

## HYDRATION STATES OF INTERLAMELLAR CHROMIUM IONS IN MONTMORILLONITE

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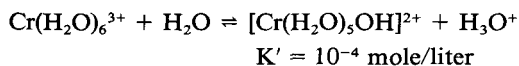
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**Abstract**—Hydroxychromium montmorillonites were prepared from solutions containing chromium nitrate and varying amounts of NaOH. The reactant Cr ions were hydrolyzed and, in some experiments, were dimerized to a significant extent. The extent of polymerization in the product formed from a solution containing a maximum amount of  $[\text{Cr}_2(\text{H}_2\text{O})_8(\text{OH})_2]^{4+}$  was compared with that in products obtained from solutions containing monomer,  $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ , and lesser amounts of the dimer. Despite the uncertainty about the nature and amounts of product interlamellar species, the catalytic effect of the montmorillonite interlayer on the hydrolysis and polymerization of Cr(III) appears to be independent of the nature of the reactant species. The validity of this conclusion depends to a large extent on the reliability of water determination in the clay mineral species, which is estimated to be no better than 5%. The assumption that  $\text{H}_2\text{O}^+$  is 'combined' and  $\text{H}_2\text{O}^-$  is 'free' water is shown to be partially true, thereby causing some uncertainty in the interpretations of interlayer compositions.

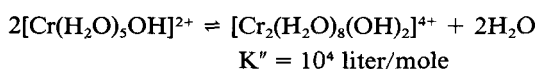
**Key Words**—Catalysis, Chromium, Hydration, Interlayer, Montmorillonite, Water.

### INTRODUCTION

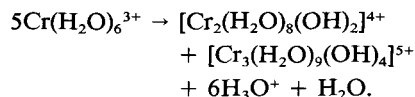
The intercalation of polymeric hydroxychromium cations into montmorillonite was reported by Brindley and Yamanaka (1979) who demonstrated that, with increasing amounts of hydroxide ion, polymeric cations are formed in the clay with increasing numbers of chromium ions and with a higher ratio of OH/Cr than in the external solution. This result supports the view that the montmorillonite structure catalyzes the hydrolysis and polymerization of hexaaquachromium(III) ions in the interlayer environment. On the other hand, it is known that these processes of hydrolysis and polymerization occur in aqueous solutions of chromium(III) ions in the absence of catalysts (Earley and Cannon, 1965). The polymerization in which  $[\text{Cr}_2(\text{H}_2\text{O})_8(\text{OH})_2]^{4+}$  and  $[\text{Cr}_3(\text{H}_2\text{O})_9(\text{OH})_4]^{5+}$  are formed is slow at 25°C (Baes and Mesmer, 1976), but quite rapid at 100°C (Laswick and Plane, 1959; Earley and Cannon, 1965). Cr(III) aqueous chemistry may be summarized as follows: A solution containing 0.1 mole/liter Cr(aq) has a pH of 2.4 due to the hydrolysis and dimerization of the hexaaquachromium(III) ion:



and



Assuming the above hydrolysis system only, the calculated pH is 2.5. Further polymerization and hydrolysis is possible but occurs very slowly at room temperature; e.g.,



The maximum amount of dimeric species can be obtained by heating a solution in which the OH/Cr ratio is unity.

The present study was designed to test the effect of the extent of hydrolysis and polymerization in the reactant Cr species on the extent of polymerization in the product interlamellar montmorillonite complexes. Because it is possible to prepare a more extensively dimerized Cr species than any of those used by Brindley and Yamanaka (1979), it was of interest to determine whether or not a dimerized reactant will be changed into a more extensively polymerized product than a reactant containing less of the dimer.

