

Chromium speciation in residues after sequential extraction of a thermally treated sludge analog

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XANES fitting indicates that non-Cr₂O₃ form of Cr(III), transformed from CrO₃ by four-hour heat application at 1100°C, is the key species sorbed onto or lattice-diffused into kaolin matrices that exhibits strong leaching resistance to sequential extraction using various combined solutions including HNO₃, H₂O₂, and HF. The EXAFS spectra are all in agreement with the XANES results. It is suggested that some Cr₂O₃ might have reacted with kaolin to form new compounds such as Cr₂O₃·Al₂O₃·2SiO₂ to account for the slight dissimilarity between the EXAFS spectra of samples and that of Cr₂O₃.

Keywords: chromium immobilization, thermal treatment, sequential extraction, kaolin, industrial sludge

1. Introduction

Synchrotron-based X-ray absorption spectroscopy (XAS) can reveal speciation, distribution, transformation, mobility, and bioavailability of trace metal contaminants in environmental matrices (US Department of Energy, 1995). Although the thermal immobilization of chromium contaminant in sludge analog mineral at elevated temperatures, such as 1100°C, has proven to meet environmental regulation, there are concerns about various harsh weathering effects, including acid rain effect, on chromium leaching from the immobilized materials. The natural fluxes of chromium compounds into the environment are small compared to anthropogenic activities (Nriagu, 1979; Nriagu, 1989; Veron et al, 1987); the hexavalent chromium can cause severe health risks for mankind through food chain (Nriagu & Pacyna, 1988). The U.S. Environmental Protection Agency (EPA) has recently decided that the most needed remedial technology is for heavy metals in Superfund sites (Reed & Moore, 1994).

Sequential extraction methods have been designed to determine the speciation of heavy metal contaminants in soils and sediments (Tessier et al, 1979). The bound heavy metals include those (i) bound to the exchangeable fraction, (ii) bound to carbonates, (iii) bound to Fe-Mn oxides, (iv) bound to organic matter, and those that constitute (v) the final residual portion. Although the sequential extraction does not reflect the real binding sites of soils, it has been extensively applied and criticized in soil and environmental research since 1979.

2. Experimental

We used a furnace to thermally immobilize 4 % hexavalent chromium in kaolinite at 1100°C for four hours. The kaolin used for this study contains 3.51% CaO, MgO, Fe₂O₃, TiO₂, K₂O, and Na₂O. The experimental steps were as follows. (i) CrO₃-contaminated materials are prepared by mixing one liter of CrO₃ solution (i.e., 76.925g CrO₃ in one liter of de-ionized water) into 1000g kaolinite. The slurry material was then oven-dried at 105°C for three days after it was thoroughly mixed in a polyethylene bottle rotating at 30 rpm for one day. The dry Cr(VI)-containing material is thermally immobilized at 1100°C for four hours. (ii) Each of five portions of the material was extracted with 1, 2, 3, 4, or 5-step procedure specified by the soil sequential extraction method. Total chromium contents in the five extracts were measured with a flame atomic absorption spectrometer (FAAS). The five extracted residues are analyzed with a synchrotron radiation facility. (iii) The XAS data are analyzed.

The sequential extraction includes the following five steps: (i) extraction with MgCl₂ solution of a pH=7.0, followed by the extraction with (ii) NH₄OAc solution of a pH=5.0, (iii) NH₂OH.HCl of a pH=2.0, (iv) HNO₃, H₂O₂, and NH₄OAc solutions of a pH=2.0, and (v) HF and H₂O₂ solutions. X-ray absorption spectra, except that of reference compounds, at the Cr-K edge (5989eV) were collected in fluorescence detecting mode at room temperature on the wiggler beamline S-5B at the Synchrotron Radiation Research Center (SRRC) in Taiwan, Republic of China; the reference compounds were run in transmittance mode. The fluorescence-detecting mode was chosen for our samples due to their weak edge jumps and the resulted poor absorption spectra in transmittance mode. The ring operates at 1.5 GeV with a beam current of 100-200 mA. Data of the spectra were analyzed using WinXAS software (Ressler, 1998).

3. Results and Discussion

The results of sequentially extracting the thermally treated 40000-mg/kg Cr-doped kaolin indicate that only 6.24, 4.4, 9.2, and 26.2-mg/kg chromium were respectively extractable by steps i, ii, iii, and iv. Although 2980-mg/kg Cr was extracted during step v by the solutions of strong acid HF and oxidizer H₂O₂, it only represented 7.5% of the doped chromium. Because all the extraction combinations failed to remove significant amounts of Cr, it is concluded that the sequential extraction method may fail to achieve its objective of differentiating multiple species of Cr. In other words, most of the doped Cr is so tightly immobilized by kaolin matrices after 4-hour thermal treatment at 1100°C that even strong acid and oxidizer used in step v can not dissolve the immobilized Cr species. It should be noted that HF, coupling with an FAAS, has usually been used to leach and determine the total heavy metals in various inorganic and organic matrices.

