ADSORBED Cr(III) ON CHLORITE, ILLITE, AND KAOLINITE: AN X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY

M. H. KOPPELMAN,¹ A. B. EMERSON,¹ AND J. G. DILLARD

Department of Chemistry, Virginia Polytechnic Institute and State University

Blacksburg, Virginia 24061

Abstract The adsorption of Cr(III) was studied at pH 1, 2, 3, 4, 6, 8, and 10 on chlorite and kaolinite and at pH 1, 2, 3, and 6 on illite. The amount of chromium adsorbed on chlorite varied from 3.1×10^{-5} mole/ **g** at pH 1 to 16.6 \times 10⁻⁵ mole/g at pH 4, and on illite from 4.9 \times 10⁻⁵ mole/g to 9.2 \times 10⁻⁵ mole/g at pH 1 and 3, respectively. Kaolinite adsorbed 3.7 \times 10⁻⁵ mole Cr/g at pH 1, 2, and 3 and 5.5 \times 10⁻⁵ mole Cr/ g at pH 4. Measurements of the Cr 2p core-level binding energies indicate that chromium is probably adsorbed as a Cr(III) aqua ion at pH values below 4. The binding energies for the Cr 2p level for samples prepared above pH 4 compare favorably with the value determined for chromium hydroxide and lead to the conclusion that the chromium species present at pH 6, 8, and l0 is chromium hydroxide.

Key Words-Adsorption, Binding energy, Chlorite, Chromium, Illite, Kaolinite, XPS.

INTRODUCTION

The adsorption and reaction of metal ions with suspended solids are of interest in many areas of interface science. Riley and Chester (1971) noted that hydrogenous processes for removal of metals from seawater include ions exchange, adsorption, and co-precipitation. Chemical processes associated with the transport of metal ions between sediments and seawater under a variety of redox conditions were examined by Lu and Chen (1977). Among the factors that influence adsorption of metal ions are cation charge, cation hydration radius, and polarizability (Swartzen-Allen and Matijevic, 1974).

From a study of the thermochemistry of metal ion adsorption on silica, Dugger *et al.* (1964) suggested that the nature of aqueous OH^- and of $-SiO^-$ oxygen environments was similar so that the reactions with metal ions may be comparable. James and Healy (1972a) observed that the adsorption density of $Cr(III)$ on $SiO₂$ was greater than that predicted by electrical doublelayer theories. The abrupt increase in adsorption with increasing pH (James and Healy, 1972a; 1972b) was qualitatively related to hydrolysis of the metal ion. Using electron spin resonance and optical absorption techniques, Cornet and Burwell (1968) studied the chemical and physical properties of Cr(III) and Cr(III) compounds on silica. For the nitrates of $Cr(H_2O)_6^{3+}$ and $Cr(NH₃₎₆³⁺$, the ESR results indicated that the metal ions appear to be in the same environment in solution impregnated into silica pores and in bulk solution (Cornet and Burwell, 1968). The electronic spectra of chromium adsorbed on zeolites (Coughlan *et al.,* 1977) and of chromium in minerals (Bish, 1977) are consistent with octahedrally coordinated Cr(III).

In a series of investigations where the details of the oxidation reduction processes of Cr(III) and (VI) with soils were examined, Cary *et al.* (1977a; 1977b) reported that Cr(VI) was reduced to Cr(III) more rapidly in acidic than in basic soils. Bartlett and Kimble (1976a) found that Cr(III) was not oxidized to Cr(VI) at high pH levels with maximum aeration. However, Cr(VI) was spontaneously reduced to Cr(III) by organic matter in soils (Bartlett and Kimble, 1976b). For soils containing oxidized manganese, Cr(III) was oxidized to Cr(VI) (Bartlett and James, 1979). An additional feature of these studies (Bartlett and Kimble, 1976a) was the observation that Cr(III) formed soluble and stable soilorganic complexes at pH levels when chromium hydroxide should precipitate.

