

CHROMATE REMOVAL BY DITHIONITE-REDUCED CLAYS: EVIDENCE FROM DIRECT X-RAY ADSORPTION NEAR EDGE SPECTROSCOPY (XANES) OF CHROMATE REDUCTION AT CLAY SURFACES

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Abstract—Chromium(VI) in the environment is of particular concern because it is toxic to both plants and animals, even at low concentrations. As a redox-sensitive element, the fate and toxicity of chromium is controlled by soil reduction-oxidation (redox) reactions. *In-situ* remediation of chromium combines reduction of Cr(VI) to Cr(III) and immobilization of chromium on mineral surfaces. In this study, Fe-rich smectite, montmorillonite, illite, vermiculite, and kaolinite were examined to determine reactivity in sorption-reduction of Cr(VI). The clays were compared to forms that were reduced by sodium dithionite. Clays containing Fe(II) efficiently removed soluble Cr(VI) from solution. Chromium K-edge X-ray absorption near edge structure (XANES) suggested that clays containing Fe(II) reduced Cr(VI) to Cr(III), immobilizing Cr at the clay/water interface. Adsorption of Cr(VI) by the Fe(II)-containing clay was a prerequisite for the coupled sorption-reduction reaction. Sodium dithionite added directly to aqueous suspensions of non-reduced clays reduced Cr(VI) to Cr(III), but did not immobilize Cr on clay surfaces. The capacity of clays to reduce Cr(VI) is correlated with the ferrous iron content of the clays. For dithionite-reduced smectite, the exchangeable cation influenced the sorption reaction, and thus it also influenced the coupled sorption-reduction reaction of Cr(VI). The pH of the aqueous system affected both the amount of Cr(VI) reduced to Cr(III) and the partition of Cr(III) between aqueous and adsorbed species. A plot of pH vs. amount (adsorption envelope) adsorbed for the coupled sorption-reduction reaction of Cr by reduced smectite exhibited a similar pattern to that of typical anion-sorption.

Key Words—Illite, IMt-2, Kaolinite, KGa-2, Montmorillonite, Reduction, Smectite, Sorption, SWa-1, SWy-1, XANES.

INTRODUCTION

Chromium contamination in soils and water is a consequence of many industrial activities, including mining, electric-power production, electroplating, leather tanning, and chemical manufacturing, and these activities generate waste products containing solid and aqueous forms of Cr(VI) (Forstner and Wittman, 1981). Cr(VI) is of particular concern because it is toxic to both plants and animals at low concentration (Turner and Rust, 1971; Bartlett and Kimble, 1976; Ajmal *et al.*, 1984). Speciation, mobility, and toxicity of heavy metals in soils are largely controlled by chemical reactions that occur at the solid-water interface. In neutral and alkaline soils, Cr(VI) is mobile owing to weak adsorption on the mineral surface. In acidic soils, Cr(VI) is removed from solution by adsorption on positively charged sorption sites (Bartlett and James, 1988; Zachara *et al.*, 1989).

Reduction of Cr(VI) to Cr(III) is of particular interest because this process usually immobilizes Cr in soils (Saleh *et al.*, 1989). Cr(VI) can be reduced by soil organic and inorganic reductants. Whereas organic matter may be a primary source for Cr(VI) reduction in soils (Bartlett and Kimble, 1976), Fe(II)-containing minerals are more important for Cr(VI) reduction in subsurface formations (Eary and Rai, 1991; Anderson

et al., 1994; Kent *et al.*, 1994). Gan *et al.* (1996) demonstrated that the reduction of structural Fe(II) increased the Cr(VI) removal efficiency of clays.

Chromate reduction by Fe(II)-containing minerals is most rapid under acid conditions (Bartlett and Kimble, 1976; Eary and Rai, 1991). Eary and Rai (1989, 1991) showed that Fe(II)-containing minerals, dissolving under acid conditions, released Fe(II) into solution, which rapidly reduced Cr(VI) to Cr(III). Under neutral and alkaline conditions, mineral dissolution and Fe(II) release become less significant, yet Cr(VI) reduction still occurs in soils and clays (Eary and Rai, 1989; Anderson *et al.*, 1994; Cifuentes *et al.*, 1996). White and Yee (1985) proposed an electron-cation transfer mechanism where the electron transfer from structural Fe(II) to aqueous Fe(III) was coupled by cation release from silicates to solution. Eary and Rai (1989) suggested that Cr(VI) reduction by Fe(II), which was produced by a coupled electron-cation transfer process, occurred in the solution rather than at the mineral surfaces even in neutral and alkaline conditions.

