Chromium leaching vs. oxidation state for a contaminated solidified/stabilized soil

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Abstract

The toxicity, solubility, and mobility of chromium in soil are strongly dependent upon its oxidation state. Solidification/stabilization (S/S) is a potential method for preventing Cr leaching from contaminated soil. We evaluated the leaching behavior of untreated and solidified/stabilized chromium contaminated soil samples obtained from two locations at a military facility in Louisiana. The leaching of chromium, as measured by the Toxicity Characteristic Leaching Procedure (TCLP), was expected to be dependent upon the chromium oxidation state. The pH, cation exchange capacity and particle size distribution were obtained for each sample and portions of each sample were solidified with Type I Portland cement. The oxidation state of chromium was determined by X-ray absorption spectroscopy (XAS). The sample from Site 1 contained 478 $mg\,kg^{-1}$ total chromium while the sample from Site 2 contained 1272 $mg\,kg^{-1}$ total Cr. The TCLP chromium concentration for Site 1 untreated soil was 3.4 $mg\,L^{-1}$ and 2.0 $mg\,L^{-1}$ for the S/S treated sample. The sample from Site 2 had TCLP chromium concentrations below the analytical detection limit (< 1.0 $mg\,L^{-1}$) for both untreated and S/S samples. The XAS data showed the presence of the more mobile and soluble Cr^{+6} at Site 1 but not at Site 2. The use of Portland cement alone was not effective in reducing the Cr^{+6} to the less soluble and less mobile Cr^{+3}, or in physically preventing leaching of Cr^{+6}. © 1997 Elsevier Science B.V.

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1. Introduction

Chromium is widely used for electroplating, leather tanning, steelmaking, corrosion control, and wood preservation. At low levels it is an essential element for animal metabolism. At high concentrations it can cause nausea, skin ulcerations, and lung cancer, and levels near 0.1 $mg\,g^{-1}$ body weight can be lethal [1].

In natural systems chromium is found in either the hexavalent (Cr^{+6}) or trivalent (Cr^{+3}) oxidation state. Hexavalent chromium is an oxyanion commonly occurring as relatively water soluble chromate $(CrO_4)^{-2}$ or dichromate $(Cr_2O_7)^{-2}$. In temperate region soils, where negatively charged clay minerals predominate, these Cr^{+6} anions are repelled by the negative charge on the soil particles. Due to the charge repulsion and the solubility of the Cr^{+6} compounds, hexavalent chromium is quite mobile in soils [2]. The Cr^{+6} form is a strong oxidizer which makes it the more toxic form to biological systems [3]. Trivalent chromium is relatively non-reactive and less toxic due to its slow ligand exchange kinetics [3]. Trivalent chromium most commonly occurs as a cation in soils, forming relatively insoluble oxide and hydroxide compounds. With its large positive charge, Cr^{+3} is attracted to negatively charged soil particles, and has been found to associate with the smallest size fractions in soils [1]. Thus, Cr^{+3} is less mobile in soils than Cr^{+6}.

In the soil, Cr^{+6} compounds may be reduced to Cr^{+3}. Eary and Rai [4] evaluated the reduction of chromate by five subsurface soils and concluded that low pH increased the rate of Cr^{+6} reduction by organic acids and enhanced the release of Fe^{+2} from soil minerals.

Molecular oxygen and manganese oxides are the only naturally occurring oxidizing agents of Cr^{+3}. Oxygen will oxidize Cr^{+3} to Cr^{+6} but only when the pH is greater than 9. Fendorf and Zasoski [2], evaluated the oxidation of Cr^{+3} in soil and found that chromium oxidation by MnO_2 occurred over a range of pH and Cr^{+3} concentrations. However, they found that as pH and Cr^{+3} concentrations increased, the amount of Cr^{+3} oxidized to Cr^{+6} decreased.

Channell and Kosson [5] evaluated the use of S/S for the treatment of soils contaminated by a chromium wood preserving waste. The binders used in their study were Portland cement, kiln dust and lime/fly ash. None of the selected binders were effective in reducing the leaching of chromium from the treated samples as measured by TCLP.

