

## BRØNSTED ACIDIFICATION OBSERVED DURING HYDROTHERMAL TREATMENT OF A CALCIUM MONTMORILLONITE

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**Abstract**—An aluminous Ca-montmorillonite from southern Manitoba, Canada, has been shown to generate very low pH values in clay/groundwater slurries over a range of ionic strength of the groundwater (fresh and saline) and temperatures from 25°–90°C. Dialysis experiments as well as results of X-ray diffraction and FTIR vibration spectroscopy point to an acidification mechanism that involves hydrolysis of exchangeable Al<sup>3+</sup> ions, thus releasing protons, and the subsequent intercalation of gibbsite-like hydroxy-Al complexes into the smectite lattice forming a non-expandable “Al”-montmorillonite.

**Key Words**—Aluminium, Ca-smectite, Gibbsite-type intercalates.

### INTRODUCTION

Interaction of Al ions with smectite has been studied widely because of its importance for a variety of natural and technical processes ranging from ecological and toxicological problems in acidified terrestrial and aquatic environments (Lou and Huang, 1988) to property improvement of Al-exchanged montmorillonite as highly selective acid catalyst (“solid proton source”) for conversion of a variety of hydrocarbons (Laszlo, 1987), including thermally stable pillared Al<sub>13</sub> smectites (Pinnavaia, 1983), to mechanical stabilization of formation clays (Reed, 1972). Similar studies have been carried out to investigate problems related to maintaining integrity, i.e., high swelling capacity and thus low permeability in a nuclear fuel waste vault (Johnston and Miller, 1984) since it is well known that incorporation of Al into montmorillonite reduces its swelling capacity considerably (El-Rayah and Rowell, 1973; Oades, 1984).

The present study was undertaken to investigate a natural aluminous Ca-montmorillonite of Upper Cretaceous age from southern Manitoba, Canada, that produces very low pH values quickly when brought in contact with groundwaters of both low and high ionic strength at low and high temperatures. The significance of this behavior is underscored by the importance of retaining swelling properties, sorption capacity for radionuclides, and mechanical integrity of smectites to be used as buffer materials as proposed by several national nuclear waste management programs in countries such as Canada, the United States, Sweden, Switzerland, and others. Also, the increasing use of swelling clays such as bentonites to seal immobilized/stabilized industrial and domestic waste makes the retention of the swelling properties over the lifetime of the repos-

itory very desirable. Besides this, polymer/montmorillonite composites (Theng, 1974) attracted attention as new materials with improved properties and reduced product cost for applications such as a water-stopping agent in enhanced oil recovery operations (Rong *et al.*, 1985) and as a soil amelioration agent. The beneficial properties of these composites could be seriously compromised by a low pH generated on interaction with groundwater since the swelling-shrinking behavior of such composites is strongly controlled by the pH of the surrounding aqueous medium (Gao and Heimann, 1993).

### MATERIALS CHARACTERIZATION AND METHODS

The clay investigated was a smectite with a mineralogical composition of 80% montmorillonite, 10% illite-smectite mixed layer mineral, 6% quartz, 3% gypsum, 1% carbonate, and 0.5% organic matter (Quigley, 1984). This material comes from the Pembina Member of the Vermillion River Formation of Upper Cretaceous age, in southern Manitoba, Canada.

The clay fraction <0.63 μm was obtained by gravitational settling, repeating the sedimentation cycle twelve times. The suspended clay was concentrated by membrane filtration, dried at room temperature, and homogenized manually in an agate mortar. To characterize the mineralogical nature of the clay, the cation exchange positions were first saturated with Mg<sup>2+</sup> ions to yield a homoionic material by shaking the water-dispersed clay with 0.5 N MgCl<sub>2</sub> solution in a test tube for 20 min. After this treatment, the clay was separated from the solution by membrane filtration and washed Cl-free with distilled water.

The X-ray diffraction pattern (CoK $\alpha$  radiation) of an oriented aggregate (Kinter and Diamond, 1956) showed that the <0.63 μm-fraction consists of almost pure montmorillonite with only a trace of quartz (Figure 1,