Reduction of Cr(VI) directly by structural Fe(II) in minerals is another possible mechanism. Peterson and co-workers (Peterson *et al.*, 1996; White and Peterson, 1996) provided evidence for Cr(VI) reduction at magnetite surfaces. With X-ray photoelectron spectroscopy

Table 1. Total Fe and Fe(II) contents of the clay samples as determined by the method of Komadel and Stucki (1998).

Clay	Sample	(% clay)	(cmol kg ⁻¹ clay)	Fe(II) content	
				(Fe(II)/ Fe _T *)	(kg ⁻¹ clay)
Smectite	SWa-1	17.7	316.6	0.61	1.9
	API-25	2.55	45.6	5.78	2.6
	SWy-1	3.50	62.6	3.04	1.9
Illite	Imt-2	4.80	85.7	26.1	22.4
	Fithian	4.65	83.0	25.4	21.0
Vermiculite	Libby	6.28	11.2	18.6	20.9
Kaolinite	KGa-2	0.80	14.3	5.9	0.9

py, Ilton and Veblen (1994) demonstrated the coupled sorption and reduction of chromate at the biotite/water interface. Using atomic force microscopy (AFM), Gan *et al.* (1996) showed that Cr(VI) directly reacted with an Fe(II)-containing smectite, forming precipitates on the smectite surface. Gan *et al.* (1996) also found chromium oxide in Cr(VI)-treated smectite SWa-1, based on an infrared vibration at 540 cm⁻¹ that is assigned to a Cr-O lattice vibration (Amonette and Rai, 1990). We are not aware of published studies reporting the direct oxidation-state measurements of Cr sorbed by clay surfaces.

Chromium K-edge X-ray absorption near-edge structure (XANES) is a useful tool for quantifying Cr oxidation states of contaminated soils (Peterson *et al.*, 1997; Szulczewski *et al.*, 1997). The intensity and area of the pre-edge peak in Cr XANES spectra is proportional to the Cr(VI) content in the sample (Bajt *et al.*, 1993; Kendig *et al.*, 1993; Peterson *et al.*, 1997; Szulczewski *et al.*, 1997). The objectives of this study were to determine the amount of chromate removed from solution by dithionite-reduced clays and to measure directly the oxidation state of Cr sorbed to clay surfaces with XANES.

MATERIALS AND METHODS

Clay minerals used in this study included: ferruginous smectite SWa-1, montmorillonite SWy-1, illite IMt-2, kaolinite KGa-2 (each from the Source Clay Repository of the Clay Minerals Society, Columbia, Missouri), and montmorillonite API-25 (America Petroleum Institute distributed by Ward's Natural Science Establishment, Rochester, New York). Illite, Fithian, Illinois, and vermiculite, Libby, Montana, were obtained from Ward's Natural Science Establishment. These samples were chosen to represent a wide range of clay mineral types and structural Fe contents (Table 1). The clay samples were washed three times with 1 M NaCl (or 1 M KCl), then with deionized water until the resistivity exceeded 18 Mohm-cm, then the exchange sites were saturated with Na⁺ ions (or K⁺ ions). The samples were fractionated by centrifugation and

the <2- μ m clay fraction was freeze-dried for storage until used.

Reduction of the structural Fe in the clay minerals was performed using the dithionite method described by Shen *et al.* (1992) and Shen (1994). The following procedure was used for sodium-saturated clays whereas the procedure for preparing potassium-saturated is described below. A 200-mg portion of each sample was weighed and placed in a 50-mL centrifuge tube and suspended in 10 mL of deionized water and mixed with 20 mL sodium citrate-bicarbonate (C-B) buffer (8 parts by volume of 0.3 M sodium citrate, Na₃C₆H₅O₇-H₂O and 1 part of 1 M sodium bicarbonate, NaHCO₃).

With a modified procedure of Chen *et al.* (1987), potassium-saturated clays were prepared by suspension in 1 M KCl solution followed by centrifugation and resuspension in a mixture of 10 mL deionized water and 20 mL potassium citrate-bicarbonate (C-B) buffer (8 parts by volume of 0.3 M potassium citrate, K₃C₆H₅O₇-2H₂O and 1 part of 1 M potassium bicarbonate, KHCO₃).

