Kinetics and Mechanisms of Metal Retention/Release in Geochemical Processes in Soil

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RESEARCH OBJECTIVES

The long-term fate of toxic metals in soils cannot be precisely predicted, and often remediation recommendations and techniques may be ineffective or unnecessary. This work will generate basic knowledge on the kinetics and mechanisms of heavy metal retention/release by soil mineral colloids. The information should assist in improving remediation strategies for toxic heavy metal contaminated soils. The objectives are:

- To determine the effects of residence time on the mechanisms of Cr(VI), Cu(II), Co(II), Cd(II), Pb(II), and Ni(II) sorption/release on Fe and Al oxide and clay mineral surfaces using kinetic studies coupled to X-ray Absorption Near Edge Structure (XANES) spectroscopy, Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy.

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- To study the effect of temperature, pH, and phosphate on metal sorption by oxides and clays, and to derive thermodynamic parameters to describe the sorption process.

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, which generate waste products containing solid and aqueous forms of Cr(VI). Cr(VI) is of particular concern because it is toxic to both plants and animals at low concentration. Speciation, mobility, and toxicity of heavy metals in soils are largely controlled by chemical reactions that take place at the solid-water interface. In neutral and alkaline soils, Cr(VI) is mobile due to its weak adsorption on mineral surface. In acidic soils Cr(VI) is removed from solution by adsorption on positively charged sorption sites.

Oxidation-reduction (redox) reaction is among the most fundamental processes that occur in soil and environment. Reduction of Cr(VI) to Cr(III) is of particular interest as this process immobilizes Cr in soils. Cr(VI) can be reduced by soil organic and inorganic reductants. While organic matter may be primary source for Cr(VI) reduction in surface soil, Fe(II)-containing minerals are more important for Cr(VI) reduction in subsurface soil and aquifer.

Chromate reduction by Fe(II)-containing minerals is most rapid under acid conditions. Studies showed that Fe(II) was released to solutions as a result of mineral dissolution under acid conditions. Aqueous Fe(II) rapidly reduced Cr(VI) to Cr(III), forming precipitates. Under neutral and alkaline conditions, mineral dissolution and Fe(II) release become less significant, while Cr(VI) reduction was still observed in soils and clays. A possible mechanism is reduction of Cr(VI) directly by structural Fe in minerals via coupled reduction-sorption process. But little direct evidence has been published to show the oxidation state of Cr on clay surfaces.

X-ray Absorption Near-Edge Structure (XANES) was proved to be a useful tool for determining Cr oxidation state of Cr-contaminated soils. The intensity and area of pre-edge peak in a Cr XANES spectrum is proportional to Cr(VI) content in the sample. Thus, XANES can be used to characterize the oxidation state of Cr formed on clays in the reduction-sorption processes. Therefore, the objectives of our current work were to determine the amount of chromate removed from solution by the dithionite-reduced clays and to characterize Cr oxidation state on the clay surfaces with XANES. The hypothesis to be tested was that reduced clay minerals can function as both reducing agents and adsorbents for Cr(VI) removal in aqueous systems.

MATERIALS AND METHODS

Materials

Clay minerals from different sources were used in this study. Ferruginous smectite SWa-1, montmorillonite SWy-1(Crook county, Wyoming), illite IMt-2, kaolinite KGa-1b, and KGa-2 were from the Source Clay Repository of the Clay Minerals Society (Columbia, Missouri). The sample obtained from America Petroleum Institute was montmorillonite API 25. Fithian illite (Fithian, Illinois) and Libby vermiculite (Libby, Montana) were obtained from Ward's Natural Science Establishment (Rochester, New York). These samples were chosen to represent a wide range of clay mineral types and structural Fe contents (Table 1).

The smectite and illite samples were Na-saturated by washing with 1 *M* NaCl three times, then four times with de-ionized water to remove excess salts. Impurities were removed from the clay by centrifugation. The clay fraction (<2 µm) was freeze-dried before being used in the experiments. The vermiculite and kaolinite samples were used in the study as received.

Fe Reduction and Cr Reaction

A 200-mg portion of each clay sample was weighed and placed in a 50-ml centrifuge tube. The clay was first washed with 1 *M* KCl solution by centrifugation. Then the clay was suspended in 10 ml de-ionized water and mixed with 20 ml potassium citrate-bicarbonate (C-B) buffer. The tubes were then transferred to an inert-atmospheric glove box. Sodium dithionite was added to each tube to form an aqueous concentration of 0.1 *M.* All samples were reacted in the glove box for 4 hrs at 70°C. For comparison, another 200-mg portion of the clay was treated identically except that 0.1 *M* sodium sulfate was used in place of sodium dithionite to maintain similar electrolytes, but without Fe reduction. After the reaction, the clay suspension was centrifuged to discard the supernatant and the clays were washed with deoxygenated, de-ionized water to remove excess salt under N_2-gas flow. All treatment were done in triplicates. One replicate of each treatment was used for the determination of total structural Fe content and Fe(II) to total Fe ratio in the clay.

Under N_2-gas flow, the tube with the reduced (dithionite-treated) or unreduced (sulfate-treated) clay was mixed with 20 ml 1 *mM* Cr(VI) solution (in form of $Na_2Cr_2O_7$), and gently shaken for 3 days at 22°C. The reaction mixture was separated by centrifugation at 22°C. The supernatant was measured for total Cr and Cr(VI) concentrations. The clay sediment was used for spectroscopic characterization.

Cr and Fe Analysis

Total Cr concentration was determined by atomic absorption and assumed as the sum of Cr(III) and Cr(VI) species. Cr(VI) concentration was determined by colorimetric assay with s-diphenylcarbazide indicator reagent (Bartlett and James, 1979) and a Beckman DU-70 spectrophotometer. 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.

One replicate of each reduced clay was used for the determination of total structural Fe content and Fe(II) to total Fe ratio in the clay by the method of Komadel and Stucki (1988). The dissolved Fe content in the treatment solutions was determined by atomic absorption.

XANES Spectra Collection and Analysis

The clay sediments after the treatments were freeze-dried. The treated clay samples were packed in plastic sample holders. The X-ray absorption spectra at the Cr K-edge (5989 eV) was collected at Beamline X23B of the National Synchrotron Light Source (Brookhaven National Laboratory, New York). The detector used was a Stern-Heald fluorescence ion chamber positioned 90 degrees of the incident beam. Calibration was done using 2 µm Cr evaporated on aluminum foil (the standard material from EXAFS Materials Co.). The purging gases were 100% Ar for the Stern-Heald fluorescence ion chamber, 100% He for the sample chamber, and 50% He and 50% N_2 for the 15 cm incident ion-chamber. The XANES spectra were collected in the range of -100 to +450 eV relative to the first inflection point of the Cr standard. The scan parameters for the region of concern (-10 to +10 eV) were 0.2 eV steps with a 4 second integration. The number of scans for each sample varied from 1 to 6 depending on the signal-to-noise ratio.

