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DEVELOPMENT OF LAYER CHARGE AND KINETICS OF EXPERIMENTAL SMECTITE ALTERATION

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Abstract—Sodium-saturated Wyoming bentonite was hydrothermally reacted at 150° and 250°C for 30 to 180 days to determine smectite alteration rates that might be applied to nuclear-waste repository design. Na-Ca solutions deficient in K were used to determine the role of interlayer cations in the creation of high layer-charge in the smectites. The results provide insight into the mechanism and timing of various steps in the diagenetic alteration of smectite to illite. X-ray powder diffraction (XRD) analyses of the reacted clay showed little effect on the character of the 17-Å reflection even after 180 days at 250°C. Potassium saturation of these reacted clays and re-examination by XRD indicated collapse of some smectite layers, leaving at most only 60% expandable layers. The development of layer charge sufficient to cause collapse on saturation with a low hydration energy exchange-cation does not require K in the reacting fluid. Rate constants for the illitization reactions as determined by K-saturated collapse are between 1.0×10^{-3} and 2.8×10^{-3}/day with activation energies <3.5 kcal/mole. Ca in a Na-silicate-bicarbonate solution slightly reduced the illitization rate constants. These rate constants are higher than expected from extrapolation of studies of beidellite-composition glasses at higher temperatures, but lower than values obtained in studies of natural clays in artificial sea water. The release of Si, Al, and Mg in the 150°C experiments suggests congruent dissolution of the smectite. In contrast, at 250°C the release of Al was not stoichiometric with Si; as little as one half of the relative available Si was released. Rather than different mechanisms for dissolution at the two temperatures, the conclusion is that noncrystalline Al-rich phases formed at greater rates at higher temperatures. The cation-exchange capacities for several of these reacted smectites were significantly less than expected, suggesting a clogging of interlayer sites, perhaps by Al-complexes.

Key Words—Alteration, Hydrothermal, Illite, Layer charge, Nuclear waste repository, Smectite.

INTRODUCTION

The use of smectite as a major component for backfill barriers and seals in radioactive waste repositories is based upon its dual properties as a permeability barrier and an adsorber (ion exchanger) of transuranic ions and fission products. For smectite to retain its swelling behavior and high cation-exchange capacity it must remain stable under anticipated repository conditions. Of greatest concern is the transformation of smectite to illite or other collapsed phases that have been observed in natural burial diagenesis settings and laboratory experiments. The formation of illite would lessen the barrier's performance due to a reduction in swelling properties and decreased cation-exchange capacity.

The major problem that needs to be resolved, both for geotechnical uses such as repository design and for a clearer understanding of the controls on clay mineral diagenesis, is the mechanism of smectite transformation. To form illite from smectite additional layer charge in the tetrahedral sheet must be created by the substitution of Al for Si and K must be fixed into these high-charged layers (Eberl and Hower, 1976). There is some disagreement as to the timing of these steps. Fixation of interlayer cations involves the balance of ionic forces between the attraction of the negative layer and the positive cation in the interlayer against the repulsion caused by the hydration sphere around the cation (Eberl, 1980). The question is essentially whether K is required in the interlayer for the creation of layer charge (Lahann and Roberson, 1980; Inoue, 1983) or whether the layer charge is created independently of the presence of K and collapse occurs only when K is supplied to the high-charged interlayer site (Howard, 1981). Current barrier designs in basalt repositories assume that the absence of K in the ground waters will effectively inhibit the illitization of smectite backfill. Barrier designs in granite repositories also assume that the supply of K will be minimal and that illitization of the smectite backfill will be limited. Neither design considers the effect of other low-dehydration energy cations that may find themselves in high-charged, expandable layer sites.

A series of experiments at different temperatures, run durations, and solution compositions was conducted to see if layer charge could be created by structural substitution in K-deficient systems.

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Table 1. Major oxide chemical analyses and cation-exchange capacity of starting smectite.[1]

Oxide	Wt. %
SiO_2	67.8
Al_2O_3	23.4
Fe_2O_3	3.87
MgO	2.14
CaO	1.37
Na_2O	1.20
K_2O	0.33
Total	100.11
CEC	80 meq/100 g

[1] Analysis on ignited basis; total Fe as Fe_2O_3.

PROCEDURE

The smectite used in this study was a Wyoming Na-bentonite, ground to <200 mesh, obtained from the Benton Clay Company, Elizabeth, New Jersey. A <1-μm size fraction was collected by centrifugation methods to remove much of the quartz and other non-smectite material commonly found in this bentonite. Wet chemical analyses of the major elements and a series of cation-exchange capacity (CEC) measurements using 1.0 N $BaCl_2$ were made on the starting material (Table 1).