In view of the previous studies, it seemed appropriate that an investigation of Cr(III) adsorption on clay minerals by X-ray photoelectron spectroscopy (XPS) be carried out to probe the clay surface for possible oxidation/reduction processes and for the formation of chromium hydroxide or chromium oxide. Such information on the chemical nature of adsorbed Cr(III) could aid in understanding the mode of metal ion-clay mineral interactions and provide data that could be useful in surface studies where hydrolysis of metal complexes is a significant feature of adsorption reactions (Koppelman and DiUard, 1978).

Previous investigators have used XPS to examine the chemical nature of chromium in simple inorganic compounds (Allen *et al.,* 1973; Allen and Tucker, 1976). The binding energy for the Cr 2p electrons was found to depend on the oxidation state of chromium (Allen *et al.,* 1973). Binding energies for Cr(VI) and Cr(III) were measured in the ranges 578.6-577.1 and 575.8-575.2 eV, respectively. The magnitude of the Cr $2p_{1/2}$ -Cr $2p_{3/2}$ energy separation measured for a series of Cr(III)-containing coordination compounds increased with in-

¹ Present address: Georgia Kaolin Research Laboratories, 25 Route 22, East, Springfield, New Jersey 07081.

	Kaolinite	Illite	Chlorite	
Color	White	gray	gray-green	
Source	Georgia Kaolin Company Hydrite-R	API $#35$ Fithian, Illinois: Illinois Geol, Survey	Ishpeming, Michigan; Ward's Natural Science Establishment	
BET-N, Surface Area (m^2/g)	12	49	14	
CEC (meg/100 g)		20	16	

Table 1. Characteristics and sources of clay minerals.

creasing ionic character in the chromium ligand bond (Allen and Tucker, 1976). In the study of Cr(VI) compounds, DeAngelis (1976) noted that reduction of Cr(VI) to Cr(III) occurred during the recording of XPS spectra. The suspected reducing agent was hydrocarbon contamination in the vacuum system. Cimino *et al.* (1976) reported that XPS is useful in examining the textural nature and chemical characteristics of chromium in CrO_x/SiO_2 catalysts.

In this paper, the adsorption of Cr(III) on the clay minerals chlorite, illite, and kaolinite is reported, and the chemical nature of adsorbed chromium as a function of pH is discussed from XPS binding-energy measurements. The results indicate that chromium is likely adsorbed as an aqua ion at low pH values and is present as the hydroxide at high pH levels.

EXPERIMENTAL SECTION

Materials

The clay minerals used in this study are listed in Table 1. They were obtained from commercial suppliers or from geological laboratories and have been characterized in earlier publications (Koppelman and Dillard, 1975; 1978). A crystal of uvarovite, from Outokumpu, Finland, was obtained from Dr. J. Craig, Department of Geological Sciences, Virginia Polytechnic Institute and State University. Chemical composition data appear in Deer *et al.* (1962). Kammererite from Siskiyou County, California, was supplied by Dr. J. White of the Smithsonian Institution, U.S. National Museum (designated as USNM $#104723$). The uvarovite and kammererite were studied to obtain XPS binding-energy data for silicate-lattice substituted Cr(III).

Chromium solutions (100 ppm) were prepared by dissolving $Cr(NO₃)₃·9H₂O$ (Fisher certified reagent grade) in argon-saturated, double-distilled, deionized water. The pH of the test solutions was adjusted to the desired value by the addition of 0.13 N NaOH or 0.10 N HC1 prepared in argon-saturated water. Cr(III) solutions were added to 2.5 g of the clay mineral contained in a Teflon-coated or polyethylene vessel maintained under an argon atmosphere. Following addition of the solutions and agitation of the samples for about 1 min, the pH of the solution was adjusted to the desired value by adding acid or base. Additions to the slurries were accomplished by piercing a rubber septum seal on the vessel with a hypodermic syringe. The suspensions were agitated for about 10 min each day during the reaction period. The clay slurries were held at $25^{\circ} \pm 0.5^{\circ}$ C throughout the 6- or 10-day reaction period. Sample aliquots were removed periodically from the suspension for pH, metal-ion, and silicon analysis, pH was measured under an inert atmosphere flow of $N₂$ or Ar with a Fisher combination electrode and a Coming model 703 pH meter. The electrode was standardized using pH 4 and 7 buffers. Metal-ion concentrations were measured by atomic absorption spectrophotometry (AA) (Perkin-Elmer, model 503 instrument). Silicon was determined spectrophotometrically using the silicon-molybdate method (Fanning and Pilson, 1973).