The raw data collected from the beamline was converted. The pre-edge background was then subtracted. The absorption coefficient was normalized relative to the intensity of the “White-line” peak so that all the spectra were plotted on the same scale.

RESULTS

Table 2 displays the Fe reduction level achieved by dithionite treated and the sorption of Cr in reduced and unreduced clays from 1 mM sodium dichromate solution. Table 3 shows the amounts of Cr(Vi) reduced to Cr(III) and Cr adsorbed in clays after reaction of sodium dithionite with 1 mM sodium dichromate in the presence of clays.

Figure 1 to 5 are the experimental results from the reactions of dithionite-reduced smectite SWa-1 with sodium dichromate under different conditions. Figure 1 displays time series of residual Cr concentration for the reaction of reduced SWa-1 with 5 mM Cr(VI). Figure 2 shows that coupled reduction-adsorption of Cr on reduced SWa-1 increased with solution Cr(VI) concentration and reached a maximum. Figure 3 exhibits the effects of cation type on the coupled reduction-sorption of Cr(VI) by reduced SWa-1. Figure 4 and 5 The pH profile of 5 mM Cr(VI) reaction with dithionite-reduced SWa-1, showing Cr(III) in final solution, adsorbed Cr, total Cr(VI) disappeared, and the amount of Fe dissociated from smectite SWa-1 at different pH after reaction.

Figure 6 and 7 display XANES spectra of Cr in clays reduced by sodium dithionite and then treated with 1 mM sodium dichromate. Figure 8 to 10 are showing XANES spectra of Cr adsorbed in reduced smectite SWa-1. The Cr(VI) was estimated by curve-fitting of the pre-edge peak, indicating about 10 - 15% Cr(VI) of total Cr in the clay treated with 5 mM Cr (pH above 8), and 40% in the clay treated with 30 mM Cr (pH 7.2).

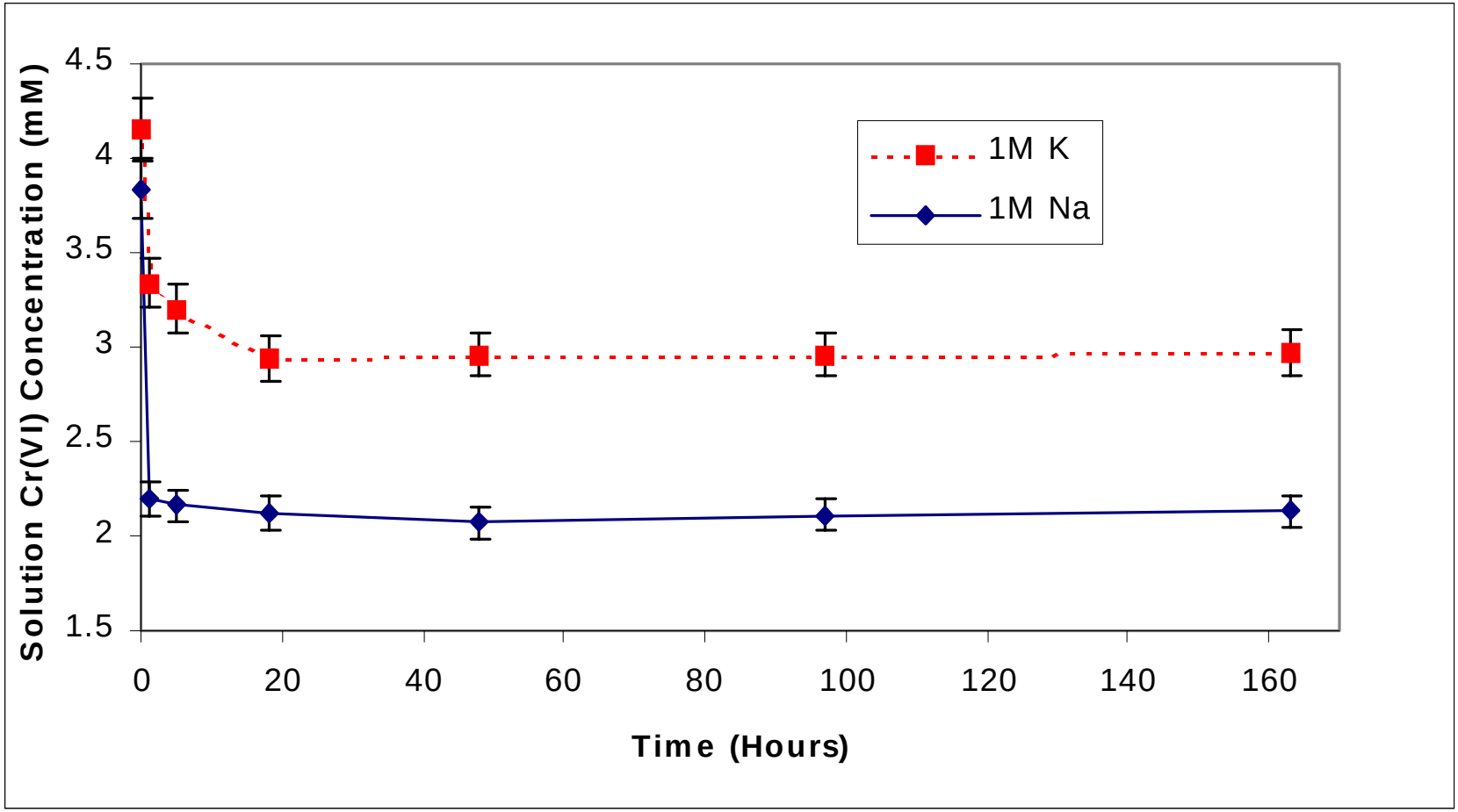

Figure 1. Residual Cr concentration at different time intervals after reaction of 5 mM Cr(VI) with the reduced smectite SWa-1. The rate of Cr removal was very rapid. The amount of removal depended on the cation type of the system with greater removal capacity for Na-smectite.

