desiccant, because with hydration the structural integrity of the system is reestablished. Earlier research demonstrated that several of the high-temperature polymorphs of Ca_2SiO_4 could be stabilized by doping the compound with CaNaPO_4 . These stabilized compounds are the β and α' forms of Ca_2SiO_4 doped with 10 mole percent CaNaPO_4 . Compounds doped with 5 percent CaNaPO_4 lacked long-term stability, and they invert to a form called γ .

The stabilized, high-temperature forms of Ca_2SiO_4 can be preserved; however, the effect of this stabilization on the rate of hydration was unknown. For this reason, hydration experiments were conducted on stabilized high-temperature forms of Ca_2SiO_4 and for comparison on material which had partly inverted to the low temperature γ forms.

3.2.2 Procedure

A high-temperature form of dicalcium silicate was synthesized from a mixture of CaCO_3 , SiO_2 , and NaH_2PO_4 heated to 1380C for 48 hours. The product had a composition of $\text{Ca}_2\text{SiO}_4)_{90} \text{CaNaPO}_4)_{10}$ and it consisted of the high temperature phases. In a similar manner, a product with the composition $\text{Ca}_2\text{SiO}_4)_{95} \text{CaNaPO}_4)_{5}$ was formed, but this product inverted on cooling to give the low-temperature, γ , form. These materials were crushed and sized. Sized fractions were used in the hydration experiments, but microscopic examination showed that all fractions, except the finest, contained aggregates instead of single crystal fragments. As a result, the surface area of the different size fractions cannot be accurately calculated.

The microscopic examination of the size fractions of the low temperature, γ , form of the doped dicalcium silicate showed that the synthesized material was heterogeneous. The inversion to γ involves a large volume change that causes the synthesized product to crumble. However, only about 28 percent of the material inverted to the low temperature, γ , form, and the other 72 percent of the material remained the typical high temperature forms. Attempts to separate a pure γ form of Ca_2SiO_4 using heavy liquids and different sieve sizes were unsuccessful. Consequently, hydration experiments involving the γ form are on heterogeneous material of which 28

percent is γ , and the balance is the high-temperature form similar to the high-temperature products with the composition $\text{Ca}_2\text{SiO}_4)_{90} \text{CaNaPO}_4)_{10}$.

Both the γ bearing material and the synthesized material lacking the form were reacted in water at 20, 60, and 150C in a manner similar to the MgO. After reaction, the products were X-rayed and the water of crystallization expelled by heating. Differential thermal analysis was completed on some products.

3.2.3 Results

Stabilized high-temperature dicalcium silicate was maintained under water for periods to 1300 hours at 20C. After drying at 150C to eliminate surface water, no additional water was expelled by heating to 630C, a temperature above the stability temperature of any hydrous product for this system. Thus no hydrous compound was formed in detectable amounts that had thermal stability above 150C, the temperature at which the products were dried after the attempted hydration.

At 60C the stabilized dicalcium silicate reacted partially to yield hydrous compounds, as shown by a 1 to 2 percent water loss with heating from 150 to 630C (Figure 3). An X-ray shows that the compound is hillebrandite $[\text{Ca}_2\text{SiO}_3(\text{OH})_2]$, but it has poor crystallinity. Hillebrandite contains about 10 percent water, indicating that after 550 hours at 60C only 10 to 20 percent of the stabilized dicalcium silicate had hydrated. Particle size has a significant effect on the reaction rate even though the coarser sizes were aggregates of crystals. Material in the size range of 62.5 to 88 μm is about twice as reactive as material in the size range of 125 to 177 μm or 250 to 350 μm .

Figure 3. Hydration of doped Ca_2SiO_4 as a function of grain size.

Note: Hillebrandite, the hydrous product, ideally contains about 10% water of crystallization.

At 150C, under a total pressure of 4.7 atmospheres, dicalcium silicate was extensively hydrated in 70 hours to hillebrandite. After 550 hours, the material contained 6 to 9 percent water depending on the grain size of the starting material. In comparison, hillebrandite, the product ideally contains about 10 percent water (Figure 3).

The γ bearing fraction of dicalcium silicate was reacted at 20 and 150C. The γ phase is the less reactive low temperature phase. The sample contained 28 percent γ and the balance appeared to be the usual high temperature phases.

At 20C the γ bearing material failed to hydrate in 1300 hours, and at 150C for 1300 hours only 2 percent water of crystallization was contained in the product. Thus, the γ bearing material is only 20 to 30 percent as reactive as the stabilized high temperature dicalcium silicate. Consequently, to maintain the most reactive dicalcium silicate, the inversion to the γ form must be prevented. This can be accomplished by the substitution of 10 mole percent CaNaPO_4 in the high temperature dicalcium silicate structure.

In comparison, the extent and rate of hydration and the stability of the hydrates of dicalcium silicate are inferior to that of MgO . The hydrates of dicalcium silicate have a cementous nature, whereas the hydrates of MgO form a noncoherent mass.

