*Smectite Dehydration and Stability:
Applications to Radioactive Waste Isolation
at Yucca Mountain, Nevada*

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SMECTITE DEHYDRATION AND STABILITY: APPLICATIONS TO RADIOACTIVE WASTE ISOLATION AT YUCCA MOUNTAIN, NEVADA

by

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ABSTRACT

Montmorillonite-beidellite smectites are present in amounts up to 50% in the rocks directly underlying the potential high-level radioactive waste repository horizon at Yucca Mountain, Nevada. Smectites can be significantly affected by minor changes in temperature and water vapor pressure, leading to changes in rock strength, porosity, and permeability. It is thus important to consider their behavior in a repository environment because emplacement of waste will increase temperatures and as a result change the water vapor pressures in the rocks. The thermal reactions of concern include (1) reversible collapse/expansion of the smectite layers due to loss/gain of interlayer water; (2) irreversible collapse due to loss of interlayer water and migration of interlayer cations into the 2:1 silicate layers; (3) irreversible reduction of the osmotic swelling ability through reaction in a steam atmosphere; and (4) inhomogeneous transformation of the smectite into an interstratified illite/smectite. Reversible collapse should be of minor importance because any thermally driven collapse will be reversed when water is introduced and temperatures go down. The amounts of smectite in the potential repository horizon itself are probably insufficient to give rise to rock strength problems due to reversible collapse. Reactions 2 and 4 will probably be of negligible importance due to the high temperatures and long times required for reaction. However, the irreversible reduction of osmotic swelling capacity in a steam environment may be significant in the rocks near the repository horizon. This effect on naturally occurring Na-rich smectites would probably increase permeabilities but would also provide for increased cation exchange by the smectite. Exposure of Na-smectites used for packing/backfill to a steam environment may eliminate or severely reduce the beneficial properties of the smectites in a short time, arguing against using Na-smectites for this purpose unless saturated conditions will be maintained.

I. INTRODUCTION

The clay mineralogy of the rocks at Yucca Mountain, Nevada, is being studied in detail as part of a project to determine the suitability of Yucca

Mountain to host a geologic repository for high-level radioactive waste. This research has been sponsored by the Nevada Nuclear Waste Storage Investigations (NNWSI) Project of the U.S. Department of Energy and directed by the Waste Management Project Office of the Department's Nevada Office of Operations. In the context of clay minerals, naturally occurring smectites in Yucca Mountain are of primary concern to the NNWSI Project, but smectites are also being considered as packing materials in some radioactive waste isolation applications at other sites (Dayal and Wilke 1982; Allen et al. 1984, 1986; Krumhansl 1986).

Previous work on the mineralogy-petrology of the tuffs at Yucca Mountain demonstrated that smectites are ubiquitous throughout the mountain, generally in low concentrations (Bish 1981; Bish et al. 1981; Caporuscio et al. 1982; Vaniman et al. 1984). The devitrified Topopah Spring Member of the Paintbrush Tuff, the unit currently under consideration as the potential host rock, generally contains less than 5% smectite; however, smectites are abundant in the smectite- and zeolite-rich zone immediately underlying the Topopah Spring Member. This zone contains up to 50% smectite and represents the closest occurrence of abundant sorptive minerals to the potential repository horizon.

The importance of smectites in a repository environment lies in their ability to sorb cations by cation exchange (Grim 1953), their ability to exert significant controls on rock porosity and permeability (Longstaffe 1981), and their ability to be significantly and rapidly affected by small changes in temperature and partial pressure of water (Bish 1981). This sensitivity to minor changes in temperature and water vapor pressure is perhaps the most important property of smectites in a potential geologic repository. Johnstone et al. (1984), Montan (1984), and Travis and Nuttall (1987) modeled the thermal history of a repository in the Topopah Spring Member for specific waste loadings. The results of their calculations showed that significantly elevated temperatures may be maintained for up to 10^3 years in the lower Topopah Spring Member and the upper Tuff of Calico Hills, units containing high concentrations of smectite and clinoptilolite. The zone within 20 m of the repository may be heated to temperatures in excess of 100°C. In addition, Travis and Nuttall (1987) showed that an area of reduced saturation will surround waste canisters, which in turn will be surrounded by a small volume of increased saturation that levels off to ambient saturation conditions farther out from the canister. Fluid pressures will be in excess of 1 atm and temperatures will be above 100°C in the area of reduced saturation. Thus it is quite important to consider the

effects of elevated temperatures and variable water vapor pressure on smectites in a repository environment. Research to clarify the consequences of exposure of the clinoptilolite in the units underlying the potential repository horizon to elevated temperatures is ongoing (Bish 1984, 1985); the dehydration and thermal stability properties of the smectites will be discussed in this report.