The tubes containing either sodium- or potassium-saturated clay were transferred to an inert-atmospheric glove box. Sodium dithionite (Na₂S₂O₄) was added to each tube to yield an aqueous concentration of 0.1 M. All samples were reacted in the glove box for 4 h at 70°C. For comparison, another 200-mg portion of the clay was treated identically except that 0.1 M sodium sulfate (Na₂SO₄) was used in place of sodium dithionite to maintain similar electrolytes, without Fe reduction. After the reaction, the clay suspensions were centrifuged, the supernatant discarded, and the clays washed with deoxygenated, deionized water (18 Mohm-cm resistivity) to remove excess salt under N₂-gas flow (Shen *et al.*, 1992; Stucki *et al.*, 1984).

All reactions between clay suspensions and solution chromate involved the following basic procedure. Immediately after dithionite treatment, 20 mL 1 mM Cr(VI) as sodium dichromate and 0.1 M NaCl were added to the tubes containing either dithionite-reduced or non-reduced clay under N₂-gas flow. Dichromate spontaneously dissociates to chromate monomers at concentrations <10 mM. The tubes were then gently shaken for 3 d at 22°C. The reaction mixture was separated by centrifugation at 22°C and the supernatant measured for total dissolved Cr and Cr(VI). All measurements were done in triplicate. The clay sediment was examined by X-ray absorption methods.

In experiments varying the initial Cr(VI) concentration (Figure 1), suspensions of reduced SWa-1 were mixed with 20 mL solutions containing 0.1, 0.5, 1, 2, 5, 10, 20, or 30 mM Cr(VI) and 0.1 M NaCl. To determine the pH-dependent adsorption envelope (Figure 2), reduced SWa-1 smectite was suspended in 20 mL of 5 mM Cr(VI) and 0.1 M NaCl. The suspension was titrated to different initial pH values, ranging from 2.5

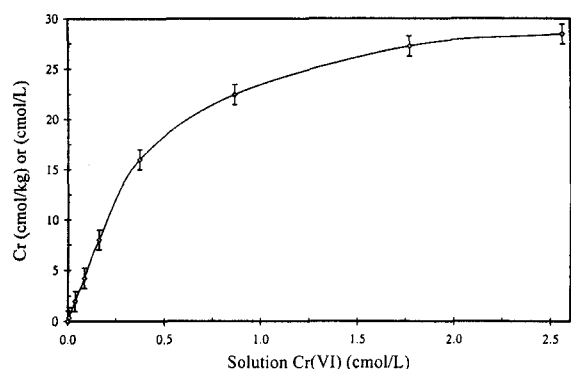


Figure 1. Sorption of Cr(III) by dithionite-reduced SWa-1 smectite with a structural Fe(II) content of 109 cmol kg^{-1} , equivalent to 10.9 mM structural Fe(II) in suspension, as a function of increasing Cr(VI) solution concentrations. All suspensions contained 200 mg SWa-1.

to 8.8, using 0.1 M NaOH or HCl. The final pH was measured before centrifugation. Other experimental conditions were identical to those given above.

For experiments measuring the effect of ionic strength and saturating cation (Figure 3), Na^+ -saturated (or K^+ -saturated) dithionite-reduced SWa-1 was suspended in NaCl (or KCl) solutions of varying concentration (0.01, 0.1, and 1 M) containing 5 mM Cr(VI) and reacted for 3 d. Similarly, in experiments measuring the effect of saturating cation on the Cr removal rate (Figure 4), Na^+ -saturated (or K^+ -saturated) dithionite-reduced SWa-1 was suspended in 1 M NaCl (or KCl) solution with 5 mM Cr(VI) and reacted for varying durations.

A portion of each clay was freeze-dried immediately after dithionite reduction. The freeze-dried samples

