

PROPERTIES OF HYDROXY-AL AND -Cr INTERLAYERS IN MONTMORILLONITE

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Abstract—In environments contaminated with Cr, the interlayers of expandable layer silicates may serve as sinks for this potentially toxic element. As a means of determining the potential for smectites to serve as sinks for Cr, the precipitation products of Al and Cr in the interlayers of a montmorillonite were examined. Five montmorillonite (SWy-1) clay suspensions were treated with preweighed amounts of AlCl_3 and CrCl_3 to give five $\text{Al}/(\text{Al} + \text{Cr})$ molar ratios (1.0, 0.67, 0.5, 0.33, 0) with a total trivalent cation (M^{3+}) concentration of 600 $\text{cmol}(+)/\text{kg}$ clay. The clay-cation suspensions were titrated with 0.1 N NaOH to give a $\text{NaOH}/\text{M}^{3+}$ molar ratio of 2.5. Analysis of the solid-phase reaction products showed that the cation exchange capacity and specific surface of all clays were reduced. Chromium reduced the exchangeability of the interlayers while Al increased the thermal stability. X-ray diffraction analysis revealed that all Al-containing interlayer materials formed similar gibbsite-like polymers. Data from infrared spectroscopy indicated that both Al and Cr were present within the same polymer. Differential thermal analysis and thermogravimetric tracings showed that the rapid collapse of the interlayer in the Cr end-member upon heating was due to a low-temperature loss of hydroxyls. It was not possible to identify all interlayer structures in the Cr end-member. Data from X-ray photoelectron spectroscopy showed all Cr to be Cr(III). Displacement of the interlayer material became more difficult as Cr content increased. The least exchangeable interlayers, therefore, may be found in environments containing the most Cr.

Key Words—Aluminum, Chromium, Interlayering, Montmorillonite, XPS.

INTRODUCTION

Intercalation of hydroxy-Al polymers in expandable layer silicates is a well-known natural process. Laboratory studies have also been successful in producing hydroxy interlayers of Al (Rich, 1968; Goh and Huang, 1986; Barnhisel and Bertsch, 1989), Fe (Carstea *et al.*, 1970; Martin-Luengo *et al.*, 1989), Zr (Yamanaka and Brindley, 1979), Ni (Yamanaka and Brindley, 1978), and Cr (Brindley and Yamanaka, 1979; Carr, 1985). The hydroxy-Cr interlayered montmorillonite prepared by Brindley and Yamanaka (1979) displayed a basal spacing near 16.8 Å, considerably larger than the 14.4 Å spacing of chlorite. As the first observed diffraction peak was broad and higher orders were weak or absent, the authors suggested that the basal spacings were probably variable. These workers were unable to determine the structure of the hydroxy-Cr polymers. While studying hydration states of interlamellar Cr in montmorillonite, Carr (1985) observed that the interlayer region catalyzed the formation of larger hydroxy-Cr polymers. The first-order reflections of the interlayered clays varied from 10 Å to 15 Å and tended to be broad, indicating variable basal spacings. As the exact composition of the hydroxy-Cr polymers was not known, the structures of the interlayered species were not determined.

Hydroxy-aluminochromium interlayers have been synthesized by those interested in the petrochemical applications of clays (Carrado *et al.*, 1986). Upon calcination, the hydroxy polymers convert to fixed oxide pillars, which give the clay catalytic properties. Although the properties of the oxide pillars have received much attention, the nature of unheated hydroxy-aluminochromium species remains unclear. In environments contaminated with Cr, the interlayers of expandable layer silicates may serve as sinks for Cr, which can be toxic when in solution (Bartlett and Kimble, 1976). The structure and stability of the hydroxy-aluminochromium polymers, therefore, merit attention.

In this study, hydroxy interlayers were formed with five different $\text{Al}/(\text{Al} + \text{Cr})$ molar ratios in a standard montmorillonite. The structure and stability of the interlayer material were examined to determine the possible interactions between Al and Cr.

MATERIALS AND METHODS

The montmorillonite (SWy-1, Crook County, Wyoming) was obtained from the Source Clays Repository of The Clay Minerals Society. Prior to fractionation, the clay was Na-saturated by washing five times with 1 N NaCl then washed free of Cl^- as determined by the AgNO_3 test. Five grams of the $< 2 \mu\text{m}$ fraction were

Table 1. Selected properties of the six clays.

