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Speciation of Copper in a Contaminated Soil

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In 1960s, due to the heavy scrap metal recycling activities (such as burning, fusing, and acid washing), a serious soil contamination was found at Wan-Li (a small town in Tainan County) (Chena et al. 2000). Toxic metals such as Cu, Zn, Pb, Cr, and Cd have contaminated the soil. Copper with even an extremently low concentration may induce behavioral responses in fresh water biota (Xue and Sunda 1997). Cu(II) also exerts adverse effects at concentrations slightly higher than its physiological range (Bosshard et al. 1996). Copper has been suspected to be carcinogenic and may cause breast and brain cancers (Yucel et al. 1994).

The toxicity characteristics leaching procedure (TCLP) is usually used in determining the impact of toxic metals in soil or other environmental solids to the environment. However, the sequential chemical extractions can provide only operationally defined forms of elements. Little chemical structure information has been observed (Hesterberg et al. 1997).

Generally, status of coordination, bond distance, and occupied ratio of energy of elements can be determined by EXAFS (extended X-ray absorption fine structural) spectroscopy. In addition, X-ray absorption near edge structure (XANES) spectroscopy can provide information regarding binding energy and oxidation state of select elements (Hsiao et al. 2001). EXAFS and XANES, in fact, offer molecular-scale data of toxic elements in a very complex matrix that may help the development of effective methods for disposal of hazardous wastes (Oday et al. 1998). Thus, the purpose of this work was to investigate the speciation of copper in a contaminated soil. Specifically, the representative soil samples were collected from a copper contaminated site nearby a printed circuit board waste recycling plant and studied by EXAFS and XANES spectroscopies.

MATERIALS AND METHODS

The soil samples were collected at the contaminated site using the standard procedure. The soil samples were dried at 313 K for 16 hours and the standard TCLP tests were conducted (Taiwan EPA 1994). Concentrations of leachable

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toxic elements in the soil were determined by ICP-AES (Jobin Yvon (JY32/38)). Structures of the soil were also studied by X-ray diffraction spectroscopy (Rigaku Model D/MAX III-V). The samples were scanned from 5 to 60° (2θ) at a scan rate of 4° /min.

The EXAFS spectra of the soil sample were determinated at 298 K on the Wiggler beamline of the Taiwan Synchrotron Radiation Research Center (SRRC). The electron storage ring provided energy of 1.5 GeV (current of 80-200 mA). A Si(111) double-crystal monochromator was used for selection of energy with an energy resolution ($\triangle E/E$) of 1.9×10^{-4} (eV/eV). The absorption spectra were collected in ion chambers that were filled with helium gas. Beam energy was calibrated by the adsorption edge of Cu foil at an energy of 8979 eV. The isolated EXAFS data were normalized to the edge jump and converted to the wavenumber scale. Coordination numbers were systematically varied in the course of the analysis within a given fitting range. Fitting of the data was performed using FEFFIT from UWXAFS 3.0 in combination with FEFF 8.0. The Fourier transform was performed on k^3-weighted EXAFS oscillations in the range of 3.5-11.5 $Å^{-1}$. An over 90% reliability of the EXAFS data fitting for Cu was obtained. The fits had an error of ± 0.01 Å in radius and of ± 10% in coordination number (CN) for the first shell atoms, and of ± 0.02 Å and ± 25% for the second shell atoms, respectively.

XANES spectra of model compounds such as Cu_2O, $Cu(OH)_2$, CuO, $CuCO_3$, $CuCO_3 \cdot Cu(OH)_2$ and Cu foil were also measured on the Wiggler beamline. The absorption edge was determined at the half-height (precisely determined by the derivative) of the XANES spectra of samples after pre-edge baseline subtraction and normalization to the maximum post-edge intensity. Principal component (factor) analysis (PCA) was used in the data treatment to optimize the quantitative extraction of relative concentrations of copper species. Semi-quantitative analyses of the edge spectra were conducted by the least-square fitting of linear combinations of standard spectra to the spectrum of the sample.

RESULTS AND DISCUSSION

Table 1 shows concentrations of leachable Cu, Zn, Cr, Pb, and Cd in the contaminated soil. It is clear that the TCLP concentrations of Cu, Zn, and Pb were excess the limits. The XRD pattern in Figure 1 indicates that CuO was the main copper in the soil (total copper concentration = 12,000 mg/kg). However, the chemical structure of copper in soil could not be observed in detail by XRD, simply due to the very complex matrix of the soil.

In order to further understand the oxidation state, bond distance, and coordinate number of copper in the soil, their EXAFS and XANES spectra were also determined. In Figure 2(a) the pre-edge XANES spectra of copper in the soil exhibit a very weak 1s-to-3d transition (8976.5 eV) that is forbidden by the selection rule in the perfect octahedral symmetry (Grunet et al. 1994). A shoulder at 8986 eV and an intense band at 8996 eV may be attributed to the 1s-to-4p transition that indicates the existence of Cu(II). The pre-edge band for Cu(0) (8999 eV) or Cu(I) (8982 eV) was not observed in the soil. Figure 2(b) also shows the distinguishable Cu(II) in the first derivatives of the XANES spectra.

Table 1. TCLP concentrations (ppm) of the contaminated soil.