After the designated interaction time, solids were separated from the solution by centrifugation. Collected solids were washed twice with distilled water and placed in a vacuum desiccator to dry.

XPS measurements

A DuPont model 650 and an AEI ES 100 spectrometer were used to measure the XPS spectra. Procedures for measurements with the AEI instrument have been described previously (Koppelman and Dillard, 1975). For measurements on the DuPont instrument, samples were prepared by suspending the clay sample in acetone or in water and sonifying the suspension for 1 min (Koppelman and Dillard, 1978). A drop of the suspension was then placed on a brass sample probe and allowed to stand in the atmosphere until the liquid had evaporated.

Calibration of the XPS energy scale was accomplished by depositing a thin film of gold onto the sample surface and measuring the binding energy of gold and the elements in the clay sample (Koppelman and Dillard, 1975). Once the binding energies for the elements in the clay had been determined they could then be used for calibration. In another calibration procedure, background carbon from the spectrometer was the calibrant. The background-carbon binding-energy value, 284.4 \pm 0.1 eV, was established using gold, copper, and zinc as reference standards (Seals *etal.,* 1973; Dillard and Tay-

Chlorite Illite Kaolinite Adsorp- Duration Adsorp- Duration Adsorp- Duration pH tion (days) tion (days) tion (days) **I 3.1 6 4.9 6 3.7 6** 2 9.8 6 4.3 6 3.7 6 3 13.5 6 9.2 6 3.7 6 $4 \t16.6 \t6 \t— \t5.5 \t6$ 6 - 10 - 10 - 10 $8 - 6 - - - - 6$ 10 - 6 - - 10

Table 2. Cr(III) adsorbed on clays.¹

¹ [mole Cr(III)/g clay][\times 10⁵] \pm 1.2 \times 10⁻⁵.

lor, 1974). The background-carbon binding energy was measured independently several times during these studies to assure that the value used for calibration was unchanged. The binding-energy values presented in this work represent the averages of no less than three separate measurements for each sample. No variation in the binding energies or relative peak intensities was noted with time of exposure to the X-rays, or with variation of the X-ray power. For each XPS run, the sample was exposed to the X-rays for less than 2 hr. Integrated peak intensities were evaluated by measuring the peak area and correcting the measured counts for the photoionization cross section (Scofield, 1976). Spectra were plotted using the Madcap IV routine (Koppelman and Dillard, 1977). X-rays were generated from a magnesium (DuPont) and an aluminum anode (AEI). Pressure in the sample and analyzer chambers was about $10⁻⁷$ torr during the measurements. The precision of the measurements is ± 0.1 eV, and the accuracy is ± 0.2 eV. XPS spectra were measured for lattice elements Si, A1, and O to discover whether the binding energies for these elements had changed as a result of the solution experiments.

RESULTS AND DISCUSSION

Results for Cr(III) adsorption on chlorite, illite, and kaolinite at various pH values are presented in Table 2. The major dissolved chromium species at pH 2 is $Cr(H₂O)₆³⁺$, while at pH 3 and 4 polymeric chromiumcontaining ions are the most abundant species in solution (Sillen and Martell, 1964; Baes and Mesmer, 1976).

Table 3. Kaolinite binding energies vs. pH for Si $2P_{1/2,3/2}$, Al $2p_{1/2,3/2}$, and O $1s_{1/2}$ after Cr(III) adsorption.

	рH						
				6		10	
Si 2p	102.7	102.8	102.7	102.6	102.7	102.8	
Al 2p	74.2	74.2	74.4	74.3	74.3	74.3	
O _{1s}	532.0	532.0	532.0	531.9	532.0	532.0	

Values in electron volts $(\pm 0.1 \text{ eV})$.