Al/ (Al + Cr) molar ratio	pH		CEC	KCl extraction		CaCl ₂ extraction		Specific surface (m ² /g)
	Initial	Final		Al	Cr	Al	Cr	
Control	7.36	7.43	95.1	0	0	0	0	781
1.0	5.31	4.62	34.4	21.0	0	27.3	0	403
0.67	5.59	4.90	30.4	12.7	3.6	15.3	2.7	383
0.5	5.82	5.24	27.6	6.3	2.6	9.8	1.8	388
0.33	5.97	5.48	25.5	3.9	1.8	6.6	1.0	385
0	6.63	6.31	45.2	0	0	0	0	652

suspended in 2 liters deionized water. Prewedged amounts of AlCl₃ and CrCl₃ were added to separate clay suspensions to give five Al/(Al + Cr) molar ratios (1.0, 0.67, 0.5, 0.33, 0). The total trivalent cation (M³⁺) concentration in each suspension was 600 cmol(+)/kg clay. The five clay-cation suspensions were stirred vigorously and titrated at 1 ml/min with 0.1 N NaOH until a final NaOH/M³⁺ molar ratio of 2.5 was reached. A sixth clay suspension containing 5 g of the <2 μ m fraction, which did not have any Al, Cr, or NaOH added, served as the control. All six suspensions were brought to final volumes of 3 liters and then transferred to capped bottles. The suspensions were aged at 23 \pm 0.5°C for 30 days and were agitated daily. After aging, each suspension was separated into its filtrate and solid phase by ultrafiltration through a Millipore filter of 0.025 μ m pore size. The solid phase of each sample was washed free of Cl⁻ as determined by the AgNO₃ test.

Cation exchange capacity (CEC) of each whole solid-phase reaction product was determined by first saturating the clay with Ca using 1 N CaCl₂ and then displacing the Ca with 1 N MgCl₂ (Rich, 1961). The displaced Ca was measured with atomic absorption spectroscopy (AAS). Exchangeable Al and Cr were determined by washing 100 mg clay subsamples five times (9 ml each) with 1 N KCl. Separate 100 mg subsamples were washed using 1 N CaCl₂. Aluminum and Cr in the extracts were determined by AAS. Specific surfaces of the clays were determined by adsorption of ethylene glycol monoethyl ether (EGME) as described by Carter *et al.* (1986). X-ray powder diffraction (XRD) analysis of oriented specimens was carried out with a Philips PW 1710 diffractometer using CuK α radiation. For infrared (IR) analysis, KBr wafers were prepared (1.5% w/w) and scanned from 4000 to 600 cm⁻¹ in a Perkin Elmer 881 spectrometer. Differential thermal analysis (DTA) and thermogravimetric (TG) tracings were obtained by heating the clays from ambient to 1000°C at 10°/min in an argon atmosphere (PL Thermal Sciences, model PL-STA 1500). X-ray photoelectron spectroscopy (XPS) was carried out using a Perkin Elmer PHI-5300 ESCA spectrometer; the spectra were produced using MgK α radiation.

RESULTS AND DISCUSSION

Chemical analysis and surface area

The pH values of all clay suspensions except the control decreased over the aging period (Table 1). The final pH values of the suspensions were the result of the relative amounts of Al and Cr. Specifically, those with more Al had lower pH values, indicating the greater hydrolyzing power of Al (Baes and Mesmer, 1976). At the end of the aging period, there was no Al or Cr detected in the supernatant (data not shown). The treated clays displayed varying amounts of CEC reduction. Generally, the trend in CEC values mimicked the trend in final solution pH values. Smaller hydroxy polymers are known to predominate at lower pH values (Hsu, 1989). Smaller polymers, as they display a greater positive charge per cation than larger polymers, are more effective at reducing CEC. The greatest CEC reductions, therefore, were observed for samples that had the lowest final solution pH values. However, one cannot rely entirely on final solution pH to predict relative CEC values. Variation in CEC was also due to the formation of external phase hydroxy polymers. As the Al in external phase hydroxy polymers does not contribute to CEC reduction, the CEC would be higher than if all Al were interlayered. The Al end-member, therefore, which contained external phase hydroxy polymers, had a higher CEC than what one would have predicted from pH alone.