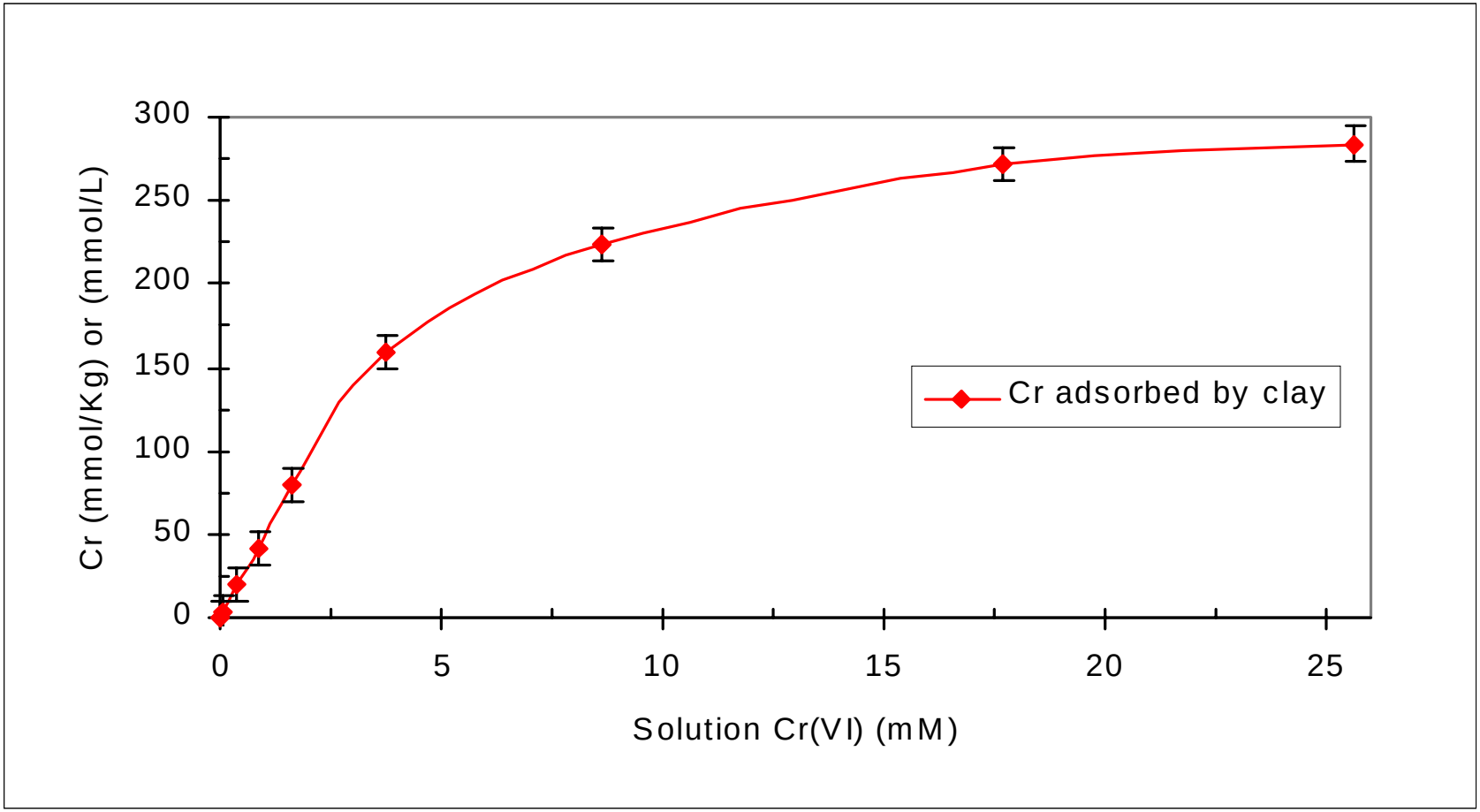

Figure 2. Coupled reduction-adsorption of Cr on dithionite-reduced smectite SWa-1 at different solution Cr(VI) concentrations. Cr sorption reached a maximum in a typical Langmuir fashion. The maximum of coupled reduction-sorption was correlated to the clay structural Fe(II).

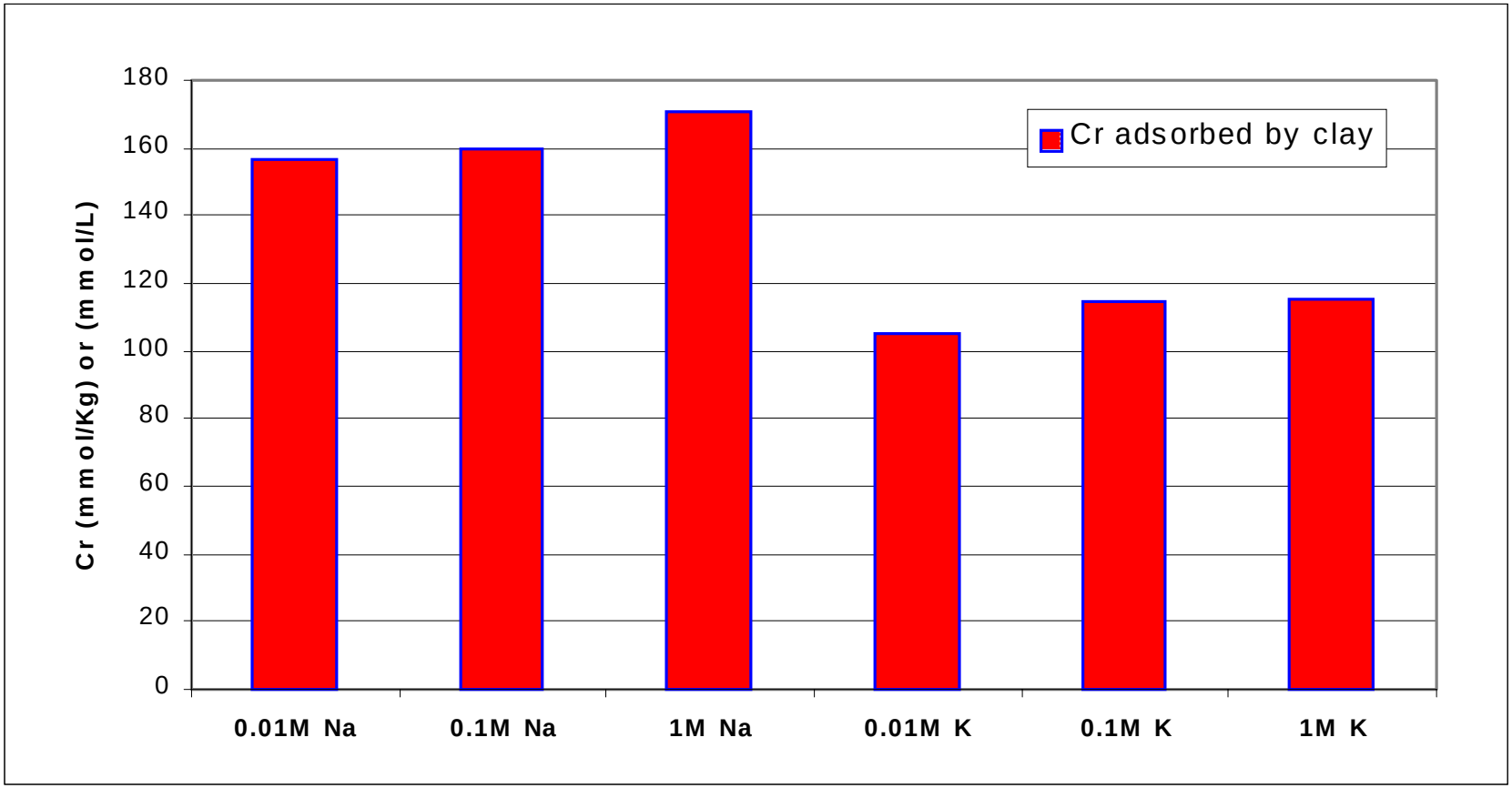

Figure 3. Coupled reduction-sorption of Cr(VI) by smectite SWa-1 with various ion concentration of Na^+ or K^+. Cation type had a significant effect on the amount of Cr adsorbed, while ion-strength played little role.