The thermal reactions of concern for smectites include several major phenomena: (1) reversible collapse/expansion of the smectite layers due to loss/gain of interlayer water coordinated to interlayer cations at water vapor pressures less than 1 atm; (2) irreversible collapse of the smectite layers due to loss of interlayer water and migration of interlayer cations into the 2:1 layers; (3) irreversible reduction of the osmotic swelling capacity of smectites through reaction in a steam atmosphere (Couture 1985a,b); and (4) inhomogeneous transformation of some of the low-charge smectite layers to higher-charge layers producing a less expandable interstratified illite/smectite. This report summarizes the literature on these four major types of reactions and includes an assessment of the importance of these reactions in a geologic repository for high-level radioactive waste.

II. CLAY MINERALOGY OF YUCCA MOUNTAIN TUFFS

The clay mineralogy of Yucca Mountain tuffs has been summarized by Bish (1981, to be published). The dominant clays in Yucca Mountain tuffs are dioctahedral montmorillonite-beidellites with variable amounts of Na, Ca, and K as exchangeable cations. These smectites are generally close to 100% expandable at depths shallower than 900 m, but they become increasingly interstratified with illite at greater depths. Interstratified illite/smectites (I/S) are most common at depths in excess of 1500 m in the northern portion of Yucca Mountain, and the transformation to $R = 2$ and $R \geq 3$ I/S is well developed (see Reynolds, 1980, for a discussion of R , Reichweite, and ordering terminology). The transformation of smectite to illite is not well developed in the southern portion of Yucca Mountain, where I/S have expandabilities greater than 80% and only random interstratifications ($R = 1$) exist. Some of the I/S at depth in the northern portion of Yucca Mountain show evidence for chloritic interlayers in the smectite layers.

Smectites in Yucca Mountain contain variable amounts of Na, K, and Ca, but few analyses of smectites are available due to the difficulty of analyzing hydrous, fine-grained minerals using the electron microprobe. In general, deeper smectites typically contain subequal amounts of Na, K, and Ca (Bish et

al. 1981; Levy 1984; Caporuscio et al. 1985), with a tendency for increased amounts of Na in shallower smectites and increased K in deeper smectites (Vaniman et al. 1984). Smectites that have replaced glass underlying devitrified Topopah Spring Member tuff from drill hole USW H-5 are Ca rich, with very low K and Na contents (Levy 1984).

All thermal models of the potential repository in the Topopah Spring Member at Yucca Mountain show that thermal effects due to emplacement of high-level waste are minimal at depths greater than about 100 m below the repository (Johnstone et al. 1984; Montan 1984; Travis and Nuttall 1987). All of the I/S at Yucca Mountain shallower than this depth are essentially pure smectites. Therefore, thermal reactions of I/S with significant amounts of illitic layers or with chloritic interlayers will not be addressed here, and only reactions involving pure smectites will be discussed.

Of the four types of thermal reactions listed above, only the first, reversible collapse, and the third, collapse in a steam environment, are probably important in a repository environment. Emphasis will be placed on these two phenomena, and the remaining two types of reactions are included here in abbreviated form.

III. THERMAL REACTIONS

A. Reversible Expansion with Water

The reversible expansion/collapse of smectites due to the addition/loss of interlayer water is one of the best-known phenomena associated with smectites and has been studied for over 50 years (Hofmann and Bilke 1936; Nagelschmidt 1936; Bradley et al. 1937). The relative ease with which smectites expand and contract results from attractive (collapsing) and repulsive (expanding) forces of approximately the same magnitude. Attraction results from the interaction between the negatively charged 2:1 silicate layers and the positively charged interlayer cations (Figure 1). Repulsion (expansion) forces result from hydration of the interlayer cations, which increases the number of interlamellar water molecules and causes a stepwise increase in the repeat spacing of the smectite layers. At low water contents, interlamellar water molecules occupy relatively fixed crystallographic positions, giving rise to one, two, three, or four layers of water in the interlayer. These interlayer interactions are a sensitive function of the nature of the interlayer cation and of

Figure 1.

Diagram of the smectite structure showing the 2:1 silicate layers and the interlayer region normally occupied by exchangeable cations and water molecules (modified from Grim 1953).

the water vapor pressure in equilibrium with a smectite. The amount of inter-layer water is also a function of temperature as a consequence primarily of the correlation between temperature and water vapor pressure in a system of constrained volume. A secondary but measurable effect is the influence of the charge on the 2:1 layers, including magnitude, location (tetrahedral or octahedral sheet), and homogeneity. Abundant data exist demonstrating the relationship between exchangeable cation, water vapor pressure, and basal spacing (MacEwan 1972). However, only the relevant data for Na-, Ca-, and K-exchanged smectites will be summarized here since these three are the dominant cation forms at Yucca Mountain. Readers wishing more detail or information on other exchangeable cations are referred to MacEwan (1972), Mering (1975), Barrer (1978), and MacEwan and Wilson (1980).