The amounts of Al and Cr extracted from the five samples are shown in Table 1. The interlayer which was the most difficult to displace was the Cr end-member (Al/(Al + Cr) = 0). Neither KCl nor CaCl₂ displaced any Cr from this clay. The presence of Al, however, increased the extractability of the Cr by inducing the formation of smaller polymers, resulting in greater total polymer surface area. In all samples there was less extractable Cr than Al, even where the interlayer material contained more Cr. The major reason for this difference is that Cr is more strongly sorbed than Al on the 2:1 layer surface (Mengel and Kirkby, 1987; Drljaca *et al.*, 1992).

All interlayered clays had lower specific surfaces than the control (Table 1). The specific surface of the Al end-member (Al/(Al + Cr) = 1.0) was 403 m²/g. The clays of intergradient composition had even smaller specific surfaces. Their smaller specific surfaces may be explained by the presence of smaller interlayer polymers. As noted, the presence of both Al and Cr in the interlayer induced the formation of smaller polymers. Clays that contained smaller polymers must also have contained a greater number of those polymers. A larger number of polymers would have caused the packing of the ethylene glycol molecules to be interrupted more frequently, thereby resulting in less efficient packing. The result would be a lower measured specific surface. The Cr end-member had a specific surface of 652 m²/g.

As the XRD data indicated the interlayer had a spacing of 7–8 Å before addition of EGME (Figure 1), the ethylene glycol molecules could have formed a bilayer similar to that found in non-interlayered smectites without any further expansion of the interlayer. Upon addition of EGME, further expansion would have allowed even greater amounts of ethylene glycol to be adsorbed, resulting in the relatively high measured specific surface.

X-ray powder diffraction

The basal spacing of the control prior to heating was 11 Å (Figure 1). Interlayering of the montmorillonite with a gibbsite-like sheet was indicated by the nearly 14 Å spacings observed for samples with Al/(Al + Cr) molar ratios = 1.0, 0.67, 0.5, 0.33 (Figure 1). A basal spacing of 16.7 Å was calculated for the Cr end-member, which is similar to the 16.8 Å spacing reported by Brindley and Yamanaka (1979). As the basal reflection of the Cr end-member was broad, the basal spacings were shown to be variable. A secondary basal spacing of 19.2 Å was also present. This spacing would arise if Keggin molecules were present in the interlayer (Pinnavaia *et al.*, 1984; Plee *et al.*, 1985; Schutz *et al.*, 1987; Fripiat, 1988). The Keggin molecule, which consists of a central tetrahedron surrounded by four sets of three octahedra, is approximately 9 Å in size and can accommodate many different cations (Cotton and Wilkinson, 1988). Although two gibbsite-like sheets stacked in the c-direction would also yield a spacing of approximately 19 Å, such gibbsite-like structures are unlikely in the Cr end-member because even a simple 14 Å spacing was not observed. A basal spacing of approximately 19 Å would also arise from the intercalation of hydrolytic trimers where the three octahedra are arranged linearly. Dimensions of individual Cr(III) hydrolytic oligomers were determined by Drljaca *et al.* (1992). Based on the dimensions these workers calculated for a dimer, a linear hydrolytic trimer would be 9.5–10 Å along the longest axis. Intercalation of these trimers with their long axes oriented parallel to the c-axis would give the observed 19 Å basal spacing.

The clays of intergradient composition and the Al end-member displayed basal spacings of about 14 Å, which indicated the formation of a similar gibbsite-like structure in each (Figure 1). It is likely that Cr substituted for Al in the hydroxy polymers. If there were separate hydroxy-Cr polymers, one would expect basal spacings of about 16.7 Å as well as the 14 Å spacings due to the gibbsite-like interlayers. In a system containing both Al and Cr, therefore, the data indicate that Al determines the structure which will form. Diffraction peaks at about 4.83 Å showed that all clays treated with Al also contained minor amounts of external phase Al hydroxide. As these diffraction peaks were broad, one cannot easily attribute them to either gibbsite or nordstrandite. Whether gibbsite or nord-

