Bull. Environ. Contam. Toxicol. (2003) 71:860–865
© 2003 Springer-Verlag New York Inc.
DOI: 10.1007/s00128-003-0215-x

Environmental
Contamination
and Toxicology

Speciation of Chromium in an Electroplating Sludge During Thermal Stabilization

C.-C. Ku,[1] H. P. Wang,[1] P.-H. Lee,[1] M. C. Hsiao,[1] H.-L. Huang,[1] H. C. Wang[2]

[1] Department of Environmental Engineering, National Cheng Kung University, Tainan, Taiwan, Republic of China
[2] Division of Chest Medicine, Department of Medicine, Veterans General Hospital-Kaoshiung, Kaoshiung, Taiwan, Republic of China

Received: 31 August 2002/Accepted: 18 June 2003

Chromium species are abundant in the earth's crust and frequently found in the ground water and soil. Contamination of Cr in the environment is mostly caused by the anthropogenic activities such as mining, fuel combustion, leather tanning, and metal plating (Katz and Salem 1994; Armienta et al. 1995). Chromium is a carcinogenic element associated with certain tumors (Katz and Salem 1994; Stern 2000; Freeman and Stern 1997). The toxicity of Cr depends highly on its chemical structure (Freeman and Stern 1997; Carter 1995). Generally, Cr(VI) has a higher toxicity and mobility than Cr(III) which is generally found in the sediments of rivers and oceans (Katz and Salem 1994; Armienta et al. 1995; Carter 1995; Tan and Wang 1996).

X-ray absorption spectroscopy can be used in characterization of valence and local structure (<10 Å) of elements in a solid matrix (Mansour 1998). Speciation data such as coordination number (CN), bond distance, and oxidation state for toxic elements in the complex environmental solids can be determined by extended X-ray absorption fine structural (EXAFS) spectroscopy (Szulczewski et al. 1997; Foster et al. 1998). The molecular-scale data are also of great importance and interest in the development of effective methods for treatments of hazardous wastes(Lin and Wang 1999; Lin and Wang 2000). For instance by EXAFS, we found that copper oxides (in ZSM-5 or ZSM-48) involved in the catalytic decomposition of NO (Huang and Wang 1999) and oxidation of chlorophenols in supercritical water (Lin and Wang 2000). The speciation data were very useful in revealing the nature of active centers in the catalysis processes.

Toxic species in the environmental solids can be stabilized by thermal treatments which may reduce their toxicity, solubility, and mobility in the environment (Wei et al. 2001; Humayoun et al. 1997; Eddings et al. 1994; Zorpas et al. 2001; Peterson et al. 1997). The possible reaction pathways and structure of toxic elements in the thermal stabilization processes have not been well studied (Karius and Hamer 2001; Kirk et al. 2002). Many reactions such as oxidation, reduction, physical and complexation may occur simultaneously in the high-temperature reactions. Basic understanding at the molecular scale is of increasing importance in revealing the fate of toxic elements in the stabilization process. Thus, the main objective of this work was to investigate the speciation of Cr in a Cr-contaminated sludge in the thermal stabilization processes by EXAFS spectroscopy.

Correspondence to: H. P. Wang

MATERIALS AND METHODS

The sludge samples were obtained from an electroplating plant in Taiwan. The Cr-contaminated electroplating sludge (Cr/sludge) as well as model compounds (Cr/SiO_2) (prepared by impregnation of $Cr(NO_3)_3 \cdot 9H_2O$ onto SiO_2) were dried at 433 K for eight hours and heated in air at 373, 673, or 1073 K for 60 minutes. Structures of the Cr/sludge and Cr/SiO_2 samples were studied by X-ray diffraction spectroscopy (RIGAKU model D/MAX III-V CuK_α radiation) (scanned from 15 to 60° (2θ) with a scan rate of 4°/min).

The XANES (X-ray absorption near-edge structure) and EXAFS spectra of the Cr/sludge and Cr/SiO_2 were collected on the Wiggler beamline at the Taiwan Synchrotron Radiation Research Center (SRRC). The electron storage ring provided energy of 1.3 GeV. A Si(111) double-crystal monochromator was used for selection of energy with an energy resolution of 1.9×10^{-4} (eV/eV). Beam energy was calibrated by the adsorption edge of Cr-foil at an energy of 5,989 eV. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. The absorption edge was determined at the half-height (precisely determined by its derivative) of the XANES spectrum after pre-edge baseline subtraction and normalization to the maximum above-edge intensity. Each EXAFS spectrum was recorded at least twice. The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 8.0 programs. The isolated EXAFS data was also converted to the wavenumber scale. The Fourier transform was performed on k^3-weighted EXAFS oscillations in the range of 2.4-12.5 $Å^{-1.}$