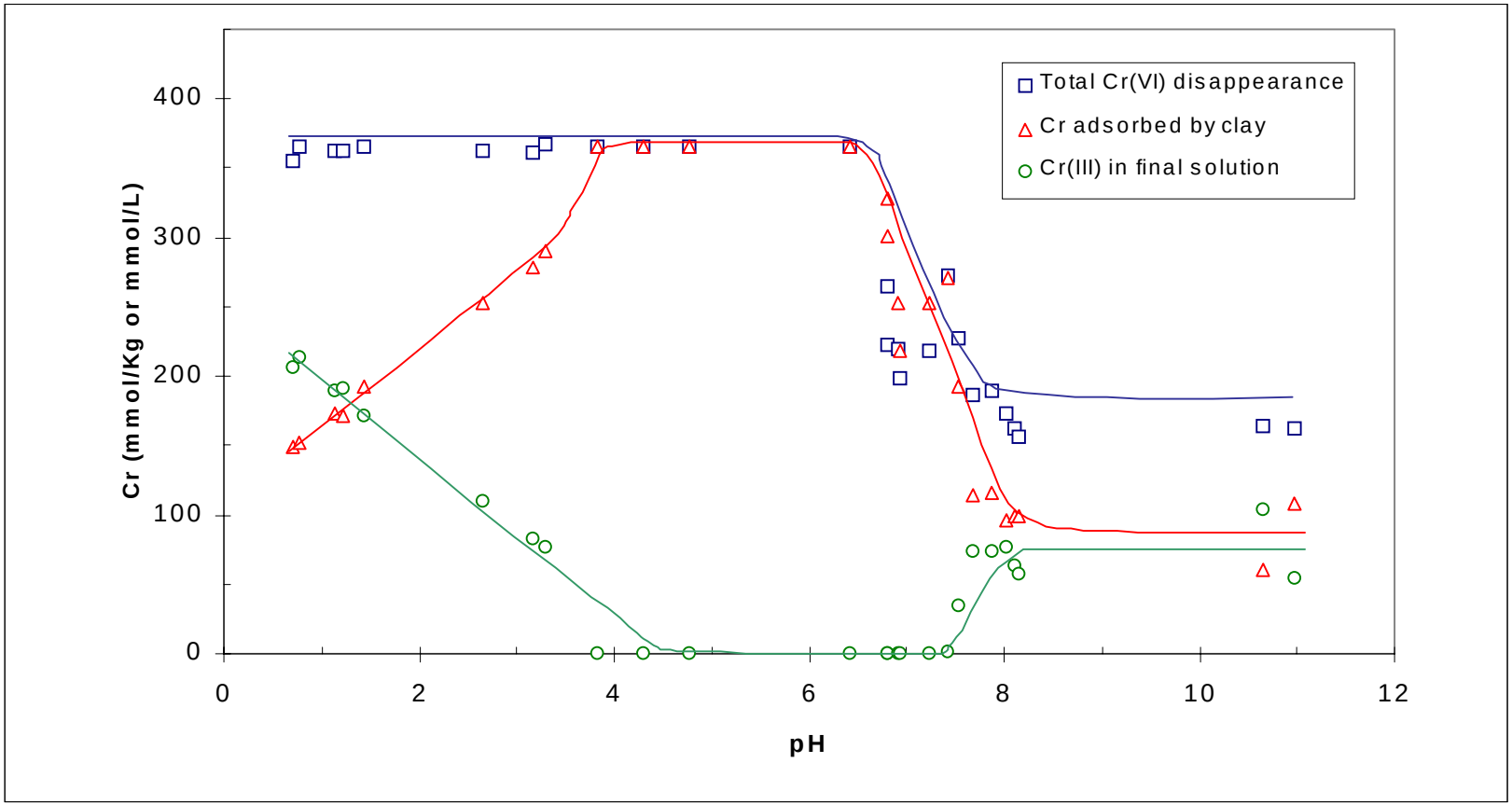

Figure 4. The pH profile of 5 mM Cr(VI) reaction with dithionite-reduced SWa-1, showing Cr(III) in final solution, adsorbed Cr, and total Cr(VI) disappeared at different pH after reaction. The coupled reduction-sorption exhibited a similar pH-edge as anion adsorption.