Chemical analyses resulted in the following structural formula for the starting material.

$$K_{0.02}Na_{0.13}Ca_{0.08}(Si_{3.98}Al_{0.02})(Al_{1.59}Fe_{0.16}Mg_{0.21})_{1.97}O_{10}(OH)_2$$

K-saturation by repeated washings with 1.0 N KCl, followed by washings with distilled water, of the starting smectite produced no significant collapse of expandable layers.

The experimental runs consisted of 20 mg of smectite in 0.50 ml of an artificial basalt ground water. Two Na-silicate-bicarbonate solutions were prepared (Table 2); one with Ca that best approximated Hanford Reservation ground-water chemistry, and the second without Ca in order to work with a simpler system (Pennsylvania State University, Materials Research Laboratory solutions E-19 and E-20). The initial pH of these solutions was adjusted to 9.8 to correspond to near surface values of basalt ground waters (Deutsch *et al.*, 1982). Slurries having a 25:1 water to solid ratio were loaded into gold capsules, cold-seal crimped, and placed in autoclaves at 150° or 250°C and 300 bars pressure for 1 to 6 months.

Upon completion of a run the capsule was weighed; any weight loss or gain was attributed to leakage and the results from that run invalidated. Capsules that remained sealed were then opened, and the solution and solid were washed with distilled water and filtered to yield 25 ml for solution analyses. These analyses were performed on a dc-arc plasma emission spectrometer (DCP) using standards prepared with similar background chemistry. Oriented mounts on glass slides were prepared from slurries of the filtered solids. The mounts were analyzed by X-ray powder diffraction with an automated Philips diffractometer, using CuKα radiation, a theta-compensating slit, and a graphite monochromator. Slides were X-rayed in an air-dried state and after solvation with ethylene glycol at 60°C for 6 hr. The glycolated samples were then dried at <60°C to drive off the ethylene glycol complex without decomposing within the interlayers (Brindley and Brown, 1980). The clay was then saturated with K by repeated washings with 1.0 N KCl, followed by washings with a distilled water-acetone mixture. Both air-dried and glycolated samples were again X-rayed. Cation-exchange capacity (CEC) measurements were made on reacted clays from several of the longer duration runs made at 250°C. The measurements were made using 1.0 N $BaCl_2$ washings prior to saturation of the clay with K.

Table 2. Solution analyses of Pennsylvania State University/ Materials Research Laboratory solutions E-19 and E-20.

Species	E-19 (mmole/liter)	E-20 (mmole/liter)
Si^{4+}	1.78	1.60
Al^{3+}	0.004	0.002
Na^+	9.13	5.22
Ca^{2+}	—	0.80
K^+	0.004	0.003

The extent of reaction was estimated from the illite/smectite mixed-layer expandability using calculated diffractograms (Reynolds, 1980; Środoń, 1980). Expandabilities were determined by the peak location of the $(002)_{10}/(003)_{17}$ and $(003)_{10}/(005)_{17}$ reflections on glycolated samples if observed. As a last resort, the peak shift of the $(001)_{10}/(002)_{17}$ reflection was used. Środoń's (1980) technique for determining illite/smectite expandability is very sensitive to the 001 basal spacing (see Środoń, 1980, figure 8). The 001 basal spacing for the reacted smectites in this study was close to 16.9Å.

RESULTS

None of the smectites, reacted at either temperature in either of the initial solutions or over the range of run durations, exhibited strong evidence of layer collapse or alteration as recognized by XRD of glycolated samples. Several showed a slight broadening or increased low-angle background of the 17-Å reflection, but no appreciable peak shift of the 001 basal reflection or any of its integral basal reflections was noted (Figure 1). Line broadening may have been due solely to particle-size and orientation differences between the initial and reacted sample. Several samples exhibited small, diffuse reflections at 20.8° and 26.6°2θ that probably

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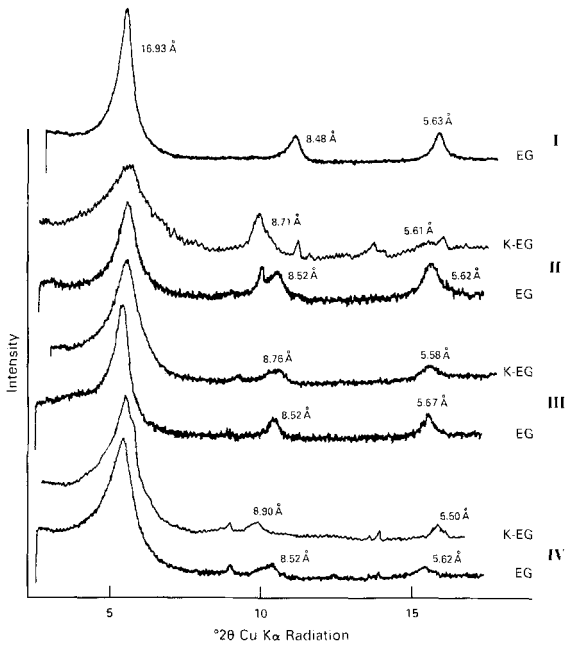