3.3 Hydration of Bentonite

3.3.1 Background

Bentonite is a finely divided clay that has attracted considerable attention as a backfill material. Bentonite is considered an expandable clay because it expands in the course of reacting with water. It has a high ion exchange capacity. Bentonite is the clay name for the mineral group called montmorillonite.

Montmorillonite, from the western United States, commonly contains an alkali between layers of the structure, and such montmorillonite expands when wet and forms a paste-like mass. Montmorillonite from the eastern United States, or when associated with calcium or magnesium carbonate rocks, commonly contains an alkaline earth between the layers; this montmorillonite fails to show the extensive expansion, suggesting that bentonite used as backfill could undergo ion exchange and lose some of its desired properties in regard to radioisotope sorption and hydration.

Bentonite has a low thermal stability, and with heating will release sorbed and water of crystallization. Thus, bentonite may serve as a low temperature sorbent for water and radioisotopes and expand. However, with heating to less than 150C in an open system, hydrated-expanded bentonite will release the water and may release the radioisotopes. In a closed system, the hydrated bentonite will retain water to a higher temperature. Consequently, bentonite, which is a low temperature sink, becomes a moderate temperature source. Because of this nature the hydration and properties of bentonite were determined for comparison to the reaction of the mineral in brine.

3.3.2 Procedure

Commercially available bentonite from Osage, Wyoming was used for all experiments. The material is a finely divided powder. The stock material was X-rayed to determine the interlayer spacing before and after heat treatment. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were completed to determine the temperature at which there is weight loss or energy changes.

Stock bentonite was reacted with water at 20, 60, and 150C and the product determined with X-ray diffraction.

3.3.3 Results

Stock bentonite was slowly heated in a thermogravimetric apparatus. Weight loss began at 30C and was continuous to 105C with the total weight loss being nearly 10 percent. There was no further weight loss with heating to 330C. With DTA the first distinct endotherm starts at 105C; however, background drift beginning at 20C may represent the loss of sorbed water. A broad small endotherm starts at 680C. The X-ray diffraction results for this untreated stock bentonite are given in Table 1. A distinctive feature of this X-ray pattern is a strong basal reflection at $13.0\text{\AA}$. This basal reflection is subject to change with hydration or dehydration. After drying at 150C, the basal reflection is reduced to $10\text{\AA}$.

Stock bentonite was hydrated in water at 20C for 140 days and then X-rayed by using the moist sample slurried with alcohol on a slide. There are two basal reflections. One is at $20.8\text{\AA}$ and the other is at $15.3\text{\AA}$.

After 140 days at 60C in water, the reacted bentonite showed a basal reflection at $20.2\text{\AA}$ and another at $15.6\text{\AA}$. This indicates that the hydration involved substantial expansion of the bentonite.

TABLE 1
X-Ray Diffraction Data for Bentonite

Stock Bentonite		Bentonite Hydrated @						Bentonite Over NBT-6a Vapors @							
		20°C		60°C		150°C		20°C		60°C		20°C then dried @ 150°C		60°C then dried @ 150°C	
"d"	I	"d"	I	"d"	I	"d"	I	"d"	I	"d"	I	"d"	I	"d"	I
		20.8	22	20.2	21	17.8	26								
		15.3	100	15.6	39	13.5	48								
13.0	90							12.4	68	11.6	26	12.4	36	11.8	26
		10.3	5	9.8	13										
6.48	5	6.37	9												
				5.30	35										
4.48	78	4.50	3	4.50	12	4.52	57	4.49	75	4.49	81	4.49	80	4.48	95
				4.30	15	4.31	29	4.29	27	4.27	29	4.27	36	4.26	33
								4.18	20						
4.04	52	4.07	12	4.10	21	4.07	43	4.05	47	4.05	46	4.05	51	4.04	54
		3.37	21	3.37	59	3.37	100	3.35	100	3.35	100	3.77	84	3.76	5
		3.24	14	3.24	47	3.25	25					3.35	100	3.34	100
														3.27	14
3.19	45	3.19	18	3.20	59	3.17	32			3.16	43	3.17	70	3.15	54
		3.14	42	3.12	100			3.13	46	3.13	34	3.14	42		
						2.77	10	2.85	5	2.84	9				
2.57	60					2.58	23	2.57	29	2.57	34	2.57	36		
2.47	30							2.48	27	2.48	35	2.46	33		
2.03	22							2.03	80	2.03	44				

Bentonite under water at 150C, at a pressure of 4.7 atmospheres for 140 days, gave a new basal reflection at $17.7\text{\AA}$ and a basal reflection at $13.5\text{\AA}$. The $13.5\text{\AA}$ may correspond to the $13.0\text{\AA}$ of the untreated material. The complete X-ray diffraction data is shown in Table 1.

3.3.4 Hydration with Low Vapor Pressure

With increasing salt concentration, the water vapor pressure of a solution is decreased. For example a 6 molar NaCl solution lowers the vapor pressure of water by 23 percent. A brine as NBT-6a contains 10 percent MgCl_2 , 10 percent CaCl_2 , 5 percent NaCl, and 5 percent KCl and, as a result, the lowering of the vapor pressure is more pronounced than with NaCl. Using the data presented by Simpson (1980), the water vapor pressure of an NBT-6a type brine at 60C is about 0.1 atmospheres, and at 20C it is .011 atmospheres. In comparison, pure water has nearly twice the vapor pressure at these temperatures, namely 0.196 and 0.023 atmospheres, respectively.