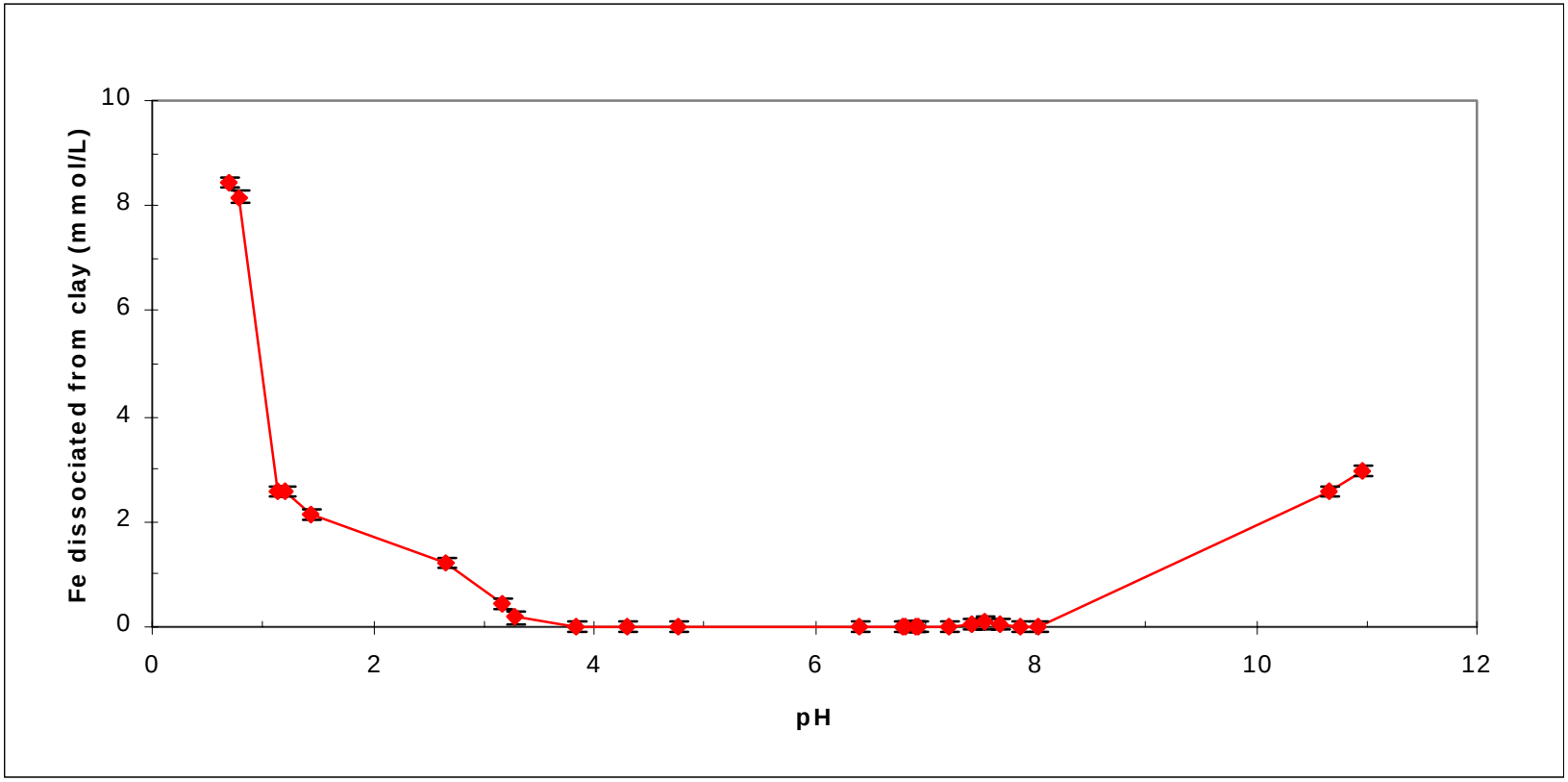

Figure 5. The amount of Fe dissociated from smectite SWa-1 when reacting with 5 mM Cr(VI) at different pH. The dissolved Fe stayed at zero between pH 3 - 8, and increased below pH 3 and above pH 8.

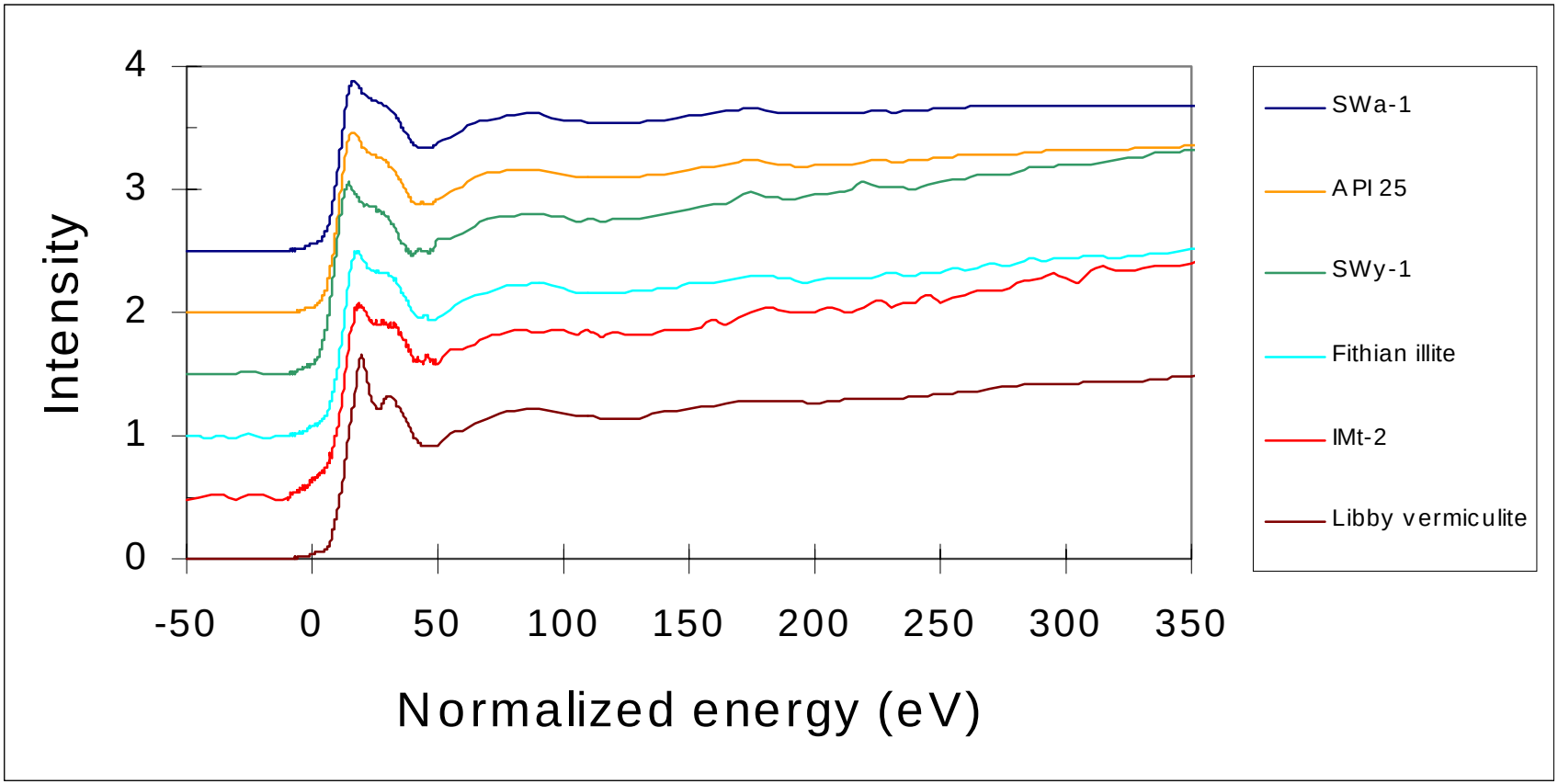

Figure 6. XANES spectra of Cr in different clays treated with 1 mM sodium dichromate. No pre-edge peak can be seen in the spectra, indicating all Cr sorbed by clays was Cr(III).