Figure 1. X-ray powder diffractograms of glycolated (EG) and K-saturated, glycolated (K-EG) smectites from runs in E-19 solution at 250°C. I. Starting smectite. II. 90 days. III. 120 days. IV. 180 days. EG-symmetry of 001/001 and location of 001/002 amd 002/003 reflections suggest minimal alteration of smectite. K-EG-shifts of 001/002 and 002/003 reflections indicate the presence of non-expandable layers.

corresponded to quartz. No other new phases were recognized.

The reacted samples that were saturated with K and glycolated showed a recognizable shift in the smectite basal reflections. The 17-Å reflection was broader and had greater assymmetry in its low and high background than the diffractions from unsaturated samples (Figure 1). The spacings of the higher-order basal reflections were no longer integral, the shifts of these maxima suggested random interstratifications containing as much as 40% collapsed (illite) layers (Table 3). Expandability estimates by both the Reynolds (1980) and Środoń (1980) methods were made.

Solution analyses are presented as the concentration of cation released during the reaction (Table 4) and as a reaction progress variable, the percentage released relative to that available in the starting solid material (Table 5). The contribution of the initial fluid composition has been subtracted from the raw analyses. The amounts of released Mg and K were generally quite low, <1.5 mmole/liter, although they amounted to several percent of the available Mg and as much as 10% of the available K. The solution analyses indicate that a small amount of Ca was released in the Na-silicate solution experiments (E-19), yet no Ca was detected in the final solutions of runs that began with Na-Ca silicate compositions (E-20). No clear relationship is

Table 3. X-ray powder diffraction data for K-saturated, glycolated, mixed-layer illite/smectite.[1]

Temp. (°C)	Days	°2θ 001/002	°2θ 002/003	°2θ 003/005	% Exp. layer Reynolds (1980)	% Exp. layer Środoń (1980)	CEC meq/ 100 g
			E-19 solution				
150	30	10.34	15.77	26.50	95	90	—
150	90	10.28	15.85	—	90	75	—
150	120	10.20	15.87	26.42	83	75	—
150	180	10.20	15.90	—	80	70	—
250	30	10.28	15.80	26.45	90	85	—
250	90	10.16	15.77	—	90	85	—
250	120	10.10	15.88	—	75	76	40
250	180	9.94	16.11	26.50	62	58	40
			E-20 solution				
150	30	10.38	15.77	—	100	90	—
150	90	10.28	15.81	26.50	90	85	—
150	120	10.22	15.84	—	85	75	—
150	180	10.25	15.88	26.45	83	75	—
250	30	10.27	15.80	26.50	90	83	—
250	90	10.20	15.90	—	77	74	—
250	120	10.15	15.86	—	80	77	50
250	180	10.02	16.06	—	65	63	—

[1] Peak locations of major reflections and estimates of percentage of expandable layers are based on methods of Reynods (1980) and Środoń (1980) and cation-exchange capacity of reaction product.

apparent between the amounts of these elements released and the original solution composition or temperature. Abundant Na, both in terms of absolute concentrations and in relation to the amount available from the starting material, was released during exper-

Table 4. Material released from smectite during hydrothermal alteration.[1]

Temp. (°C)	Days	Al	Ca	K	Mg	Na	Si
			E-19 solution				
150	30	5.67	—	0.51	0.79	6.87	20.57
150	90	4.59	0.25	0.51	0.58	14.04	15.36
150	120	6.30	0.32	0.46	1.25	25.22	23.21
150	180	6.52	0.30	0.51	1.25	23.83	22.32
250	30	1.03	—	0.49	—	8.26	7.75
250	90	2.07	1.40	0.32	1.50	15.39	17.68
250	120	5.37	—	1.15	1.04	32.61	19.07
250	180	2.81	1.02	0.61	1.58	30.56	16.36
			E-20 solution				
150	30	9.62	—	1.02	1.67	24.25	30.18
150	90	7.41	—	0.51	1.50	49.13	23.75
150	120	6.48	—	0.64	1.60	37.35	21.78
150	180	7.78	—	0.79	1.50	30.87	25.18
250	30	1.67	—	0.28	0.21	20.00	10.18
250	90	4.44	—	0.59	1.08	76.90	21.54
250	120	3.07	—	0.41	0.79	21.74	17.86
250	180	1.67	—	0.51	0.16	26.09	10.57

[1] Corrected for the original solution composition. In terms of mmole/liter.

