Chemical stability of CuO and ZnO artificially added to a soil material

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1 Introduction

The Geological Survey of Japan, AIST has provided 42 kinds of geochemical reference materials (rocks, sediments, ores, and so on) for the analysis of elemental concentrations and isotopic compositions from 1964. The analytical data of elemental concentrations, isotopic compositions, and isotopic ages in these materials have been obtained. These geochemical reference materials are worldwide references to test a reliability of analytical data obtained from different methods and different laboratories.

Recently, we try to identify chemical species in geochemical reference materials. This is because physicochemical properties and toxicities of elements in materials change according to their chemical species. Elemental speciation would be informative to conduct more appropriate risk assessment in environment. For such purpose, the concentrations of 38 elements extracted by a sequential extraction procedure were determined for geochemical reference materials sediment series [1]. The sequential extraction scheme developed by the Community Bureau of Reference (BCR) [2] was used for speciation analysis. Furthermore, XANES spectroscopy was measured to identify whether Cr, Cu, and Zn are successfully extracted from intended phases by sequential extraction procedure [3-5]. In this study, we elucidate the chemical stability of Cu and Zn in a soil substance associated with the report about Cr(VI) stability in soil [5].

2 Sample materials

An artificially produced soil material is used for a chemical stability test [6, 7]. A brownish black forest soil collected from Tukuba City was dried in air for six months and further for one week at about 40 °C. An artificial mixture of 31 chemicals (mainly metal oxides) was added to the dried soil material, mixed for 192 h at 85 °C (repeated twice), followed by 8 HF-HNO3-HClO4, 3h 120°C. Consequently, about 1000 μg/g of Cr, Cu, and Zn was added to the dried source materials. Analytical results of Cr, Cu, and Zn in the contaminated soil are 1118 μg/g, 1276 μg/g, and 1174 μg/g, respectively [7]. The produced sample has been archived under dark and dry conditions for more than a dozen year.

3 Experimental methods

The Cr, Cu, and Zn in the contaminated soil was extracted using the BCR scheme [2]. Table 1 summarizes the procedure used in this investigation. BCR protocol is intended to extract metal weakly absorbed on material or carbonate phase in step 1, Fe hydroxide and Mn oxide phases in step 2, and organic phase and metal sulfide in step 3. The residue after each step of extraction was filtrated by a 0.45 μm membrane filter and freeze dried. For comparison, chemical reagents of K2Cr2O7, CuO, and ZnO that were diluted with BN powder, JSO-1, and metal doped humic acid were also prepared. JSO-1 is the geochemical reference material and similar to base material of the contaminated soil [7]. The Cu, Cr, and Zn concentrations in JSO-1 is 71 μg/g, 169 μg/g, and 105 μg/g, respectively [7]. The Cu and Zn were reacted with humic acid at pH 6.0 for 5 days [3-5].

The Cu and Zn K-edge XANES spectra were recorded in a fluorescence mode at the BL-12C of KEK-PF. The monochromator was calibrated at the peaks of Cu and Zn at 8984 eV and 9663 eV using CuO and ZnO powder in transmission mode, respectively. The fluorescence X-ray was measured by a 19 element pure-Ge SSD. The energy regions around the Cu-Kα and Zn-Kα fluorescence were selected from elastic scattering using single-channel analyzers, respectively.

Table 1: Outline of the sequential extraction procedure

<table>
<thead>
<tr>
<th>Step</th>
<th>Extractant</th>
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<tbody>
<tr>
<td>1</td>
<td>CH3COOH (0.11 mol/L), 16 h</td>
</tr>
<tr>
<td>2</td>
<td>NH2OH·HCl (0.5 mol/L), 16 h</td>
</tr>
<tr>
<td>3</td>
<td>H2O2 (8.8 mol/L), 1h at 20–30 °C and 1h at 85 °C (repeated twice), followed by CH3COONH4 (1 mol/L), 16 h</td>
</tr>
<tr>
<td>4</td>
<td>HF-HNO3-HClO4, 3h 120°C</td>
</tr>
</tbody>
</table>