Bajt et al. [6] evaluated the inclusion of a synthetic chromate waste in a Type II Portland cement matrix and used a synchrotron X-ray microprobe to identify the oxidation state of the chromium within the solidified matrix. Slag materials, containing Fe^{+2} and sulfide compounds, were added to some of the samples in an attempt to reduce the added Cr^{+6} to Cr^{+3}. The sample containing slag had a much lower percentage of Cr^{+6} than the sample containing no slag, indicating that with proper additives, the Cr^{+6} could be reduced as curing took place.

Methods for chromium oxidation state determinations vary. Chemical methods convert all of the chromium to the hexavalent form for extraction, then the Cr^{+6} is measured by a colorimetric procedure or by atomic absorption [7].

X-ray absorption spectroscopy (XAS) employing a synchrotron X-ray source may be utilized to determine the oxidation state of chromium in treated and untreated soil samples. XAS is a non-destructive technique well suited for differentiating chromium compounds due to the structural differences in the Cr^{+3} and Cr^{+6} ions. The portion of XAS relevant to this study is the X-ray absorption near-edge structure (XANES), which provides information on element valence and coordination number [8]. In an XAS analysis, monochromatic X-rays are impinged upon a sample and the energy of the incident X-rays is scanned over a region encompassing the binding energy of core electrons in the atom of interest. At the K-edge of an element, the point at which the energy of incident X-rays is optimal to excite 1s electrons to the continuum, the absorption coefficient increases dramatically. When the incident X-ray energy is lower than the energy required for a transition to the continuum, the 1s electrons can still be promoted to unoccupied orbitals below the continuum, if such orbitals exist. In this case pre-edge resonance(s) will appear in the XANES spectrum. In special cases, as with elements having an empty d orbital and without a center of inversion (Ti^{+4}, V^{+5}, Cr^{+6}, and Mn^{+7}), the pre-edge peak is very strong [9]. It is this pre-edge peak which enables the differentiation of Cr^{+6} and Cr^{+3} in a sample.

This research focused on chromium contaminated soils obtained near a chromic acid cleaning and etching facility. Based on the sources of chromium contamination, it was suspected that both oxidation states should be present at the site, with distribution dependent upon where the sample was collected. Solidification/stabilization has been proposed as a possible treatment method to prevent the movement of chromium into the groundwater. The purpose of this study was to evaluate the effectiveness of S/S for treatment of chromium contaminated soils at this site. In addition, the relationship between chromium leaching data and the oxidation state, as determined by the XANES method, was examined experimentally.

2. Materials and methods

Soil samples were collected from the Louisiana Army Ammunition Plant (LAAP) located near Shreveport, LA. The soil at this site is a Ruston very fine, sandy loam, classified as a fine-loamy, siliceous, thermic Typic Paleudult according to the US Soil Taxonomy [10]. The LAAP operates a small facility where chromic acid is used to clean 155 mm shell casings prior to the application of a paint primer coat. In addition, chromic acid is also used in an etching process during quality control evaluations of the 155 mm shells.

Samples from two different sites were evaluated in this study. The sample identified as Site 1 was collected at a depth of 2–6 in. near a chromic acid etching tank. This sample had a distinct yellow color. The second sample, identified as Site 2, was collected at a depth of 2–6 in. near a downspout which drained rain water from the roof of the building in which the chromic acid was used. Exhaust hoods over the etching tanks had transported Cr-containing aerosols to the roof of the building, and these aerosols were subsequently washed to the ground. Light green deposits were visible in this sample.

The soils were stored at 4°C in a secure, temperature controlled environment until they were required for testing. Before analyses were initiated, the moist samples were passed through a No. 10 sieve to remove particles larger than 2 mm, and homogenized with a Gilson Model SP-1 sample splitter.

Chemical characterization included pH measurement according to EPA Method 9045[7] using both deionized, distilled water and a 0.01 M calcium chloride solution. Particle size distribution was determined with a hydrometer using the Bouyoucos procedure [11]. The cation exchange capacity (CEC) was determined by EPA Method 9081 [7], in which the samples are saturated with Na using an excess of sodium acetate, followed by extraction of the Na with ammonium acetate. The displaced sodium was measured by atomic absorption spectrometry to determine the CEC of the sample. Total metals were determined by microwave digestion with HNO_3 following EPA Method 3051 [7]. Total chromium was determined in triplicate by flame atomic absorption spectrometry.