The behavior of a smectite as a function of water vapor pressure is usually depicted by relating the basal (001) spacing from the x-ray powder diffraction pattern to some measure of water vapor pressure, such as relative humidity (RH). Figure 2 illustrates the relationship between basal spacing and RH for several Na-smectites (Gillery 1959), and Figure 3 shows an independent determination of this relationship for three smectites, including the effects of immersing the samples in liquid water (Suquet et al. 1975). Figure 4 shows the same relationship for K-smectites (Suquet et al. 1975). Figure 5 shows the behavior of several Ca-smectites, including the effects of varying the layer charge (Gillery 1959), and Figure 6 illustrates an independent determination of the basal spacing/vapor pressure relationship for Ca-smectites, including the effects of immersion in liquid water (Suquet et al. 1975). These figures dramatically illustrate the strong link between water vapor pressure and the basal spacing of smectites. Under room conditions, between 0 and 100% RH, Na-smectites typically yield three distinct basal spacings. At very low relative humidities, Na-smectites yield a zero-water-layer complex, with a basal spacing at, or slightly below, 10 Å. Between approximately 20 and 60% RH, these smectites have a one-water-layer complex, with a basal spacing of between 12.4 and 12.7 Å. They exhibit a two-layer complex at higher humidities up to about 90%, with basal spacings of about 15.2 to 15.5 Å. At greater humidities and in saturated conditions, Na-smectites exhibit osmotic swelling, which is discussed below. Moore and Hower (1986) showed that some Na-smectites yield additional reflections due to interstratification of zero-water-layer and one-water-layer units. They found that Na-SWy-1, a Wyoming bentonite, gave a basal

Figure 2.

Basal spacing/relative humidity (RH) relations for Na-smectites (modified from Gillery 1959). All smectites in a-c have a layer charge of 0.33 per half-unit cell. Note the two horizontal steps at about 12.5 and 15.5 Å representing the one- and two-water-layer complexes, respectively.

Figure 3.

Basal spacing/vapor pressure relations for Na-smectites (modified from Suquet et al. 1975). Note the two horizontal steps at about 12.5 and 15.5 Å representing the one- and two-water-layer complexes, respectively. The vertical lines represent the presence of interstratification between one and two-water-layer structures within a range of about 10% RH. The notation p/p_0 represents the relative partial pressure of water and is equivalent to RH.

Figure 4.

Basal spacing/vapor pressure (p/p_0) relation for K-saturated saponite (modified from Suquet et al. 1975). Note the horizontal step at about 12.5 Å representing the one-water-layer complex. The vertical lines represent the presence of interstratification between zero- and one-water-layer structures within a range of about 10% RH. The notation p/p_0 represents the relative partial pressure of water and is equivalent to RH.

Figure 5.

Basal spacing/relative humidity (RH) relations for Ca-saturated smectites (modified from Gillery 1959). Smectites in a-d have a layer charge (z) of 0.33 per half-unit cell unless otherwise indicated. Note the nearly horizontal step at about 15.5 Å representing the two-water-layer complex.

Figure 6.

Basal spacing/vapor pressure (p/p_0) relations for Ca-smectites (modified from Suquet et al. 1975). Note the nearly horizontal steps at about 12.2 and 15.5 Å representing the one- and two-water-layer complexes, respectively. The notation p/p_0 represents the relative partial pressure of water and is equivalent to RH.

spacing of 22 Å resulting from this interstratification at humidities of about 35%.

K-smectites typically exhibit a zero-layer complex below about 30% RH, with a basal spacing about 10 Å. Above 30% RH, K-smectites have a one-water-layer complex, with a basal spacing between 11.9 and 12.5 Å. Some K-smectites exhibit osmotic swelling under saturated conditions, but most retain a one-layer complex. Ca-smectites are typically two-layer hydrates over an extended range of RH due to the stabilization of the two-layer complex by the formation of octahedrally coordinated Ca-hexahydrate groups (Mering 1946). The two-layer hydrate of Ca-smectite is stable between about 35 and 100% RH, yielding a basal spacing of 15.1 to 15.2 Å. Under saturated conditions, Ca-smectites often yield a three-layer hydrate with a basal spacing between 18 and 19 Å. Below an RH of about 20%, Ca-smectites exhibit a complex range of basal spacings, with one- and two-layer hydrates and intermediate hydrates. Ca-smectites do not normally yield a zero-hydrate (10 Å) structure under room conditions at any humidity. However, these smectites can be dehydrated and collapsed by heating. There is little literature on the behavior of mixed-cation smectites, but available data suggest that the resultant behavior is intermediate between the end-member smectites (Gillery 1959).

The amounts of water lost during the dehydration reaction (and before dehydroxylation, the loss of structural hydroxyl) vary considerably depending on the smectite and the interlayer cation (Grim 1953; Van Olphen and Fripiat 1979; El-Barawy et al. 1986). Smectites may contain in excess of 30 wt% water in a saturated atmosphere (Gillery 1959), and much of this water can be lost at low temperatures at low heating rates, demonstrating that smectites can be an important source of water. El-Barawy et al. (1986) demonstrated the dependence of smectite water content on exchangeable cation content. Monovalent-cation smectites were completely dehydrated by 100°C at 1 atm, and weight losses ranged from 6.6 to 14.5% for Cs, Rb, K, Na, and Li smectites respectively. Divalent- and trivalent-cation smectites retained their interlayer water to about 175°C, and weight losses for these smectites ranged between 15 and 18%. There is apparently a relationship between the ionic strength of the exchangeable cation and the total amount of interlayer water contained in the smectite.