### EXPERIMENTAL

The experimental procedure adopted was similar to that used by Brindley and Yamanaka (1979). Samples of Na-montmorillonite were obtained from 'Volclay' (a Wyoming montmorillonite supplied by the American Colloid Company) by exchange in NaCl solutions, followed by decantation and dialysis to remove  $\text{Cl}^-$ . Hydroxychromium solutions of composition OH/Cr = 0, 0.33, and 1.0 were prepared by slowly titrating 100 ml of 0.1 mole/liter  $\text{Cr}(\text{NO}_3)_3$  solution with appropriate volumes of 0.1 mole/liter NaOH followed by dilution to 300 ml. A solution (300 ml) containing the maximum amount of dimeric Cr(III) (designated 'dimer') was prepared by heating a solution containing 100 ml of each of 0.1 mole/liter  $\text{Cr}(\text{NO}_3)_3$ , 0.1 mole/liter NaOH, and distilled water to about 80°C for 40 min. No at-

Table 1. Chemical analyses and structural formulae of Na- and hydroxy-Cr-montmorillonites obtained with various initial OH/Cr solution ratios.

	Na-mont.	Hydroxy-Cr-montmorillonites			
		OH/Cr = 0.0	0.33	1.0	1.0 (dimer)
SiO <sub>2</sub>	61.37	60.26	58.89	55.77	58.74
Al <sub>2</sub> O <sub>3</sub>	21.46	21.06	20.88	19.48	20.49
Fe <sub>2</sub> O <sub>3</sub>	3.85	3.74	4.03	3.62	4.07
MgO	2.45	2.44	2.52	2.00	2.42
CaO	0.19	0.14	0.15	0.11	0.18
TiO <sub>2</sub>	0.14	0.15	0.14	0.13	0.14
K <sub>2</sub> O	0.17	0.14	0.14	0.12	0.16
Na <sub>2</sub> O	2.61	0.00	0.00	0.09	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.00	2.50	4.18	7.57	5.99
H <sub>2</sub> O+	6.24	8.91	9.09	11.03	9.05
Total	98.48	99.34	100.02	99.92	101.24
Compositions per formula unit containing O <sub>10</sub> (OH) <sub>2</sub>					
Si	3.93	3.94	3.89	3.94	3.91
Al(VI)	0.07	0.06	0.11	0.06	0.09
Al(IV)	1.55	1.56	1.52	1.56	1.52
Fe	0.18	0.18	0.20	0.20	0.20
Mg	0.24	0.24	0.25	0.21	0.24
Ca	0.01	0.01	0.01	0.01	0.01
Ti	0.01	0.01	0.01	0.01	0.01
K	0.02	0.01	0.01	0.01	0.02
Interlayer compositions and ratios					
Na	0.32	—	—	0.01	—
Cr	—	0.13	0.22	0.42	0.31
OH	—	0.10	0.34	0.94	0.61
H <sub>2</sub> O	0.37	0.90	0.81	1.15	0.70
OH/Cr	—	0.77	1.55	2.24	1.97
(OH + H <sub>2</sub> O)/Cr	—	7.69	5.23	4.98	4.23

tempt was made to estimate the concentrations of dimeric Cr(III) in these solutions, but data obtained by Laswick and Plane (1959) indicate that about 50% of the available Cr in the heated solution could have been polymeric.

Five-gram samples of Na-montmorillonite were dispersed in 100 ml of each Cr solution and stirred periodically. After standing for 24 hr the samples were centrifuged, the solutions decanted, and fresh chromium solutions added. Dispersion and periodic stirring during a second 24-hr period was followed by a third treatment with fresh solution to ensure completeness of the reaction. The Cr uptake of the clay was monitored by comparing the optical absorptions of the spent solutions in the wavelength range 570–580 nm using a Cary 10 spectrophotometer. For each sample Cr uptake appeared to be complete after two exchange treatments. The resulting solids were washed several times to remove excess exchange solution and dried in an air oven at 105°C.

Chemical analyses of the products and the reactant Na-montmorillonite were made by X-ray fluorescence (XRF) using a lithium tetraborate fusion technique and a Philips PW1410 spectrometer. An electrically heated aluminum block containing a thermistor sensor adja-

cent to four sample cavities was used for water determinations. Each sample was heated at 110°C for 16 hr. Constancy of temperature was ensured by a cavity design which minimized the volume of air surrounding the sample trays. Total water was determined by ignition at 1050°C for 40 min.