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Table 5. Solution analyses converted to relative percentage released from original material.

Temp. (°C)	Days	Al	Ca	K	Mg	Na	Si
			E-19 solution				
150	30	1.34	—	8.00	1.60	19.39	1.99
150	90	1.04	1.11	8.00	1.18	39.63	1.50
150	120	1.50	1.44	7.20	2.52	71.16	2.23
150	180	1.55	1.33	8.00	2.52	67.24	2.15
250	30	0.24	—	7.60	—	23.31	0.74
250	90	0.49	6.22	3.60	3.02	43.44	1.53
250	120	1.27	—	18.00	2.10	92.02	1.84
250	180	0.67	4.55	9.60	3.19	86.25	1.57
			E-20 solution				
150	30	2.29	—	16.00	3.36	68.71	2.90
150	90	1.76	—	8.00	3.02	138.65	2.28
150	120	1.54	—	10.00	3.24	104.90	2.10
150	180	1.85	—	12.40	3.02	87.12	2.42
250	30	0.40	—	4.40	0.42	56.44	0.97
250	90	1.06	—	9.10	2.18	217.18	1.77
250	120	0.73	—	6.60	1.60	61.34	1.72
250	180	0.40	—	8.00	0.34	73.62	1.02

iments with both kinds of solution. Several samples "released" more Na than was available in the starting smectite, a reflection of both Na contamination and the imprecision of Na analyses. The amount of Na released was not dependent on temperature, although the E-20 solution runs released a greater proportion of available Na than the Ca-deficient E-19 runs. This difference may reflect a Ca-Na exchange in the E-20 samples, a result consistent with Benson's (1982) values for exchange constants for monovalent and divalent cations on smectites.

CEC measurements on several of the high-temperature samples from runs of 120 and 180 days revealed a significant loss in capacity (Table 3). The starting smectite had a CEC of 80 meq/100 g. Two samples reacted in E-19 solutions at 250°C for 120 and 180 days had capacities of 40 meq/100 g, and a third sample reacted in E-20 solution at 250°C for 120 days had a capacity of 50 meq/100 g.

More Si and Al were released at low temperature than in the 250°C experiments, a relationship that was most noticeable in the Na-Ca silicate E-20 solutions. In addition, the release of Si and Al tended to be more stoichiometric in the low-temperature runs (Table 6), whereas the solution Si:Al ratio in the 250°C runs was twice that of the original smectite.

DISCUSSION

The collapse of a small percentage of smectite layers after the reacted samples were saturated with K suggests that highly charged expandable layers were formed during the hydrothermal process. It is not certain whether the increase of layer charge was localized within the tetrahedral or the octahedral sheets. The extent

Table 6. Comparison of smectite alteration rate constants.[1]

	Temp. (°C)	Solution	K (days^{-1})
This study	150	E-19	2.01×10^{-3}
	250	E-19	2.62×10^{-3}
	150	E-20	1.65×10^{-3}
	250	E-20	2.20×10^{-3}
Eberl and Hower (1976)	260	Distilled water	1.2×10^{-3}
	300	Distilled water	4.3×10^{-3}
	340	Distilled water	13.0×10^{-3}
	390	Distilled water	45.0×10^{-3}
Roberson and Lahann (1981)	270	400K/9400Na	6.0×10^{-3}
	270	400K	7.8×10^{-3}
	350	400K	74.0×10^{-3}

[1] K/Na values are in ppm.

of reaction and the production of highly charged expandable layers was tracked by saturating the reaction products with K and determining the percentage of resultant collapsed layers as a function of run duration. A plot of the percentage of collapsed layers vs. time (Figure 2) produced a series of straight lines, the slopes of which are equal to reaction rates (Eberl and Hower, 1976). The strong linear correlation is suggestive of a first-order kinetics process, with greater rates being observed at higher temperatures. Slopes for these lines were forced through the origin on the reasonable assumption of 100% expandable smectite at the start of each experiment. At each temperature, the reaction rate was slower in the Ca-bearing solution (E-20) than in the Na-only solutions. These reaction rates are somewhat greater than those obtained by Eberl and Hower (1976) in their illitization experiments using ideal beidellite compositions at higher run temperatures (Table 6). In contrast, the rates from this present study are significantly less than those observed in high-temperature experiments with Na-K fluids (Roberson and Lahann, 1981).