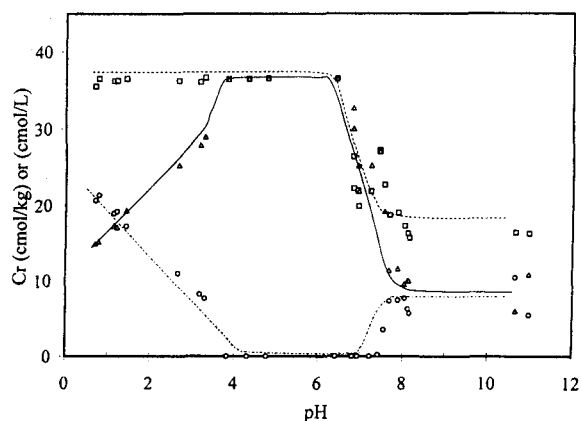


Figure 2. Effect of pH on the reduction of Cr(VI) and sorption of Cr(III) following a single addition of 5 mM Cr(VI): total Cr(VI) removed from solution (squares), total Cr sorbed by clay (triangles), and Cr(III) remaining in solution at equilibrium (circles). The suspensions contain 200 mg of dithionite-reduced SWa-1 [109 cmol kg^{-1} structural Fe(II) smectite, equivalent to 10.9 mM structural Fe(II) in suspension] saturated with Na^+ .

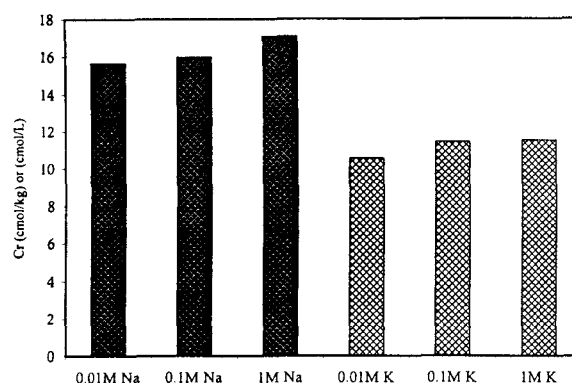


Figure 3. Effect of exchangeable cation and ionic strength on the removal of Cr(VI) by reduction following a single addition of 5 mM Cr(VI). The suspensions contain 200 mg of dithionite-reduced SWa-1 [109 cmol kg^{-1} structural Fe(II) smectite, equivalent to 10.9 mM structural Fe(II) in suspension], saturated with either Na^+ or K^+ .

were used for the determination of total structural Fe and Fe(II) contents by the method of Komadel and Stucki (1988). The dissolved Fe content in the treatment solutions was determined by atomic absorption.

The total Cr-solution concentration, including both Cr(III) and Cr(VI), was determined by atomic absorption spectrometry. Solution Cr(VI) concentrations were determined by colorimetric assay with s-diphenylcarbazide indicator reagent (Bartlett and James, 1979). Cr(III) concentration in the final solution was calculated as the difference between the total Cr and Cr(VI) concentrations. The difference in total Cr concentration between the initial and final solutions was assumed to be Cr sorbed by the clay. All Fe and Cr measurements were done in duplicate.

X-ray absorption spectra at the Cr K-edge (5989 eV) were collected at beamline X23B of the National

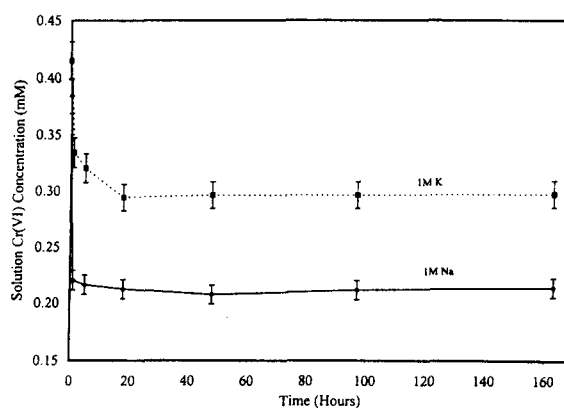


Figure 4. Kinetics of Cr(VI) removal by reduction and the effect of exchangeable cation following a single addition of 5 mM Cr(VI). The suspensions contain 200 mg of dithionite-reduced SWa-1 [109 cmol kg^{-1} structural Fe(II) smectite, equivalent to 10.9 mM structural Fe(II) in suspension], saturated with either Na^+ or K^+ .

Table 2. Chromium sorbed from non-reduced and dithionite-reduced Na-saturated clay suspensions. Initial Cr(VI) concentration was 1 mM and clay content was 10 g/L.

Clay type	Sample	Cr (cmol kg ⁻¹)	Fe(II) (cmol kg ⁻¹)	Cr (cmol kg ⁻¹)	pH ⁵
Smectite	SWa-1	0.37	5.91	109	7.85
	API-25	0.56	6.01	45	5.00
	SWy-1	0.41	6.19	62	5.23
Mite	Imt-2	0.53	4.98	42	2.66
	Fithian	0.94	5.35	49	3.86
Vermiculite	Libby	2.22	5.77	31	4.32
Kaolinite	KGa-2	0.2	4.90	11	2.09

¹ Total Cr sorbed by non-reduced clay.