Since bentonite reacts with water and expands, the possibility of desiccation under reduced vapor pressure must be considered. For this reason, samples of stock bentonite were exposed to the water vapor from the NBT-6a brine at 20C and 60C for 112 days. As shown in Table 1, stock bentonite has a basal spacing at $13.0\text{\AA}$, but long exposure to the lowered water vapor pressure at 20C reduced the basal spacing to $12.4\text{\AA}$. Exposure to the low vapor pressure at 60C reduced the basal spacing to $11.6\text{\AA}$. Brines are a desiccant. These experiments show that NBT-6a brine is a sufficiently strong desiccant to provide a vapor phase which will remove water from the stock bentonite, which appears as a dry powder, and partially collapse the structure as shown by the reduced basal spacing. This desiccation is caused by a drying vapor and is not the result of reaction of ions in the brine with

the mineral. Such contraction of the bentonite by the drying vapor results in increased porosity. As will be presented in a later section, heat flow decreases as the porosity increases.

4.0 REACTION OF BENTONITE WITH BRINE

4.1 Background

Bentonite readily undergoes ion exchange which causing a change in the basal spacing. For example, there are sodium bearing bentonites and calcium bearing bentonites, and these different compounds have desiccating properties and expansion in water. Ion exchange, as a surface-related process, occurs rapidly compared to diffusion of ions within a crystal. However, both the surface ions of a crystal and those within a crystal can be exchanged, and the exchange process is accelerated by increased temperature.

Bentonite, or the mineral montmorillonite, undergoes ion exchange with magnesium, calcium, and the alkali ions depending on the activity of these ions in a solution. It has been suggested that a magnesium exchanged montmorillonite with heat treatment may undergo a magnesium ion "place exchange" in that the magnesium ion migrates from the interlayer site to an octahedral site (Theng, 1974). Such a "place exchange" of sorbed ions will change the properties of the montmorillonite and if extensive, may lead to a new compound.

Montmorillonite lacks a unique composition; however, a typical formula given by Fleischer (1974) is shown in Table 2. For comparison, the formula for vermiculite is also given. The two groups of minerals are similar; the major difference is that the montmorillonites contain two ions in three octahedral sites, whereas the vermiculites contain three ions in the three

sites. Thus, a place exchange in an interlayer magnesium of montmorillonite yields an additional ion for an octahedral site, thereby making the compound a vermiculite. The distinction between montmorillonite and vermiculite can be difficult because one can grade into the other. The physical and chemical nature of the two groups is different, but the intermediate compositions may have intermediate properties. The distinction and identification of clays is further complicated by some compounds having mixed layers; namely, layers of one type of clay are interspersed with layers of a second type of clay.

Table 2

Representative Formulas of Montmorillonite and Vermiculite

<u>Name</u>	<u>Formula</u>
Montmorillonite	$(\text{NaCa})_{0.33}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
Vermiculite	$(\text{MgFeAl})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

Clays are commonly identified on the basis of a characteristic basal spacing as determined by X-ray diffraction. Some clays, of which montmorillonite is an excellent example, sorb organic molecules such as ethylene glycol. These organic molecules may change the basal spacing. For example, montmorillonite is expanded by the sorption of ethylene glycol, whereas vermiculite undergoes a lesser expansion. The behavior of clays in the presence of organic molecules aids in their identification. Differential thermal analysis (DTA), which records the temperature of endothermic and exothermic reactions, is also useful for identification. All of these

methods were used, but the basic problem remains the gradational nature between the montmorillonite and vermiculite groups.

4.2 Procedure

Stock bentonite was mixed with a synthetic brine, NBT-6a. This brine contains 30 percent salts of CaCl_2 , MgCl_2 , NaCl , and KCl . On a mole basis, the brine is slightly enriched in MgCl_2 and depleted in KCl relative to the CaCl_2 and NaCl_2 . The bentonite, 10 grams, and 10 ml. of brine, were sealed in plastic bottles and maintained at 20 and 60C for 100 days, then resealed and maintained for a total of 250 days. Similar samples were sealed in Teflon containers in a pressure vessel at 150 and 200C for 100 days and 50 days, respectively.

After reaction with the brine, part of the sample was mixed with alcohol and an X-ray diffraction slide prepared. The prepared mount air dried before X-raying. The remaining reacted material was air dried or dried over silica gel before DTA and other determinations were made.

Some reacted material was repeatedly washed in water to determine the reversibility of the reaction. This washed material was dried over silica gel.

The reacted material, after the initial X-rays were completed, was exposed to ethylene glycol vapors. The same X-ray mounts were reX-rayed to determine the effect of glycolation.

Thermogravimetric analysis and DTA runs were made with material air dried, or dried over silica gel, using a heating rate of 4-5C/minute.