All of the data depicted in Figures 2-6 were obtained at room temperature and 1 atm total pressure, with water vapor pressures considerably below 1 atm. Thus these results may not be directly applicable to the behavior of clays in a high-level waste repository, where total pressures may exceed 1 atm and water

vapor pressures will likely exceed those generated under room conditions. Limited data have been obtained at elevated temperatures and pressures. Colten (1986) examined a Na-saturated smectite in a high-pressure, high-temperature x-ray powder diffraction cell in NaCl solutions at temperatures up to 200°C and pressures up to 456 bar. This smectite exhibited a basal spacing of 15.2 to 15.7 Å over the P-T range studied and in solutions up to 5 molal NaCl, suggesting that Na-smectite exists as a two-water-layer complex under diagenetic conditions (temperatures up to 200°C and hydraulic pressures up to 456 bar). Colten (1986) and Colten-Bradley (1987) concluded that the temperatures and hydraulic pressures associated with diagenesis do not significantly affect dehydration. Extending her earlier work (Colten 1986), Colten-Bradley (1987) used a simple thermodynamic model coupled with experimental data for water and Na-montmorillonite to calculate dehydration curves for smectite under both hydrostatic and lithostatic (differential) pressure conditions. Under hydrostatic conditions with zero applied pressure, the dehydration temperatures were calculated to be 58° to 75°C, 67° to 81°C, and 172° to 192°C, for removal of the third, second, and first water layers, respectively. These dehydration temperatures increase with hydraulic pressure such that dehydration of smectite should not occur in saturated rocks under hydraulic pressure conditions with geothermal gradients less than about 160°C/km. Results of analyses under lithostatic conditions show that smectites will dehydrate at lower temperatures than under hydraulic pressure conditions. However, the effects of lithostatic (nonhydrostatic) pressure should not be great enough to dehydrate smectite completely at depths even as deep as 3 km, much deeper than the proposed repository horizon at Yucca Mountain. Assuming a repository depth of 311 m (1020 ft) and a lithostatic gradient of 0.22 bar/m (1.0 psi/ft), the maximum lithostatic pressure at repository depth will be 69.4 bar. This pressure is insufficient to cause a significant shift in the dehydration temperature of smectite.

Koster van Groos and Guggenheim (1984, 1986, 1987) conducted numerous experiments on the effect of pressure on the dehydration of Na-, K-, Ca-, and Mg-montmorillonites using high-pressure differential thermal analysis. The total water pressure in their experiments was approximately equal to the total pressure, i.e., $P_{H_2O} = P_{total}$. Their results were consistent for all compositions analyzed and indicated two distinct dehydration reactions occurring at discrete temperatures above the boiling curve of water for each composition. Figure 7 compares the effects of pressure on the first dehydration reaction for

Figure 7.

Pressure-temperature diagram showing the first dehydration reaction of Na-, K-, and Ca-smectites (SWy-1 = Wyoming bentonite) (modified from Koster van Groos and Guggenheim 1984, 1986, 1987). The solid curve is the boiling curve of water.

Na-, K-, and Ca-smectites. The first dehydration reaction ranged from 40° (Na) to 50° (K, Mg) to 70°C (Ca) above the liquid-vapor curve of water and was thought to represent the loss of the first hydration sphere around the interlayer cations. All samples examined also yielded a second endotherm about 100° to 110°C above the boiling curve of water. This second dehydration event was thought to represent the loss of the inner hydration shell around the interlayer cations. Koster van Groos and Guggenheim concluded from their results that all water in smectites is not bonded equally. These results are consistent with data obtained by others using thermogravimetric analysis and differential scanning calorimetry. Above the critical point of water (374.1°C, 216.9 bar), only a modest increase in dehydration temperature was observed with an increase in pressure. The important conclusions to be drawn from the work of Koster van Groos and Guggenheim (1984, 1986, 1987) (Figure 7) are that, in geological systems in which the partial pressure of water is less than the total pressure, for example, in the presence of electrolytes, dehydration of smectites can occur below the boiling temperature of water. The smectites in these systems will thus buffer the water pressure. However, it is also very important to note the large increase in stability of hydrated smectites with only a modest increase in water vapor pressure. For example, the first dehydration reaction for Na-smectite occurs at 148°C at 1 bar, but this dehydration reaction occurs at 219°C at a pressure of only 5.3 bars.