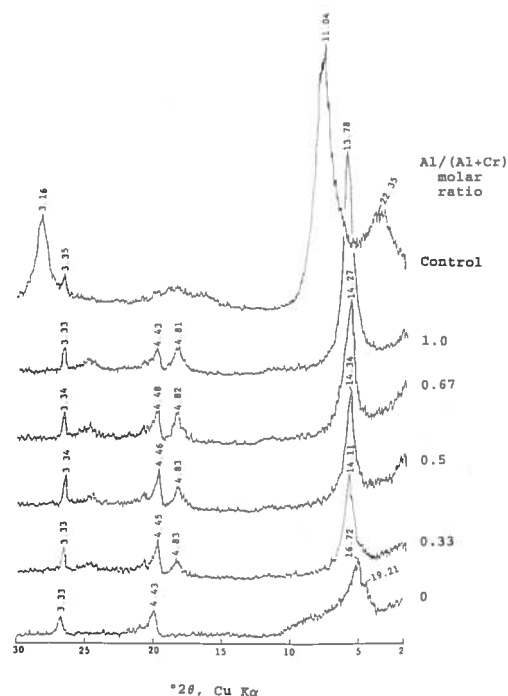


Figure 1. X-ray diffraction patterns of the six clays under ambient conditions. All clays were analyzed at 54% relative humidity. (Spacings are in Å.)

strandite, however, the broad diffraction peaks showed the Al hydroxide to be poorly crystalline.

The intensity of the basal reflections decreased as Cr content increased (Figure 1). This indicated that Cr increased the disorder of the interlayer material. As the clays were heated to increasingly higher temperatures, the interlayers began to collapse (Figure 2). The least heat-stable interlayer was the Cr end-member. At 300°C the interlayer collapsed so that there were no discernible peaks. At 400°C, however, the montmorillonite basal spacing of 9.7 Å appeared. The other hydroxy polymers displayed greater heat-stability. The basal spacings of these other four clays decreased gradually to 11–12 Å at 550°C. The presence of Al increased heat-stability, possibly by promoting the formation of gibbsite-like "islands" that prop open the interlayer.

Glycerol solvation increased the basal spacings of all samples (Figure 2). The basal spacings of most interlayered clays increased only slightly (about 1 Å). The basal spacing of the Cr end-member, however, increased by about 5 Å. This indicates that the hydroxy-Cr polymers may be distributed mainly around the margin of the interlayer region. Such an arrangement would allow for easier expansion of the interior of the interlayer space.

Infrared spectroscopy

The OH-stretching absorption band of the control sample was 3635 cm⁻¹ (Figure 3). This is nearly iden-

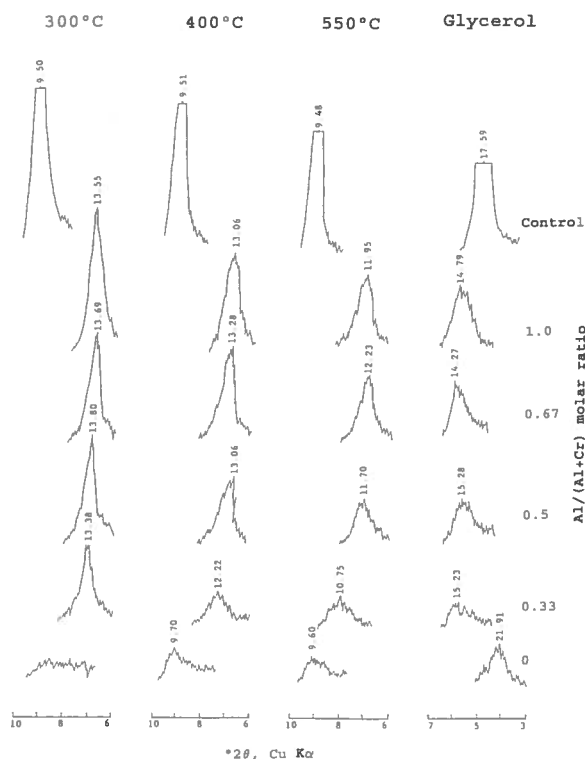


Figure 2. Basal reflections of the six clays after each of four pretreatments. All clays were analyzed at 54% relative humidity. (Spacings are in Å.)