An Arrhenius plot of reaction rates with only two

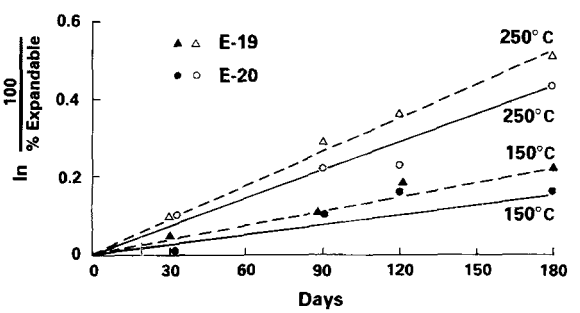


Figure 2. First-order kinetics plots of data in Table 3. Calculated slopes are reaction rates for each temperature and solution composition. Note that E-20 (Ca-present) experiments have lower reaction rates at each temperature than E-19 runs.

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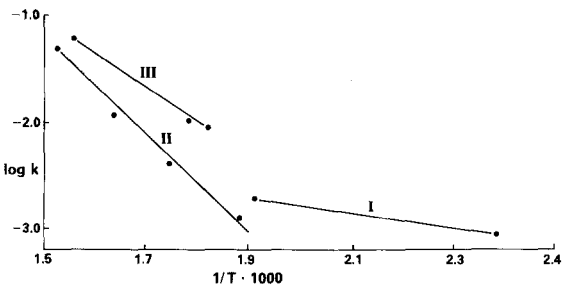


Figure 3. Arrhenius plot of smectite alteration rates vs. inverse of absolute temperature for several different studies in smectite alteration rates. I. Present study. II. Eberl and Hower (1976). III. Roberson and Lahann (1981). Change in slope may indicate either temperature dependent activation energies or differences in experimental design.

run temperatures is a rather brash effort in evaluation of these results, but the comparison with previous workers' results is intriguing enough to warrant attention. The slopes of the lines are proportional to the activation energy of reaction. The activation energy of the Na-only solution is 3.5 kcal/mole, whereas the Ca-bearing solution has an activation energy of 3.0 kcal/mole (Figure 3). The quasi-activation energies from these experiments are significantly less than those obtained by Eberl and Hower (1976), 19.6 kcal/mole, and Roberson and Lahann (1981), 30 kcal/mole.

At least four possible explanations for the large difference in activation energies between this study and previous work exist:

(1) A different reaction mechanism exists between the high- and low-temperature experiments. The change in slope on the Arrhenius plot suggests separate low- and high-temperature processes. Curvature in the plot may also indicate temperature-dependent activation energies (Lasaga, 1984). The accepted interpretation of the higher activation energies is that they represent the energy required to break Si–O and Al–O bonds, a mechanism expected in the illitization process (Eberl and Hower, 1976; Roberson and Lahann, 1981; Lahann and Roberson, 1980). Activation energies from the present study are more suggestive of a reaction controlled by the diffusion of material to and from the surface (Berner, 1980). The results from this study suggest then that low-temperature illitization reactions are diffusion controlled, a conclusion that is difficult to reconcile with possible mechanisms of transformation.

(2) The reduced activation energies may be the result of catalytic activity on the smectite surfaces due to the adsorption of ions or surface defects (Lasaga, 1984). The high activation energies obtained by Eberl and Hower (1976) were from experiments in distilled water, thereby minimizing catalytic activity. Numerous experiments of silicate minerals dissolution in a variety of solution compositions have resulted in activation energies intermediate to pure diffusion-controlled values and those associated with the breaking of Si–O–Al bonds (Lasaga, 1984). Silica release from smectite in several brine compositions also resulted in intermediate activation energies (Lahann and Robertson, 1980). It is reasonable that the reduced activation energies in this present study are at least partially due to catalysis of the breaking of bonds on the smectite surface by the presence of ionic species in the reacting fluid.

(3) The present and previous studies reflect two different processes and reaction products. The present experiments actually did not create illitic layers; rather they produced sufficient layer charge so that saturation with K led to collapse of some layers to a 10-Å spacing. Eberl and Hower (1976) assumed that sufficient K was available for complete illitization, although it was possible that the subsquent addition of K might have collapsed more layers. Greater collapse in the Eberl and Hower (1976) experiments would have resulted in faster reaction rates and lower activation energies. In essence, their study and those that preceded it attempted to estimate activation energies of the overall smectite to illite transformation without utilizing similar elementary reactions that make up the reaction mechanism.

(4) Differences may exist in the surface effects function A/M (surface area of reacting solid over the mass of solution, Rimstidt and Barnes, 1980). The water/clay ratio was greatly different in the present experiments compared with those of Eberl and Hower (1976) and Roberson and Lahann (1981). Because it was not possible to estimate the surface area of the glass/synthetic clay in Eberl and Hower's (1976) study, it was difficult to determine A/M values for the normalization of the rate data. The similarity in starting materials for the present study and for the experiments by Roberson and Lahann (1981) suggested that any difference in reaction rates should be a response to differences in the mass of water available or the water/clay ratio in the reaction vessel. Roberson and Lahann (1981) used a water/clay ratio of 100:1, in contrast to the 25:1 ratio in the present study, and obtained reaction rates 2.0 to 3.6 times faster at 270°C, depending upon the solution chemistry, than those observed in the present study (Table 6).