Figure l. Chromium 2p photoelectron spectra. A. Cr(III) adsorbed on chlorite, pH 6, 29,000 net counts: 24 repetitive scans. B. Cr(II) adsorbed on chlorite, pH 3, 19,000 net counts: 64 repetitive scans.

In the solutions, at pH values ≥ 4.8 , precipitation of chromium hydroxide was anticipated. Visual evidence of a blue-green precipitate was noted at pH 6, 8, and 10. The dissolved chromium content of aliquots of these suspensions indicated that virtually no chromium remained in solution at these pHs.

Adsorption of chromium on chlorite at pH 2.0 is significantly greater than at pH 1.0. Similarly, the amount of chromium adsorbed on chlorite and illite at pH 3.0 is greater than at pH 2.0. At pH 4 an increase of $23%$ and 49% Cr(III) adsorption was observed for chlorite and kaolinite, respectively, compared to pH 3. These results may be due to two different phenomena: (1) the cation-exchange capacity of the clay increases from pH 1 to 4 as a result of hydrolysis of Si-OH and A1-OH groups; (2) at pH 1 the hydrogen ion concentration is almost 100 times the concentration of Cr(III) and hydrogen ions compete effectively with Cr(III) for surface sites. As the pH increases, $[H^+]$ decreases, and the

Table 4. Cr $2p_{3/2}$ binding energies vs. pH after Cr(III) interaction with clays.

	pН					
	$\mathbf{2}$	3	4	6	8	10
Chlorite		577.2 577.3 577.5 576.9 576.8 576.7				
Illite	577.3	577.3	المستردات	576.9		
Kaolinite	577.3	577.4 577.5 576.9 576.8 576.7				
Kammererite		578.2				
Uvarovite		578.3				
Cr(OH)		576.8				
Cr_2O_3		576.4				
$Cr(NO3)3·9H2O$		577.9				

Values in electron volts $(\pm 0.1 \text{ eV})$.

Chlorite **Illite** Kaolinite pH AFSi Cr/Si AI/Si Cr/Si Al/Si Cr/Si $2 \quad - \quad - \quad 0.52 \quad 0.0027 \quad 0.89 \quad 0.0098$ 3 0.86 0.061 0.56 0.010 0.91 0.010 $4 \t 0.99 \t 0.25 \t - \t - \t 0.91 \t 0.015$ Pure clay $0.94 - 0.52 - 0.91$

Table 5. Experimental (ESCA) atom ratios on chlorite, il-

competition for these sites is reduced. The increased adsorption at pH 3 and 4 may be due also to adsorptivity

of polymeric chromium species which are the dominant cations at those pH values. The present experiments were not conducted such that a detailed analysis of polymeric species could be carried out; however, attempts were made to characterize the chemical nature of adsorbed Cr(III) using XPS.

The measured absolute binding energies (calibrated using carbon and gold) for silicon, aluminum, and oxygen are summarized in Table 3 as a function of pH for kaolinite. Within experimental error, the binding energies are equivalent at all pH values. Further, the shapes of the photoelectron peaks for these three elements were unaltered after interaction with Cr(III). Similar results were obtained for chlorite and illite. The absolute binding energies are in excellent agreement with those measured in previous studies (Koppelman and Dillard, 1975). The near equality of the binding energies and the unaltered peak shape for each lattice element in the three clays suggest that no significant alteration in the chemical nature of surface silicon, aluminum, or oxygen occurred after the clay reacted with Cr(III).

Initial XPS examination of the pure clays before adsorption revealed no evidence of chromium on the surface of the samples. XPS spectra measured after reaction of Cr(III) with the clays revealed intense Cr $2p_{1/2}$ and Cr $2p_{3/2}$ photopeaks.

Cr 2p spectra are shown in Figure 1 for Cr(llI) adsorbed on chlorite at pH 3 and at pH 6. Spectra, similar in appearance to those shown here, were obtained for Cr(III) adsorbed on kaolinite and illite. The 2p spectra are devoid of satellite features in agreement with previous XPS studies on chromium compounds (Allen *et al.,* 1973; Allen and Tucker, 1976). The significant aspects of the XPS measurements are related to the binding-energy measurements.