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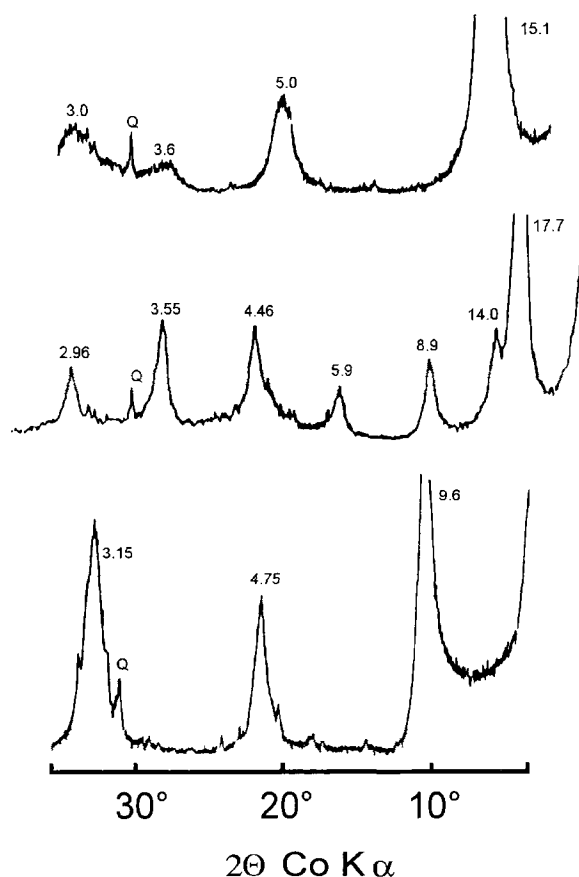


Figure 1. X-ray diffraction pattern (CoK $\alpha$  radiation) of smectite saturated with Mg<sup>2+</sup>-ions (top), saturated with Mg<sup>2+</sup>-ions and glycol solvated (middle) and saturated with Li<sup>+</sup>-ions, heated to 300°C and glycol solvated (Greene-Kelly test, bottom). Q = quartz.

top). On ethylene glycol solvation, the d(001) interplanar spacing shifted from 15.1 to 17.7 Å. A small peak at 14.0 Å was thought to indicate some hydroxy-Al interlayers in the montmorillonite (Figure 1, middle). The Greene-Kelly test (Greene-Kelly, 1953), applied to determine the location of charge deficiency, failed to show swelling by shifting of the d(001) interplanar spacing, thus indicating the absence of beidellite (Figure 1, bottom).

To obtain information on the chemical composition of the montmorillonite the <63  $\mu\text{m}$  clay fraction was analyzed by Inductively Coupled Plasma Spectrometry (ICPS; ARL Model 3580B). Total Fe was determined as Fe<sub>2</sub>O<sub>3</sub> using SnCl<sub>2</sub>. Fe<sup>2+</sup> was analyzed colorimetrically using TPTZ (2,4,6-Tripyridyl-1,3,5-triazine). Fe<sup>3+</sup> was calculated by difference. The amount of adsorbed cations in the interlayer was as follows: Na<sup>+</sup> 12.1, Ca<sup>2+</sup> 27.2, Mg<sup>2+</sup> 15.6 and Al<sup>3+</sup> 5.0 meq/100 g according to Quigley (1984) and Singh (1982). The cation exchange capacity (CEC) was measured by Na acetate exchange of the Mg<sup>2+</sup> homoionized clay and found to be 136

Table 1. Nominal composition in mg/liter of groundwaters used (Abry *et al.*, 1982).

| Element          | GGW                    | WN-1                   | SCSSS                  |
|------------------|------------------------|------------------------|------------------------|
| Na               | 8.0 ± 0.5              | 1900 ± 100             | 5000 ± 155             |
| K                | 2.6 ± 0.3              | 13 ± 0.3               | 44 ± 3                 |
| Mg               | 3.8 ± 0.3              | 69 ± 3                 | 210 ± 4                |
| Ca               | 13.0 ± 0.5             | 2130 ± 150             | 13,800 ± 300           |
| Sr               | <0.05                  | 26 ± 0.5               | 19 ± 0.5               |
| Fe               | <0.1                   | <0.1                   | 0.7 ± 0.1              |
| Si               | <1.0                   | 3 ± 1                  | 19 ± 1                 |
| Cl               | 5.0                    | 6460 ± 400             | 34,300 ± 1700          |
| SO <sub>4</sub>  | 8.9 ± 0.2              | 632 ± 10               | 790 ± 10               |
| NO <sub>3</sub>  | 0.6                    | n.d.                   | 50 ± 2                 |
| F                | 0.2                    | n.d.                   | n.d.                   |
| HCO <sub>3</sub> | n.d. <sup>1</sup>      | n.d.                   | 10                     |
| TDS <sup>2</sup> | 1.0 × 10 <sup>-4</sup> | 1.3 × 10 <sup>-2</sup> | 7.0 × 10 <sup>-2</sup> |
| I <sup>3</sup>   | 1.4 × 10 <sup>-3</sup> | 2.7 × 10 <sup>-1</sup> | 1.37                   |
| pH               | 6.5 ± 0.5              | 7 ± 0.5                | 7 ± 0.5                |

<sup>1</sup> n.d. = not determined.

<sup>2</sup> TDS: total dissolved solids in [kg/liter].