4.3 Results

Stock bentonite reacted with NBT-6a type brine showed an expansion from 13.0 $\overset{\circ}{\text{\AA}}$, for the basal spacing of the untreated bentonite, to 15.2 $\overset{\circ}{\text{\AA}}$ for reacted material at 20C for 100 days. Reacted material at 60C and 150C over 100 days gave basal spacings of 14.7 and 13.8 $\overset{\circ}{\text{\AA}}$, respectively (Table 3). Thus, the reaction of bentonite with brine causes an increase in the basal spacing of the clay. However, this increase is diminished at increased temperatures of reaction.

After 250 days, bentonite reacted with brine at 20 and 60C gave basal spacings of 14.0 and 12.8 $\overset{\circ}{\text{\AA}}$, respectively (Table 3).

A single experiment was conducted at 200C for 50 days. The product had a basal spacing of 13.0 $\overset{\circ}{\text{\AA}}$.

Bentonite reacted with brine at 150C was heated in air to 150C. There was no change in the basal spacing after reaction compared to the reacted material heated in air. For comparison, untreated bentonite is dehydrated and the basal spacing reduced to 10 $\overset{\circ}{\text{\AA}}$ with heating to 150C. Thus, a reaction with the brine produces a compound with increased thermal stability.

To summarize, the brine reacts with bentonite to yield a clay with an increased basal spacing. The increase is diminished by increasing temperature from 20 to 200C. It is further diminished by increasing time from 100 to 250 days at 20 to 60C (Figure 4). Both the time and temperature effects indicate that the reaction is sluggish, and is therefore more than a surface process. Furthermore, the kinetics, temperature, and basal spacing effects suggest a reaction as the "place exchange" reaction where the

TABLE 3

X-Ray Diffraction Data of Bentonite and Reaction Products

Stock Bentonite		Unwashed After Reaction in NBT-6a Brine For 100 Days @								Unwashed After Reaction in NBT-6a Brine For 250 Days @			
		20°C		60°C		150°C		Reacted @ 150°C Dried @ 150°C		20°C		60°C	
"d"	I	"d"	I	"d"	I	"d"	I	"d"	I	"d"	I	"d"	I
13.0	90	15.2	3	14.7	26	13.8	6	13.8	35	14.0	20		
6.48	5											12.8	28
4.48	78	4.49	9	5.0	20	4.68	5	4.73	10				
				4.46	72	4.46	17	4.49	69	4.50	37	4.49	56
				4.25	30			4.26	27	4.28	15	4.26	24
4.04	52			4.03	45	4.04	12	4.04	42	4.07	20	4.05	30
								3.76	6				
		3.35	13	3.33	100	3.34	50	3.35	99	3.36	100	3.35	100
3.19	45			3.17	26					3.29	26		
		3.14	9	3.13	60	3.14	10	3.14	49	3.19	22	3.21	33
		2.82	26	3.04	26							2.99	81
2.57	60			2.92	25								
				2.81	65	2.82	100	2.83	90			2.82	31
				2.57	37			2.56	34	2.58	19	2.56	50
2.47	30			2.34	37			2.47	23	2.48	11		
				2.22	42			2.34	100				
								2.22	39			2.16	13
2.03	22	2.02	16	2.02	77			2.02	73

Figure 4. Basal spacing of bentonite and its reaction products at different temperatures.

Note: B = NBT-6a brine, VB = water vapor from NBT-6a brine, EG = treatment with ethylene glycol of product from NBT-6a brine reaction after 100 days.

interlayer alkaline ion migrates to a vacant octahedral site. This new compound has increased thermal stability.

After exposure to ethylene glycol, both the reacted and the unreacted clays have a basal spacing of $16.4\text{\AA}$.

DTA of clays principally show the temperature at which water is expelled. Stock bentonite shows the start of an endothermic reaction at about 115C and the maximum thermal effect at 160C. In contrast, bentonite reacted with brine at 20C shows two endotherms. The first begins at 180 with a maximum at 190C, and the second begins at 250 with a maximum at 270C. The condition of the reaction, nature of the sample, total weight loss, and graphic DTA data is given in Table 4. All reacted-unwashed bentonite has two distinct endotherms at higher temperatures than the single endotherm of the stock bentonite. The two endotherms are shifted to lower temperatures as the brine-bentonite reaction temperature is increased. Or, in view of the X-ray data, the two endothermic peaks are shifted to lower temperatures concomitantly with the decreased basal spacing of the reacted bentonite.

Bentonite reacted with brine at 150C and then repeatedly washed in water shows a single endotherm peaking at 190C. In contrast, untreated bentonite has an endotherm peak at 160C. This indicates that the reacted bentonite cannot be washed without modification of the product.

Since the reacted bentonites were unwashed, the possibility that one of the endotherms is from salts from the brine was investigated. Salts from the brine gave a large sharp endotherm at 180C and several small endotherms at lower temperatures. Mixtures of 10 and 20 percent salts with the stock bentonite still showed the 180C endotherm. The mixture of 20 percent salt and stock bentonite also showed a 260C endotherm, which is lacking in the

pure salt DTA pattern. The 260 endotherm of the 20 percent salt-bentonite mixture is probably the result of a salt-bentonite reaction during the DTA heating cycle. The distinctiveness and the peak positions of the salt DTA pattern preclude the possibility that either of the two endotherms of the reacted bentonite are the result of salt contamination. Thus, a characteristic feature of the reacted bentonite is the double endotherms between 160 and 280C. The precise position of the two endotherms depends on the nature of the reaction product, which is a function of the time and temperature of the reaction (Tables 3 and 4).