² Final suspension pH for reactions involving non-reduced clays.

³ Fe(II) content of dithionite-reduced clay.

⁴ Total Cr sorbed by dithionite-reduced clay.

⁵ Final suspension pH for reactions involving dithionite-reduced clays.

Synchrotron Light Source (Brookhaven National Laboratory, New York) using a Stern-Heald fluorescence ion chamber (Lytle *et al.*, 1984). The purging gases were: 100% Ar (fluorescence ion chamber), 100% He (sample chamber), and 50% He—50% N₂ (15-cm incident ion-chamber). The XANES spectra were collected in the range of -100 to +450 eV relative to the Cr K-edge, using 0.2 eV steps with a 4-s integration in the energy range of ± 10 eV. The number of scans for each sample varied from one to six, depending on the signal-to-noise ratio.

All XANES spectra were subsequently merged and normalized using programs developed by Stern *et al.* (1995) and Boudin *et al.* (1995). The normalized XANES spectra with the pre-edge peak were fitted with one arctangent and four gaussian curves following the procedure of Szulczewski *et al.* (1997).

RESULTS AND DISCUSSION

Coupled sorption-reduction of Cr(VI) by reduced clays

The chromate anions, CrO₄²⁻ or Cr₂O₇²⁻, rarely adsorb on negatively charged clay surfaces. The total Cr sorbed by non-reduced clays from 1 mM sodium chromate solutions was <1.0 cmol/kg for most clays (Table 2) with one exception, the non-reduced Libby vermiculite, which adsorbed 2.22 cmol/kg of Cr. The amount of structural Fe reduced by the sodium dithionite treatment is given also in Table 2. The amount of Cr sorbed by dithionite-reduced clays ranged from 2.0 to 7.9 cmol/kg (Table 2). The linear regression of Cr sorbed vs. the initial structural Fe(II) content (Figure 5), using data from Tables 1 and 2, yields a correlation coefficient of $r^2 = 0.93$.

The initial Fe(II) content of the non-reduced clays, except the Libby vermiculite and dithionite-reduced KGa-2 kaolinite, resulted in sorbed Cr levels too low

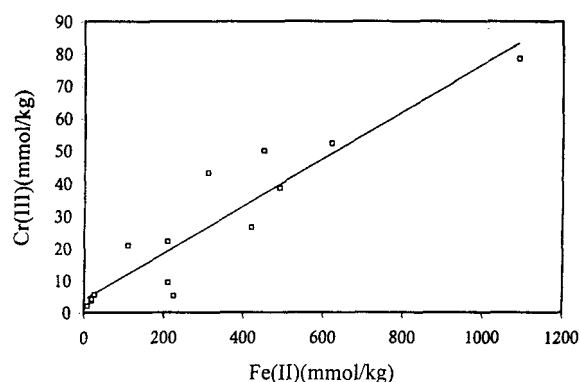


Figure 5. Total chromium(III) sorbed by non-reduced and dithionite-reduced clay as a function of the initial structural Fe(II) content of the clays.

for quantitative XANES analysis. Normalized XANES spectra of sorbed Cr for the remaining dithionite-reduced clays yielded XANES spectra with signal-to-noise levels suitable for quantitative analysis of Cr(VI):Cr(III) ratios. The XANES spectrum for untreated Libby vermiculite, not shown, resembled the dithionite-reduced clays shown in Figure 6, revealing no Cr(VI) in the Cr sorbed by the clay minerals. Expanding the energy range near the Cr K-edge to a larger scale (Figure 7) failed to reveal any pre-edge peak indicative of Cr(VI). These XANES spectra provide direct evidence that structural Fe(II) from the clay minerals reduces Cr(VI) and immobilizes Cr(III) on the clay surface. The removal of Cr(VI) from aqueous solutions by reduced clays appears to be a coupled sorption-reduction process (Uton and Veblen, 1994).