<sup>3</sup> Ionic strength in [mol/liter].

cmol<sub>c</sub>/kg. The composition of the montmorillonite was tentatively calculated from the results of the chemical analyses assuming that the partition of Al between tetrahedral and octahedral sites was determined by the molar fractions and charge balance of, respectively, Si and (Mg + Fe). The interlayer charge was based on oxygen equivalency (Gast, 1977) and was found to be remarkably high. This is in accord with the high cation exchange capacity measured. The calculation suggests a very tentative formula: M<sub>0.51</sub><sup>+</sup>[Si<sub>3.88</sub>Al<sub>0.12</sub>][Al<sub>1.38</sub>-Fe(II)<sub>0.21</sub>Fe(III)<sub>0.07</sub>Mg<sub>0.42</sub>]O<sub>10</sub>(OH)<sub>2</sub>.

The <0.63  $\mu\text{m}$  clay fraction was suspended in synthetic groundwaters of different ionic strengths at temperatures of 25°, 70°, and 90°C. The groundwaters used were a granitic groundwater (GGW) and two saline groundwaters (WN-1 and Standard Canadian Shield Saline Solution, SCSSS) (Abry *et al.*, 1982). These groundwaters were selected to represent shallow fresh groundwater and deep saline groundwater, respectively, as frequently encountered in granitic rocks of the Canadian Shield (Frape *et al.*, 1984). The compositions of the three groundwaters are shown in Table 1.

Three types of experiments were performed. First, hydrothermal dissolution experiments were carried out on clay/groundwater mixtures with ratios of 2, 25 and 50 g/liter in polypropylene vessels for 28 days. After reaction, the solutions were filtered through 0.45  $\mu\text{m}$  Nucleopore filters. The pH values of the solutions were measured with a Beckman 170 pH meter and corrected to the temperatures of the experiments with an algorithm provided by the geochemical equilibrium code SOLMNQ (Goodwin and Munday, 1983). The number of data points obtained at 90°C were 17 for SCSSS, 8 for WN-1, and 7 for GGW. The solutions were then acidified with nitric acid, and the concentrations of Si and Al were determined by Atomic Absorption Spec-

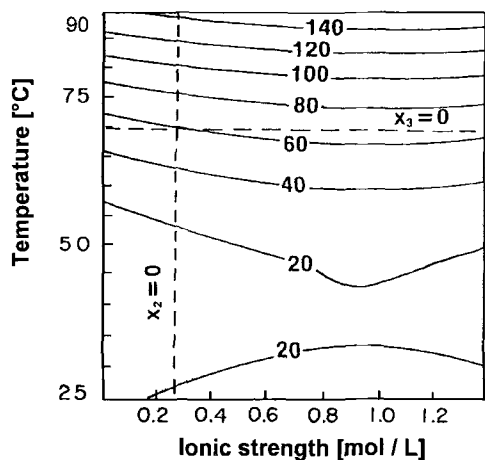


Figure 2. Isopleths of equal concentration of silicon released during hydrothermal dissolution of montmorillonite as a function of the ionic strength of the groundwater and the temperature (for details, see text).

trospecty (AAS) and ICPS, respectively. The solid clay was washed, dried at 60°C, and analyzed by XRD and FTIR.

Second, clay/solution mixtures with ratios of 5 and 10 g/liter were immersed in polypropylene vessels for 14 days at 90°C. Solutions selected were double distilled water (DDW), granitic groundwater (GGW), the two saline groundwaters (WN-1 and SCSSS), sodium citrate (0.5 mol/liter) and sodium tartrate (0.5 mol/liter). After reaction, the solution concentrations of Mg, Al and Fe were measured by ICPS.

Third, dialysis experiments were performed using a montmorillonite/SCSSS slurry (50 g/liter). Initially this slurry was allowed to react under constant stirring for 60 min. Then it was transferred to a dialysis tube and immersed into SCSSS. The solution was changed daily for 28 days, and the pH values were measured just before changing the solution. In the exchanged solutions, the Al concentrations were measured by ICPS.

## EXPERIMENTAL RESULTS

Hydrothermal experiments were performed in groundwaters of different ionic strengths ( $X_2$ ) (see Table 1) at temperatures of 25°, 70°, and 90°C ( $X_3$ ) and with clay/groundwater ratios of 2, 25, and 50 g/liter ( $X_1$ ). Figure 2 shows the isopleths of the concentration of dissolved Si in mg/liter as a function of the ionic strength of the groundwater and the temperature (Heimann, 1985; Heimann and Stanchell, 1984). The values  $X_i = 0$  denote the medium values of the selected parameter levels according to the applied Box-Behnken experimental design (Box and Behnken, 1960). The equation of the response surface, i.e., the Si concentration in mg/liter,

$$[\text{Si}] = 32.0 + 18.1X_1 - 17.1X_1^2 + 6.25X_2 - 8.1X_2^2 + 61.0X_3 + 57.1X_3^2, \quad (1)$$

Table 2. pH of clay/groundwater slurries as a function of contact time (clay/groundwater ratio 50 g/liter).