The soils were solidified with Type I Portland cement using a 0.2 binder to soil ratio (by weight) and a 0.2 water to soil ratio (by weight). The S/S samples were cured for 28 days in an environmental chamber at 23°C and 95% rh. After curing, the S/S treated samples and untreated soils were crushed to pass a 9.5 mm sieve and evaluated in triplicate for chromium leaching with the TCLP test [12]. A liquid to solids ratio of 20:1 (by weight) was used and both untreated and S/S treated soils were leached with a mixture of acetic acid and deionized, distilled water. Leachates were analyzed by atomic absorption spectrometry.

In preparation for the XANES analysis, oven dried S/S samples were crushed to pass a 230 mesh (63 μm) sieve. A thin layer of the powdered sample was sandwiched between two pieces of 4 μm Prolene film (Chemplex Industries, Inc., Tuckahoe, NY), held in a Chemplex X-ray fluorescence sample cup. The untreated soils were used without drying or crushing to minimize any changes and were simply packed into sample cups and covered with Prolene film.

The XANES data was obtained using beamline X26A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. This beamline is used primarily as an X-ray fluorescence microprobe with a collimated (8 × 10 μm) white beam, or for micro-XANES measurements with a focused (150 × 300 μm) monochromatic beam. In this experiment the synchrotron X-ray fluorescence microprobe was used in its normal configuration [13–15] with a Si(111) channel-cut monochromator and a focusing mirror. The monochromator operated between 4 and 20 keV and had an energy resolution of about 1 eV. The focusing mirror served to focus X-rays and to reject the higher harmonics (high energy cutoff is at ≈ 14 keV). An ion chamber, filled with helium and located downstream of the slit assembly, was used for the incident beam intensity normalization. An energy dispersive Si(Li) detector with energy resolution of 155 eV for Mn Kα was mounted at 90° to the incident beam. Such geometry minimizes the Compton scattering causing most of the background radiation. The samples were mounted at 45° to the incident beam and 45° to the Si(Li) detector, on an x-, y-, z-, θ-stage which had a 1 μm precision. The sample could be observed at all times using a microscope that views the sample at normal incident and had a CCD camera connected to a monitor outside the experimental hutch.

The intensity of chromium fluorescence X-rays was measured as a function of incident X-ray energy. A typical XANES spectrum was collected from about 20 eV below the chromium pre-edge peak energy to 30 eV above the pre-edge peak with 0.3 eV steps. A second scan was taken over a 100 eV region at energies about 500 eV above the pre-edge peak for intensity normalization as previously described by Bajt et al. [6]. Fluorescence detection is especially appropriate for dilute and thick samples. All samples in this study contained very low concentrations of chromium so that self absorption effects could be neglected. The detection limit for the above experimental conditions was below 100 ppm.

Three chromium reference compounds with known concentrations of Cr^{+6} were used as a basis for quantifying the chromium oxidation state in each sample. The first standard consisted entirely of Na_2CrO_4 and had a Cr^{+6} mole fraction ($Cr^{+6}/Cr^{+6} + Cr^{+3}$) of 1.00. The second standard was a combination of Na_2CrO_4 and Cr_2O_3 and had a Cr^{+6} mole fraction of 0.39. The third standard consisted entirely of Cr_2O_3 and had a Cr^{+6} mole fraction of 0.00. The different concentrations of Cr^{+6} produced varying peak intensities. The area of the pre-edge peak was determined using a curve fitting procedure, which has been previously described by Bajt et al. [6]. In this procedure, the normalized peak area is linearly proportional to the mole fraction of Cr^{+6} present in the sample.

3. Results and discussion

The characteristics of the soil for both sites are listed in Table 1. The pH of ≈ 9.5 is much higher than normal (4.2–4.8) for this soil type, and the data showed no significant variation between deionized water and 0.1 M $CaCl_2$ solutions for either site. The extremely high pH suggests the site was limed, perhaps to neutralize chromic acid, and that considerable sodium is present. The CEC results for both sites indicate sufficient cation exchange capacity for potential binding of the Cr^{+3} cation. Based on particle size distribution data, these soils have sandy loam textures.