Cr $2p_{3/2}$ binding energies for the three clays after reaction with Cr(III) at various pHs are summarized in Table 4. Binding energies for chromium in octahedral sites in the minerals kammererite and uvarovite are presented also in Table 4, along with the experimental binding energies for $Cr(OH)_3$, Cr_2O_3 , and $Cr(NO₃)·9H₂O.$

The data in Table 4 indicate that the chromium bind-

ing energies center around three values. At low pH values (pH 2 and 3), the binding energy is approximately 577.3 \pm 0.1 eV for all three clays. At pH 4, the binding energy for kaolinite and chlorite is 577.5 eV. At pH 6, 8, and 10 for kaolinite and chlorite and at pH 6 for illite, the binding energy is 576.8 ± 0.1 eV. The binding energies for samples at pH 6, 8, and 10 are equivalent within experimental error to that measured for chromium hydroxide. This result is not unexpected since at pH 4.8, chromium hydroxide forms. This result is unlike that reported by Bartlett and Kimble (1976a) who noted that soil organic complexes of Cr(III) were soluble and stable above pH levels where $Cr(OH)$ ₃ would precipitate. The results reported here are not in conflict with the earlier report (Bartlett and Kimble, 1976a) since in the present work no complexing agents were added to aid in solubilizing Cr(III) at pH values above 4.8.

The Cr $2p_{3/2}$ binding energies determined at pH 2 and 3 are about 0.5 eV higher than those measured at the highest pH values. In comparing the binding energy for the Cr $2p_{3/2}$ level of chromium substituted in an octahedral site in the silicate lattice (uvarovite and kammererite) with that of Cr(III) adsorbed on the clays at pH values of 2 and 3, the following points are important: (1) the binding energy for adsorbed Cr(IIl) and latticesubstituted Cr(III) are not equivalent; (2) the lower binding energy (0.9 eV) for the adsorbed Cr(III) species is similar to the observation by Koppelman and Dillard (1975) that adsorbed Fe(III) has a binding energy considerably lower than lattice Fe(III); and (3) the adsorbed species is not chromium hydroxide or chromium oxide. In addition, the adsorbed chromium is not $Cr(NO₃)₃·9H₂O$ which may not have been removed during the washing of the clay after the adsorption experiment.

It should be noted also that the binding energy of chromium in chromium nitrate differs from that of chromium adsorbed on the clays. The chromium species in chromium nitrate can be represented as the hexaaqua chromium ion, $Cr(H_2O)₆³⁺$. Thus, while the adsorbed chromium species on the clay surface may be $Cr(H₂O)₆³⁺$, the binding energy for the adsorbed species is lower than for chromium in $Cr(NO₃)₃ \cdot 9H₂O$ because of the additional bonding with the surface. Evidently the surface site is a better electron donor than the coordinated $H₂O$ ligand. The results indicate that the donation of negative charge to the adsorbed chromium species from the surface site lowers the binding energy for chromium in the adsorbed chromium species relative to $Cr(NO_3)_3.9H_2O$. It would be informative to examine the oxygen:chromium ratio for each sample to specify the approximate stoichiometry of the adsorbed chromium species. This is not possible with these materials, because the clays contain large stoichiometric quantities of oxygen compared to the quantity of oxygen in the adsorbed complex chromium ion.

lite, and kaolinite.

The binding energy for chromium measured at pH 4 is slightly greater than that determined at lower or at higher pH values. The dominant chemical species for chromium at pH 4 include the polymeric chromium ion, $Cr_3(OH_4)^{5+}$ (Baes and Mesmer, 1976). If this ion was adsorbed at the clay surface, the binding energy data or the Cr/A1 or Cr/Si ratios should have been indicative of the adsorption of polymeric chromium species *(vide infra*). The binding energy measurements at pH 4 on chlorite and kaolinite are not significantly different from those measured at pH 2 and 3. Thus, from the XPS binding energy data it is not possible to demonstrate that polymeric species are indeed adsorbed. It is clear, however, that at pH 4, chromium is not present as a hydroxide or oxide.