Osmotic Swelling

A different phenomenon leading to much greater degrees of swelling can occur with smectites having the higher water contents typical of saturated conditions. As opposed to the interlayer swelling depicted in Figures 2-6, osmotic swelling gives rise to layer separations greater than about four water layers or 10 Å. Beyond this interlayer separation, surface hydration energies and interlayer cation-water interactions are no longer as important, and electrical double-layer repulsion is the major repulsive force between the layers. The exact nature of osmotic swelling in smectites depends on the surface charge density and charge localization of the smectite and on the nature of the exchangeable cation. Norrish (1954, 1972) and Foster et al. (1955) demonstrated that individual layers of Na- and Li-montmorillonite dissociate completely as the water content is increased. Figure 8 shows the relationship between interlayer spacing and the water:smectite ratio for a Na-exchanged montmorillonite. Osmotic swelling is obviously of considerable importance for

Figure 8.

Interplanar spacing versus water/smectite ratio for Na-montmorillonite showing the region of osmotic swelling, region 2 (modified from Norrish 1972).

Na- and Li-smectites, giving rise to interlayer expansions more than an order of magnitude greater than that produced by intracrystalline expansion due to hydration of interlayer cations. It is this osmotic swelling that yields the very low permeabilities of Na-bentonites proposed for use as packing materials. However, the amount of osmotic swelling is an inverse function of the ionic strength of the solution (MacEwan and Wilson 1980) and will thus be less significant in fluids of elevated salt concentrations. Thus Na-bentonite used as a backfill in a repository in salt may not exhibit significant osmotic swelling if the ionic strength of solutions is sufficiently high, and the bentonite may not act as an efficient permeability barrier (Krumhansl 1986). Although Na-bentonites typically swell osmotically, not all Na-smectites yield unlimited swelling in water. Suquet et al. (1975) showed that some beidellites and saponites yield only a two-water-layer interlayer in their fully hydrated forms, probably because the source of layer charge in these minerals is in the tetrahedra. In addition, smectites saturated with cations other than Na and Li typically behave quite differently. Whereas K-saturated montmorillonite may show complete expansion in water, K-beidellites and K-saponites usually form a single-layer hydrate. Divalent-cation smectites do not completely disperse in water and instead form two- and three-layer hydrates with 15- to 19-Å basal spacings.

B. Irreversible Collapse

It was demonstrated above that smectites readily expand and collapse in response to changes in water vapor pressure and temperature. The majority of smectites collapse to a zero-water-layer structure (approximately 10-Å basal spacing) upon heating to 110°C (Martin-Vivaldi et al. 1963). However, not all smectites rehydrate in a hydrous atmosphere, and the ability of smectites to reexpand depends on several factors, including the smectite structure and exchangeable cation. In general, saponites (trioctahedral smectites) dehydrate less readily than montmorillonites of similar exchangeable cation composition (Farmer and Russell 1967). Saponites exchanged with divalent cations will not rehydrate after being heated higher than 450°C, but Li-, Na-, and K-saponites still rehydrate after heating to 700°C. This behavior is in contrast to that exhibited by montmorillonite, in which no cation forms will rehydrate after heating to 450°C. Mg- and Li-montmorillonites will not reexpand significantly after heating to just 250°C (Russell and Farmer 1964). In fact, the thermal reactions of Li-exchanged smectites are used to differentiate montmorillonite

from beidellite (Hofmann and Klemen 1950). If the Li-exchanged smectite expands after heating to 250-300°C, it is interpreted to be a beidellite, a smectite with the layer charge originating in the tetrahedral layer. Saponite also expands after this treatment. Montmorillonite is the primary smectite with the site of negative charge in the octahedral sheet, and it is presumed that heating causes migration of Li into the vacant site in the octahedral sheet, resulting in a mineral that will no longer expand.

Migration of the interlayer cation into the hexagonal hole in the tetrahedral layer or into a vacant octahedral site in the octahedral layer, with concomitant reduction of layer charge, will have significant effects on the physical properties of a smectite. The most obvious result is the reduction in swelling ability, but the cation-exchange capacity will also be reduced. If the layers cannot be initially expanded, osmotic swelling of the smectite will be severely restricted.

Heating experiments conducted at Los Alamos on Clay Minerals Society Repository clays yielded slightly different results than those outlined above. Wyoming bentonite, SWy-1, and Cheto, Arizona, montmorillonite, SAz-1, were exchanged with Ba, Ca, Cs, K, Li, Mg, Na, and Sr, heated for 24 hours at temperatures up to 700°C, and solvated with ethylene glycol to assess the clays' reexpandability. With increasing temperature, Li-montmorillonites irreversibly collapsed at 250°C, followed by Mg-montmorillonites (400°-450°C) and Ca-montmorillonites (500°-600°C). The remaining montmorillonites did not irreversibly collapse until heated to at least 550°C. Long-term dry heating experiments at 100° and 200°C on Mg-saturated SWy-1 mounted on silica glass slides were conducted to assess the importance of kinetics in the irreversible collapse reaction. No change in expandability was observed after three years at 100°C, but the sample heated at 200°C began to exhibit discernible changes after three years. Apparently the montmorillonite layers began to collapse randomly, as the x-ray diffraction pattern indicated approximately 20% collapsed layers randomly interstratified with expanded layers. This experiment demonstrates the importance of kinetics in this reaction and suggests that Mg- and Li-smectites can collapse irreversibly at low temperatures given sufficient time. The migration of Mg or Li into the 2:1 layer must be the controlling factor in determining how fast and at what temperature these smectites will collapse irreversibly. However, due to the large ionic radii of Ca, Na, and K, and the high collapse temperatures of Ca-, Na-, and K-smectites, it is unlikely

that significant irreversible collapse will occur with these smectites at the temperatures expected in any high-level waste repository.