It is recognized that hexavalent Cr species is extremely water soluble and highly toxic, while trivalent ones are nearly water insoluble and non-toxic. Thus the doped hexavalent Cr has been suggested to transform into trivalent Cr through thermal decomposition that evolves O₂ after the thermal treatment at 1100°C, which is justified with the absence of the pre-edge peak that characterizes hexavalent Cr species in the XANES spectra shown in Figure 1. The respective XANES spectra of the residues after 1, 2, 3, 4, and 5-step extraction are quite similar to each other; this means that the thermally transformed Cr species are generally acid-digestion resistant under various pH conditions and various extracting reagents. We also have carried out the

XANES fitting of these samples and the results indicate that Cr_2O_3 represents $\geq 94\%$ of the total doped chromium in all samples.

Basically, there are three major bonding mechanisms to describe Cr compound bonded to kaolin. They are: (i) physical sorption, or precipitation of discrete metal compounds to kaolin, (ii) chemisorption to fine grained particles of kaolin, (iv) chemical dissolution into kaolin through lattice diffusion. The EXAFS data are discussed in two parts as follows: (i) k^2 -weighted, and (ii) their Fourier Transforms.

For k^2 -weighted EXAFS, Figure 2 demonstrates that there is a fair spectral similarity between the k^2 -weighted EXAFS of the extracted residues of the heated sample and that of reference compound Cr_2O_3 . This indicates that Cr(III) is the main Cr species in Cr-doped kaolin after heating at 1100°C for 4 hours and extraction at various acid digestion conditions, although there is some discrepancy in the EXAFS fitting between samples and Cr_2O_3 . It is suggested that some Cr (III) might have reacted with kaolin to form new compounds, such as $\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, to account for the slight discrepancy between the EXAFS spectra of samples and that of Cr_2O_3 . As more sequential extraction steps are applied, there is an increasing similarity between the k^2 -weighted EXAFS of Cr_2O_3 reference and that of extracted sample due to the leaching-out of Cr (VI).

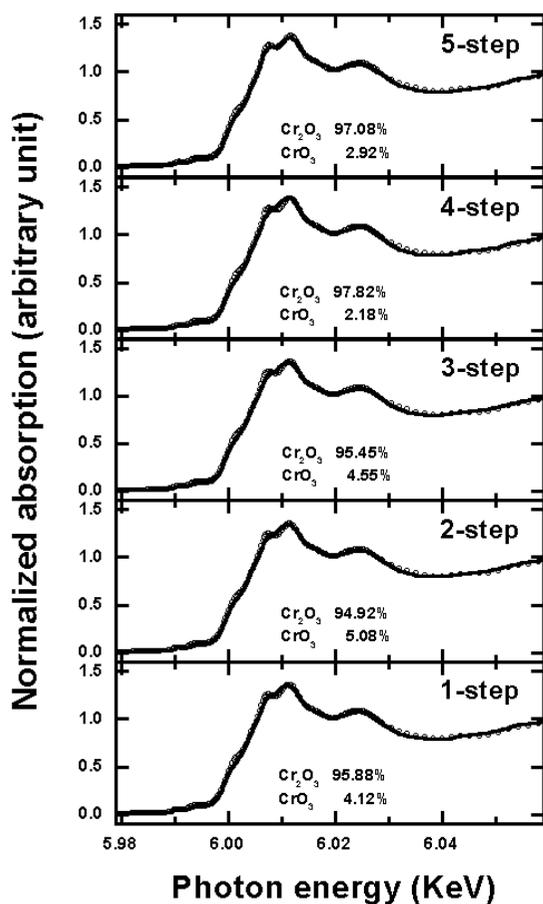


Figure 1 XANES spectra of the residues of sequentially extracted Cr-doped kaolin (solid line: sample curve; open circle: fit curve). The percentages in each compartment are fit results. Lettering in each compartment: for example, 4-step represents that the sample was extracted with 4-step sequential extraction).

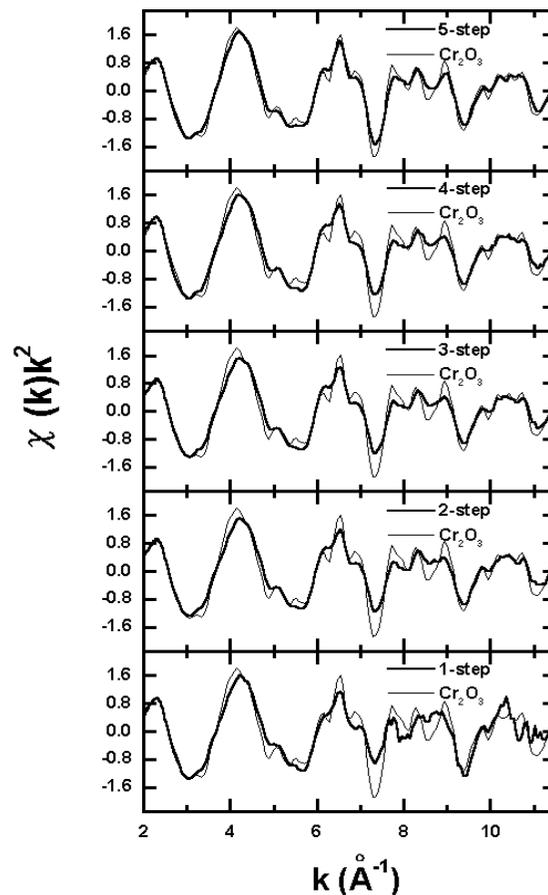


Figure 2 EXAFS spectra of the residues of sequentially extracted Cr-doped kaolin (thin curve: Cr_2O_3 reference; thick curve: sample).