The scanning electron microscope was used to determine the morphology of the stock bentonite and the reacted material. As shown in Figure 5, there is no distinct morphological difference between the stock bentonite and the reacted material.

4.4 Summary

Bentonite used in the experiments reacted with the NBT-6a composition brine. The initial product of the reaction shows an increased basal spacing compared to unreacted bentonite, but with extended time, or increased temperature of reaction, the basal spacing approached $13\text{\AA}$, a value which fortuitously is the value of the unreacted material. The reaction product contains more water, yet it has increased thermal stability. Both unreacted and reacted bentonite expanded to yield a basal spacing of $16.4\text{\AA}$ when exposed to ethylene glycol. A characteristic feature of the reacted bentonite is two endothermic reactions with heating from 160 to 280C; whereas, unreacted bentonite has a single endotherm at a lower temperature. Finally, a distinct

Table 4. DTA and Weight Loss Data for Bentonite and its Reaction Products

Stock
Bentonite

After
Reaction

Figure 5. SEM of stock bentonite and bentonite reacted in NBT-6a brine at 150°C for 96 days. Scale bar is 10 μm .

morphological difference between the reacted and unreacted bentonite is lacking.

These findings indicate that the bentonite reacted with the brine. The initial reaction was probably an ion exchange and the long term reaction is a "place exchange" where the sorbed magnesium ion migrates to and occupies an octahedral site of the clay. With such site occupation by magnesium, the bentonite becomes a vermiculite. The data clearly indicates that the change is gradational and the ion exchange process involves the entire crystal framework and not just the surface. The DTA patterns of the reaction products are identical to published patterns for vermiculite. Typical vermiculite is not considered to expand to $16.4\text{\AA}$ when exposed to ethylene glycol; however, the reaction products, concluded to be vermiculite, did expand. This may indicate that the reaction was incomplete or the product is atypical because of other ion exchange.

5.0 THERMAL CONDUCTIVITY MEASUREMENTS

5.1 Background

Many of the materials which are reactive, desiccants, and sorbents have these properties because they tend to be finely divided and therefore have a large surface area. Finely divided material has a high porosity which imports thermal insulating properties. Thus, in selecting a material, the desiccant and sorbent properties must be considered with regard to the thermal conductivity. This selection should be further evaluated in view of thermal conductivity data obtained on backfill materials after they have reacted with water. Such reaction with water will change the porosity of the backfill and the thermal properties of the reaction products. Because of a

paucity of data, thermal conductivity was measured for several backfill candidate materials before and after hydration.

There are many types of apparatus for measuring thermal conductivity. One method involves a cylinder, packed with the sample, with a heating wire coaxial with the cylinder. The thermal gradient from the wire to the perimeter and the energy input is measured. From this the thermal conductivity is calculated. This method is known as the hot wire technique. A modification of this method is to heat the cylindrical sample container and sample until they are at a uniform temperature. Then the sample container is cooled and the thermal gradient measured with a thermocouple at the center of the sample and a second thermocouple at the container wall. With this arrangement, the sample is the heat source and the container the sink. Since energy input is unmeasured, the measurements lead to thermal diffusivity (α) instead of thermal conductivity (λ). The two results are related by considering the density and specific heat of the sample. Thermal diffusivity (α) = $\beta r^2 / 4 \Delta T$, which has dimensions of cm^2/sec .

β = cooling rate (deg/sec)

r = radius of the cylinder

ΔT = temperature difference between center of the
sample and the perimeter

4 = the volume/surface of a cylinder = $r/2$ which
with subsequent integration yield $1/4$

Thermal conductivity = $\frac{c}{\alpha \rho}$ where

α = thermal diffusivity (cm^2/sec)

ρ = density (gr/cm^3)

c = specific heat ($\text{cal}/\text{gr. deg}$)

The dimensions of the thermal conductivity are: $\text{cal}/\text{cm. sec. deg}$. In this study, the thermal diffusivity and density were measured. The specific heat is taken for the species of material constituting the sample. Differences between specific heats of the samples are small compared to differences in the other parameters.

Published thermal conductivity data for a given rock type generally show a decrease in the conductivity value with an increase in temperature at which the value is determined. A study by Woodside and Messmer (1961) gives the conductivity of six different sandstones under dry conditions and after saturation with water. These six sandstones have a range in porosity from 3 to 59 percent. A plot of the thermal conductivity of the sandstones as a function of porosity is shown in Figure 6. The data closely fits a straight line on a semi-log plot, meaning that the conductivity is an exponential function of the porosity. Specifically, porosity bears an e^{-x} relation with the conductivity. Kunii, et al (1960) published data for four different sandstones and Moiseyenko, et al (1972) give data for three other sandstones. Each set of data points approximately fits a straight line, but the lines have an increased negative slope. The differences are greatest for the rocks with low porosity (Figure 6). These studies indicate that porosity is the major factor controlling conductivity.

