

In-situ EXAFS study of copper in the electrokinetic remediation process

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The speciation of copper in the early stage of the electrokinetic remediation (EKR) process has been studied by extended X-ray absorption fine structure (EXAFS) spectroscopy in the present work. By in-situ EXAFS, we found that copper in a contaminated soil possessed a Cu-O bond distance of 1.98 Å with a coordination number (CN) of 5.8. In the second shell, the bond distance of Cu-(O)-Cu was 2.87 Å with a CN of 6.4. However, possibly due to the fact that incompact copper atoms in the outer shells were distorted by EKR, the Cu-(O)-Cu (2nd shell) bond distance and the CN of copper in the contaminated soil decreased by 0.08 Å and 5.4, respectively in the early stage of the EKR process. Interestingly, after prolonging the contact time to about 80 minutes, the 1st-shell copper atoms were also perturbed by EKR. This work is an example of usefulness of the in-situ EXAFS spectroscopy for detailed studies of the speciation of copper in the contaminated soil during EKR process.

Keywords: EXAFS; XANES; electrokinetic remediation; copper; contaminated soil.

1. Introduction

Soil pollution has been a serious environmental problem in the highly industrialized countries. In recent decades, soils contaminated by heavy metals have increased significantly, that may cause serious problems with respect to plant nutrition and food chains. Over 160 heavy metal contaminated sites in Taiwan have been found (Sah & Chen, 1998). In the USA, about 5000 hazardous waste contaminated sites that may be leaking toxic chemicals into soil and then to the ground water have been reported (Khan & Alam, 1994). Electrokinetic remediation (EKR) is one of the feasible technologies for in-situ soil decontamination (Probst & Hicks, 1993; Lageman, 1993; Trombly, 1994; Acar & Alshawabkeh, 1993). EKR has been used successfully in removal of more than 90% of heavy metals (copper, cadmium, cobalt, chromium, arsenic, mercury, nickel, manganese, lead, antimony and zinc) from clay, kaolinite, montmorillonite and argillaceous sands (Hicks & Tondorf, 1994; Acar & Alshawabkeh, 1996; Acar *et al.*, 1994; Yeung *et al.*, 1996).

Although the EKR has been proven to be feasible in laboratory or bench-scale experiments and small-scale field tests (Lageman, 1993), an understanding of the complex transport phenomena and electrochemistry involved in the EKR is not well understood. These reactions may include: ion diffusion, ion exchange, mineral decomposition, precipitation of salts, hydrolysis, oxidation,

reduction, physical and chemical sorption and complexation with humic substances (Mitchell, 1993).

X-ray absorption near-edge structure (XANES) can provide information about the oxidation state of an excited atom, the coordination geometry, and the bonding of its local environment in unknown compounds. Speciation information such as bond distance, as well as the number and chemical identity of atoms can be determined by EXAFS spectroscopy. Thus, the main objective of the present work was to investigate the speciation of copper in the electrokinetic extraction process by EXAFS. An in-situ EXAFS cell was used to reveal the structural change of Cu in the EKR experiments.

2. Experimental

A contaminated soil near several printed circuit board waste recycling plants was obtained. The EKR reaction was carried out in a home-made in-situ XAS cell (see Figure 1). The reaction system consisted two Ru electrode, two electrode reservoirs, a power supply, a cation-selective membrane (Nafion[®] 417, Aldrich) and glass filters. The soil samples were packed in the cell and filled with 0.01 M potassium nitrate as a conductive solution. A DC voltage of 100 volts was constantly applied to the electrodes.

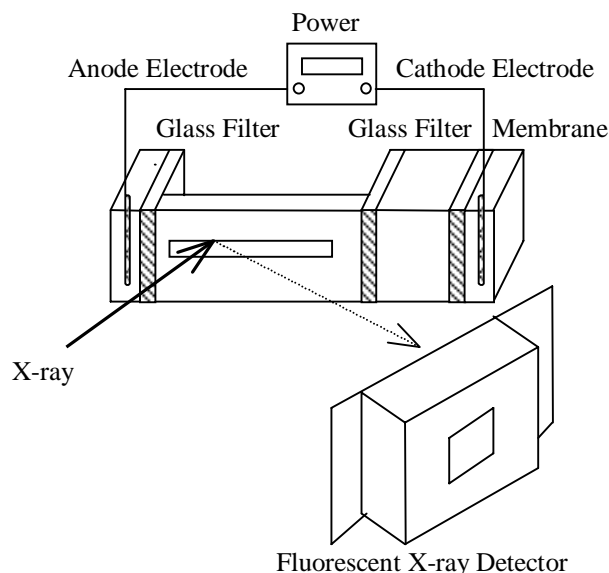


Figure 1

A schematic diagram of the in-situ EXAFS cell for studies of speciation of copper during EKR of the contaminated soil.