| Time (days)     | GGW <sup>1</sup> (90°C) | WN-1 <sup>2</sup> (90°C) | SCSSS <sup>3</sup> (90°C) | SCSSS <sup>4</sup> (25°C) |
|-----------------|-------------------------|--------------------------|---------------------------|---------------------------|
| 0.001 (1.5 min) | 6.10                    | 7.49                     | 7.18                      | 7.18                      |
| 0.004 (5 min)   |                         |                          |                           | 6.61                      |
| 0.01 (15 min)   | 4.80                    | 4.32                     | 4.20                      | 5.10                      |
| 0.04 (1 hour)   |                         |                          |                           | 4.61                      |
| 1 (1 day)       | 3.45                    | 3.50                     | 3.31                      | 3.65                      |
| 2               |                         |                          | 3.35                      | 3.27                      |
| 3               |                         | 3.35                     | 3.03                      |                           |
| 4               | 3.46                    | 3.32                     | 3.07                      | 3.10                      |
| 5               |                         |                          | 3.10                      |                           |
| 6               |                         |                          | 3.04                      |                           |
| 7               | 3.42                    | 3.20                     | 3.00                      | 3.08                      |
| 8               |                         |                          | 2.96                      |                           |
| 9               |                         |                          | 2.92                      |                           |
| 10              |                         |                          | 2.89                      |                           |
| 11              |                         |                          | 2.90                      |                           |
| 12              |                         |                          | 2.84                      |                           |
| 13              |                         |                          | 2.93                      |                           |
| 14              | 3.39                    | 3.10                     | 2.95                      | 3.06                      |
| 28              | 3.55                    | 3.11                     | 2.95                      | 3.08                      |

<sup>1</sup>  $\Gamma = 3.86$ ,  $n = -0.06$ ,  $r^2 = 0.90$ .

<sup>2</sup>  $\Gamma = 3.71$ ,  $n = -0.08$ ,  $r^2 = 0.87$ .

<sup>3</sup>  $\Gamma = 3.50$ ,  $n = -0.08$ ,  $r^2 = 0.90$ .

<sup>4</sup>  $\Gamma = 3.70$ ,  $n = -0.09$ ,  $r^2 = 0.96$ .

obtained by standard statistical treatment of the analytical data, shows that the dissolved Si concentration is strongly positively correlated with the parabolic temperature parameter. A weaker correlation exists between the Si concentration and the clay/groundwater ratio. The ionic strengths of the groundwaters play only a minor role. The negative parabolic term of  $X_2$  indicates, however, that an increase in ionic strength, i.e., an increase in Ca in the solution, may lead to Ca uptake on the clay and reduction in the rate of silica dissolution (Lahann and Roberson, 1980).

During hydrothermal treatment of the montmorillonite, the solution pH dropped in all groundwaters at all temperatures and concentration ratios investigated. The  $\Delta\text{pH}$  values ranged from 1.0 and 2.6 in GGW at 25°C and 90°C, respectively, to 5.4 and 4.2 in SCSSS at 25°C and 90°C, respectively. Initially, the pH values showed a sharp drop followed by a more gradual decrease. Table 2 shows the measured pH values for the three groundwaters investigated at a clay/groundwater ratio of 50 g/liter and at 90°C and for SCSSS at a clay/groundwater ratio of 50 g/liter and at 25°C. The time dependence of the pH can be described by a power function  $\text{pH} = \Gamma \cdot t^n$  for  $t \leq 28$  days. The pre-exponential factors ( $\Gamma$ ), the exponents ( $n$ ) and the regression coefficients ( $r^2$ ) are also given in Table 2. The value of  $n$ , i.e., the rate of pH change, is the slope of a line in the log pH-log t plane.

The observation that low pH can be generated during interaction of smectitic clays with electrolytes is not new (e.g., Mortland, 1968; Eberl, 1978; Gerstl and Ban-

Table 3. Solution concentrations in mg/liter of Mg, Al, and Fe dissolved from Ca-montmorillonite and pH (clay/solution ratios 5 and 10 g/liter, 90°C, 14 days).