Allen et al. (1984) examined the dehydration behavior of Na-montmorillonite at 1 atm pressure and temperatures from 250° to 550°C for times up to one year. Their results showed that significant changes in the dry-heated montmorillonite occurred above 370°C. Samples heated to 370°C rehydrated, whereas those heated to 440°C and above would not reexpand. The difference between these results and those outlined above is probably due to reaction kinetics.

Krumhansl (1986) performed unconfined swelling measurements in brines on Na-Ca-montmorillonites that had been dehydrated for up to 500 days at temperatures up to 320°C. His experiments showed that heating to 150°C for 50 days resulted in a significant loss of expandability, but these samples expanded much more than those heated to 250° or 320°C. Most of the loss in expandability occurred in the first 100 days of heating. He also showed that reexpansion differed in brines of different compositions; a saturated NaCl solution produced greater swelling than a synthetic brine containing Mg, Ca, K, Na, SO₄, and Cl did. Although unheated samples required more than a day to hydrate completely, samples heated to 250° and 320°C finished their limited expansion after only 30 min. The loss of swelling observed by Krumhansl (1986) may be similar to the effects described by Couture (1985a,b) and may not be directly related to the phenomenon discussed in this section on irreversible collapse.

C. Irreversible Reduction in Osmotic Swelling Capacity

In contrast to the reactions discussed above, in which irreversible changes require either high temperatures or long time periods, Couture and Seitz (1984) and Couture (1985a,b) documented several unusual effects that occur over short reaction times at relatively low temperatures in a steam environment. These important experiments involved Na-montmorillonites with minor amounts of quartz and plagioclase or packed columns of 25% Na-montmorillonite mixed with either 75% quartz or basalt sand. For about one week these samples were heated dry at 250°C and in closed systems at 150-250°C with variable water:clay ratios. Both deionized water and synthetic basaltic groundwater were used. The initial, unheated montmorillonites swelled greatly in water to specific volumes of 25 to 40 cm³ g⁻¹ and formed thick, gummy pastes.

The behavior of montmorillonites as a function of temperature and water/montmorillonite ratio is illustrated in Figure 9. Closed-system experiments with total water/montmorillonite ratios ≤1.0 produced montmorillonites

Figure 9.

Hydrothermal degradation of smectite as a function of temperature and water/smectite ratio (modified from Couture 1985b). Samples above the line showed significant changes in swelling properties.

with significantly reduced swelling capacities, down to values on the order of $4\text{--}13\text{ cm}^3\text{g}^{-1}$. Maximum reduction in swelling capacity occurred with water/montmorillonite ratios of 0.15–0.25 at 250°C . This reduction in swelling capacity occurred at temperatures as low as 150°C for reaction times as short as seven days. Reheating of steam-altered montmorillonite with excess water at 250°C did not result in material that would reexpand; thus the loss of swelling capacity does not appear to be reversible over the time scale of the experiments. In addition, the reaction appeared to be insensitive to water composition. Apparently the concentration of solutes in typical groundwaters is insignificant compared with the concentration of soluble impurities and exchangeable ions in the natural montmorillonites. Dry heating for seven days at 250°C also reduced the swelling capacity, from 37 to $28\text{ cm}^3\text{g}^{-1}$, results similar to those obtained by Krumhansl (1986). However, as explained below, it appears that this reduction in swelling resulted from reaction with the water present in the interlayers of the unaltered montmorillonite rather than from an irreversible collapse reaction. This is important because it suggests that significant losses in swelling capacity can result even when liquid water is not present. Couture (1985a,b) conducted two experiments to elucidate the effects of liquid water versus vapor. In one experiment, the partial pressure of water was kept at 93% of saturation; in other words, no liquid water was present. A companion experiment involved a water/montmorillonite ratio of 20, in which the clay was always in a gel state. The montmorillonite in the former experiment experienced a reduction in swelling capacity to $10\text{ cm}^3\text{g}^{-1}$, whereas the montmorillonite in the latter experiment suffered no loss in swelling capacity. Thus it appears that reaction with water vapor and not liquid water is responsible for the observed reductions in swelling capacity.

The water/montmorillonite ratios at which maximum reductions in swelling capacity occur correspond to one to three layers of water in the smectite interlayers. The concentration of solutes in the interlayer water is apparently too low to produce a reaction when significant liquid water is present. Apart from the greatly reduced swelling capacity in water, no significant mineralogical changes were observed. Starting and altered montmorillonites were dioctahedral, and both exhibited similar behavior in a humid atmosphere and with ethylene glycol. The reaction is not due to Ca for Na exchange, although some Mg was fixed during the reaction. There was also no indication that any interaction occurred with the reaction vessels. Couture (1985a) suggested several possible explanations for the observed reaction,

including hydrolysis of exchangeable cations, attack of the octahedral layer with release of Al into the interlayer positions, or oxidation of ferrous iron.