Figure 6. Thermal conductivity as a function of porosity of sandstones.

Note: Curve 1 and 2 from data by Woodside and Messmer (1961), 3 from Kunii, et al (1960), and 4 from Moiseyenko, et al (1972).

Specific heat or heat capacity is used in the relation between thermal conductivity and thermal diffusivity. The values used are from $H_{400^{\circ}\text{K}}$ to $H_{298^{\circ}\text{K}}$ as given by Robie and Waldbaum (1968). These values were converted to cal/gr. deg., and are the following:

MgO ——— 0.245 cal/gr. deg.

$\text{Mg}(\text{OH})_2$ - 0.324

Ca_2SiO_4 - 0.193

Data is unavailable for montmorillonite; however, the three layer silicates muscovite, phlogopite, and talc have specific heats of 0.212, 0.218, and 0.225, respectively. These values are similar to most silicate and oxide minerals. Consequently, a thermal conductivity of 0.22 was used for the montmorillonite.

5.2 Procedure

Sample cells were machined from a 316SS block. Each sample cavity was 5/8" diameter by 1-3/4" in length and was separated from an adjacent cavity by a 1/2" wall. Each block contained seven cavities. Each cavity was sealed with a thin Teflon gasket and covered with a 1/4" thick flat plate. Thus, each cavity is cylindrical in a block that is massive relative to the dimensions of the cylinder.

Coaxial in the cylinders is a small diameter sheathed thermocouple, with the tip of the thermocouple central in the cylinder. This thermocouple gives the temperature of the center of the sample in the cylinder. The temperature at the perimeter of the sample is also required; this is also the temperature

of the cylinder wall. Initially, a thermocouple was embedded in the stainless steel block close to the wall, but this was modified after the first feasibility experiments. Each sample block contained seven cylindrical sample wells. Each sample well contained a central thermocouple. Three alternate sample wells were filled with the same sample packed to the same density. Three unpacked sample wells were used with the central thermocouple to measure the cylinder wall temperature. Thermocouples from the three samples containing cells were connected in parallel, and the three thermocouples from the empty cells were connected in parallel. The two sets of thermocouples were then connected to yield a differential electromotive force between the empty and the sample bearing cells. With this arrangement, there are the advantages of signal averaging and measurement of differentials. The seventh cell of the block was used simply to measure the block temperature and cooling rate.

The seven-cell block becomes a massive heat sink when cooled. Depending on the temperature range of the experiment, either air or water was used to cool the block. Typical cooling rates were 0.05 to 0.005°/sec. These rates gave a sufficient differential temperature between the center and perimeter of the sample for precise measurement, and yet the rates permitted the block, which is the heat sink, to be essentially isothermal at any moment.

The blocks with the sealed samples and cavities were heated to the desired temperature until the sample and block equilibrated. The apparatus was then cooled with the differential and the cooling rate measured. This differential temperature and cooling rate at a given temperature are directly used in the thermal diffusivity equation. The conversion to thermal

conductivity was made using the specific heat of the sample species and the density of the powder in the sample cells.

5.3 Samples

Commercially available pelletized MgO was crushed and sized to $-62.5\ \mu\text{m}$ for the thermal experiments. This material was fine-grained, but granular, in contrast to some flocculent MgO powders. Dicalcium silicate was synthesized by doping with CaNaPO_4 , thus it is a solid solution variant with the composition $\text{CaSiO}_4)_{90} \text{CaNaPO}_4)_{10}$. The synthesized material had either the α' or β form, these are the forms that most readily hydrate. This synthesized material was crushed to $-62.5\ \mu\text{m}$. Bentonite is the typical fine powdery material described earlier, none was pre-compacted or pelletized to a high density.

The dry samples of a known weight were packed or pressed into the sample cell of known volume, from which the density was calculated. This density, compared to the density of the solid, gave the porosity of the sample. The density of pure bentonite is unknown because it has poor crystallinity and extensive chemical variation. A density of the bentonite used in these experiments was assumed to be 2.35, and this value was used to calculate the porosity of the bentonite in the packed cells.

Water was added to some of the samples in different experiments to determine the thermal conductivity of the hydrous product. These samples plus the added water were held in the sample cells at elevated temperature until the hydration reaction had gone to completion or until the water phase was exhausted. Then the thermal conductivity of the hydrous product was determined.

With granular samples, the added water entered the interstices and the cell is sealed. However, when water is added to bentonite, the clay expands making packing and sealing impossible. To overcome this problem, water was added to the empty cell, and the water was frozen. The bentonite was then packed on top of the ice. In several thermal conductivity experiments, water was present as a separate phase. Such a mobile phase has a profound effect on heat transfer.

