Tracking of copper in contaminated soils

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Abstract

Tracking of copper in the soils contaminated by a nearby printed circuit board (PCB) waste recycling plant and the wire-burnt residue has been studied by X-ray absorption near edge structure (XANES) spectroscopy. The contaminated soils have a very high total and leaching concentrations of copper which are in excess of limit (15 mg/L). By XANES, we found that Cu(OH)\textsubscript{2} (44%), CuCl\textsubscript{2} (34%), and CuSO\textsubscript{4} (16%) were the main copper compounds in the soil contaminated by the copper slag that was discharged from the PCB recycling plant. The additional contaminated site caused by the illegally wire-burnt residue also has high total and leaching copper concentrations. The main copper compounds in the contaminated soil were CuSO\textsubscript{4} (41%), CuCl\textsubscript{2} (39%), and Cu\textsubscript{2}O (19%). In the downstream soil (nearby a river (2 m)), the main copper compounds such as Cu(OH)\textsubscript{2} (46%), Cu(NO\textsubscript{3})\textsubscript{2} (35%), and Cu\textsubscript{2}O (9%) were found. The speciation of copper in the contaminated soils can be very helpful in the development of effective remediation methods.

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1. Introduction

In 1980s, the soils nearby a plant for recycling of valuable metals from printed circuit board (PCB) wastes were contaminated by copper at Wonlee, Tainan County, Taiwan. The contaminated soils containing a high concentration of copper has caused seriously negative impact to the environment. The potential toxicity of copper might affect the ecological cycles under different redox and chemical environments [1]. Copper in the contaminated soils may also cause a pollution of ground water and aggravate the environment and human health.

The main scientific issues concerning speciation of contaminants ultimately depend on their molecular-scale structures. Basic understanding at molecular scale is essential in the management of environmental contaminants, which may also help in the development of effective methods for remediation. X-ray absorption near edge structural (XANES) spectroscopy can provide information about oxidation states of select elements in environmental solids [2–4]. By XANES, we found that copper oxides involved in the catalytic decomposition of NO [5], solidification of fly ashes [6] and oxidation of chlorophenols in supercritical water [7]. Copper oxides may also catalyze the formation of PCDD/DFs in an incineration process [8]. The aim of the present work was to study speciation as well as fate of copper in the contaminated soils between the pollution sources and the downstream soil nearby a river at Wonlee by XANES spectroscopy.

2. Experimental

The soil samples were collected from contaminated sites between a printed circuit board (PCB) recycling plant and the downstream river. Three contaminated soil samples were collected from the top 15 cm layer soil at the contaminated sites. The sites which contaminated by copper slag (discharged from the PCB recycling plant (site A)) and wire-burnt residue (site B) are about 3 and 400 m away from the Son-Yae-Kong river, respectively. A soil was also sampled at the downstream (2 m from the river (site C)) of the pollution sources.

The leaching concentrations of copper in the contaminated soils were determined by the EPA TCLP method [9,10]. Copper in the soils was extracted with an acetic acid solution (pH 2.88) for 18 h. The total concentration of copper was determined by microwave digestion (in a solution containing 9 mL of H\textsubscript{2}O\textsubscript{3} (65%, MERCK), 5 mL of HBF\textsubscript{4} (50%, Lancaster), and 3 mL of H\textsubscript{2}O\textsubscript{2} (30%, MERCK) in a microwave (250–650 W)}
for 24 min) of the contaminated soils. Concentrations of copper were determined by inductively coupled plasma optical emission spectrometer (ICP-OES).

Chemical structure of the contaminated soils was characterized by XRD (X-ray diffraction) spectroscopy (Riguka, D/MAX III-V). Sample were scanned from 5 to 60° (2θ) with a scan rate of 4°/min. XANES spectra of copper in the contaminated soils were recorded on the Wiggler BL17C beamline at the National Taiwan Synchrotron Radiation Research Center (NSRRC). The energy storage ring was operated at an energy of 1.5 GeV. A Si (1 1 1) double-crystal monochromator was used at the energy resolution ΔE/E of 1.9 × 10−4 (eV/eV). The beam energy was calibrated by the Cu k-edge of a Cu foil (99.9%) at 8979 eV. The Cu K-edge absorption spectra were collected in fluorescence mode using a Lytle fluorescence detector filled with helium gas (99.99%).

XANES spectra of model compounds such as CuSO4, CuO, Cu foil, Cu2O, CuCl2, CuCO3, Cu(NO3)2 and Cu(OH)2 were also measured on the Wiggler beamline. Fractions of copper compounds in the soil samples were determined using least-square fittings of the XANES spectra. 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 analysis 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.

### 3. Results and discussion

Table 1 shows the concentrations of total and leaching copper in the contaminated soils between the PCB recycling plant and the nearby river. Very high concentrations (13,000–47,000 mg/L) of copper in the contaminated soils were found. It should be noted that the TCLP leaching concentrations of copper in the contaminated soils were 45–220 mg/L which were in excess of the limit (15 mg/L) [11].

The XRD patterns of the contaminated soils are shown in Fig. 1. It is clear that SiO2 was the major species in the contaminated soils. Copper compounds were barely observed by XRD in the contaminated soils at sites B and C. Cu2O, Cu(OH)2, CuCl2, CuSO4, Cu(OH)2, CuNO3, and Cu(OH)2 were found in the copper slag contaminated soil (site A).

![Fig. 1. XRD patterns of major species in the soils contaminated by (a) copper slag (discharged from the printed circuit board waste recycling plant), and (b) wire-burnt residue, and (c) the downstream soil of the two pollution sources (2 m away from the nearby river).](image1)

![Fig. 2. Component-fitted XANES spectra of copper in the soils contaminated by (a) copper slag (discharged from the printed circuit board waste recycling plant) and (b) wire-burnt residue, and (c) the downstream soil of the two pollution sources (2 m away from the nearby river).](image2)

<table>
<thead>
<tr>
<th>Contamination source</th>
<th>Copper slag</th>
<th>Wire-burnt residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance (m) from the near by river</td>
<td>400</td>
<td>3</td>
</tr>
<tr>
<td>Total concentration</td>
<td>47000</td>
<td>17000</td>
</tr>
<tr>
<td>TCLP concentration</td>
<td>220</td>
<td>120</td>
</tr>
</tbody>
</table>
that was contaminated by copper slag discharged from the PCB recycling plant. Additional contaminated site caused by the illegally wire-burnt residue also have high copper total and leaching concentrations. The main copper compounds in the contaminated soil were CuSO₄ (41%), CuCl₂ (39%), and Cu₂O (19%).

4. Conclusions

The soils contaminated by wire-burnt residue and copper slag discharged from the nearby printed circuit board waste recycling plant contain high leaching (TCLP) and total concentrations of copper which are in excess of the limit. The component-fitted XANES spectra show that Cu(OH)₂ (44%), CuCl₂ (34%), and CuSO₄ (16%) were the main copper compounds in the copper slag that was discharged from PCB recycling plant. Additional contaminated site caused by the illegally wire-burnt residue also have high copper total and leaching concentrations. The main copper compounds in the contaminated soil were CuSO₄ (41%), CuCl₂ (39%), and Cu₂O (19%). In the downstream soil (near a river (2 m)), the main copper compounds such as Cu(OH)₂ (46%), Cu(NO₃)₂ (35%), and Cu₂O (9%) were found. Tracking of copper (the main toxic heavy metal) between the pollution sources and the nearby river and determination of speciation of copper compounds in the soils would help to develop effective methods for remediation.

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References