Although the solution analyses shed little light on the reaction kinetics, they do provide some information on the mechanism of the transformation of smectite to illite. The uptake of Ca and release of Na is most likely associated with cation exchange, although the data do not balance stoichiometrically (Table 5). That divalent Ca is preferentially exchanged over the alkali Na is due to their differences in hydration energy and valence (Eberl, 1980; Benson, 1982).

The release of Al and Si, and to a lesser degree Mg, appears to be stoichiometric with respect to original

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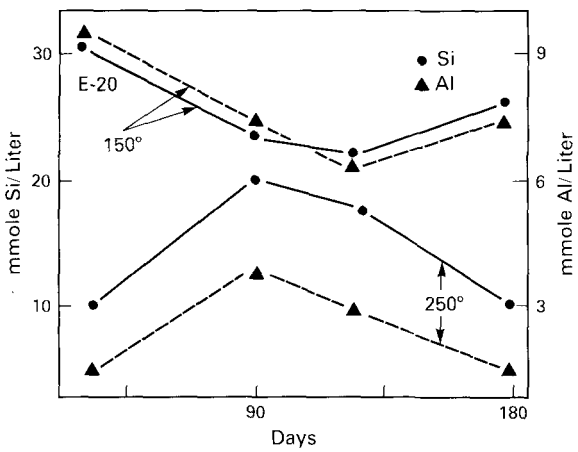


Figure 4. Al and Si released from smectite vs. time in E-20 experiments. Relationships between Si and Al values for individual runs show greater release of Si relative to Al at 250°C than at 150°C. Behavior suggests reprecipitation of Al-rich phases in the 250°C experiments.

smectite composition in the low-temperature (150°C) experiments (Figure 4). Stoichiometric balance would be expected if illitization was a solution-reprecipitation process, wherein both tetrahedral and octahedral sheets were dissolved congruently. The results from the 250°C runs (Figure 4) indicate that twice as much of the available Si was removed from the clay compared to Mg and Al. Rather than evidencing incongruent dissolution for the higher-temperature reaction, the solution analyses more likely represent a minimum amount of dissolved smectite; perturbations from stoichiometry probably resulted from the reprecipitation of new phases. Small amounts of quartz were recognized in several of the runs, even though the reflections were usually too faint and diffuse for a quantitative estimate. No crystalline Al-Mg phases were recognized, although the initial solution pH favored the formation of noncrystalline $(Al,Mg)(OH)_n$ phases. Thus, the distribution of ionic species in solution does not reflect selective dissolution, but rather selective precipitation or interlayer adsorption of phases having compositions different from the starting material (Churchman and Jackson, 1976). That this phenomenon is more noticeable at higher temperatures in these experiments most likely reflects increased rates of nucleation and precipitation rather than shifts in thermodynamic stability fields (Holdren and Adams, 1982).

A plot of solution analyses vs. reaction time produced no clear trend, either in terms of reaction kinetics or the absence of time-dependent changes that would suggest equilibration. The absence of linear or parabolic curves is not surprising because in many previous works on aluminosilicate dissolution kinetics most of the change in curve character occurred with the first few days (Holdren and Adams, 1982; see Fleer, 1982, for review).

CEC differed from what might have been expected by the creation of additional layer charge in expandable layers. Inasmuch as the measurements were made prior to K-saturation and collapse, the CEC should have increased, reflecting the formation of vermiculite-like layers. The observed decrease therefore suggests that many exchange sites were filled or clogged with material that did not dramatically affect the smectite's XRD behavior. It is possible that noncrystalline Al-Mg hydroxides were formed within the interlayer on available exchange sites (Roberson and Sass, 1982; Churchman and Jackson, 1976).

CONCLUSIONS

The results of this study have several implications for understanding the mechanism of the smectite to illite transformation along with the geotechnical behavior of smectite-rich barriers in basalt repositories. The creation of layer charge sufficient to lead to the transformation of smectite to illite requires no K in the starting solution. For illitization to proceed, K must be introduced only when sufficient layer charge is present. This study illustrates the importance of the presence in solution of other interlayer cations, all of which have higher energies of dehydration than K, in inhibiting the reaction rate. The reduced reaction rate with Ca-bearing solutions supports Eberl's (1980) contention that the relative extent of inhibition is directly correlative to the hydration energy of the interlayer cation.