| Sample           | pH   | Mg     | Al    | Fe     |
|------------------|------|--------|-------|--------|
| DDW-blk          | 6.43 | <0.001 | <0.10 | <0.001 |
| DDW-5 g/liter    | 3.27 | 32     | 20.8  | 3.0    |
| DDW-10 g/liter   | 3.26 | 63     | 46    | 3.8    |
| GGW-blk          | 7.09 | 4.2    | <0.10 | <0.01  |
| GGW-5 g/liter    | 3.38 | 39     | 21.1  | 2.27   |
| GGW-10 g/liter   | 3.27 | 68     | 51    | 4.0    |
| WN-1-blk         | 7.54 | 63     | <1.0  | <0.1   |
| WN-1-5 g/liter   | 3.32 | 115    | 119   | 3.8    |
| WN-1-10 g/liter  | 3.15 | 165    | 187   | 6.7    |
| SCSS-blk         | 7.01 | 185    | <1.0  | <0.1   |
| SCSS-5 g/liter   | 3.14 | 250    | 185   | 6.3    |
| SCSS-10 g/liter  | 2.97 | 310    | 360   | 9.4    |
| Na-Ci-blk        | 8.76 | 0.66   | 0.47  | 0.36   |
| Na-Ci-5 g/liter  | 7.00 | 70     | 213   | 42     |
| Na-Ci-10 g/liter | 6.71 | 139    | 420   | 88     |
| Na-Ta-blk        | 7.87 | 0.06   | 0.15  | 0.10   |
| Na-Ta-5 g/liter  | 5.63 | 63     | 219   | 51     |
| Na-Ta-10 g/liter | 5.35 | 132    | 420   | 100    |

blk = blank, DDW = double distilled water, GGW = granitic groundwater, WN-1 and SCSS = saline groundwaters, Na-Ci = sodium citrate (0.5 mol/liter), Na-Ta = sodium tartrate (0.5 mol/liter).

in, 1980; Johnston and Miller, 1984). There is, however, considerable controversy about the nature of this acidification. In a review paper on chemical reactions on clays, Laszlo (1987) attributed higher surface acidity of smectites to terminal hydroxyl groups and bridging oxygen atoms on clay surfaces (Brønsted acidity) as well as to adsorption of bases at Lewis acidic sites.

Bulk acidity, on the other hand, is thought to be due to the polarizing effect of the highly charged cation on water molecules in the restricted interlayer space. Several lines of reasoning suggest that the experimental results reported here can indeed be explained by assuming the operation of a Brønsted acidity mechanism based on hydrolysis of Al ions.

The amounts of Mg, Al, and Fe leached during hydrothermal treatment of the Ca-montmorillonite at 90°C for clay/solution ratios of 5 and 10 g/liter are shown in Table 3. The element concentration in solution is directly proportional to the mass of clay. In saline solutions the amounts of Mg and Al leached from the Ca-montmorillonite are much higher than those in DDW or GGW. Sodium citrate and sodium tartrate solutions leach preferentially Al and Fe from the clay.

To support the conjecture that the reason for acidification is the hydrolysis of exchangeable Al ions, a set of dialysis experiments were performed. Figure 3 shows the concentration of  $Al^{3+}$  in mmol/liter as well as the pH development of SCSSS contacted with 50 g/liter Ca-montmorillonite. During prolonged contact (curing) for 60 min, the pH dropped from an initial value of 7.3 to a value of around 3.6. After this, the slurry was transferred to a dialysis tube and immersed into SCSSS. The solution was changed daily, and the pH measured. Dialysis for 28 days shows a gradual recovery of the pH whose value can be described by a power function  $pH = 3.46 \cdot t^{0.22}$  ( $r^2 = .97$ ; solid curved line). Within a day, the concentration of extractable  $Al^{3+}$  ions reached a sharp maximum at 2.5 mmol/liter, and then fell gradually off over a period of 10 days to very low values. Thus, the Al concentration behaves in a complementary fashion, e.g., the steep drop in pH during curing is accompanied by an Al peak that grad-

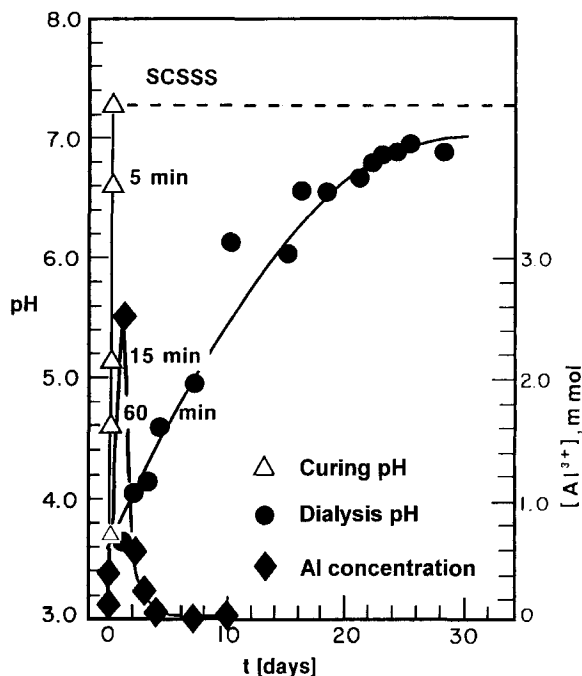


Figure 3.  $Al^{3+}$  concentration and development of pH during curing and dialysis of Ca-montmorillonite in SCSSS at 25°C over 28 days. The time intervals on the "curing line" are counted from the beginning of the reaction.

ually disappears as the pH increases. This points to adsorption of Al ions at the surface and/or in the interlayer space of the clay. Such adsorption sites show a strong preference for trivalent cations over the competing divalent  $\text{Ca}^{2+}$  (McBride and Bloom, 1977; Foscolos, 1968) or the proton (Walker *et al.*, 1988). It should be noted that exceptionally high Al concentrations (116 mg/liter) were also observed by Singh (1982) in GGW that had been in contact with a Ca-montmorillonite from the same location (clay/groundwater ratio = 100 g/liter) for 500 hours. In his study, however, the pH values were not measured and consequently no conclusions could be drawn with respect to an acidification mechanism.