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of the Cr/sludge and Cr/SiO_2 heated at 373-1073 K are shown in Figure 1. It seems that Cr(III) ($CuCr_2O_4$ or Cr_2O_3) was the major Cr species in the Cr/sludge. Fe_2O_3 and CuO were also found in the sludge. Thermal treatments of the Cr/sludge at 1073 K led to an increase in the crystallinity of the Cr(III) species. High-oxidation state Cr such as Cr(VI), however, was not observed by XRD. In the parallel experiments, Cr on SiO_2 behaved differently in the thermal treatment process. Crystalline Cr was found on SiO_2 at the thermal treatment temperatures of 373-673 K. At 1073 K, Cr_2O_3 was the main Cr species on SiO_2.

The pre-edge XANES spectra of the thermally treated Cr/sludge and Cr/SiO_2 as well as Cr model compounds (CrO_3 and Cr_2O_3) are show in Figure 2. A prominent pre-edge feature was observed at 5993.5 eV that may be due to the weak 1s-to-3d transition for Cr(VI). Cr(VI) was not found in the Cr/Sludge during the thermal treatments. However, a small amount of Cr(VI) was found for the Cr/SiO_2 sample thermally treated in air at 673 K for 60 minutes. At higher temperatures (e.g., 1073 K), Cr(VI) might be self reduced.

In order to more thoroughly examine the speciation changes of Cr during thermal treatments at elevated temperatures. EXAFS spectra of the Cr/sludge and Cr/SiO_2

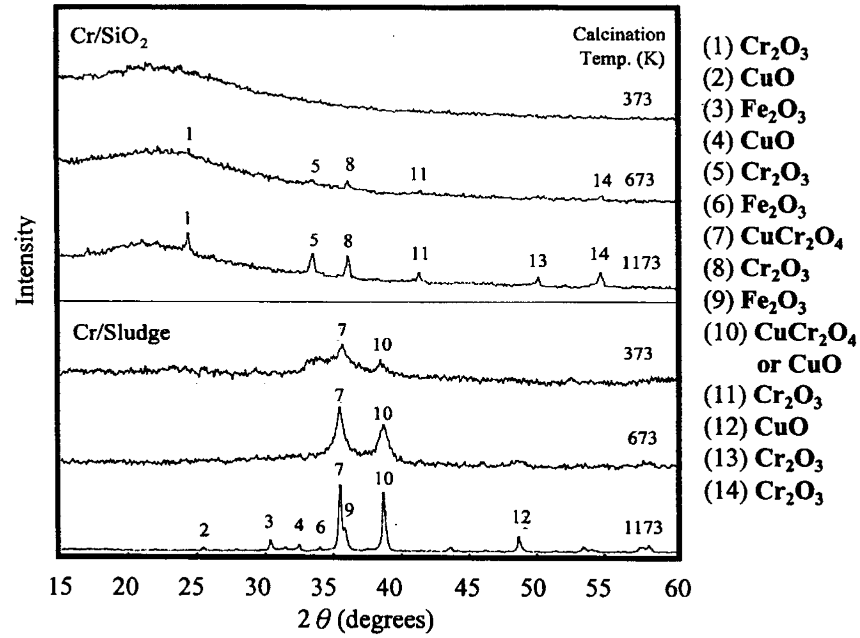

Figure 1. X-ray diffraction patterns of Cr/SiO$_2$ and Cr/sludge thermally treated at (a) 373, (b) 673, and (c) 1073 K in air for 60 minutes.

were also recorded and analyzed in the k range of 2.4-12.5 Å^{-1}. An over 99% reliability of the Fourier-transformed EXAFS data fitting for Cr was obtained. In Figure 3, experimental EXAFS spectra and nonlinear least-squares fitting results are observed. In all EXAFS data analyses, the Debye-Waller factors (σ^2) were less than 0.01 Å^2. Table 1 shows that bond distances of Cr-O for Cr/sludge and Cr/SiO$_2$ are 1.98 and 1.97 Å with CNs (coordination numbers) of 5.3 and 1.1, respectively. The Cr-O bonding in the first shells in the sludge was little perturbed in the thermal treatment process. The bond distances of Cr-(O)-Cr in the sludge thermally treated at 1073 K were, however, significantly decreased by 0.05 Å, suggesting that the Cr might be stabilized. Note that the high mobility Cr(VI) in the sludge was not observed by XANES. Similar results were also observed for the model compound Cr/SiO$_2$.