tical to the 3632 cm^{-1} band observed in montmorillonite by Farmer and Russell (1967). The hydroxy-Al interlayered clay gave a high frequency shoulder at 3700 cm^{-1} . Other workers have found similar high frequency absorption bands in hydroxy-Al interlayered montmorillonite and assigned them to the gibbsite-like interlayer (Weismiller *et al.*, 1967; Ahlrichs, 1968; Ocelli and Tindwa, 1983). The pure hydroxy-Cr clay gave an OH-stretching frequency of 3656 cm^{-1} , lower than that for the pure hydroxy-Al clay. The greater atomic mass of Cr contributed to the decreased frequency in the pure hydroxy-Cr clay.

Hydroxyl stretching frequencies of the clays with intergradient interlayer compositions were similar to OH-stretching frequencies of the control clay. In fact, OH-stretching frequencies of the interlayer material were so close to those of the 2:1 silicate layer that only one absorption band could be discerned. As only one OH-stretching frequency was observed for the intergrades, their interlayers would not contain separate hydroxy-Cr and -Al polymers. If there were separate polymers, the IR spectra of the intergrades would be a composite of the end-members.

Thermal analysis

As the thermal analysis tracings of all clays with intergradient compositions were similar, only one (Al/

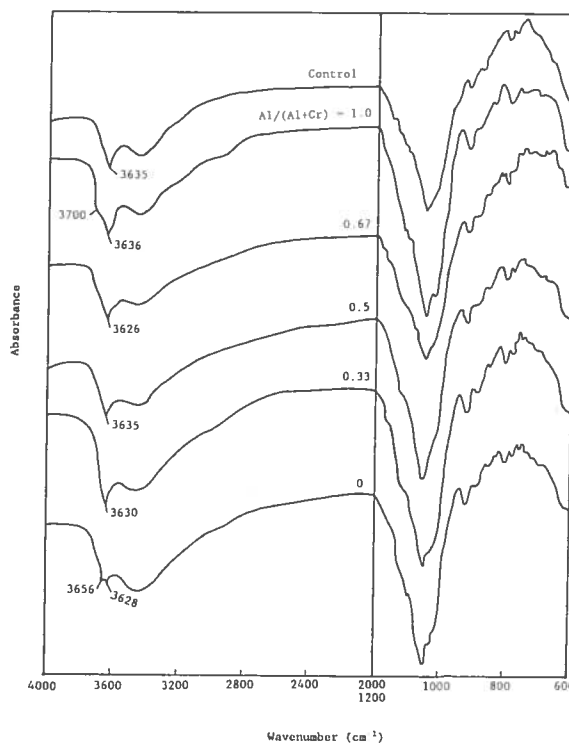


Figure 3. Infrared spectra of the six clays.

(Al + Cr) = 0.5) is shown (Figure 4c). Differential thermal analysis of all clays except the Cr end-member showed endotherms at about 75°C (Figure 4). These endotherms were attributed to the loss of adsorbed water (Tan *et al.*, 1986) and represent 5–7% of the total clay weight (TG data not shown). The corresponding endotherm for the Cr end-member occurred at 90°C and represented 12% of the clay weight. This higher temperature and greater weight loss was due to loss of structural water from the interlayer hydroxy-Cr polymers (Carr, 1985). The endotherm at 347°C for the Al end-member was attributed to a discrete $\text{Al}(\text{OH})_3$ phase (Hsu, 1989). There were no corresponding peaks for the clays containing Cr. Endotherms at $430^\circ\text{--}440^\circ\text{C}$ from the Al end-member and the intergrades represented loss of hydroxyls from the interlayer (Glenn and Nash, 1964; Barnhisel and Bertsch, 1989). The absence of a corresponding endotherm for the Cr end-member supports the idea of a low-temperature loss of structural water from the hydroxy interlayer. Dehydroxylation of the control occurred at 676°C and that of the 2:1 portion in the interlayered clays occurred at $603^\circ\text{--}609^\circ\text{C}$. This decrease of the dehydroxylation temperature has been attributed to the expanded interlayer (Rich, 1968).