Atom ratios for AI/Si and Cr/Si calculated by the method of Alvarez *et al. (1976),* using the photoelectric cross sections published by Scofield (1976), are presented in Table 5. Ratios at pH values where chromium precipitated are not presented because it is not evident what information such ratios would convey. For illite and kaolinite, the A1/Si ratio does not change significantly with pH. For chlorite, however, the A1/Si ratio is lower at pH 3 than at pH 4, suggesting that aluminum may be removed from the clay and not readsorbed.

The increase in the Cr/Si ratios with increasing pH is consistent with the results of solution analysis for chromium uptake. Only a slight increase in the Cr/Si ratio was noted for kaolinite from pH 2 to pH 4. On the other hand, the amount of surface Cr increased by about a factor of four for chlorite from pH 3 to pH 4 and for illite from pH 2 to pH 3. The increase in the Cr/Si ratio at pH 3 and at pH 4 is significant for chlorite only. The Cr/Si ratio for kaolinite is equivalent within the experimental error at pH 3 and pH 4. If polymeric species were adsorbed at pH 4 on kaolinite, it might be anticipated that the Cr/Si ratio would increase. That such an increase was not observed, and the fact that the binding energy is unchanged for chromium between pH 3 and pH 4 provide no evidence for the adsorption of polymeric chromium-containing ions. The situation with chlorite is complicated by the fact that a significant increase in the Cr/Si ratio was noted when comparing the data obtained at pH 3 and pH 4. This result taken alone could support the presence of polymeric-chromium species, but the binding-energy data cannot be interpreted to indicate the presence of surface species of polymeric chromium.

In conclusion, the XPS results indicate that chromium is adsorbed, but not as the hydroxide or oxide at the low pHs (2-4) investigated. The XPS results neither support nor deny the adsorption of polymeric chromium ions at these pH values. From binding-energy measurements on chromium-clay samples prepared at pH 6, 8, and 10, it is suggested that chromium is present as $Cr(OH)_{3}.$

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant OCE-76-11458. Grateful thanks are expressed also to Drs. J. White and J. Craig who provided some of the samples used in this investigation.