Cr(VI) in the model compound Cr/SiO$_2$ (thermally treated in air at 673 K) was found by XANES. However Cr(III) was the main Cr species in the sludge. The EXAFS data showed that the bond distance of Cr-O in the sludge was 1.98 Å with a CN of 5.3. Little perturbation in the first shell of Cr was observed during the thermal treatment at 1073 K. However, in the second shells, the bond distance of Cr-(O)-Cr in the sludge was decreased by about 0.05 Å, which might be attributed to the fact that Cr was stabilized in the high-temperature thermal treatment process. Similar results for the model compound Cr/SiO$_2$ were also observed. This work exemplifies the utilization of EXAFS and XANES for studying the speciation of Cr in a very complex sludge specifically in the thermal stabilization process.

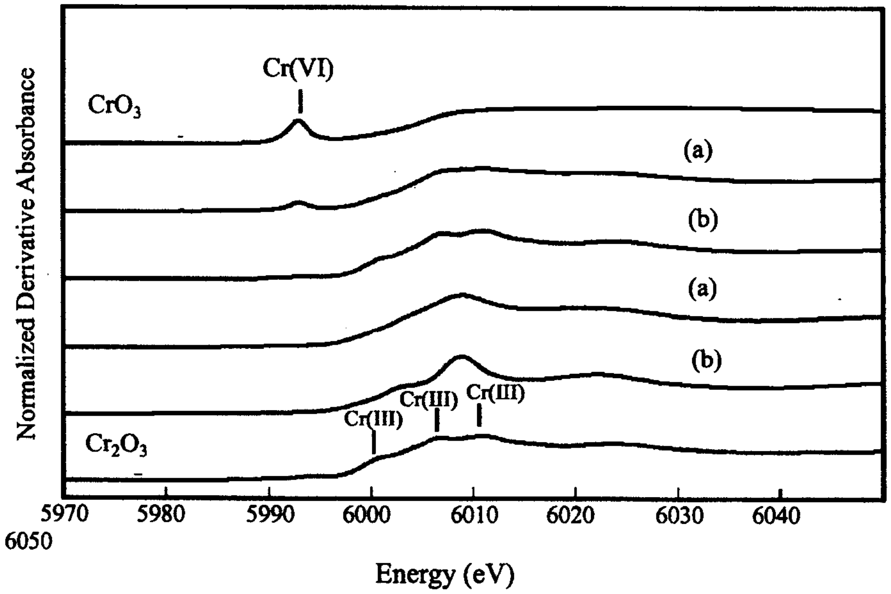

Figure 2. Normalized Cr K-edge XANES spectra for model compounds: CrO$_3$ and Cr$_2$O$_3$ and for the Cr/SiO$_2$ and Cr/sludge thermally treated at (a) 673 and (b) 1073 K in air for 60 minutes.

Table 1. Speciation of Cr for the model compound (Cr/SiO$_2$) and the electroplating sludge (Cr/sludge) during thermal treatments at 373-1073 K.

	Thermal	Shells	Bond Distance	Coordination
Cr/sludge	373	Cr-O	1.98	5.3
		Cr-(O)-Cr	2.96	1.1
Cr/sludge	673	Cr-O	1.98	5.0
		Cr-(O)-Cr	2.96	2.1
Cr/slud	1073	Cr-O	1.97	5.0
		Cr-(O)-Cr	2.91	3.6
Cr/SiO$_2$	373	Cr-O	1.97	3.3
		Cr-(O)-Cr	2.95	0.4
Cr/SiO$_2$	673	Cr-O	1.97	4.0
		Cr-(O)-Cr	2.95	1.1
Cr/SiO$_2$	1073	Cr-O	1.97	4.9
		Cr-(O)-Cr	2.91	2.4

