Speciation of Copper in a Contaminated Soil

M. C. Hsiao, H. P. Wang

Department of Environmental Engineering, Cheng Kung University, Tainan City, Taiwan, Republic of China

Received: 31 August 2002/Accepted: 18 June 2003

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 extremely 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 (Booshart et al. 1996). Copper has been suspected to be carcinogenic and may cause breast and brain cancers (Yu 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
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 determined 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 (∆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 Cu₂O, Cu(OH)₂, CuO, CuCO₃,
CuCO₂Cu(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 exceed 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