Oscarson and Dixon (1987) recently confirmed Couture's results that a steam atmosphere significantly reduces the swelling ability of montmorillonite. The results of their experiments, conducted for different times at several temperatures and with different moisture contents in autoclaves, suggested that temperature was the most important factor. Increasing the temperature decreased the free swelling volume (FSV), and increasing time of reaction, up to 14 days, decreased the FSV. Treatments as short as 1 day resulted in a significant decrease in FSV. Additional experiments conducted with compacted montmorillonite heated to 200°C at 85 to 90% water saturation for 7 days also produced significant changes in properties. After this treatment, the clay samples developed swelling pressures about one order of magnitude lower and had hydraulic conductivities approximately two orders of magnitude higher than those of the untreated material.

The reduction in swelling has important implications for the use of Na-montmorillonite (Na-bentonite) as a packing or backfill material in a high-level radioactive waste repository. One of the primary purposes of a packing or backfill material surrounding high-level waste canisters is to limit the access of water to the waste. Na-bentonite, either pure or mixed with another component, has the ability to swell osmotically. As a result, such mixtures have very low initial permeabilities. In addition, natural Na-smectites have the ability to swell and fill fractures and thus further limit the ingress of water. However, most high-level waste repository designs will result in temperatures in excess of 150°C for significant times in the vicinity of the waste canister. The results of Couture's (1985a,b) experiments suggest that the swelling ability of the Na-smectites will be largely lost in a short time under these conditions. Thus one of the primary functions of the packing material will be lost. Couture's (1985a,b) results argue strongly against using Na-bentonites as backfill or packing materials in any high-level waste repository to limit water access and flow. Any Na-smectites in the host rock in the vicinity of the waste canisters would also be affected, resulting in an opening of fractures and a possibly significant modification of flow paths, although amounts of smectite in the host rock at Yucca Mountain are probably insufficient to give rise to any significant changes. Since the cation exchange capacity is not appreciably affected by this dehydration reaction, open fractures in the host rock would provide avenues for increased sorption by

any Na-smectites in fractures. In this case, water flow through such fractures would be greater than if the smectite retained its ability to osmotically swell.

D. Reaction of Smectite to Illite/Smectite

The reaction of smectite to illite through a series of interstratified intermediates I/S has been thoroughly documented in a wide range of rock types in diagenetic sequences, in hydrothermal alteration, in contact metamorphism, and in numerous laboratory experiments. This reaction involves an increase in tetrahedral aluminum, interlayer potassium, and layer charge, giving rise to a mineral with decreased expandability and cation exchange capacity. The reaction is a function of several variables, including temperature, time, fluid composition, and type of smectite (Eberl and Hower 1976; Howard 1981; Howard and White 1981; McCubbin and Patton 1981; Roberson and Lahann 1981; Hower and Altaner 1983; Anderson 1984; Thompson and Jennings 1985; Altaner 1986). The temperature dependence makes consideration of this reaction important in the context of a high-level radioactive waste repository. Howard and White (1981) used kinetic data from Eberl and Hower (1976) to estimate times necessary for transformation of 100% expandable smectite to illite. At temperatures below 100°C, transformation to a 20% expandable I/S would take approximately 10^4 to 10^5 years. These geologically rapid rates are not observed in nature due to the effects of competing ions on the I/S reaction (Eberl 1978; Howard 1981; Roberson and Lahann 1981), and the I/S reaction in natural systems is slower than that predicted by the Eberl and Hower (1976) data.

No experiments have been conducted specifically on a smectite-tuff assemblage, but numerous experiments on smectite stability have been conducted in relation to radioactive waste repository applications (Howard and Roy 1983; Allen et al. 1984; Peacor et al. 1984; Allen et al. 1986; Krumhansl 1986). Na-montmorillonite-basalt mixtures reacted at 300°C for 12 months with a fluid/solids ratio of 1:1 yielded interstratified illite/smectite with as much as 65% collapsed layers (Allen et al. 1986). Similar experiments performed with a fluid/solids ratio of 10:1 resulted in no significant alteration of the montmorillonite. In addition, all experiments with basalt yielded significant amounts of a trioctahedral iron-rich smectite that resulted from virtually complete alteration of the glassy basalt mesostasis.

Krumhansl (1986) conducted experiments on Na-Ca-montmorillonite between 150° and 250°C in several brines to assess the hydrothermal stability of montmorillonite used as a backfill in a high-level waste repository in rock salt.

He found little change in the montmorillonite after two months at 250°C in pure NaCl brines, but smectite heated in brines rich in potassium formed interstratified illite/smectites. The presence of magnesium in the brines inhibited the formation of interstratified illite/smectite, and a Mg-smectite formed instead.