The expansion of the montmorillonite basal spacing by exchange of hydroxychromium species and the subsequent collapse by heat treatment to 500°C was followed by X-ray powder diffraction of thin layers of the clays (aggregates were crushed with an agate mortar and pestle) on glass slides. Usually, only the first-order reflections corresponding to spacings in the range 10–15 Å were measurable, and even these tended to be broad indicating variable basal spacings.

Surface areas were determined by nitrogen sorption at liquid nitrogen temperature using a gravimetric procedure. Samples were degassed at 200°C under high vacuum prior to the sorption measurements.

## RESULTS

The chemical analyses and derived formulae are given in Table 1. The weight loss of samples from 110° to 1050°C is listed as H<sub>2</sub>O+ and was determined from the difference between the weight loss from room con-

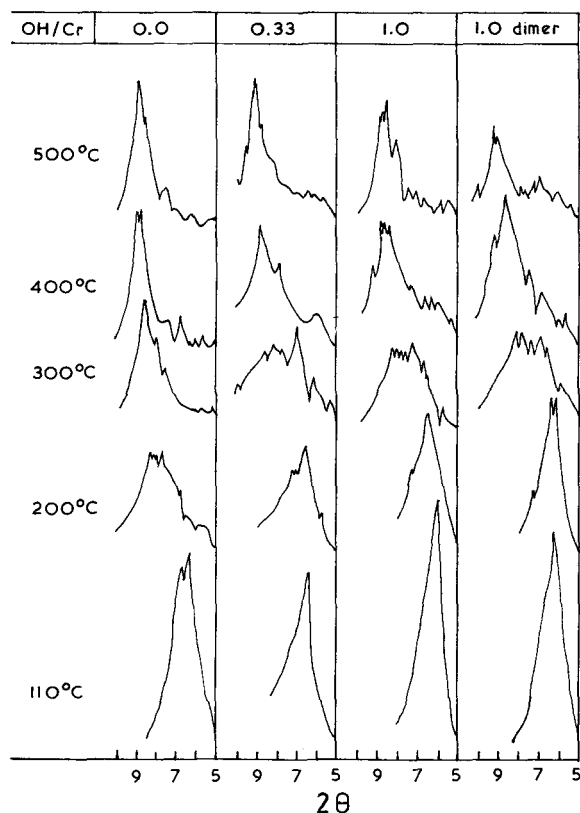


Figure 1. X-ray powder diffractograms showing the effect of heat treatment on the basal spacings of hydroxychromium montmorillonites obtained from solutions of different compositions.

ditions ( $\sim 20^\circ\text{C}$  and 52% RH over saturated  $\text{NaHSO}_4$  solution) to  $1050^\circ\text{C}$  and the weight loss from room conditions to  $110^\circ\text{C}$ . Fe was determined as  $\text{Fe}_2\text{O}_3$  and Cr as  $\text{Cr}_2\text{O}_3$ . The formula of the reactant Na-montmorillonite was derived on the basis of a total cation valence of +22 and the anion  $\text{O}_{10}(\text{OH})_2$ . The layer charge was +0.32 per formula unit. Formulae for the hydroxychromium montmorillonites were obtained by assuming no net charge in the formula composition.

Although the dimeric Cr solution and the titrated  $\text{OH}/\text{Cr} = 1.0$  solution were identical in Cr content, the amount in the product montmorillonite complex was smaller for the dimeric reactant. This apparent anomaly may be explained in terms of the relative magnitudes of interactions which influenced the reaction pathway. The initial absorption step must have consisted of van der Waals contact between the aqueous Cr species and the crystal edges and interlayer surfaces of the montmorillonite particles. After exchange with  $\text{Na}^+$  was complete, any subsequent hydrolysis and polymerization was probably accompanied by a temporary excess of interlayer positive charge in the form of

Table 2. Surface areas of hydroxy-Cr-montmorillonites after heating to  $200^\circ\text{C}$ .