The in-situ Cu K-edge XANES and EXAFS spectra of Cu-contaminated soils were collected on the Wiggler SL-3B beamline at the Taiwan Synchrotron Radiation Research Center (SRRC). The electron storage ring operated at an energy of 1.3 GeV (current of 80-200 mA). A Si(111) double-crystal monochromator was used for selection of energy with an energy resolution of 1.9×10^{-4} . The X-ray absorption spectra were collected using a fluorescence detector (Lytle detector) and the beam energy was calibrated by the adsorption edge of Cu foil at an energy of 8980 eV. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. Samples were measured in the fluorescence mode. Each EXAFS spectrum was recorded at least twice.

The EXAFS data were analyzed using the UWXAFS 3.0 (Stern *et al.*, 1995) and FEFF 7.0 programs (Zabinsky *et al.*, 1995). The

absorption edge was determined at the half-height (precisely determined by the derivative) of the XANES spectra after pre-edge baseline subtraction and normalization to the maximum above-edge intensity. The background of all the data was justified by an AUTOBK program (Stern *et al.*, 1995). The isolated EXAFS data was normalized to the edge jump and converted to the wavenumber scale. The Fourier transform was performed on k^2 -weighted EXAFS oscillations in the range of 3.3–10.5 \AA^{-1} . To reduce the number of fit variables, the many-body factor (S_0) was fixed at 1.0.

3. Results and Discussion

The in-situ Cu K-edge XANES spectra and the first derivatives of the Cu-contaminated soil during the EKR process are shown in Figure 2. A bump in the pre-edge region and an obvious shoulder in the edge jump were observed in XANES spectra of tetrahedral complex. The pre-edge XANES spectra of the Cu-contaminated soil exhibited a very weak absorbance band for the 1s to 3d transition (8975–8980 eV) which is forbidden by the selection rule in the case of perfect octahedral symmetry (Denise *et al.*, 1989; Lin & Wang, 1999; Huang & Wang, 1999; Lin & Wang, 2000). A shoulder at 8984–8988 eV and an intense feature at about 8995–9002 eV were attributed to the 1s to 4p transition that indicated the existence of Cu(II) species.

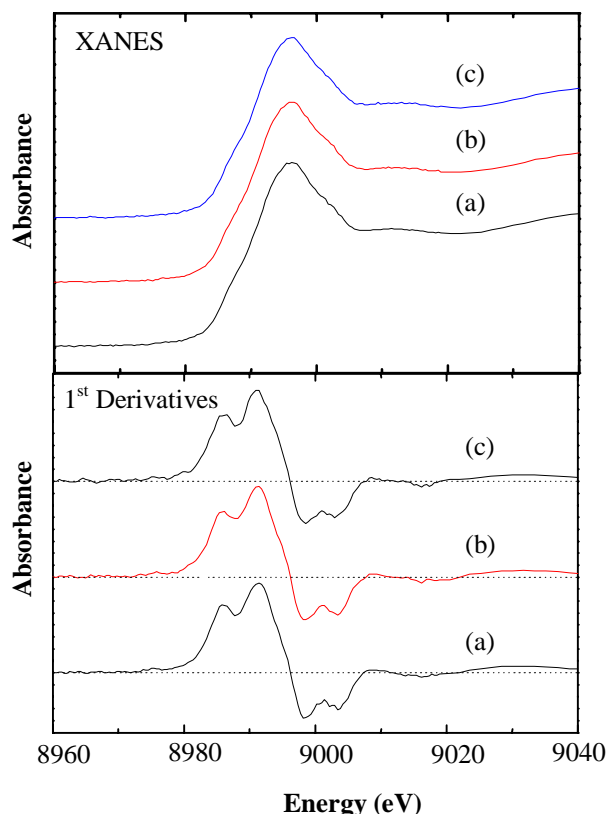


Figure 2
XANES spectra of the Cu-contaminated soil effected by EKR for (a) 0, (b) 40, and (c) 80 minutes.

The in-situ EXAFS spectra were also recorded and analyzed in the k range of 3.3–10.5 \AA^{-1} . The feature centered at 1.5 \AA (not phase shift corrected) arised from Cu atoms in the first coordination shell while a small feature at about 2.2 \AA represented scattering from atoms in the second coordination shell (see Figure 3). An over 99%

reliability of the EXAFS data fitting for copper in the EKR process was obtained. In Table 1, copper in the contaminated soil has a Cu-O bond distance of 1.98 \AA with a coordination number (CN) of 5.8. In the second shell, the bond distance of Cu-(O)-Cu was 2.87 \AA with a CN of 6.4. However, the Cu-(O)-Cu (2nd shell) bond distance and CN of the Cu-contaminated soil decreased by 0.08 \AA and 5.4, respectively in the early stage of the EKR process, that may be due to the fact that incompact copper atoms in the outer shells were distorted by EKR. After prolonging the contact time to about 80 minutes, the CNs of Cu-O (1st shell) and Cu-(O)-Cu (2nd shell) were reduced. The outer shell copper atoms were distorted to a great extent, and the first shell copper atoms were also perturbed in the EKR process.