Site 1 had a total chromium concentration of 478 $mg\,kg^{-1}$ and the TCLP leachate of the untreated soil had a chromium concentration of 3.3 $mg\,L^{-1}$ (Table 1). This site was near the chromic acid tank and the more mobile and soluble Cr^{+6} was expected at this location due to the proximity to the tank and yellow deposits observed on the soil surface. The total chromium concentration was higher at Site 2, 1272 $mg\,kg^{-1}$, but the concentration of chromium in the TCLP leachate of the untreated soil was below the detection limit of 1 $mg\,L^{-1}$ for our procedure. The lower concentration of chromium in the TCLP leachate from Site 2 is likely due to the absence or much lower concentration of the more soluble Cr^{+6}.

Fig. 1 shows the XANES spectra of the chromium compounds used as standard references. The total chromium in the reference standards ranged from 10.0 to 22.1 $g\,Cr\,kg^{-1}$, which is low enough to prohibit chromium self absorption effects. Note the increase in intensity of the pre-edge peak, indicative of the Cr^{+6} ion, as the mole fraction of Cr^{+6} increases. The peak areas obtained for the reference compounds,

Table 1

Selected soil characteristics. The data for Cr concentration in the soil and TCLP leachate is an average of three replicates. The numbers in parentheses are the standard deviations. All other data was obtained from a single replicate

Parameter	Site 1	Site 2
pH		
Distilled, deionized water	9.5	9.6
0.01 M $CaCl_2$	9.5	9.5
CEC ($cmol_c$ kg^{-1})	6.1	9.0
Particle size distribution		
% Sand	77	74
% Silt	15	19
% Clay	8	7
Total chromium, wet basis ($mg kg^{-1}$)	478.0	1272.0
TCLP Cr concentration ($mg L^{-1}$)		
Untreated samples	3.3 (0.4)	< 1.0
Treated samples	2.0 (0.1)	< 1.0
XANES Data, mole fraction Cr^{+6}		
Untreated samples	0.033	< 0.001
Treated samples	0.095	< 0.001

normalized to average counts at higher energy (approximately 500 eV above the pre-edge peak energy as described above), were used to develop the calibration curve shown in Fig. 2.
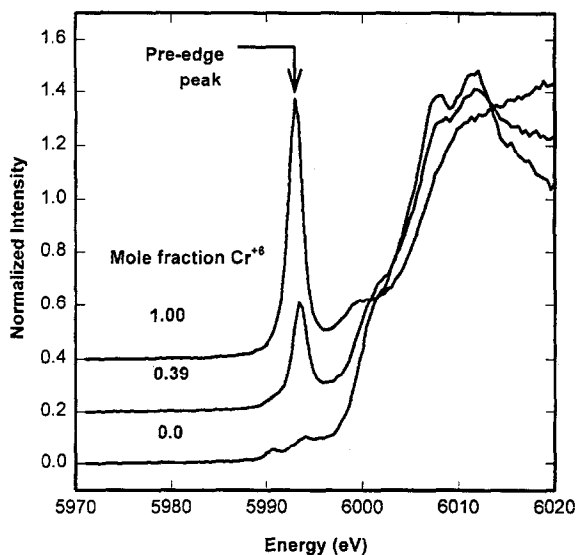

Fig. 1. XANES spectra for chromium standards. Successive spectra are offset by 0.2 intensity units for clarity.
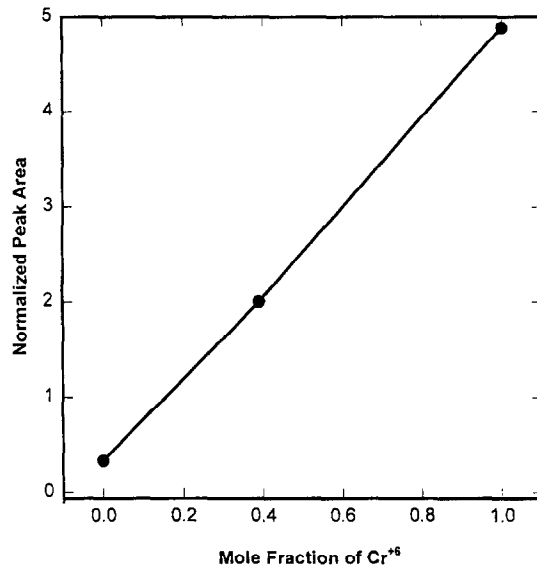
Fig. 2. Calibration curve obtained from chromium reference compounds.