The low-temperature (150°C) dissolution analyses suggest that the breakdown of smectite involves the congruent dissolution of octahedral and tetrahedral sheets. The mechanism as to how sufficient Al replaces Si in the tetrahedral sheet is still unclear, although the present closed-system study and other analyses of natural and experimental diagenetic systems indicate that sufficient Al can be derived from the smectite alone (Eberl, 1978; Roberson and Lahann, 1981; Boles and Franks, 1979; Howard, 1981).

The reaction rates obtained here are faster than those of some previous studies, but are the only ones determined at the low temperatures that might be expected in a repository. In addition, the activation energies calculated here are much lower than those obtained in high-temperature experiments (Eberl and Hower, 1976; Roberson and Lahann, 1981). The difference between a mechanism controlled by surface reactions, e.g., breaking of Si–O and Al–O bonds, and one influenced by diffusional processes, e.g., rate of supply of K to the interlayer, needs to be considered further. The lack of agreement among studies in the literature on illitization kinetics also needs to be considered with respect to fundamental reaction rates. All of the previous work

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on illitization kinetics reports rates specific to localized and individual surface effects, such as water/clay ratio and effective surface area. A surface area term to correct for these individual effects is needed to determine the fundamental reaction rate for the illitization of smectite.

The present study suggests that even at relatively low repository temperatures of 150°C and in the presence of waters devoid of K, smectite is susceptible to alteration. The rate of alteration is dependent upon temperature, the fluid composition and its content of inhibiting cations, and the surface effects function which considers water/clay ratio and available surface area. The very low water content of a barrier, along with the limited permeability which inhibits the removal and supply of various ions, will effectively reduce the reaction rate and the development of layer charge in the smectite.

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Резюме—Насыщенный натрием бентонит из Уаиоминга подвергался термальной реакции при 150° и 250°С в течение от 30 до 180 дней для определения скоростей перемены смектита, которые могут быть использованы для проекта хранилища отходов атомной промышленности. Использовались растворы Na-Ca, обедненные калием для определения роли межслойных катионов в процессе образования слоев с высоким зарядам в смектитах. Результаты помагают объяснить механизм и историю различных стадий диагенетического превращения смектита в иллит. Рентгеновская порошковая дифракция (РПД) реагированной глины указала на малый эффект этой реакции на характер отражения 17 Å, даже после 180 дней при 250°С. Насыщение калием этих реагированных глин и вторичное исследование РПД указало на разрушение некоторых слоев смектита, оставляя не больще, чем 60% расширяющихся слоев. Построение слойного заряда достаточного для разрушения слоев после насыщения обменными катионами с низкой энергией гидратации не требует присутствия калия в реагирующей жидкости. Постоянные скорости реакции иллитизации, определенные на основании разрушения К-насыщенных слоев равны от $1,0 \times 10^{-3}$ до $2,8 \times 10^{-3}$/день с величинами энергии активации <3,5 ккал/моль. Присутствие Са в растворе Na-силиката-бикарбоната немного уменьшило постоянные скорости иллитизации. Эти постоянные скорости являются выше, чем предполагаемые на основании результатов исследований состава бейделитовых стекел при повышенных температурах, но ниже, чем значения, полученные во время исследований натуральных глин в искуственной морской воде. Удаление Si, Al, и Mg во время опытов при 150°С указывает на соответствующее этому процессу

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растворение смектита. В противоположность, при 250°C удаление Al не было стехиометрическим с Si; только половина располагаемого Si удалялась. В результате проделанных экспериментов может быть сделан вывод, что некристаллические, обогащенные Al фазы быстрее формировались при повышеной температуре более вероятно, чем имели место различные механизмы растворения при разных температурах. Катионо-обменные способности для нескольких из этих реагированных смектитов являлись значительно меньшими, чем предполагалось, указывая на закупорку межслойных мест, возможно комплексами Al. [E.G.]