OH/Cr (solution)	Surface area ( $\text{m}^2/\text{g}$ )
0.0	53
0.33	89
1.00	164
1.00 (dimeric)	156

$\text{H}_3\text{O}^+$ . In comparison with the +2 charge on the hydroxychromium monomer the larger repulsion effects between the +4 charge on the dimeric Cr species and  $\text{H}_3\text{O}^+$  probably caused a reduced uptake of Cr from the dimeric solution. Any dimeric ions which were absorbed underwent catalysis within the interlayers and were condensed to polymeric species of higher stability.

The variations in X-ray powder diffraction spacings (Figure 1) can be attributed to differences both in the nature and the orientations of the interlayer species. The complexes were stable to about  $200^\circ\text{C}$ , but at  $300^\circ\text{C}$  they showed varying amounts of collapse reaching a minimum value of  $\sim 9.7 \text{ \AA}$  at  $500^\circ\text{C}$ .

Surface areas of the product clays increased with increasing  $\text{OH}/\text{Cr}$  ratios (Table 2). The reproducibility of the values was  $\sim \pm 5\%$ .








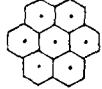
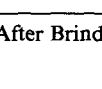
## DISCUSSION

The  $\text{OH}/\text{Cr}$  ratios listed in Table 1 suggest that the Cr ions underwent additional hydrolysis within the montmorillonite interlayers because the product complexes appeared to be enriched in hydroxide. Similarly, the  $(\text{OH} + \text{H}_2\text{O})/\text{Cr}$  ratios indicate that the clay interlayer region catalyzed the formation of polymeric forms of hydroxychromium complexes. The data are similar to, but not identical with, those given by Brindley and Yamanaka (1979) who, for example, reported that  $\text{Cr}_6$ -hydroxychromium polymers formed from  $\text{OH}/\text{Cr} = 1.0$  solutions. The present investigation, however, indicated that  $\text{Cr}_2$ -hydroxy complexes formed. On the other hand, it is significant that the trends observed in each investigation are similar and self-consistent. Significantly, the ability of the montmorillonite interlayer to catalyze both the hydrolysis and the polymerization of the aqueous Cr species appears to have been independent of the extent of polymerization in the reactant species. When the reactant was partly dimeric, the product was more polymerized (trimeric) than for the essentially monomeric reactant, which gave only dimeric product.

### Analytical uncertainty

The Cr and  $\text{H}_2\text{O}^+$  analytical values for the products prepared in the current study are significantly different from those reported by Brindley and Yamanaka (1979). Because the above interpretations depend strongly on

Table 3. Calculated and experimental OH/Cr and (OH + H<sub>2</sub>O)/Cr ratios for possible polymeric forms of interlayer complexes.

	Model <sup>1</sup>		Brindley and Yamanaka (1979)		This work	
	OH/Cr	(OH + H <sub>2</sub> O)/Cr	OH/Cr	(OH + H <sub>2</sub> O)/Cr	OH/Cr	(OH + H <sub>2</sub> O)/Cr
	1.0	6.0	0.87	6.00	0.77	7.69
	1.0	5.0			1.55	5.23
					2.24	4.98
	1.33	4.67	2.14	4.54		
	1.33	4.33				
	2.00	4.00	2.40	4.02	1.97	4.23
			2.66	3.56		
	1.71	3.43	2.54	3.54		
			2.66	3.56		

<sup>1</sup> After Brindley and Yamanaka (1979).

the compositions of these components, some comment is necessary. Although the analytical method used in each investigation was different, both the atomic absorption (Brindley and Yamanaka, 1979) and the XRF (this study) procedures were checked using international standard rock samples. In the current study, some difficulty was experienced in obtaining reproducible H<sub>2</sub>O- values. The temperature control in large ovens was no better than  $\pm 5^\circ\text{C}$  at the sample position. To minimize this uncertainty an aluminum block furnace, as described above, was constructed. A second source of error arose from the uptake of moisture by the clay during weighing of the sample trays. Rapid weighing allowed this error to be reduced to about 5%, equivalent to about  $\pm 0.2$  in (OH + H<sub>2</sub>O)/Cr ratios.