		Limit
Cu	73	15
Zn	63	25
Pb	85	5.0
Cr	0.03	5.0
Cd	0.3	1.0

The XANES spectra were also expressed mathematically in a LC XANES fit vectors, using the absorption data within the energy range of 8960-9020 eV. It was found that CuCO3·Cu(OH)2 and CuO were the main copper species in the contaminated soil. Relative contents of the copper species in the contaminated soil with an over 90% reliability in the fitting process are also shown in Figure 2(a).

The Fourier transforms of the k^3-weighted EXAFS spectra for copper in the soil and model compounds (Cu, Cu_2O, and CuO) were determined and calculated (Table 2). The bond distance of CuO was typically 1.96 Å. $CuSO_4$ and $Cu(OH)_2$ possess Cu-O bond distances of 1.87 and 2.07 Å, respectively. In the second shells, the bond distance of Cu-Cu in soil was 2.82 Å. The observation that the bond distance of Cu-O increased in the first shells and decreased in the second shell suggested a perturbation or possibly insertion of other elements into the CuO matrix.

In summary, by the least-square fits of the XANES spectra, fractions of copper species such as CuO (34%) and $CuCO_3 \cdot Cu(OH)_2$ (66%) could be determined in the contaminated soil. The refined EXAFS spectra of copper in the contaminated soil showed that the bond distances of Cu-O and Cu-(O)-Cu were 1.98 Å and 2.82 Å with the coordinated numbers of about 1.6 and 2.2, respectively. The variations of the Cu-O bond distances in the first and second shells of copper might be due to the perturbation of other elements in the soil.

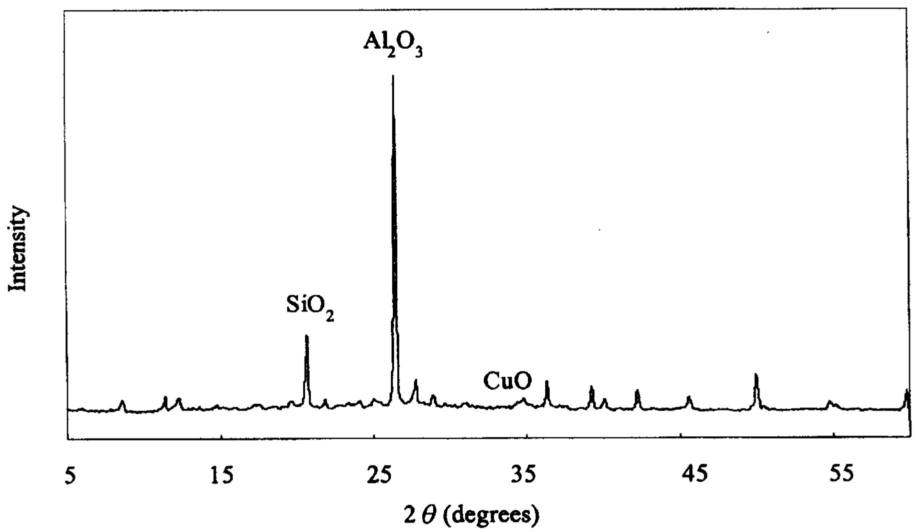

Figure 1. XRD spectra of the contaminated soil.

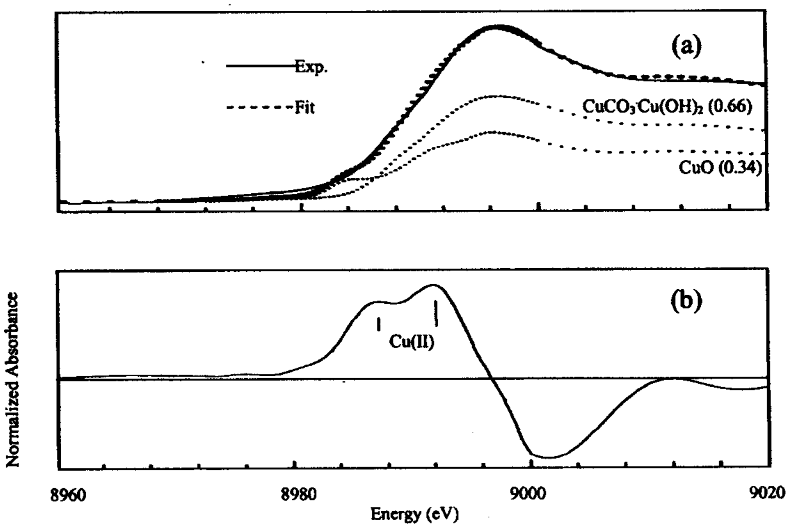

Figure 2. (a) Experimental data (solid line) and the least-square fits (circles) for the XANES spectra of the contaminated soil and (b) the first derivative spectrum. Dotted lines denote fractional contributions of the two principal components making up the fitted spectra.

Table 2. Chemical structure parameters of copper in the contaminated soil and model compounds (Cu foil, Cu_2O, and CuO).

	shell	bond distance (Å)	Coordination number	σ^2 (Å^2)^a
Cu foil	Cu-Cu	2.95	12.2	0.0067
Cu_2O	Cu-O	1.85	1.6	0.0011
	Cu-(O)-Cu	2.90	1.3	0.0263
CuO	Cu-O	1.96	2.5	0.0004
	Cu-(O)-Cu	2.95	2.7	0.0478
Contaminated Soil	Cu-O	1.98	1.6	0.0015
	Cu-(O)-Cu	2.82	2.2	0.0117

[a] σ : Debye-Waller factor

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