XPS analysis

Binding energies for the $\text{Cr}_{2p1/2}$ and $\text{Cr}_{2p3/2}$ peaks for $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were 587.4 and 577.8 eV, respectively,

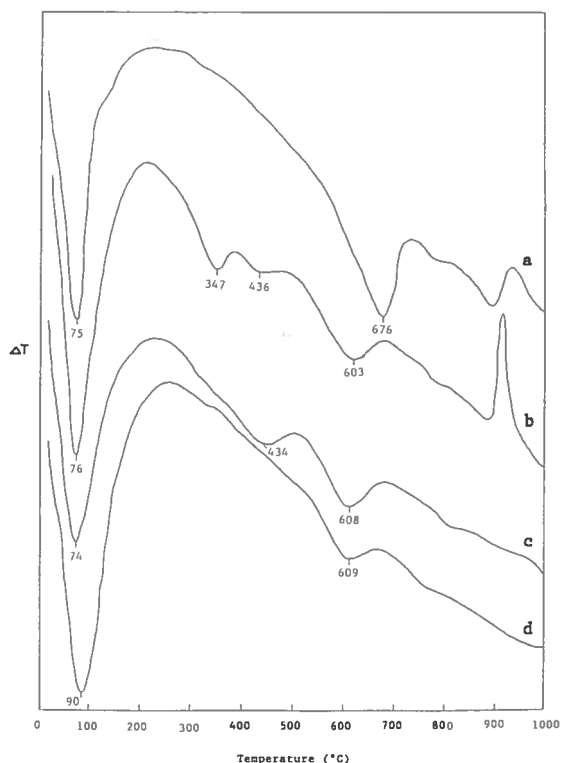


Figure 4. DTA tracings of a) the control and interlayered clay where the Al/(Al + Cr) molar ratio = b) 1.0, c) 0.5, and d) 0.

while the corresponding peaks for the Cr end-member were 588.2 and 577.6 eV. As the binding energies of Cr in the clay and the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ standard were essentially the same, the Cr in the clay detected by XPS was present as Cr(III). Previously, the presence of the Keggin structure was invoked to explain the 19.2 Å spacing of the Cr end-member. However, the central cation in the Keggin molecule is tetrahedrally coordinated to four O. As only higher oxidation states of Cr can be tetrahedrally coordinated to O, the presence of the Keggin structure must be dismissed. One must conclude, therefore, that the 19.2 Å basal spacing was caused by the intercalation of linear hydrolytic trimers. It is important to note, however, that XPS analyzes to a depth of only 10–50 Å (Hochella, 1988). If the Keggin molecules were located only within the interior of the clay particle, the higher oxidation states of Cr would not be detected by XPS. All Cr in the clays of inter-gradient composition was also present as Cr(III).

CONCLUSIONS

All interlayer materials that contain Al have formed similar gibbsite-like polymers. Substitution of Cr for Al in these polymers was supported by XRD and IR data. Data indicate, therefore, that Al may have served as a template in the formation of the gibbsite-like poly-

mers. It was not possible to determine the structures of all the pure hydroxy-Cr interlayer components. Based on XRD data, however, a simple octahedral sheet arrangement was an unlikely structure. Data from XPS, meanwhile, tended to rule out the presence of the Keggin molecule. Only intercalated linear hydrolytic trimers would give the clay properties that are consistent with the data.

Chromium increased the resistance of the interlayer to displacement. As Cr content increased, displacement of Cr by both K and Ca became more difficult. Aluminum, however, increased the thermal stability of the interlayer. As Al content increased, the interlayer became more resistant to collapse upon heating. The presence of both Cr and Al in the hydroxy polymers resulted in chemical and physical properties that seem to be contradictory. The most heat-stable interlayers (those with the most Al) were also the least resistant to displacement. Meanwhile, the least heat-stable interlayers (those with the most Cr) were the most resistant to displacement. A possible explanation for this apparent contradiction is that, while the hydroxy-Cr polymers were poorly crystalline, the Cr may have formed strong inner-sphere complexes with the 2:1 layer surface. Despite uncertainties concerning the structure of the interlayer material, however, one may conclude that expandable layer silicates serve as effective sinks for Cr.

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