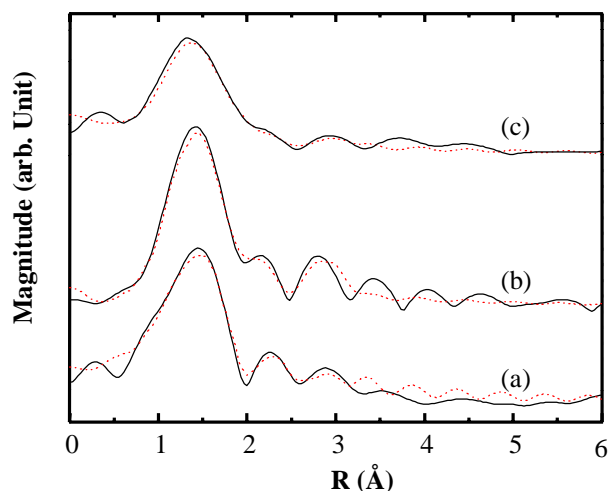


Figure 3
Fourier transformed Cu K-edge EXAFS of the Cu-contaminated soil effected by EKR for (a) 0, (b) 40, and (c) 80 minutes.

Table 1

Structural parameters of copper in the contaminated soil in the EKR process

| Contact Time (min) | Shell | R (\AA) | CN | σ^2 (\AA^2) |
|--------------------|-----------|--------------------|-----|-------------------------------|
| 0 | Cu-O | 1.98 \pm 0.02 | 5.8 | 0.001 |
| | Cu-(O)-Cu | 2.87 \pm 0.04 | 6.4 | 0.026 |
| 40 | Cu-O | 1.98 \pm 0.02 | 5.0 | 0.004 |
| | Cu-(O)-Cu | 2.79 \pm 0.04 | 1.0 | 0.020 |
| 80 | Cu-O | 1.96 \pm 0.02 | 3.6 | 0.002 |
| | Cu-(O)-Cu | 2.76 \pm 0.04 | 0.1 | 0.019 |

R: Bond distance; CN: Coordination number; σ^2 : Debye-Waller factor.

4. Conclusions

The speciation of the copper in the EKR process was studied by in-situ EXAFS. Copper in the contaminated soil possessed a Cu-O bond distance of 1.98 Å with a coordination number (CN) of 5.8. In the second shell, the bond distance of Cu-(O)-Cu was 2.87 Å with a CN of 6.4. Remediation of the Cu-contaminated soil by EKR for 40 minutes led to a reduction of the Cu-(O)-Cu bond distance (2.79 Å) and its CN. This reduction may be due to the fact that of incompact copper atoms in the outer shells were distorted by electric field in the early stage of the EKR process. Interestingly, the first shell copper atoms were also perturbed in the EKR process when the contact time of the EKR process was prolonged to about 80 minutes. The work also illustrates the utility of the in-situ EXAFS cell for studying the speciation of copper in the EKR of a contaminated soil.

References

- Acar, Y. B. & Alshawabkeh, A. N. (1993). *Environ. Sci. Technol.* **27** (13), 2638-264.
- Acar, Y. B. & Alshawabkeh, A. N. (1996). *J. Geotech. Eng.* **122** (3), 173-185.
- Acar, Y. B., Hamed, J. T., Alshawabkeh, A. N. & Gale, R. J. (1994). *Geotechnique* **44** (2), 239-254.
- Denise, B., Cherifi, O., Bettahar, M. M. & Sneed, R. P. (1989). *Appl. Catal.* **48** (2), 365-372.
- Hicks, R. E. & Tondorf, S. (1994). *Environ. Sci. Technol.* **28** (12), 2203-2210.
- Huang, Y.-J. & Wang, H. P. (1999). *J. Phys. Chem. A* **103** (33), 6514-6516.
- Khan, L. I. & Alam, M. S. (1994). *J. Environ. Eng.* **120** (6), 1524-1543.
- Lageman, R. (1993). *Environ. Sci. Technol.* **27** (13), 2648-2650.
- Lin, K.-S. & Wang, H. P. (1999). *Appl. Catal. B: Environ.* **22**, 261-267.
- Lin, K.-S. & Wang, H. P. (2000). *Langmuir* **16**, 2627-2631.
- Mitchell, J. K. (1993). *Fundamentals of Soil Behavior*, 2nd ed. New York: John Wiley & Sons.
- Probst, R. F. & Hicks, R. E. (1993). *Science* **260**, 498-503.
- Sah, J. G. & Chen, J. Y. (1998). *J. Hazardous Materials* **58**, 301-315.
- Stern, E. A., Newville, M., Ravel, B., Yacoby, Y. & Haskel, D. (1995). *Physica B* **209**, 117-120.
- Trombly, J. (1994). *Environ. Sci. Technol.* **28** (6), 289A-291A.
- Yeung, A. T. & Hsu, C. & Menon, R. M. (1996). *J. Geotech. Eng.* **122** (8), 666-673.
- Zabinsky, S. I., Rehr, J. J., Ankudinov, A., Albers, R. C., Eller, M. J. (1995). *Phys. Rev. B* **52**, 2995-3009.