In Brindley and Yamanaka's (1979) investigation the highest (OH + H<sub>2</sub>O)/Cr ratio obtained was 6.00 corresponding to the simplest, partially hydrolyzed monomer, [Cr(H<sub>2</sub>O)<sub>5</sub>OH]<sup>2+</sup>. In the present study a ratio of 7.69 was obtained, the discrepancy being possibly due, at least in part, to the uncertainty in H<sub>2</sub>O+ values. If the value of 7.69 is correct, it may be due to the fact that both partially hydrolyzed chromium monomers and isolated water molecules were present within the interlayer.

#### Assumptions concerning interlayer compositions

H<sub>2</sub>O- is generally assumed to be weakly bonded adsorbed water, whereas H<sub>2</sub>O+ is thought to be chemically combined (hydration) H<sub>2</sub>O and/or hydroxy ion. The validity of this assumption is questionable. In the salt, Cr(H<sub>2</sub>O)<sub>6</sub>Cl<sub>3</sub>, and the dimer, [Cr<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>(OH)<sub>2</sub>]<sup>4+</sup>, the H<sub>2</sub>O molecules are assumed to be bound to the Cr

atoms with coordinate covalent bonds. Because the colors of these compounds are similar it can be assumed that the Cr(III)-H<sub>2</sub>O bond energies are similar. In a separate experiment, wherein Cr(H<sub>2</sub>O)<sub>6</sub>Cl<sub>3</sub> was heated at 110°C for 16 hr, i.e., the conditions for H<sub>2</sub>O-determination, the salt melted and lost about 60% of its chemically bonded water. Because the Cr(III) hydration energy is independent of the crystal lattice energy, water loss is not influenced by the melting of the salt, and, hence, the experiment demonstrated that H<sub>2</sub>O- can include chemically combined H<sub>2</sub>O. The labile nature of ligand water was further demonstrated by drying Cr(H<sub>2</sub>O)<sub>6</sub>Cl<sub>3</sub> over concentrated sulfuric acid. About 30% of the water was removed after 9 days. Conclusions based on the assumption that the H<sub>2</sub>O+ value represents all of the combined water are therefore unwarranted without independent experimental evidence.

Table 3 compares the OH/Cr and (OH + H<sub>2</sub>O)/Cr ratios calculated from model polymeric species (after Brindley and Yamanaka, 1979) and the experimentally determined ratios. With the exception of the complexes prepared from OH/Cr = 0 solutions, the OH/Cr ratios of the products of both studies suggest more polymerization than is suggested by (OH + H<sub>2</sub>O)/Cr ratios. It is likely that this major discrepancy is due to the presence of free hydroxyl ions in the interlayer region, the negative charge being balanced by a positive charge in the hydroxychromium complex ions. The lack of a ready means of determining the structures of the interlayer species makes it impossible to ascertain the exact composition of the hydroxychromium species in any of the experimental products.

### CONCLUSION

The hydrolysis and polymerization of the Cr(III) ion in the montmorillonite interlayer appear to be independent of the nature of the reactant solution species. The product interlayer species may include one or more hydroxychromium complexes (monomeric or polymeric), hydroxyl ions, or water molecules.

In investigations where 'free' and 'combined' water compositions are important, it is essential that complete experimental details of the determinations be reported together with any other analytical uncertainties. Erroneous  $H_2O^+$  data could invalidate some, or all, of the conclusions. The assumption that 'free' water is driven off below 110°C whereas 'combined' water is released at higher temperatures may not be valid and should also be tested experimentally.

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