4 Results and Discussion

Figure 1 shows Cr K-edge XAENS spectra of the contaminated soil, JSO-1, and K2Cr2O7 taken from Ohta [5]. The K2Cr2O7 (Cr(VI)-spiking material) is not recognized in the XAENS spectrum of the contaminated soil substance. The fact suggests that Cr(VI) in soil substance is totally reduced to Cr(III) by Fe(II) and organic material as Tsuno et al. [8] suggested. They assumed that slight humidity promoted Cr(VI) reduction during the initial stage of production. Incidentally, Cr(VI) reduction in soil is confirmed to be proceeded even in dry condition [7]. In addition, Ohta [5] revealed that Cr(III) reduced from Cr(VI) was finally precipitated as Cr(OH)3 (58%), and partly bound to FeOOH (about 20%) and humic substance (about 10%) in the contaminated soil. It is concluded that a stable reference material containing Cr(VI) is difficult in preparing because Cr(VI) is highly reactive [5].
Figure 1 shows Cr K-edge XANES spectra of contaminated soil, JSO-1, and K₂Cr₂O₇ powder. The spectrum of the contaminated soil cannot be explained by the mixture of JSO-1 and CuO. The spectrum of CuO has the main peak at 8984 eV and small shoulder peak at 8974 eV. In contrast, the main and shoulder peaks of XANES spectrum of the contaminated soil shift to the lower energy side. It's main and shoulder peaks at 8982 eV and 8968 eV are rather correspond to the peaks of Cu₂O estimated from Kosugi [9], respectively (Fig. 2). The fact suggests that a part of Cu(II) is reduced to Cu(I). As with the case with Cr(VI), Cu(II) may be reduced by organic materials [10].

The analytical data on Cu concentrations extracted using the BCR scheme are summarized in Table 2. The 38%, 30%, 17% of Cu was extracted from the contaminated soil in steps 1, 2, and 3, respectively. The XANES spectrum of the contaminated soil suggest that the intensity of the shoulder peak attributed to Cu(I) gradually decreases and the main peak shifts to the higher energy side with going through the procedure (Fig. 3). Therefore, Cu(I) is selectively extracted in the BCR procedure. Because XANES spectra of Cu(I) materials such as Cu₂O were not measured in this study, it is difficult to identify the other chemical forms. However, the presence of Cu(I) in the residue after step 2 and 3 of the extraction seems to be negligible (Fig. 3).

Figure 4 depicts the XANES spectra of the residues from steps 2 and 3 of the extraction and Cu doped humic acid, and the fitting result. The spectrum of the residue after step 2 extraction is fully explained by the linear combination fitting of Cu doped humic acid (58%) and the residue after step 3 extraction (42%). Therefore, about 112 μg/g of Cu exist as Cu bound to organic matter, which is calculated as 58% of 204 μg/g of Cu extracted at step 3.

Table 2: Concentrations of Cr, Cu, and Zn in steps 1–4 obtained from BCR extraction procedure.

<table>
<thead>
<tr>
<th>Step</th>
<th>Cr (μg/g)</th>
<th>Cu (μg/g)</th>
<th>Zn (μg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39</td>
<td>465</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>168</td>
<td>364</td>
<td>341</td>
</tr>
<tr>
<td>3</td>
<td>583</td>
<td>204</td>
<td>148</td>
</tr>
<tr>
<td>4</td>
<td>427</td>
<td>175</td>
<td>362</td>
</tr>
</tbody>
</table>

* The data were taken from Ohta [5]
combination fitting of JSO-1 and ZnO. The relative ratio of ZnO determined from the XANES fitting is zero, nevertheless 1000 μg/g of Zn (156 g of ZnO added to 125 kg of a base material) was added to the source materials. The peak positions in XANES spectrum of the contaminated soil correspond to those of JSO-1.

Voegelin et al. [11] examined the speciation of Zn in contaminated soil mixed with ZnO. They confirmed that ZnO in soil was dissolved within 4–9 months and precipitated as Zn-layered double hydroxide (Zn-Al hydroxide) and partly as Zn-phyllosilicate phases. Kubota et al. [1] reported that Zn in JSO-1 is scarcely extracted in steps 1, 2, and 3. The fact suggests that Zn in JSO-1 exists dominantly as an alumino-silicate mineral. Accordingly, it is reasonable that XANES feature of the contaminated soil resembles to that of JSO-1 (Fig. 5).

![XANES spectra of contaminated soil, JSO-1, and ZnO.](image)

Fig. 5: Zn K-edge XANES spectra of contaminated soil, JSO-1, and ZnO.

The BCR scheme extracts the 26%, 30%, and 13% of Zn from the contaminated soil at steps 1, 2, and 3, respectively (Table 2). Nevertheless, XANES spectra of the contaminated soil did not change significantly (Fig. 6). It is assumed that Zn authigenic materials (Zn-layered double hydroxide and Zn-phyllosilicate) are dissolved by piecemeal in each extraction step, which are not target phases of the BCR scheme. The Zn bound to FeOOH or humic substances seem to be scarce in this material.

5 Conclusion

Speciation study is conducted for an artificially produced soil material with CuO and ZnO. The CuO and ZnO are stable chemical forms and seem to be suitable for the production of a metal speciation reference material having chemical stability. However, Cu(II) in soil is partly reduced to Cr(I) by organic material; ZnO reacts with Al and Si and subsequently is precipitated as Zn-layered double hydroxide and Zn-phyllosilicate phases. Eventually, Cu and Zn do not retain their chemical forms (also valence state) in soil. It is concluded that a stable reference material containing known chemical forms is difficult in preparing.

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References


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