A second line of evidence comes from X-ray diffraction studies of hydrothermally treated Ca-montmorillonite. Figure 4 (top) shows an X-ray diffractogram of the  $<0.63 \mu\text{m}$  fraction of Ca-montmorillonite hydrothermally treated at  $90^\circ\text{C}$  with SCSSS<sup>2</sup> and subsequently glycolated. The main feature of the diffractogram is a strong peak at  $13.8 \text{ \AA}$  and non-rational higher order peaks ( $d(002) = 4.77 \text{ \AA}$ ,  $d(003) = 3.05 \text{ \AA}$ ) that did not expand on solvation with glycol (e.g., Johnston and Miller, 1984). This suggests the formation of a nonexpandable chlorite- or sudoite-type structure of an "Al"-montmorillonite with hydroxy-Al intercalation complexes in the interlayer space. Indeed, after overnight treatment of the same clay with a 0.5 mol/liter sodium tartrate solution at  $60^\circ\text{C}$  to dissolve the Al complexes, the basal spacings expanded again on solvation with glycol and yielded the complete (001) series with  $1 < l < 7$  (Figure 4, bottom). Note that the X-ray pattern shown at the bottom of Figure 4 is almost identical to that of the original montmorillonite shown in the middle of Figure 1.

The formation of aluminous intercalates is also supported by FTIR. Figure 5 shows FTIR spectra of the two characteristic stretching vibrations at  $3707$  and  $3556 \text{ cm}^{-1}$  of an intercalated gibbsite-like ring complex  $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_2]_6^{6+}$  equidistant from the Al-OH stretching vibration of the montmorillonite structure at  $3630 \text{ cm}^{-1}$  (van der Marel and Beutelspacher, 1976). They may be indicative of a local sudoitic structural arrangement consistent with the X-ray diffraction results, and the two observed IR peaks can be attributed to the stretching vibration between Al and the inner ( $3707 \text{ cm}^{-1}$ ) and the outer ( $3556 \text{ cm}^{-1}$ ) OH-groups of the ring complex (Weismiller *et al.*, 1967). The spectrum shown in Figure 5 was obtained by subtracting the original Ca-montmorillonite ( $<0.63 \mu\text{m}$ ) spectrum from the spectrum of a Ca-montmorillonite hydrothermally reacted in SCSSS at  $90^\circ\text{C}$ .

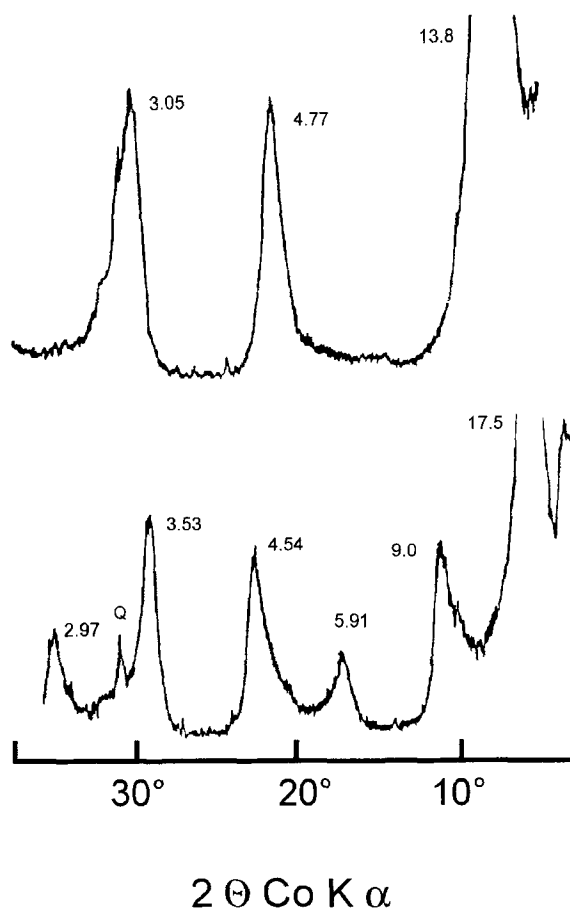
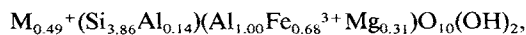


Figure 4. X-ray diffraction pattern (CoK $\alpha$  radiation) of Ca-montmorillonite treated in SCSSS at  $90^\circ\text{C}$  and solvated with glycol (top) and that of the same sample treated at  $60^\circ\text{C}$  in a 0.5 mol/liter sodium tartrate solution overnight (bottom).