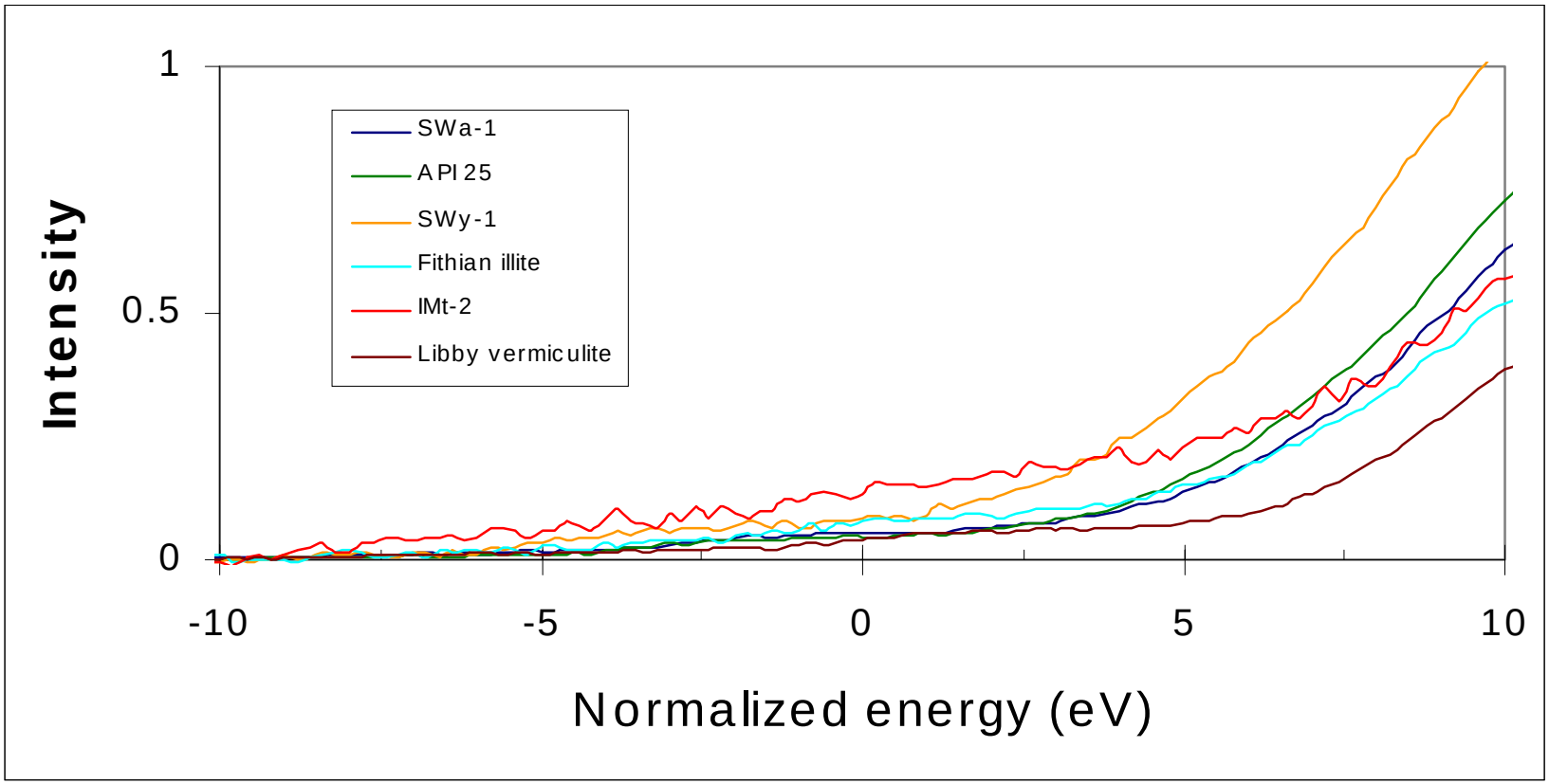

Figure 7. The expanded XANES spectra of Cr in different clays treated with 1 mM sodium dichromate. Still, no pre-edge peak can be seen in the spectra, indicating all Cr sorbed by clays was Cr(III).

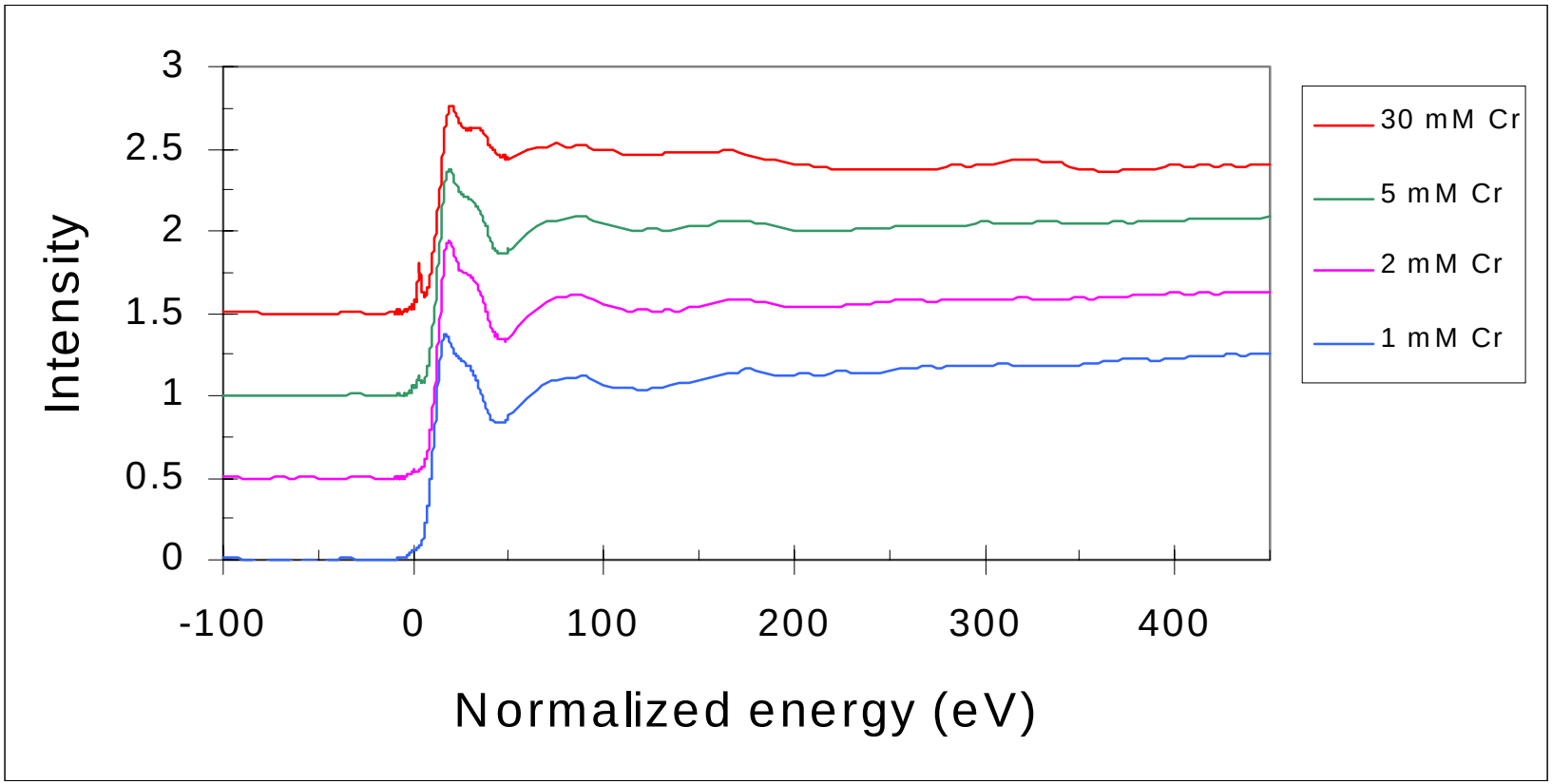

Figure 8. XANES spectra of Cr in smectite SWa-1 treated with different concentration of sodium dichromate. Pre-edge peak can be seen in the spectra of Cr in the smectite treated with high concentration of sodium dichromate, indicating some Cr(VI) in the clay.