The data (Table 2) for the reduction of Cr(VI) by structural Fe(II) leading to its immobilization on clay surfaces as Cr(III) did not involve direct contact between Cr(VI) and dithionite. An experiment was designed to determine whether coupled reduction-im-

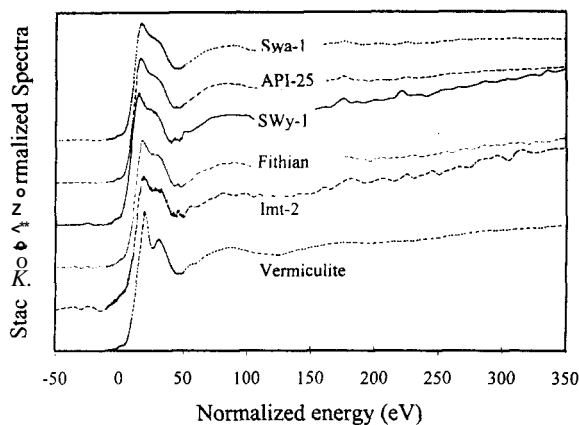


Figure 6. K-edge XANES spectra of Cr sorbed following reaction with selected dithionite-reduced clays.

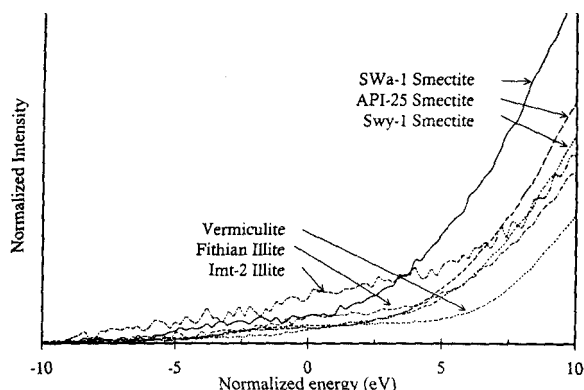


Figure 7. Pre-edge portion of the K-edge XANES spectra of Cr sorbed following reaction with selected dithionite-reduced clays.

Table 3. Chromium reduced and sorbed from non-reduced clay suspensions following the addition of sodium dithionite. Initial Cr(VI) concentration was 1.11 mM, clay content was 10 g/L, initial suspension pH was 5.07, and initial sodium dithionite concentration was 100 mM.

Clay type	Sample	Cr(VI), (mM) ¹	Cr(III), (mM) ²	Cr (cmol kg ⁻¹) ³	pH ⁴
Smectite	SWa-1	0.01	1.09	n.d. ⁵	6.61
	API-25	0.02	1.08	0.12	6.68
	SWy-1	0.02	1.09	n.d. ⁵	6.87
Illite	Imt-1	0.02	1.05	0.96	5.93
	Fithian	0.02	1.01	1.92	6.30
Vermiculite	Libby	0.02	0.91	4.55	5.99
Kaolinite	KGa-2	0.02	1.08	n.d. ⁵	6.10

¹ Solution Cr(VI) concentration.

² Solution Cr(III) concentration.

³ Total Cr sorbed by clay.

⁴ Final suspension pH clay.

⁵ Not detected.

mobilization occurs in the same way if dithionite reacted directly with Cr(VI). First, we suspended 200 mg of clay in 20 mL of a solution that was 1 mM Cr(VI) and 0.1 M NaCl, then added 348 mg of sodium dithionite crystals, yielding an initial dithionite concentration of 0.1 M that was identical to that used to pretreat an equal quantity of clay in the previous experiment. Table 3 shows the amounts of Cr(VI) reduced to Cr(III) and the amount of Cr adsorbed to clay surfaces after reduction in solution by dissolved sodium dithionite. Although sodium dithionite in solution reduced nearly all Cr(VI) to Cr(III), unlike reduction at the interface by structural Fe(II), most of the Cr(III) remained in solution and did not sorb to the clay surface. Because the non-reduced clay samples used in this experiment did contain structural Fe(II) in the untreated form (Table 1) and because this structural Fe(II) did cause sorption of Cr(III) by clay surfaces (Table 2), we expected some reduction-sorption at the interface, especially by illite and vermiculite. A linear regression of Cr(III) sorption resulting from reduction at the interface by structural Fe(III) (Table 2, col. 3) vs. Cr(III) sorption resulting from reduction by dithionite in solution (Table 3, col. 5) suggests dithionite has a kinetic advantage over structural Fe(II). The net result is that the clays sorbed nearly half as much Cr(III), the product of reduction, where the reductant was dithionite in solution rather than structural Fe(II) in the clay.