## DISCUSSION

The interlayer charge and the cationic exchange capacity of the investigated Ca-montmorillonite are remarkably high and, thus, more characteristic of a vermiculite-type structure.<sup>3</sup> This rather unique behavior is partly corroborated by the work on other smectites of western Canada inner plains origins in Saskatchewan and Alberta. Mermut *et al.* (1984) obtained for smectites from southern Saskatchewan the average composition



again showing a high interlayer charge. According to Warren *et al.* (1992), smectites from a calcareous till in east central Saskatchewan develop towards a pyrophyllitic composition when subjected to acid weathering, thus decreasing the charge sites in the octahedral sheet and concurrently increasing the interlayer charge.

<sup>2</sup> Similar patterns have been obtained during treatment in GGW and WN-1 at elevated temperatures.

<sup>3</sup> Quigley (1984) suggests adsorbed  $\text{H}_3\text{O}^{+}$ -ions to account for the high cation exchange capacity.

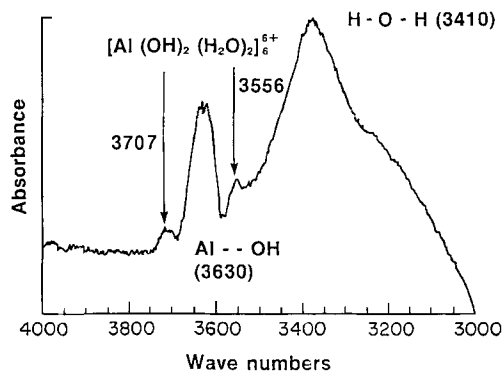
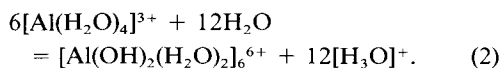


Figure 5. FTIR differential spectrum obtained by subtracting from the spectrum of Ca-montmorillonite reacted hydrothermally in SCSSS at 90°C that of the original Ca-montmorillonite.

The investigated Ca-montmorillonite is presumably the product of sedimentation in a shallow marine or lacustrine environment and probably derived from volcanic ash (Quigley, 1984). It is found in bentonite beds associated with a noncalcareous marine shale in the Vermillion River Formation of Upper Cretaceous age in southern Manitoba. Al dissolved from the octahedral sheet by acidic weathering may have been moved to and adsorbed at interlayer positions as suggested by Warren *et al.* (1992) or preferentially sorbed at the outer edges of the clay mineral platelets (Pusch, 1983). The Ca-montmorillonite transforms on contact with groundwater to non-expandable "Al"-montmorillonite whose characteristic structural features are gibbsite-like hydroxyl complexes. The formation of those complexes is coupled with the release of protons from water molecules coordinated with a solvated Al ion, according to:



This mechanism has been suggested by Rich (1968) and Oades (1984) to explain the formation of Al-montmorillonite. The low pH values resulting from Ca-montmorillonite/groundwater interaction favors the adsorption and intercalation of the hydroxy-Al complex over that of the  $\text{Al}^{3+}$  ion because the former has a much greater ionic radius, a much higher charge, and, therefore, a much lower hydration energy that promotes closer approach of the complex to the clay surface and, in turn, stronger electrostatic interaction (Bloom *et al.*, 1977). The gibbsite-like Al polyhydroxy rings may be either preferentially adsorbed in the counterion layer on planar sides of the clay mineral platelets (Pusch, 1983) or may be intercalated between smectite layer stacks to form a chloritic-sudoitic structure as observed (Figure 4). In contrast to this, hydroxy-Fe interlayers form only very slowly, if at all (Carstea,

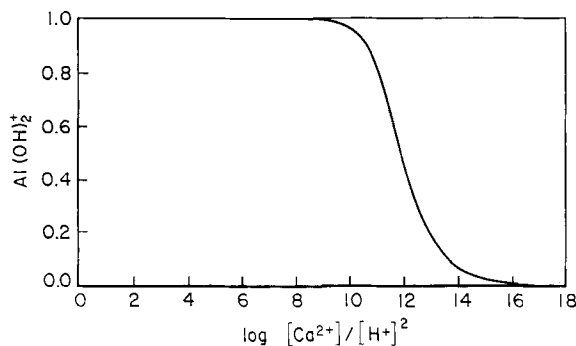
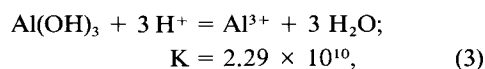


Figure 6. Equivalent fraction of aluminium in solution at equilibrium in a Ca-saturated montmorillonite as a function of  $\log[\text{Ca}^{2+}]/[\text{H}^+]^2$ .