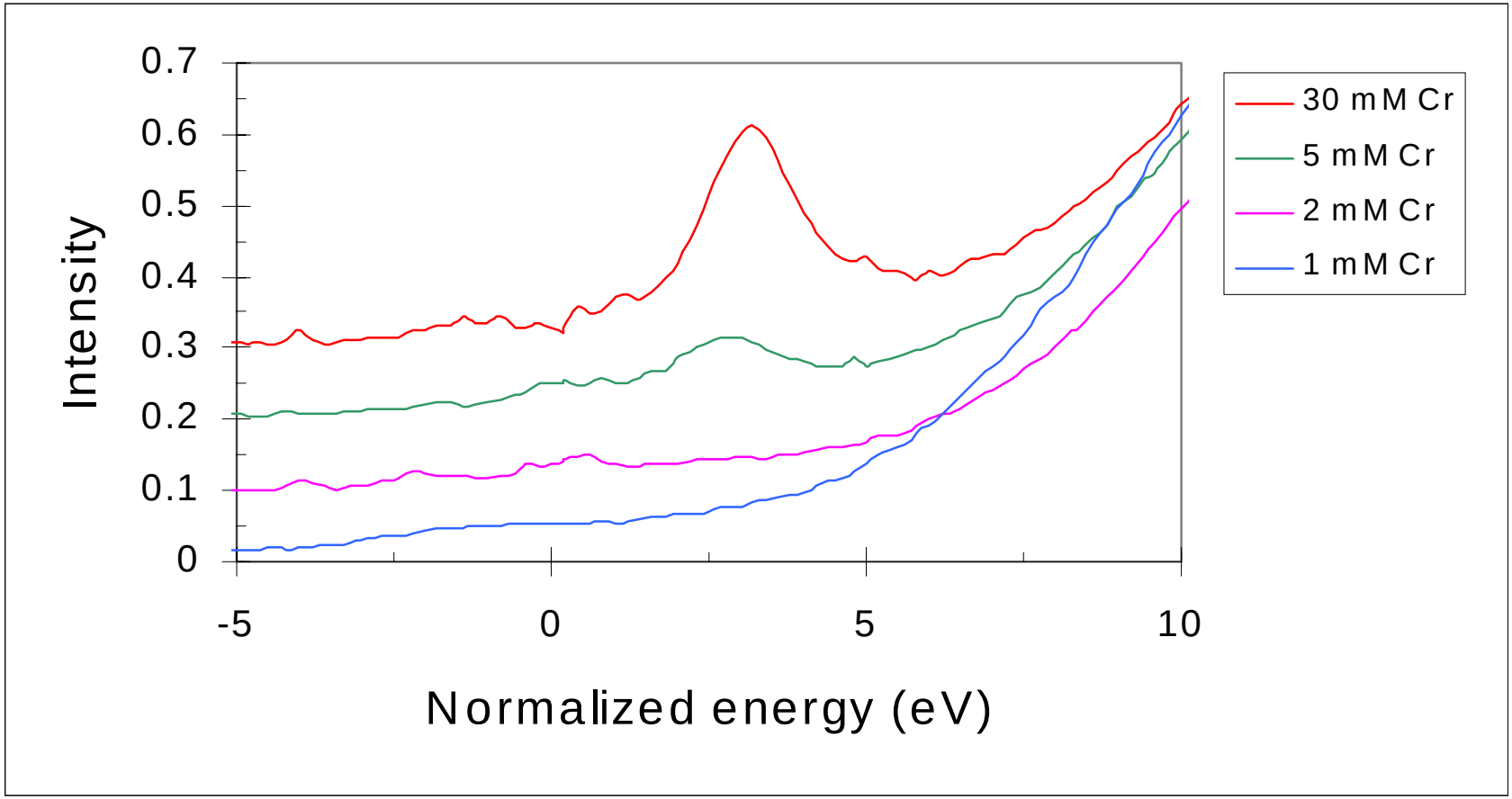

Figure 9. Expanded XANES spectra of Cr in smectite SWa-1 treated with different concentration of sodium dichromate. The Cr(VI) was estimated by curve-fitting of the pre-edge peak, indicating about 15% Cr(VI) of total Cr in the clay treated with 5 mM Cr and 40% in the clay treated with 30 mM Cr. The pH of final reaction mixture was in the range of 7.2 - 8.0