Effects of solution Cr concentration and pH

The effects of time, concentration, pH, cation type, and ion strength can provide further insight into the mechanisms of sorption reactions. The results from the reactions of dithionite-reduced SWa-1 with sodium dichromate under different conditions are given in Figures 1, 2, 3, 4, and 8.

Figure 1 shows that increasing the Cr(VI) concentration resulted in a non-linear increase in Cr(III) sorp-

tion by the dithionite-reduced SWa-1 with a structural Fe(II) content of 109 cmol/kg (Table 2). The final pH ranged from 7.2 to 8.0. Cr(III) sorption follows a curve similar to a Langmuir equation. The ratio of Cr(VI) reduced to Fe(II) oxidized will be 1:3 if all of the structural Fe(II) reacts with the Cr(VI) in the suspension. The actual ratio of Cr(VI) reduced to Fe(II) oxidized was 0.262 at the maximum Cr sorption (Figure 1), indicating a maximum efficiency of ~79% for the utilization of structural Fe(II).

Figure 4 shows the rate of Cr(VI) reduction by dithionite-reduced SWa-1 with a structural Fe(II) content of 109 cmol/kg. The rate of Cr(VI) removal by coupled sorption-reduction was very rapid. The amount of Cr(VI) removed clearly depends on the type of exchangeable cation, with Na-saturated SWa-1 removing more Cr(VI) than K-saturated SWa-1. The combined effect of exchangeable cation and ionic strength on the

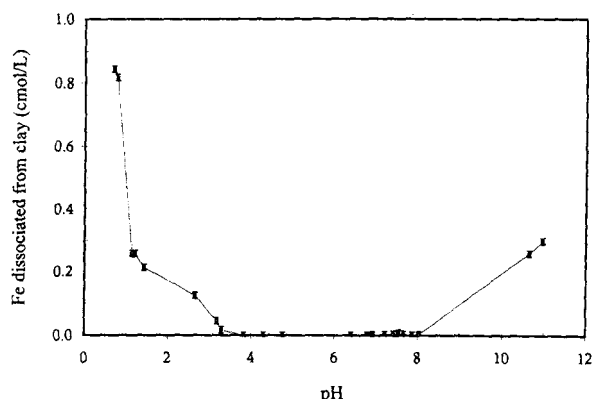


Figure 8. Effect of pH on solution Fe concentrations following a single addition of 5 mM Cr(VI) to suspensions containing 200 mg of dithionite-reduced SWa-1 [109 cmol kg⁻¹ structural Fe(II) smectite, equivalent to 10.9 mM structural Fe(II) in suspension] saturated with Na⁺.

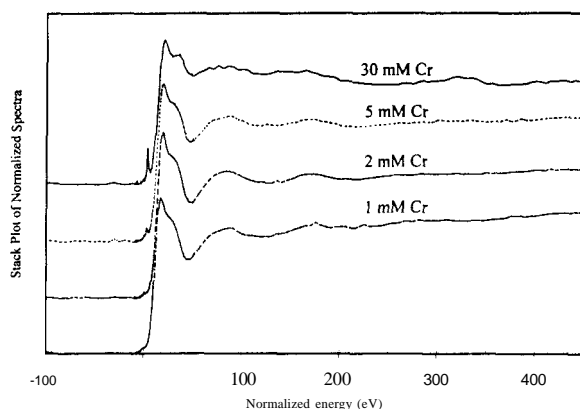


Figure 9. K-edge XANES spectra of Cr sorbed following reduction by dithionite-reduced SWa-1 [109 cmol kg⁻¹ structural Fe(II) smectite, equivalent to 10.9 mM structural Fe(II) in suspension] saturated with Na⁺.

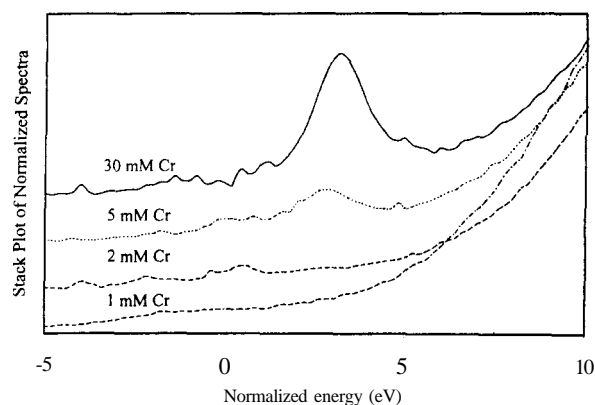


Figure 10. Pre-edge portion of the K-edge XANES spectra of Cr sorbed following reduction by dithionite-reduced SWa-1 [109 cmol kg⁻¹ structural Fe(II) smectite, equivalent to 10.9 mM structural Fe(II) in suspension] saturated with Na⁺.

coupled Cr(VI) sorption-reduction reaction by dithionite-reduced SWa-1 is given in Figure 3. Varying the ionic strength from 0.01 to 1 M has little effect.