REFERENCES

- Allen, G. C., Curtis, M. T., Hooper, A. J., and Tucker, P. M. (1973) X-ray photoelectron spectroscopy of chromiumoxygen systems: *J. Chem. Soc. Dalton Trans.,* 1675-1683.
- Allen, G. C. and Tucker, P. M. (1976) Multiplet splitting of X-ray photoelectron lines of chromium complexes. The effect of covalency on the 2p core level spin-orbit separation: *Inorg. Chim. Acta* 16, 41-45.
- Alvarez, R., Fadley, C. S., Silva, J. A., and Uehara, G. (1976) A study of silicate adsorption on gibbsite $(AI(OH)₃)$ by X-ray photoelectron spectroscopy (XPS): *Soil Sci. Soc. Amer. J.* 40, 615-617.
- Baes, C. F. and Mesmer, R. E. (1976) *Hydrolysis of Cations:* Wiley, New York, 211-219.
- Bartlett, R. J. and Kimble, J. M. (1976a) Behavior of chromium in soils. I. Trivalent forms: *J. Environ. Qual.* 5, 379- 383.
- Bartlett, R. J. and Kimble, J. M. (1976b) Behavior of chromium in soils. II. Hexavalent forms: *J. Environ. Qual.* 5, 383-386.
- Bartlett, R. and James, B. (1979) Behavior of chromium in soils: III. Oxidation. *J. Environ. Qual.* 8, 31-25.
- Bish, D. L. (1977) A spectroscopic and X-ray study of the coordination of Cr³⁺ ions in chlorite: Amer. Mineral. **62**, 385-389.
- Cary, E. E., Allaway, W. H., and Olson, O. E. (1977a) Control of chromium concentrations in food plants. I. Absorption and translocation of chromium by plants: *J. Agric. Food Chem.* 25, 300-304.
- Cary, E. E., Allaway, W. H., and Olson, O. E. (1977b) Control of chromium concentrations in food plants. II. Chemistry of chromium and its availability to plants: *J. Agric. Food Chem.* 25, 305-309.
- Cimino, A., DeAngelis, B. A., Luchetti, A., and Minelli, G. (1976) The characterization of $CrO_x/SiO₂$ catalysts by photoelectron spectroscopy (XPS), X-ray and optical measurements: *J. Catal.* 45, 316-325.
- Cornet, D. and Burwell, R. L. (1968) Chromium compounds on silica gel: *J. Amer. Chem. Soc.* 90, 2489-2494.
- Coughlan, B., McCann, W. A., and Carroll, W. M. (1977) An electron spectroscopic study of chromium complexes in zeolites L and mordentite: *Chem. Ind. (London),* 358-360.
- DeAngelis, B. A. (1976) On the surface reduction of some chromium compounds during X-ray photoelectron spectroscopy: *J. Electron Spectrosc. Relat. Phenom.* 9, 91-84.
- Deer, W. A., Howie, R. A., and Zussman, J. (1962) *Rockforming minerals:* Longman Press, London, p. 24.
- Dillard, J. G. and Taylor, L. T. (1974) X-ray photoelectron spectroscopic study of schiffbase metal complexes: *J. Electron Spectrosc. Relat. Phenom.* 3, 455-460.
- Dugger, D. L., Stanton, J. H., Irby, B. N., McConnell, B. L., Cummings, W. W., and Maatman, R. W. (1964) The exchange of twenty metal ions with the weakly acidic silanol groups of silica gel: *J. Phys. Chem.* 68, 757-760.
- Fanning, K. A. and Pilson, M. E. Q. (1973) On the spectrophotometric determination of dissolved silica in natural waters: *Anal. Chem.* 45, 136-140.
- James, R. O. and Healy, T. W. (1972a) Adsorption of hydrolyzable metal ions at the oxide-water interface. I. Co(II) ad-

sorption on SiO₂ and TiO₂ as model systems: *J. Colloid Interface Sci.* 40, 42-52.

- James, R. O. and Healy, T. W. (1972b) Adsorption of hydrolyzable metal ions at the oxide-water interface. III. A thermodynamic model of adsorption: *J. Colloid Interface Sci.* **40,** 65-81.
- Koppelman, M. H. and Dillard, J. G. (1975) An ESCA study of sorbed metal ions on clay minerals: *ACS Symp. Ser.* 18, 186-201.
- Koppelman, M. H. and Dillard, J. G. (1977) A Study of the adsorption of Ni(II) and Cu(II) by clay minerals: *Clays & Clay Minerals* 25, 457-462.
- Koppelman, M. H. and Dillard, J. G. (1978) An X-ray photoelectron spectroscopic (XPS) study of cobalt adsorbed on the clay mineral chlorite: *J. Colloid Interface Sci.* 66, 345- 351.
- Lu, J. C. S. and Chen, K. Y. (1977) Migration of trace metals

in interfaces of seawater and polluted surficial sediments: *Environ. Sci. Technol.* 11, 174-182.

- Riley, J. P. and Chester, R. (1971) *Introduction to Marine Chemistry:* Academic Press, London, p. 389.
- Scofield, J. H. (1976) Hartree-slater subshell photoionization gross sections at 1254 and 1487 eV: J. *Electron Spectrosc. Relat. Phenom.* 8, 129-137.
- Seals, R. D., Alexander, R. W., Taylor, L. T., and Dillard, J. G. (1973) Core electron binding energy study of group IIb-VIIa compounds: *lnorg. Chem.* 12, 2485-2487.
- Sillen, L. G. and Martell, E. A. (1964) Stability constants of metal ion complexes: *Chem. Soc. (London), Spec. Pabl.* 17, 754 pp.
- Swartzen-Allen, S. L. and Matijevic, E. (1974) Surface and colloid chemistry of clays: *Chem. Rev.* 74, 385-400.

