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 physic-chemical 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 ºC. An artificial mixture of 31 chemicals (mainly metal oxides) was added to the dried soil material, mixed for 192 h using a high alumina-lined mill, exposed to air to reach equilibrium with the ambient humidity of the air and subsequently bottled [6, 7]. As Cr-, Cu-, and Zn-spiking materials, 700 g of $K_2Cr_2O_7$, 156 g of CuO, 156 g of ZnO were added to 125 kg of a base material. 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 The produced sample has been archived under dark and dry conditions for more than a dozen year.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 contaminate 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 $K_2Cr_2O_7$, 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 Cr, Cu, 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 fluoresce 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

Step	Extractant
1	CH_3COOH (0.11 mol/L), 16 h
2	$NH_2OH \cdot HCl$ (0.5 mol/L), 16 h
3	H_2O_2 (8.8 mol/L), 1h at 20–30 °C and 1h at 85 °C (repeated twice), followed by CH_3COONH_4 (1 mol/L), 16 h
4	$HF-HNO_3-HClO_4$, 3h 120°C

4 Results and Discussion

Figure 1 shows Cr K-edge XAENS spectra of the contaminated soil, JSO-1, and $K_2Cr_2O_7$ taken from Ohta [5]. The $K_2Cr_2O_7$ (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].
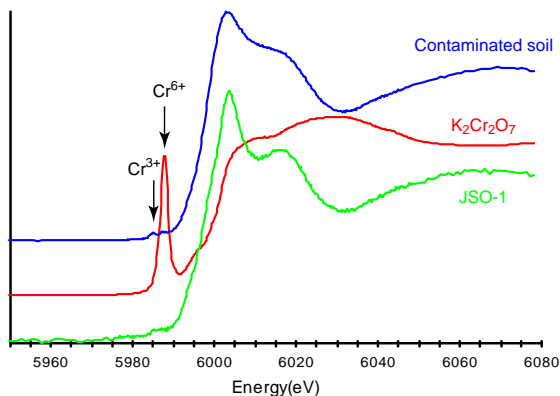
Fig. 1: Cr K-edge XANES spectra of contaminated soil, JSO-1, and K₂Cr₂O₇ powder.

Figure 2 shows Cu K-edge XAENS spectra of the contaminated soil, JSO-1, and CuO. The dotted line indicates the linear combination fitting of JSO-1 and CuO. The spectrum of the contaminated soil cannot be explained by the mixture of JSO-1 and CuO. XAENS 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 Cu_2O estimated from Kosugi [9], respectively (Fig. 2). The fact suggests that a part of Cu(I) is reduced to Cu(I). As with the case with Cr(VI), Cu(II) may be reduced by organic materials [10].
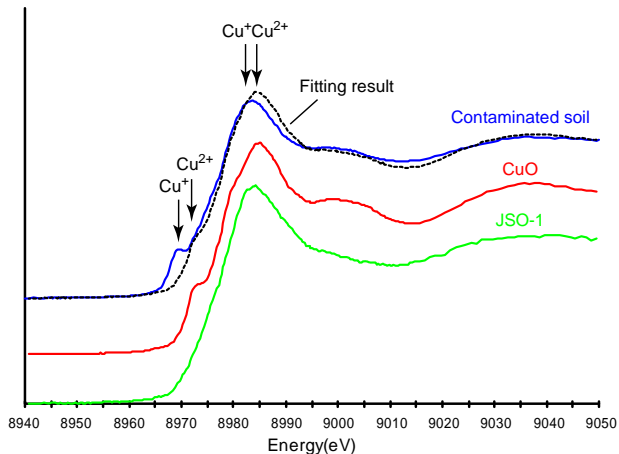

Fig. 2: Cu K-edge XANES spectra of contaminated soil, JSO-1, and CuO. The dotted line shows that the linear combination fitting of JSO-1 (44%) and CuO (56%).

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 contaminate 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 Cu_2O 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.