Thermal diffusivity was measured and thermal conductivity calculated for the following:

1. MgO	dry, packed to a density of 1.56, sample porosity of 56%
2. Doped Ca_2SiO_4	dry, packed to a density of 1.66, sample porosity of 50%
3. Bentonite	dry, packed to a density of 1.34, sample porosity of 43%
4. Bentonite	dry, packed to a density of 1.48, sample porosity of 37%
5. $\text{MgO} + \text{H}_2\text{O}$	product approximately equal moles of MgO and $\text{Mg}(\text{OH})_2$, bulk density 1.60, porosity 51%
6. Doped $\text{Ca}_2\text{SiO}_4 + \text{H}_2\text{O}$	product hydrous calcium silicate and water as a separate phase, bulk density 1.54, porosity 36%
7. Bentonite + H_2O	product is expanded bentonite, bulk density 1.25, porosity 44%
8. Bentonite + H_2O	product is expanded bentonite, bulk density 1.23, porosity 37%

5.4 Results

About 100 determinations were made of the thermal diffusivity of each sample as a function of temperature. A relation was developed using a least squares fit, and a 95.5 percent confidence limits were determined. The relation of thermal diffusivity to temperature for MgO and the partially hydrated MgO is shown in Figure 7. The partially hydrated MgO has slightly less porosity but nearly twice the thermal diffusivity of dry MgO.

Thermal diffusivity for the dry variant of Ca_2SiO_4 and the sample containing water as a separate phase is shown in Figure 8. The relation for the water bearing sample is based on 80 data points from 30 to 60C, and the dry sample relation is based on 120 data points from 30-160C. The 95.5 percent confidence limits are shown. The water bearing sample has a steeper positive relation and greater thermal diffusivity than the dry sample. Although beyond the range in which data was collected, the two trends appear likely to cross at about 15C. At temperatures below 15C, the dry sample appears likely to have the greatest thermal diffusivity, whereas at higher temperatures the water bearing sample has the highest thermal diffusivity, as is expected on the basis of thermal conductivity of water and the porosity of the sample. There is no obvious explanation for the apparent crossing of these thermal diffusivity curves.

Bentonite was packed to different bulk densities and the thermal diffusivity determined with more than 100 data points for each sample. The bentonite with the greatest bulk density has the greatest thermal diffusivity (Figure 9). Bentonite expanded with water and the thermal

Figure 7. Thermal diffusivity (α) as a function of temperature for MgO and $\text{MgO} + \text{Mg}(\text{OH})_2$. 95.5% confidence limits shown by dashed lines.

Figure 8. Thermal diffusivity (α) as function of temperature for doped Ca_2SiO_4 and doped $\text{Ca}_2\text{SiO}_4 + \text{H}_2\text{O}$ as a separate phase. 95.5% confidence limits shown by dashed lines.

Figure 9. Thermal diffusivity of bentonite packed to a density of 1.48 (upper curve) and 1.34 (lower curve). 95.5% confidence limits shown by the dashed lines.

diffusivity relations for two samples, based on more than 100 data points each, is shown in Figure 10. Similar to the dicalcium silicate relations, the relations for bentonite appear to cross the relations for bentonite plus water. The bentonite plus water curve has the steepest slope for thermal diffusivity.

5.5 Thermal Conductivity Values

Thermal conductivity values for the eight samples are calculated from the thermal diffusivity values at 20, 60, and 120C (Table 5). The diffusivity data may be used for any temperatures within the range covered by the experiments.

5.6 Conclusions

Thermal conductivity of materials decreases as porosity increases, as shown in Figure 6 for various sandstones. If the porous material is saturated with water, or contains water as a separate phase in the interstices, the thermal conductivity of the porous material is greatly increased. Because of these relations it is necessary to evaluate candidate backfill materials in terms of conductivity at a given porosity. A plot of the data in Table 5 is shown in Figure 11. MgO, as used, had the highest porosity, and tightly packed bentonite had the lowest porosity among the dry samples. This bentonite has slightly superior thermal conductivity relative to the more porous MgO. However, porosity is a function of grain size distribution in the sample and especially of packing, an extrinsic variable. More effective packing reduces porosity which increases thermal conductivity. Thus, the data

Figure 10. Thermal diffusivity as a function of temperature for bentonite + water with bulk density of 1.25 (lower curve) and 1.23 (upper curve).

Note: Brackets show 99.5% confidence limits (dashed lines) for each curve. Compare slopes to Figure 9.

TABLE 5
Thermal Conductivity

Sample	Bulk Density	Porosity	Thermal Conductivity X 10^{-3} cal/cm. sec. $^{\circ}$		
			@ 20 $^{\circ}$ C	60 $^{\circ}$ C	120 $^{\circ}$ C
1. MgO	1.56	56%	.25	.31	.41
2. Doped Ca_2SiO_4	1.66	50%	.22	.30	.41
3. Bentonite	1.34	43%	.23	.32	.45
4. Bentonite	1.48	37%	.27	.39	.53
5. MgO + $\text{Mg}(\text{OH})_2$	1.60	51%	.55	.62	.73
6. Doped Ca_2SiO_4 + H_2O	1.54	36%	.35	.85	ND
7. Bentonite expanded with H_2O	1.25	44%	.32	.55	.89
8. Bentonite expanded with H_2O	1.23	37%	.47	.69	1.02

Figure 11. Thermal conductivity of candidate overpack materials as a function of porosity.