Whether or not the results of these hydrothermal experiments are important in a high-level radioactive waste repository is ambiguous. Travis and Nuttall (1987) concluded from a modeling study that the elevated-temperature area immediately surrounding waste canisters at Yucca Mountain will be unsaturated and a zone of saturation will move outward from the canisters to cooler rocks. Therefore, conditions in the highest temperature portion of the repository will not be conducive to hydrothermal alteration. Thus, all of these data argue against the I/S reaction being of significance in a repository environment above the water table at Yucca Mountain. The importance of the I/S reaction in saturated environments must be assessed through a combination of hydrothermal experimentation and numerical modeling considering the heat load, repository design, and rock properties of the repository.

IV. SUMMARY AND CONCLUSIONS

Smectites are important in a high-level radioactive waste repository environment by virtue of their high cation exchange capacities and their ability to interact strongly with water. Most thermal reactions of smectites do not affect the cation exchange capacity, apart from the development of interstratified illite/smectites and reactions that occur at temperatures in excess of 300°C. However, other physical properties are significantly affected by exposure to slightly elevated temperatures. The molar volume of smectites is a function of temperature and partial pressure of water in an unsaturated environment and a function of the activity of water in a saturated environment. Therefore, heating smectites in the rocks around the potential repository horizon at Yucca Mountain can lead to large, reversible decreases in smectite volume with the effects on smectite-rich rocks still to be determined. Reintroduction of water will lead to reexpansion of the smectites. If smectites are significant components of the rocks in the vicinity of a repository, this volume decrease may give rise to changes in rock strength. However, the rocks in the potential repository horizon at Yucca Mountain, the lower Topopah Spring Member, generally contain less than 5% smectite, an amount probably insufficient to cause significant changes in rock strength. The available thermal models of the potential repository at Yucca Mountain suggest

that the bulk of the rock mass will not be heated above the boiling point of water. The rocks above this temperature will experience increased water vapor pressure that will tend to stabilize the hydrated, expanded forms of smectites. Accurate predictions of the effects of a repository on the smectites in the lower Topopah Spring Member and upper Tuff of Calico Hills await final, complete thermal models, including the effects of any water driven off hydrous minerals.

The phenomenon of osmotic swelling that leads to very large expansions and low permeabilities of some smectites can be important for predominantly Na-smectites, but short-term heating in a steam environment will likely lead to a significant loss of swelling capacity. Thus, Na-rich smectites near the repository horizon will probably not efficiently limit the ingress of water into the repository if unsaturated steam conditions exist. This applies both to natural Na-smectites in the repository rocks and to Na-smectites potentially used as packing or backfill materials. Apparently, any smectite that exhibits significant osmotic swelling capability is subject to large decreases in swelling capacity in a steam environment. Smectites that do not exhibit osmotic swelling are not as effective in providing a low permeability barrier to water as are those that osmotically swell. The degradation of Na-smectites in the vicinity of the canisters should not be problematic at Yucca Mountain if the Project does not use Na-bentonite as a packing or backfill. However, the behavior of a potential Na-bentonite packing or backfill in any repository should be assessed by considering available experimental data and thermal models of the repository. Present data suggest that natural Na-smectites near the potential repository horizon at Yucca Mountain will not be adversely affected if they are in a saturated environment. The long-term effects of heating smectites in a partially saturated environment below 100°C are presently unknown.

Experimental and thermal modeling results suggest that the irreversible collapse reaction will not be important in repository environments because maximum temperatures are too low. However, small interlayer cations (e.g., Mg, Li) not commonly found in abundance in natural smectites can migrate into the 2:1 layers at temperatures as low as 200°C in unsaturated conditions. In addition, the reaction of smectite to interstratified illite/smectites should not be important except perhaps in the volumetrically small region of both elevated temperature and elevated water pressure. Even in this region, it is not

presently clear whether temperatures will be high enough for periods of time sufficient to cause this reaction to proceed very far.

This summary of the literature on thermal reactions of smectites has pointed out the need for additional information in several areas. Because smectites are sensitive to changes in temperature and water vapor pressure, it is obvious that accurate predictions of the effects of a repository on smectites require comprehensive and accurate thermal models of the repository. Ideally, at least a two-dimensional picture of the temperature and fluid pressure in the repository is required as a function of time. Very different mineralogic changes would be predicted depending on whether the rocks are unsaturated or saturated. If hydrous minerals are significant components of the rock mass in an unsaturated repository, the water produced by the dehydration of these minerals should also be considered. In addition, if temperatures around a potential repository are expected to be at or below 100°C for times on the order of 10^3 years, it will be difficult to apply laboratory data collected at higher temperatures and for times usually less than one year. Thus kinetic data are needed to predict accurately the behavior of smectites in a repository environment. We are beginning a series of long-term experiments on smectites at temperatures at or below 225°C in environments ranging from dry to saturated. We anticipate that coupling results of these experiments with more accurate models of the physical processes in a repository will lead to reasonable estimates of the long-term behavior of smectites in a repository environment.

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