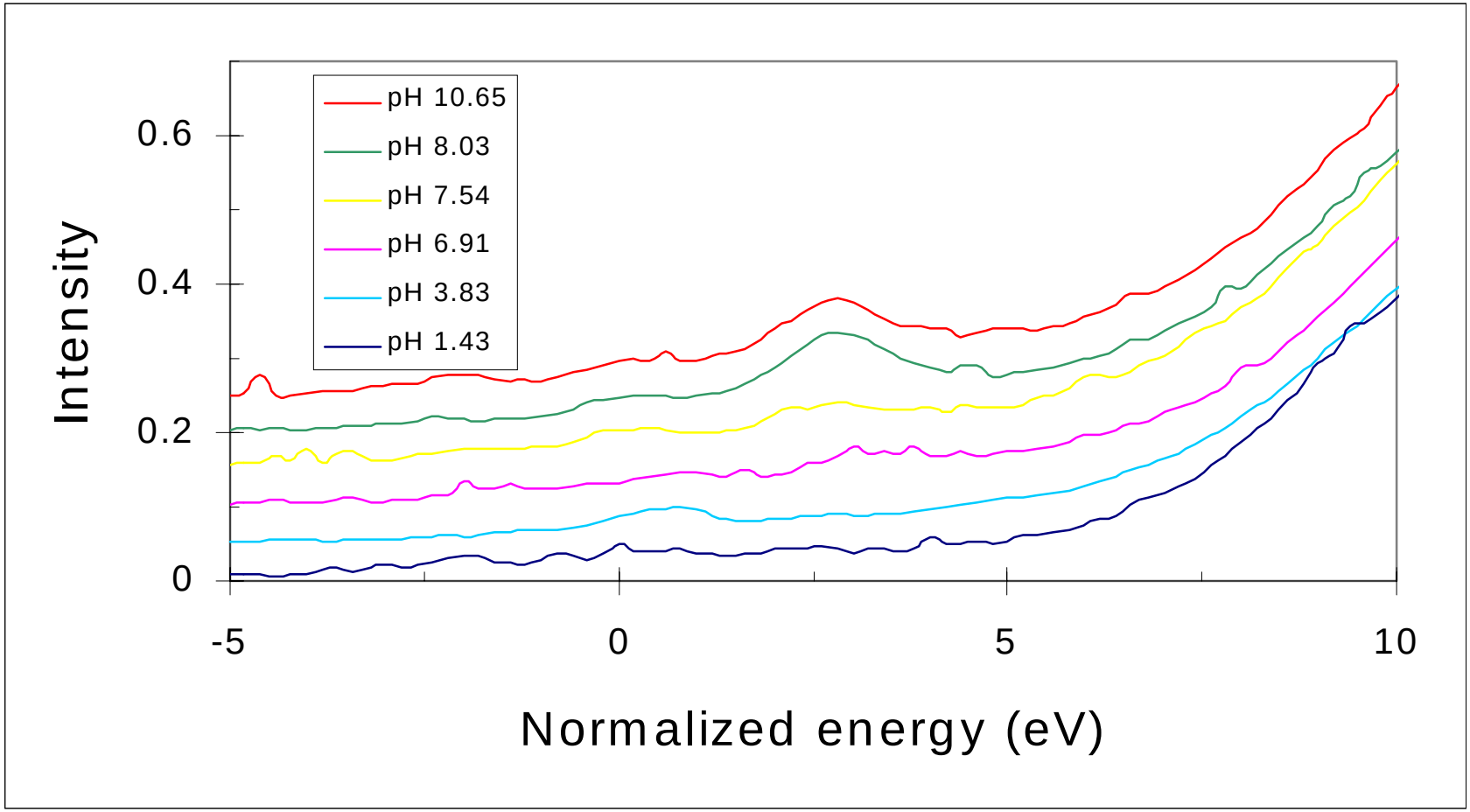

Figure 10. Expanded XANES spectra of Cr in smectite SWa-1 treated with 5 mM Cr(VI) at different pH. The Cr(VI) was estimated by curve-fitting of the pre-edge peak, indicating 10 - 15% Cr(VI) of total Cr in the clay treated at pH above 8.

Conclusions

Clays containing structural Fe(II) can act as an efficient remover of Cr(VI) from an aqueous system. The XANES spectra of such Cr-treated clays provided evidence that the clays reduced Cr(VI) to Cr(III) and immobilized Cr at the same time.

The Cr(VI) removal capacity varied with the clay mineral type in the orders of smectites > vermiculites ~ illites > kaolinite. For the reduced smectites, the surface cation type influenced sorption process, and thus the coupled reduction-sorption 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. The pH profile of coupled reduction-sorption exhibited a similar pattern as the pH-edge of anion sorption.

The reducing agent (sodium dithionite) applied directly into aqueous systems reduced Cr(VI) to Cr(III), but could not immobilize Cr even in the presence of the clays. All the above phenomena indicated that initial close contact between clay surfaces and Cr(VI) was the pre-requisite of coupled reduction-sorption processes.

Within the same type of clay minerals, reduction of Cr(VI) is correlated to the ferrous iron content of the clays. The maximum removal of Cr(VI) by the reduced smectite was determined by its structural Fe(II) content. These results indicated that the reduction of Cr(VI) to Cr(III) was coupled by the oxidation of structural Fe(II) to Fe(III).

The results of this study can be used to develop a method for in-situ remediation of chromium at contaminated sites.

Future Work

1. The studies planned for Summer 1998 will examine the coupling of Cr reduction and oxidation to Fe and Mn in soils:
   - One series of experiments will study the reduction of soluble Cr(VI) by Fe(II) within the structure of layer silicate minerals. This study will determine changes in solution conditions influencing the reactivity of Fe(II) locked within silicate minerals.
   - Another series of experiments will collect Cr, Mn, and Fe K-edge XANES from soils contaminated with Cr(VI) and later treated by additions of soluble Fe(II) to promote reduction of Mn(IV) and re-oxidation of Cr(III).
   - 2. The XANES studies for Fall 1998 will concentrate on the K-edges of two elements: S and Cr. We will examine reactions between soil humic substances and Cr(VI), seeking to verify whether humic thiol groups are acting as reducing agents.
3. Soil clay minerals will be extracted from two common soil types in Northern Alabama (Decatur and Hartsells soils). The extracted soil clays will be subjected to XRD analysis to identify the clay minerals present. All of the experiments done above involving Cr, Mn and Fe will be repeated using the extracted soil clays to see if there are differences between natural soil clays and reference clay minerals. This work is expected to take one year for completion.

TABLE 1. The total and ferrous iron contents of the clay samples

Clay Type	Clay Sample	Total Fe Content		Fe(II) Content	
		(%of clay)	(mmol/Kg clay)	(Fe(II)/ Fe_{total}, %)	(mmol/Kg clay)
Smectite	SWa-1	17.7	3.166	0.16	0.005
	API-25	2.55	0.456	5.78	0.026
	SWy-1	3.50	0.626	3.04	0.019
Illite	IMt-2	4.80	0.857	26.1	0.224
	Fithian	4.65	0.830	25.4	0.210
Vermiculite	Libby	6.28	1.121	18.6	0.209
Kaolinite	KGa-1	0.14	0.025	7.8	0.002
	KGa-2	0.80	0.143	5.9	0.009

SWa-1 is a iron-rich smectite, while API 25 and SWy-1 are low-iron smectites. In the natural state, Fe(II) in Illites and vermiculite is around 20% of their total Fe content . Kaolinites contain very small amount of Fe in their structure.

TABLE 2. Adsorption of chromium in dithionite-reduced or unreduced clays from 1 mM sodium dichromate solution

Clay Type	Clay Sample	Fe reduction level Fe(II)/ Fe_{total} (%)	Cr adsorbed by unreduced clay (mmol/Kg)	Cr adsorbed by reduced clay (mmol/Kg)	Difference of adsorbed Cr (mmol/Kg)
Smectite	SWa-1	34.5	3.7	78.5	74.8
	API-25	98.7	5.6	50.0	44.4
	SWy-1	99.8	4.1	52.3	48.2
Illite	IMt-1	49.2	5.3	26.6	21.3
	Fithian	58.7	9.4	38.6	29.2
Vermiculite	Libby	27.6	22.2	43.2	21.0
Kaolinite	KGa-1	99.8	2.1	19.9	17.8
	KGa-2	78.3	2.0	20.9	18.9

The reduced smectites behaved as good remover of Cr(VI). The amount of Cr sorbed by reduced smectites was correlated to Fe(II) content. Vermiculite in its natural oxidation state removed significant amount of Cr from aqueous system.

TABLE 3. The Cr contents and pH of the initial Cr solution and the final solutions after reduction by sodium dithionite in the presence of clays, and the amount of Cr adsorbed by clays after the reaction

Clay Type	Clay Sample	Cr(VI) (mM)	Cr(III) (mM)	Adsorbed Cr (mmol/Kg)	pH
Initial Cr solution		1.11	0		5.07
Smectite	SWa-1	0.01	1.09	-	6.61
	API-25	0.02	1.08	1.2	6.68
	SWy-1	0.02	1.09	-	6.87
Illite	IMt-1	0.02	1.05	9.6	5.93
	Fithion	0.02	1.01	19.2	6.30
Vermiculite	Libby	0.02	0.91	45.5	5.99
Kaolinite	KGa-1	0.02	1.09	-	6.06
	KGa-2	0.02	1.08	-	6.10

The reducing agent (sodium dithionite) reduced almost all Cr(VI) to Cr(III). But most of Cr(III) remained in the solution even in the presence of clays. Adsorption of Cr(III) was insignificant except by vermiculite and some illite.