Fig. 3 shows the XANES spectra for the treated and untreated samples from both sites. Treated and untreated samples from Site 1 have the pre-edge peak characteristic of Cr^{+6} while the spectra for samples from Site 2 lack this feature. Based upon the
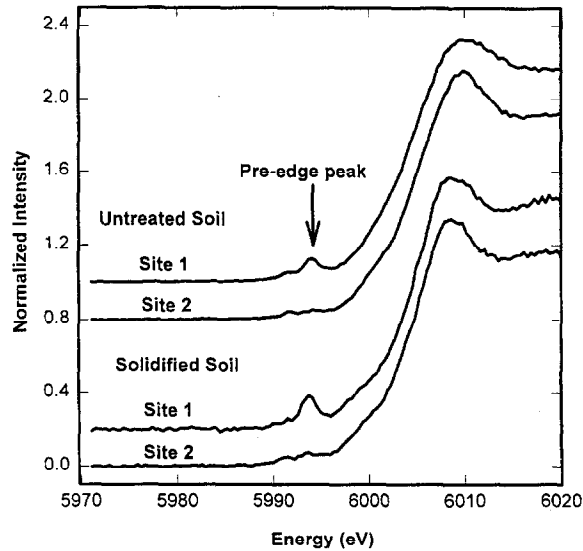

Fig. 3. XANES spectra for soils. Successive spectra are offset by 0.2, 0.8, and 1.0 intensity units along the y-axis for clarity.

normalized peak area and using the calibration curve in Fig. 2, untreated soil from Site 1 had a Cr^{+6} mole fraction of 0.033 and the S/S treated sample had a Cr^{+6} mole fraction of 0.095 (Table 1), i.e. 3.3 and 9.5% of the total Cr is present as Cr^{+6}. Both untreated and S/S treated soil from Site 2 had Cr^{+6} mole fractions below the detection limits of the analytical method (< 0.001 mole fraction Cr^{+6}). Although there is an apparent increase in Cr^{+6} in the sample from Site 1 after S/S treatment, this increase may not be real. The synchrotron beam used for this study struck the sample in an area only about 150×300 μm in size. The S/S treated samples had been crushed and sieved through a 63 μm sieve prior to obtaining the XANES spectra. Thus, the spectra of the S/S treated samples should be reasonably representative of the bulk sample. The untreated samples, however, had only been passed through a 2 mm sieve and kept in their field moist state to minimize any chemical changes prior to XANES analysis. Variations in the intensity of the Cr^{+6} pre-edge peak in the untreated samples may have been due to an inhomogeneous distribution of Cr^{+6} within the sample. Additional work is necessary to determine whether the apparent increase in Cr^{+6} is due to inhomogeneous Cr^{+6} distribution or to possible oxidation of Cr^{+3} during the S/S procedure.

Site 1, as was expected and verified by the XANES data, had a higher concentration of the more mobile Cr^{+6} than Site 2. The pre-edge peak indicating the presence of Cr^{+6} in both the untreated and S/S treated samples from Site 1 is qualitatively consistent with the leaching of Cr by the TCLP procedure from these samples, while the lack of a significant Cr^{+6} pre-edge peak in the spectra of samples from Site 2 is consistent with the lack of Cr leaching.

When applying S/S treatment to chromium contaminated soils it might be assumed the chromium would be physically entrapped in the matrix and therefore not subject to leaching during the TCLP test. This study shows, however, that this is not the case and that chromium will leach from a S/S treated sample if it is in the hexavalent form.

The XAS method of determining oxidation state is advantageous over wet chemical procedures because it is a non-destructive procedure which can be done with a minimum of sample treatment. Chemical methods for determining chromium oxidation state require the conversion of the chromium in a sample to one oxidation state and assume that all of the chromium has been converted and remains in this oxidation state during analysis. With XAS there is much less chance of change in oxidation state during analysis.

4. Conclusions

The XANES data obtained from the synchrotron X-ray microprobe verified the assumption that the oxidation state of chromium is important in explaining the difference in chromium TCLP leaching data for the contaminated soils. Treatment with Type I Portland cement alone had little effect on the oxidation state of the chromium and therefore, had only a limited effect on reducing the chromium leaching, as measured by the TCLP test. If S/S were to be used as a treatment method for these soils, an additive such as a slag containing Fe^{+2} and sulfide compounds which reduce Cr^{+6} to Cr^{+3}, may be more effective [6,16].

Acknowledgements

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