Resümee—Na-gesättigter Bentonit von Wyoming wurde hydrothermal bei 150° und 250°C für 30 bis 180 Tage zur Reaktion gebracht, um die Umwandlungsgeschwindigkeiten von Smektit zu bestimmen, die im Hinblick auf die Planung der Lagerung radioaktiver Abfälle verwendet werden können. Na-Ca-Lösungen, arm an K, wurden verwendet, um den Einfluß zu untersuchen, den Zwischenschichtkationen auf die Bildung von hohen Schichtladungen in Smektit haben. Die Ergebnisse liefern Einblick in den Mechanismus und die zeitliche Abfolge der verschiedenen Stufen bei der diagenetischen Umwandlung von Smektit in Illit. Röntgenpulverdiffraktometer-Analysen (XRD) des Tons nach der Reaktion zeigten kaum einen Einfluß auf die Art des 17 Å Reflexes, selbst nach einer Reaktion von 180 Tagen bei 250°C. Die Sättigung dieser reagierten Tone mit K und die erneute Untersuchung mit XRD zeigte die Kontraktion einiger Smektitlagen, so daß maximal nur 60% expandierbare Lagen übrig blieben. Die Entwicklung einer Schichtladung, ausreichend um eine Kontraktion durch Sättigung mit einem Austauschkation, das eine niedrige Hydratationsenergie hat, zu verursachen, benötigt kein K in der reagierenden Flüssigkeit. Beschwindigkeitskonstanten für die Illitisierungs-Reaktionen, wie sie aus der Kontraktion durch K-Sättigung bestimmt wurden, liegen zwischen $1{,}0 \times 10^{-3}$ und $2{,}8 \times 10^{-3}$/Tag mit Aktivierungsenergien <3,5 kcal/Mol. Calcium in Na-Silikatbikarbonatlösung erniedrigt die Geschwindigkeitskonstante der Illitisierung geringfügig. Diese Geschwindigkeitskonstanten sind höher als man sie aus der Extrapolation von Untersuchungen von Gläsern mit Beidellitzusammensetzung erwartet hat, aber niedriger als die Werte, die man bei Untersuchungen natürlicher Tone in künstlichem Meerwasser erhalten hat. Die Freisetzung von Si, Al, und Mg in den Experimenten bei 150°C deuten auf eine kongruente Auflösung des Smektits hin. Im Gegensatz dazu war bei 250°C die Freisetzung von Al nicht stöchiometrisch zu Si; nur etwa die Hälfte des zur Verfügung stehenden Si wurde freigesetzt. Es wird jedoch nicht ein unterschiedlicher Auflösungsmechanismus bei den zwei Temperaturen angenommen, sondern viel mehr, daß bei höheren Temperaturen nichtkristalline Al-reiche Phasen mit größeren Geschwindigkeiten gebildet werden. Die Kationenaustauschkapazitäten für einige dieser reagierten Smektite waren beachtlich kleiner als erwartet, was eine Belegung der Zwischenschichtplätze—wahrscheinlich durch Al-Komplexe—vermuten läßt. [U.W.]

Résumé—On a fait réagir de la bentonite saturée de sodium du Wyoming hydrothermalement à 150°C et 250°C pendant une période de 30 à 180 jours pour déterminer des vitesses d'altération de smectite qui pourraient être appliquées au dessin de dépôts de déchets nucléaires. Des solutions Na-Ca déficientes en K ont été utilisées pour déterminer le rôle de cations intercouche dans la création de charge de couche élevée dans des smectites. Les résultats permettent un aperçu du mécanisme et de la chronologie des différentes étapes dans l'altération de la smectite en illite. Des analyses de diffraction des rayons-X (XRD) de l'argile réagie ont montré qu'il y avait très peu d'effet sur le caractère de la réflection 17 Å, même après 180 jours à 250°C. La saturation par le potassium de ces argiles réagies, et la réexamination par XRD a indiqué la fermeture de quelques couches de smectite, laissant au plus seulement 60% de couches expansibles. Le développement de charge de couche suffisante pour causer la fermeture lors de la saturation avec un cation d'échange à basse énergie d'hydration n'exige pas K dans le fluide réagissant. Des constantes de vitesse pour les réactions d'illitisation déterminées d'après la fermeture saturée de K sont entre $1{,}0 \times 10^{-3}$ et $2{,}8 \times 10^{-3}$/jour avec des énergies d'activation <3,5 kcal/mole Ca dans une solution bicarbonate-silicate-Na n'a reduit que légèrement les constantes de taux d'illitisation. Ces constantes de taux sont plus élevées que celles anticipées à partir de l'extrapolation d'études de verres de composition beidellite à de plus hautes températures, mais sont plus basses que les valeurs obtenues dans des études d'argiles naturelles dans l'eau de mer artificielle. Le détachement de Si, Al, et Mg dans des expériences à 150°C suggère une dissolution congruente de la smectite. Par contraste, à 250°C, le détachement d'Al n'était pas stoichiométrique avec Si; aussi peu que la moitié de Si relative disponsible a été relâchée. Plutôt que des mécanismes différents pour la dissolution aux deux températures, la conclusion est que les phases riches en Al non cristalline se sont formées à des vitesses plus élevées aux plus hautes températures. Les capacités d'échange de cations pour plusieurs de ces smectites réagies étaient plus basses de manière significative, suggérant un embouchement des sites intercouche, peut-être par des complexes-Al. [D.J.]

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