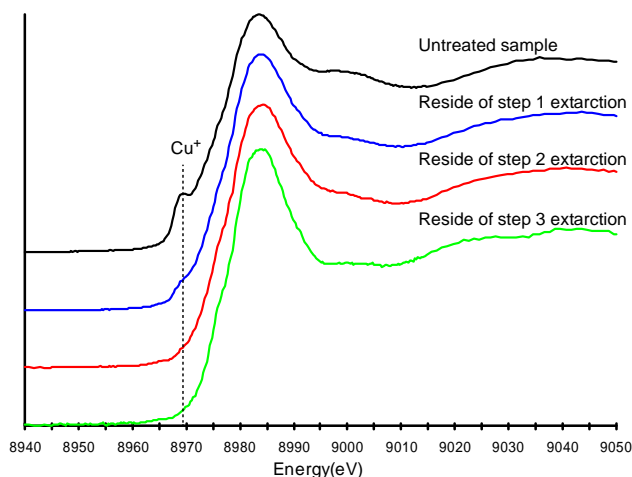| Step	Cr (µg/g)[*]	Cu (µg/g)	Zn (µg/g)
1	39	465	300
2	168	364	341
3	583	204	148
4	427	175	362

* The data were taken from Ohta [5]

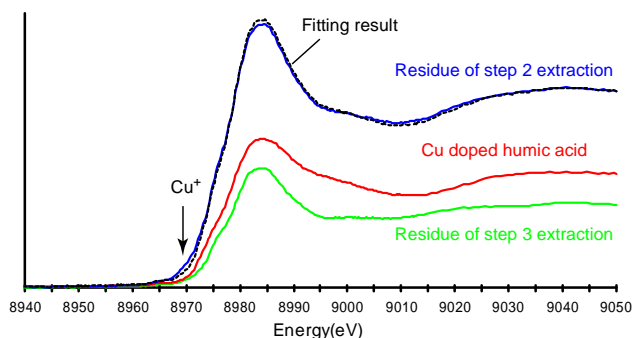Fig. 3: Cu K-edge XANES spectra of untreated sample and residue after extraction of steps 1, 2, and 3.

Fig. 4: The linear combination fitting result of residue from step 2 extraction, calculated from a set of Cu doped humic acid and residue from step 3 extraction.

Figure 5 portrays that Zn K-edge XANES spectra of the contaminated soil, JSO-1 and ZnO. The spectrum of the contaminated soil is not explained by the linear

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.
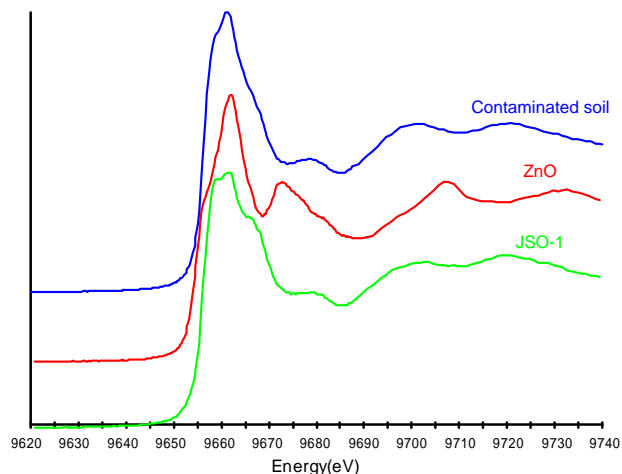

Fig. 5: Zn K-edge XANES spectra of contaminated soil, JSO-1, and ZnO.

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).
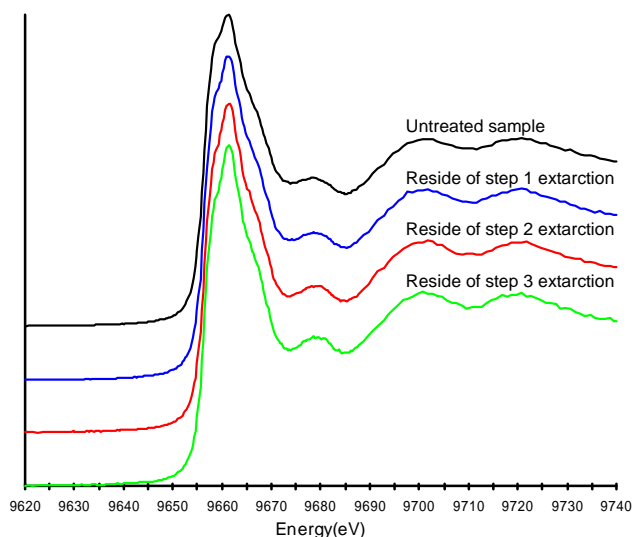

Fig. 6: Zn K-edge XANES spectra of untreated sample and residue after extraction of steps 1, 2, and 3.

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.

References
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