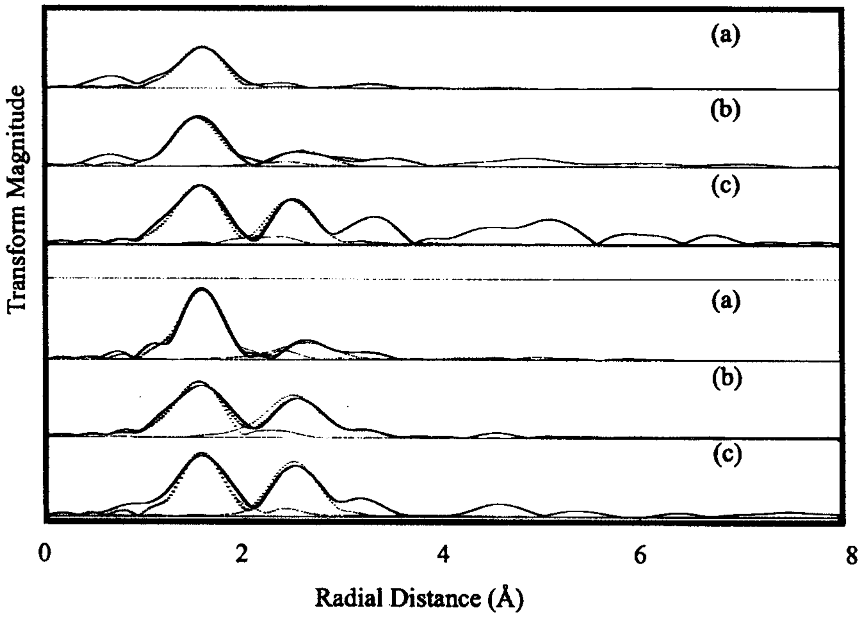

Figure 3. Fourier transformed Cr K-edge EXAFS spectra (solid line) and fittings (dotted line) of the Cr/SiO_2 and Cr/sludge thermally treated at (a) 373, (b) 673, and (c) 1073 K in air for 60 minutes.

Acknowledgments. The financial support of the National Science Council and the Taiwan SRRC is gratefully acknowledged. We also thank Dr. Y. W. Yang and Dr. Jyh-Fu Lee of the SRRC for their EXAFS experimental assistance. This paper was presented at the First International Conference on Pollution Ecochemistry and Ecological Processes, Shenyang, P. R. China, August 26-31, 2002.

REFERENCES

Armienta H, Maria, A, Rodriguez CR (1995) Environmental exposure to chromium compounds in the Vally of Leon, Mexico. Environ Health Perspect 103:47-51.

Carter DE (1995) Oxidation-reduction reactions of metal ions. Environ Health Perspect 103:17-19

Eddings EG, Lighty JS, Kozinskl JA (1994) Determination of metal behavior during the incineration of a contaminated montmorillonite clay. Environ Sci Technol 28:1791-1800

Freeman NCG, Stern AH (1997) Exposure to chromium dust form homes in a chromium. Arch Environ Health 52:213-219

Foster AL, Brown GE, Parks GA (1998) X-ray absorption fine-structure spectroscopy study of photocatalyzed, heterogeneous As(III) Oxidation on kaolin and anatase. Environ Sci Technol 62:1444-1452

Huang YJ, Wang HP (1999) Reduction of NO with CH_4 effected by copper oxide cluster in the channels of ZSM-5. J Phys Chem A 103:6514-6516

Humayoun A, Cartledge FK, Roy A, Tittlebaum, ME (1997) Solidification/stabilization of arsenic salts: Effects of long cure times. J Hazard Mat 52:247-264

Karius V, Hamer K (2001) pH and grain-size variation in leaching tests with bricks made of harbour sediments compared to commercial bricks. T Sci Tot Environ 278:73-85

Katz SA, Salem H (1994) The biological and environmental chemistry of chromium. VCH Publishers 1:1-87

Kirk DW, Chan CCY, Marsh H (2002) Chromium behavior during thermal treatment of MSW fly ash. J Hazard Mat 90:39-49

Lin KS, Wang HP (1999) Shape selectivity of trace by-products for supercritical water oxidation of 2-chlorophenol effected by CuO/ZSM-48. Appl Catal B: Environ 22:261-267

Lin KS, Wang HP (2000) Byproduct shape selectivity in supercritical water oxidation of 2-chlorophenol effected by CuO/ZSM-5. Langmuir 16:2627-2631

Mansour AN, Melendres CA (1998) Analysis of X-ray absorption spectra of some nickel oxycompounds using theoretical standards. J Phys Chem A 102:65-81

Peterson ML, Brown GB, Parks GP, Stein CL (1997) Differential redox and sorption of Cr(III/VI) on natural silicate and oxide minerals: EXAFS and XANES results. Geoch Cosmoch Acta 61:3399-3412

Stern DM (2000) Is chromium a trace essential metal. Biofactors 11:149-161

Szulczewski MD, Helmke P, Bleam WF (1997) Comparison of XANES analyses and extractions to determine chromium speciation in contaminated soils. Environ Sci Technol 31:2954-2959

Tan Z, Wang Y (1996) Removal of heavy metal (Cr^{6+}, Ni^{2+}) from polluted water. J Environ Sci 8:191-195

Wei YL, Yang YW, Cheng N (2001) Study of thermally immobilized Cu in analogue minerals of contaminated soils. Environ Sci Technol 35:416-421

Zorpas AA, Vlyssides AG, Zorpas GA, Karlis PK, Arapoglou D (2001) Impact of thermal treatment on metal in sewage sludge from the Psittalias wastewater treatment plant, Athens, Greece. J Hazard Mat 82:291-298