Note: Number keyed to sample numbers in text. Arrows indicate trend of thermal conductivity with decreased porosity.

must be evaluated in view of the porosity. Fortunately, the effect of porosity has been established, as shown in Figure 6, and the trend based on the data by Woodside, et al (1961) is shown in Figure 11. This trend was used because it is based on more data points than that by Kunii, et al or Moiseyenko, et al, and it covers the porosity range considered in the present study.

MgO packed with 56 percent porosity has a thermal conductivity of 0.25×10^{-3} cal/cm. sec. $^{\circ}$. If the porosity is reduced the conductivity increases approximately in accord with the trend shown by Woodside, et al (1961). For example, if the porosity of the MgO is reduced to 43 percent by tighter packing, the conductivity would be shifted, as shown by the arrow in Figure 11, to a new value of about 1.75×10^{-3} cal/cm. sec. $^{\circ}$. Because of a similar porosity, this projected value can be related to dry bentonite. The data show MgO to be superior to bentonite in thermal conductivity at a given porosity. In fact, among the materials tested and adjusted to a common porosity, MgO shows the superior conductivity.

The addition of water to the system increases the thermal conductivity. With some materials this is partly the result of the hydrous product having a greater volume than its anhydrous predecessor, and therefore, with hydration, the porosity is decreased. Water present as a discrete phase reduces porosity and is a mobile material of high thermal properties; therefore, thermal conductivity of a wet material is superior to that of dry material.

6.0 SUMMARY AND CONCLUSIONS

Backfill materials should be a desiccant, sorb any released radioisotopes, and preserve the integrity of the system. The materials must have adequate stability as reactants and products and they must have appropriate thermal conductivity. MgO, dicalcium silicate, and bentonite are candidate backfill materials. The purpose of this research was to determine the rate and products of reaction and the thermal conductivity of the materials.

The rate of hydration of granular MgO as a function of temperature and grain size was determined. At 150C with a water vapor pressure of 4.6 atmospheres MgO completely hydrated to $\text{Mg}(\text{OH})_2$ in less than 10 hours. At 60C extensive hydration required about 100 hours, and at 20C extensive hydration required more than 1000 hours. Grain size and therefore surface area had the greatest effect for experiments at 60C. From this data the extent of hydration for MgO with a given surface area at a given temperature and time can be determined.

A chemical variant of dicalcium silicate with the composition $\text{Ca}_2\text{SiO}_4)_{90} \text{CaNaPO}_4)_{10}$ was synthesized. The compound had the β or α' form, and this material was reacted with water in a manner similar to the MgO. The extent and rate of reaction of the doped dicalcium silicate is markedly inferior to MgO. The hydration product has a cementitious nature, but it lacks moderate temperature stability.

Bentonite was reacted with water and brine to determine the nature and stability of the reaction products. Bentonite is known to expand with water and because of enormous surface area it readily undergoes ion exchange. Unfortunately, bentonite lacks moderate temperature

stability. Thus, bentonite may be a desiccant at low temperature and sorb ions, but it becomes a water source at increased temperature as a result of its own decomposition.

Bentonite slowly heated begins to lose water at 30C and this loss continues to 105C. This weight loss causes a decrease in volume which is an increase in porosity. The vapor pressure of water from the NBT-6a type brine was sufficiently low to cause a desiccation of the bentonite, again increasing the porosity.

The NBT-6a type brine contains high concentrations of alkaline earth and alkali chloride salts. The magnesium ions of the brine reacted with the bentonite. DTA, TGA, and X-ray diffraction indicate that this reaction product is a vermiculite. Such a reaction involves ion exchange and migration of magnesium ions to an octahedral site, a process termed "place exchange". Vermiculite contains more water than unexpanded bentonite, and it is stable to a slightly higher temperature. The ion exchange with the brine will clearly affect the radioisotope ion exchange.

Thermal diffusivity and thermal conductivity determinations on MgO, dicalcium silicate, bentonite, and hydrous reaction products showed the sensitivity of the determinations to sample porosity. Thermal conductivity values for the different materials at 20, 60, and 120C with porosity ranging from 36 to 56 percent yielded values of 0.22×10^{-3} to 1.02×10^{-3} cal./cm. sec.°. Increased thermal conductivity is found with decreased porosity and increased hydration.

There is a small increase in thermal conductivity with increased temperature, in contrast to rocks that typically show decreased thermal

conductivity with increased temperature. The increased thermal conductivity with increased temperature is also reported in the Sandia National Laboratories quarterly report concerning the thermal conductivity of bentonite. The increased conductivity may result from thermal expansion of the contained or jacketed powder yielding better grain to grain contact.

If porosity is considered a extrinsic variable, controlled by the grain size and installation techniques, MgO is the superior material also in regard to thermal conductivity. In practice, the thermal conductivity of MgO can be further improved by installing and packing of anhydrous material and then controlling in situ hydration. Such a practice would reduce the porosity and increase the thermal conductivity.

MgO is found to be superior to bentonite and dicalcium silicate in regard to desiccant capacity, thermal stability of the hydrous product, and thermal conductivity.

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