Figure 2 illustrates the effect of pH on Cr(VI) reduction and Cr(III) sorption whereas Figure 8 shows the release of Fe(II) by clay dissolution. The clay used for these experiments was dithionite-reduced SWa-1, containing 109 cmol/kg structural Fe(II). In the pH range 4–6.3, SWa-1 reduced nearly all Cr(VI) in solution (Figure 2), converting it to Cr(III) that either remains sorbed to the smectite or returns to solution as dissolved Cr(III). Above pH 6.3, reduction removes less Cr(VI) as the pH increases to 8, beyond which the quantity of Cr(VI) reduced by the smectite is unchanged.

The removal of Cr(VI) (Figure 2) is highest under acid conditions. This result is typical of anion adsorption by a mineral with a positive proton-surface charge, although the ion deposited on the surface is the cation Cr(III) rather than anion Cr(VI). The results in Figure 2 provide further evidence that Cr(VI) anions probably adsorb to the clay surface before reduction occurs, provided the pH is >4. In contrast, Fe(II) released by clay dissolution below pH 4 (Figure 8) reduces some of the Cr(VI) before it adsorbs.

Figures 9 and 10 show the effect caused by varying the solution Cr(VI) in dithionite-reduced SWa-1 suspensions. Adding <5 mM Cr(VI) to the clay suspensions resulted in the complete reduction of Cr(VI) to Cr(III). Clay suspensions reacted with solutions containing >5 mM Cr(VI) did not completely reduce adsorbed Cr(VI) to Cr(III). Quantitative analysis of the XANES, following the method of Szulczewski *et al.* (1997), indicated ~85% reduction of Cr(VI) to Cr(III) in the smectite treated with 5 mM Cr and 60% reduction of Cr(VI) to Cr(III) in the clay treated with 30 mM Cr.

Figure 11 shows the effect of pH on the reduction of Cr(VI), showing only the pre-edge region of the K-edge XANES spectra for Cr sorbed to dithionite-reduced SWa-1 treated with 5 mM Cr(VI). Below pH 7.54, all of the Cr sorbed to the smectite has been reduced to Cr(III). Quantitative analysis of the XANES spectra from samples prepared at pH 8.03 and 10.65 revealed 90 and 85% reduction, respectively. Patterson *et al.* (1997) also observed the complete removal of Cr(VI) from solution yet incomplete reduction of Cr(VI) to Cr(III) at the surface following reduction by amorphous ferrous sulfide. The accumulation of a chromic oxide precipitate at the clay surface may possibly inhibit electron transfer, resulting in Cr(VI) removal by adsorption without reduction.

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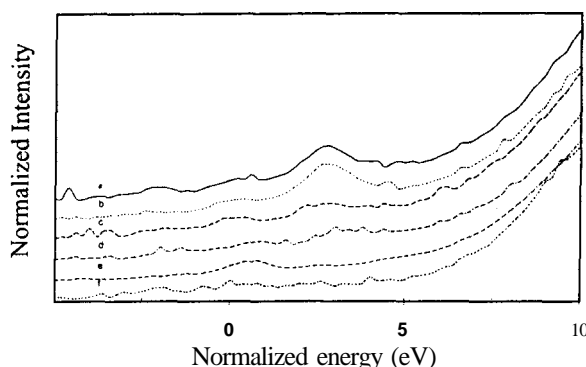


Figure 11. Effect of pH on the K-edge XANES spectra of Cr sorbed following a single addition of 5 mM Cr(VI) to suspensions contain 200 mg of dithionite-reduced SWa-1 [109 cmol kg⁻¹ structural Fe(II) smectite, equivalent to 10.9 mM structural Fe(II) in suspension] saturated with Na⁺. (a) pH 10.65, (b) pH 8.03, (c) pH 7.54, (d) pH 6.91, (e) pH 3.83, and (f) pH 1.43.

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