

Speciation of chromium in contaminated soil from dumped slag in Tokyo

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1 Introduction

Chemical states of elements in sediment or soil have often been used as an index to evaluate redox condition. In addition, the mobility of elements changes by its oxidation states. For instance, Cr(VI) species have high mobility because of its presence in highly soluble oxyanion: CrO_4^{2-} , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$. In contrast, Cr(III) rarely migrates in the environment because it precipitates as $\text{Cr}(\text{OH})_3$.

Highly Cr(VI) contaminants have often found in groundwater and soils around the chromium slag dumping site in Edogawa-ward and Koto-ward, Tokyo, although the government applied a reduction to Cr(III) by FeSO_4 treatment. We investigated Cr(VI) pollution in these areas and found that heavy rain and snowfall cause elution of Cr(VI) from the slag [1]. However, the chemical species of eluted Cr(VI) is not still understood. Further, the valence of Cr should be measured directly because liquid phase experiments such as extraction may cause some chemical changes. Therefore, we directly analyzed the Cr(VI) contaminants by using XAFS to confirm the chemical species of Cr(VI) contaminants flowing out at present.

2 Experiment

Contaminated soil sample was collected from catch basin around Ojima-Komatsugawa Park, which lies in Edogawa-ku and Koto-ku. After sampling, the collected soil sample was packed into polyethylene bag for XAFS analysis.

Cr K-edge XANES spectra and Fe K-edge XANES spectra were measured in the fluorescence mode using a Lytle type detector at the BL-9C equipped with a double crystal monochromator of Si(111). The measurements were carried out at room temperature. The spectra were treated by the REX2000 program (Rigaku Corporation).

3 Results and Discussion

Figure shows the normalized Cr K-edge XANES spectra of the Cr(VI) reference materials and the contaminated soil sample. As shown in Figure, pre-edge peak at 5992 eV, which is characteristic of Cr(VI), appeared for all samples, indicating that the soil sample present in the hexavalent oxidation states. The chromium slag under the ground at Ojima-Komatsugawa Park included sodium chromate [2]. In order to confirm the chemical species of Cr(VI) in contaminated soil, we compared the spectrum of the sample with the reference materials. The feature at 6000 eV around the pre-edge peak of the sample was mostly similar to those of

chromate and dichromate reference samples (Figure). This result indicates that Cr(VI) is mainly present as chromate or dichromate compound which is an oxyanion (CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$). Furthermore, it is considered that the origin of Cr(VI) contaminant is the chromium slag. In case of heavy rain, Cr(VI) in the slag is eluted by rainwater because sodium chromate is soluble in water. As a result, eluted Cr(VI) solution flows out and Cr(VI) pollution occurs around the Park. In addition, we measured Fe K-edge XANES spectrum of contaminated soil sample, confirming that Cr(III) in the sample is present as $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$. It is considered that eluted Cr(VI) is reduced to Cr(III) by Fe(II), and it precipitates as $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$. These findings would be helpful for understand how Cr(VI) is released from the slag in this area.

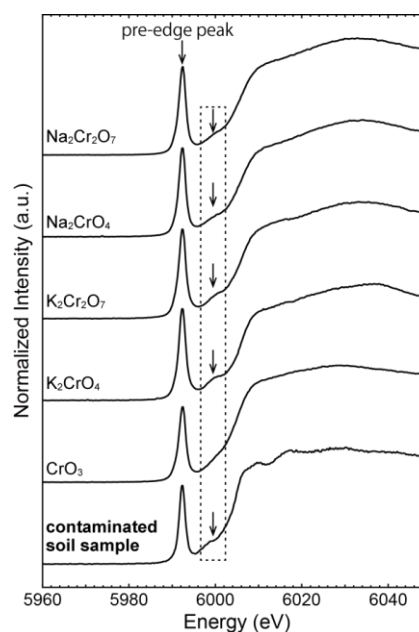


Figure Cr K-edge XANES spectra of the Cr(VI) reference materials (CrO_3 , K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, Na_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$) and the contaminated soil sample in catch basin.

References

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