(Received 21 May 1979; accepted 29 October 1979)

Резюме—Изучалась адсорбция Cr(III) хлоритом и каолинитом при рН 1, 2, 3, 4, 6, 8, и 10 и иллитом при pH 1, 2, 3, и 6. Количество хрома, адсорбированного хлоритом, изменяется от 3.1×10^{-5} MOJIb/r npn pH 1 ao 16.6×10^{-5} MOJIb/r npn pH 4, и иллитом от 4.9×10^{-5} MOJIb/r ло 9,2 \times 10⁻⁵ моль/г при pH 1 и 3 соответственно. Каолинит адсорбировал 3,7 \times 10⁻⁵ моль Cr/r при pH 1, 2, и 3 и 5,5 \times 10⁻⁵ моль Cr/r при pH 4. Измерения связывающих энергий Cr на ядерном уровне 2p показывают, что хром, вероятно адсорбируется как водный ион Cr(III) при величинах pH меньше 4. Связывающие энергии для Сг на уровне 2p для образцов, приготовленных при pH выше 4, сильнее по сравнению с величиной, найденной для гидроокиси хрома, из чего следует, что соединение хрома, присутствующее при рН 6, 8, и 10 является гидроокисью. [N. R.]

Resiimee--Die Adsorption von Cr(III) an Chlorit und Kaolinit wurde bei den pH-Werten 1, 2, 3, 4, 6, 8, und 10 untersucht, die an Illit bei pH 1, 2, 3, und 6. Die Chrommenge, die an Chlorit adsorbiert wurde, variierte von 3,1 \times 10⁻⁵ Mol/g bei pH 1 bis 16,6 \times 10⁻⁵ Mol/g bei pH 4. Die an Illit adsorbierte Menge variierte von 4,9 \times 10⁻⁵ Mol/g bis 9,2 \times 10⁻⁵ Mol/g bei pH 1 bzw. 3. Kaolinit adsorbierte 3,7 \times 10⁻⁵ Mol *Cr/g* bei pH 1, 2, und 3 und 5.5×10^{-5} Mol Cr/g bei pH 4. Messungen der Cr 2p Kernlevel-Bindungsenergien deuten darauf hin, dab das Chrom bei pH-Werten unter 4 wahrscheinlich als ein Cr(III)aqua-ion adsorbiert ist. Die Bindungsenergien für den Cr 2p-Level bei Proben, die oberhalb pH 4 präpariert wurden, stimmen sehr gut mit dem Wert überein, der für Chromhydroxid bestimmt wurde, und führen zu dem schluß, daß das Chrom bei den pH-Werten 6, 8, und l0 in Form von Chromhydroxid vorliegt. [U.W.]

Résumé—L'adsorption de Cr(III) sur la chlorite et la kaolinite a été étudiée aux pH 1, 2, 3, 4, 6, 8, et 10, et sur l'illite aux pH 1, 2, 3, et 6. La quantité de chromium adsorbée sur la chlorite a varié de $3,1 \times 10^{-5}$ mole/g à un pH 1 à 16,6 \times 10⁻⁵ mole/g à pH 4, et sur l'illite, de 4,9 \times 10⁻⁵ mole/g à 9,2 \times 10⁻⁵ mole/g aux pH 1 et 3, respectivement. La kaolinite a adsorbé 3.7×10^{-5} mole Cr/g aux pH 1, 2, et 3, et 5.5×10^{-5} mole Cr/g à pH 4. Des mesures des énergies de liens du niveau de noyeu 2p de Cr indiquent que le chromium est probablement adsorbé en tant qu'ion aqua Cr(III) à des pH plus bas que 4. Les énergies de liens pour le Cr de niveau 2p pour des échantillons préparés à un pH plus haut que 4 peuvent être favorablement comparées à la valeur déterminée pour l'hydroxide de chromium, et mènent à conclure que l'espèce de chromium présente aux pH 6, 8, et 10 est l'hydroxide de chromium. [D.J.]