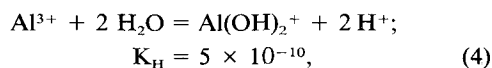
1968), and hydroxy-Mg interlayers are stable only in alkaline systems (Carstea, 1967). The former has been confirmed by long-term leaching of montmorillonite clays at elevated temperatures in the presence of Fe(II)-silicate (Oscarson and Heimann, 1988).

The pH dependence of the  $\text{Ca}^{2+}$ - $\text{Al}^{3+}$  exchange reaction is shown in Figure 6, which depicts the equivalent fraction of Al in solution at equilibrium in a Ca-saturated montmorillonite as a function of  $\log[\text{Ca}^{2+}]/[\text{H}^+]^2$ .  $\text{Al}(\text{OH})_2^+$  was assumed to be the prevalent Al species because it constitutes the core of the gibbsite-like complex and is the dominant Al species at pH values between 5.4 and 6.7 in solutions saturated with  $\text{Al}(\text{OH})_3$  (Baes and Mesmer, 1976). It is recognized, however, that other hydroxy-Al species can be present.

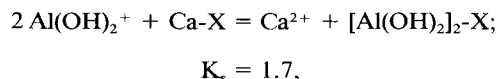
From the equilibrium constant (K) for the dissolution reaction of amorphous  $\text{Al}(\text{OH})_3$  (Benson and Teague, 1980):



the equilibrium constant ( $\text{K}_H$ ) for the second-stage hydrolysis reaction of  $\text{Al}^{3+}$  (Lindsay, 1979):



and the selectivity coefficient ( $\text{K}_s$ ) for the exchange reaction<sup>4</sup> (Bruggenwert, 1979):



where "X" refers to the smectite backbone structure, the equivalent fraction of  $\text{Al}(\text{OH})_2^+$  can be calculated according to Eberl (personal communication, 1988) as:

<sup>4</sup> There is considerable controversy about the validity of any cation exchange constant of clays since its value depends very strongly on the conditions under which the exchange experiments are conducted.

$$\begin{aligned} (\text{Al}(\text{OH})_2^+) = & (\{K_T K^4 [\text{H}^+]^4 + 4 K_T K^2 [\text{H}^+]^2 [\text{Ca}^{2+}] \}^{1/2} \\ & - K_T K^2 [\text{H}^+]^2) / 2 [\text{Ca}^{2+}], \end{aligned} \quad (6)$$

where  $K_T = K_H K_s = 8.5 \times 10^{-10}$ .

This function has been plotted in Figure 6 against  $\log[\text{Ca}^{2+}]/[\text{H}^+]^2$  (e.g., Heimann, 1988). Over a wide range of both Ca activities in solution and pH values, it is evident that the exchange positions of the montmorillonite structure are saturated by  $\text{Al}(\text{OH})_2^+$ . At  $\log[\text{Ca}^{2+}]/[\text{H}^+]^2 > 9$ , the competition for exchange sites starts; and at  $\log[\text{Ca}^{2+}]/[\text{H}^+]^2$  values of around 16, all positions are occupied by  $\text{Ca}^{2+}$ .

### CONCLUSIONS

The acidification of aluminous montmorillonites has important implications as far as their use as highly selective agents for catalytic conversion of hydrocarbons is concerned. Furthermore, reduction of swelling capacity and, thus, increase of permeability to groundwater by hydroxy-Al complex intercalation can seriously compromise the safe performance of repositories for radioactive, heavy metal, and mixed wastes. This problem may be compounded by the loss of sorption capacity for radionuclides and toxic transition metal ions since stable hydroxy-Al complexes will block potential exchange sites for high valency ions. Silica dissolved during interaction of groundwater and Ca-montmorillonite at elevated temperature, as shown in the experiments, will precipitate in the temperature gradient established in a radioactive waste repository, and will thus decrease the porosity and permeability of the clay. Embrittlement, however, would likely decrease the mechanical stability of the clay by stress-induced fracturing which, in turn, would promote Darcian flow (Fournier, 1983). This is akin to the formation of syneresis cracks in fresh-water clays exposed to saline brines (Hudec and Yanful, 1983). The investigation suggests that the very low pH-values generated by interaction of an aluminous montmorillonitic clay with groundwaters of varying ionic strengths at temperatures between 25° and 90°C can be related to hydrolysis of exchangeable Al ions.

The hydroxy-Al complexes formed can be intercalated in the montmorillonite forming locally an "Al"-montmorillonite. While this is in accord with previous findings, the most unexpected result of the study was the extremely fast exchange and thus hydrolysis reaction that led very quickly to low pH values. This is in contrast to results obtained previously on other acidic clays (Eberl, 1978; Gerstl and Banin, 1980) that showed similar but much slower pH changes.

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