The Fourier transforms of EXAFS of all samples and Cr_2O_3 are presented in Figure 3. There is some resemblance between the spectrum of Cr_2O_3 reference and that of samples in the first shell region, but not beyond that; therefore the Cr speciation is a non- Cr_2O_3 form of Cr (III). In addition, because so little Cr was sequentially extracted, the similarity of the spectra and Cr speciation between Cr_2O_3 reference and all samples was unlikely to be profound. The higher amplitude in the second shell region of Cr_2O_3 reference than that of samples might have been due to a greater multiple scattering effect in Cr_2O_3 reference and/or due to the formation of reaction product such as $\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ that tends to disorder the second shell region. This molecular information provided by XAS measurement on the sequentially extracted Cr-doped kaolin reveals the mechanism of acid-resistant characteristics of heated Cr-doped kaolin. The understanding of molecular-scale mechanism of chromium immobilization after thermal treatment will help designing a long-term safe method for treating Cr-containing sludge and soils.

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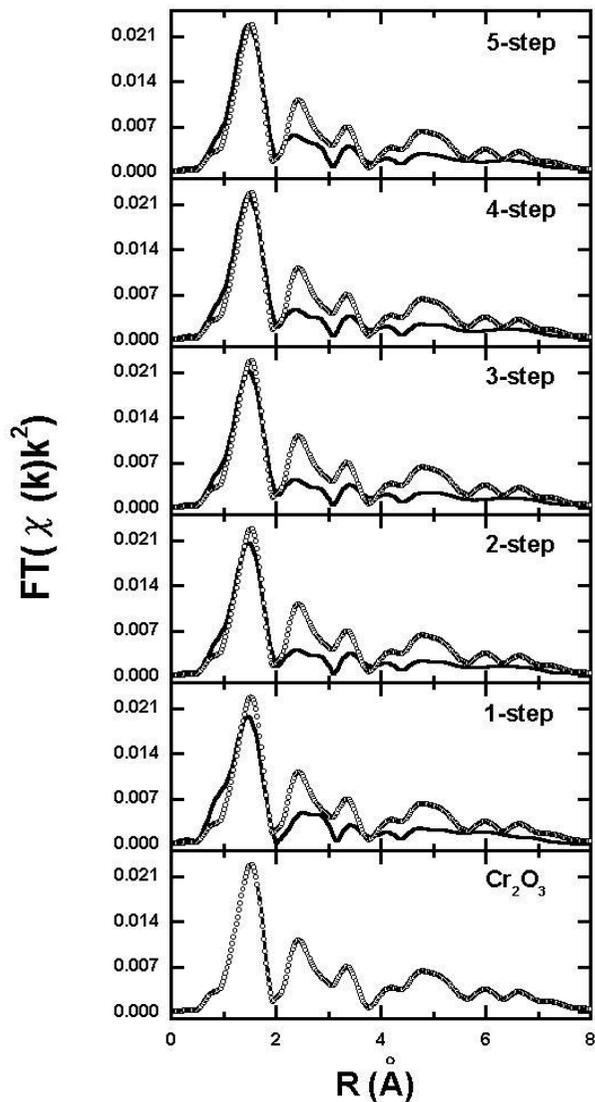


Figure 3
Fourier transforms of EXAFS spectra of the residues of sequentially extracted Cr-doped kaolin (open curve: Cr_2O_3 reference; solid curve: sample).

References

- Nriagu, J. O. (1979). *Nature* **279**, 409-411.
 Nriagu, J. O. (1989). *Nature* **338**, 47-49.
 Nriagu, J. O. & Pacyna, J. M. (1988). *Nature* **333**, 134-139.
 Reed, B. E. & Moore, R. (1994). *Proc. Twenty-sixth Mid-Atlantic Ind. Waste Conf.* Aug 7-10, University of Delaware, USA, 425-430.
 Ressler, T. (1998). *J. Synchrotron Radiat.* **5**, 118-122.
 Tessier, A., Campbell, P. G. C. & Bisson, M. (1979). *Analytical Chemistry* **51**, 844-851.
 US Department of Energy (1995). *Report of DOE Molecular Environmental Science Workshop* July 5-8, Airlie Center, VA, USA, 1-3.
 US Environmental Protection Agency. (1990). *SW-846 Method 3052*.
 Veron, A., Lambert, C. E., Isley, A., Linet, P. & Grousset, F. (1987). *Nature* **326**, 278-281.