

Reduction of hexavalent chromium in soils by X-ray irradiation

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1 Introduction

A reduction of Cr(VI) by organic materials and Fe(II) in soils is a very interesting phenomenon for environmental problems because pollutant Cr(VI) disappears in a field system easily [1, 2]. We have focused on Cr(VI) stability in soils and Cr(III/VI) reacting with humic substances using the XAFS spectroscopy method [3, 4]. However, there is a serious problem that X-ray irradiation accelerates the reduction of Cr(VI) in such experimental systems during XAFS measurement. From this reason, the Cr K-edge XANES spectra of Cr(VI)-doped soils on the first measurement was used for analysis, although multiple scans were conducted for samples. We have not explained this problem in detail so far. In this study, we discuss how X-ray irradiation affects the Cr(VI) reduction in soil materials.

2. Experiment

A 13–15 mg of $K_2Cr_2O_7$ solid reagent was mixed with 4–5 g of JSO-1, which is a soil geochemical reference material provided by Geological Survey of Japan, AIST [5]. The sample contained approximately 1000 $\mu\text{g/g}$ of Cr as Cr(VI) and 70 $\mu\text{g/g}$ of Cr as Cr(III) [3]. We further added water to an aliquot of the sample (about 20 wt%). The JSO-1 samples mixed with $K_2Cr_2O_7$ powder kept under dry and wet condition are named as the dry sample and the wet sample, respectively. The XANES spectra of these samples were recorded on the second, 20th, 120th and 240th days after the preparation.

The Cr K-edge XAFS spectra were recorded in fluorescence mode at the BL-12C of KEK-PF. A Si(111) double-crystal monochromator was used to produce a monochromatic X-ray beam. The monochromator was calibrated at the sharp pre-edge peak of Cr(VI) at 5989 eV, which is sensitive to the presence of Cr(VI), using $K_2Cr_2O_7$ powder in the transmission mode. The fluorescence X-ray (Cr $K\alpha$: 5.4 keV) was measured using a 19 element pure-Ge solid-state detector. The XAFS spectra of all samples were measured at room temperature. The energy region around the Cr- $K\alpha$ fluorescence was selected from elastic scattering using single-channel analyzers. Multiple scans (two–five times) were conducted for the samples. The $K_2Cr(VI)_2O_7$ and $Cr(III)(NO_3)_3$ 1000 $\mu\text{g/g}$ standard solutions were also measured as reference substances. These materials are used for determining molar fractions of Cr(VI) and Cr(III) of samples.

4. Results and Discussion

Figure 1 shows the XANES spectra of JSO-1 reacting with $K_2Cr_2O_7$ in wet condition for 2 days. Because the x-ray beam was focused into an area smaller than $1 \times 1 \text{ mm}^2$, the damaged area was very restricted. Figure 1 shows that the spectra dramatically changed with three repeat measurements. The sharp pre-edge peak at 5989 eV and the region around 6020–6040 eV decrease their intensities and the peak at 6003–6005 eV increase its intensity during measurements. It takes 670 seconds for measuring the whole XANES region and 150 seconds for measuring within the pre-edge region including the pre-edge peak at 5989 eV. Those changes suggest that the X-ray irradiated to samples reduced Cr(VI) to Cr(III) remarkably within only 35 minutes.

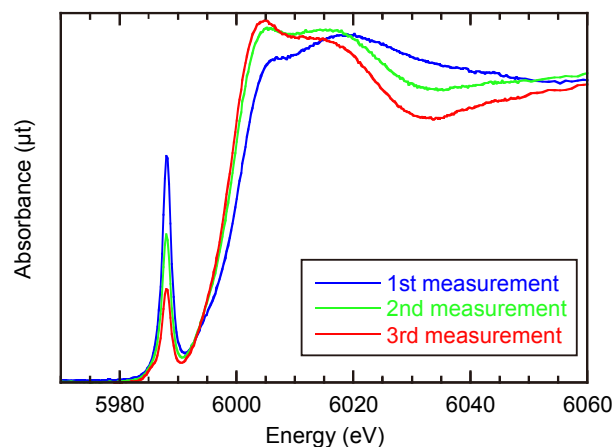


Fig. 1: XANES spectra of JSO-1 reacting with $K_2Cr_2O_7$ in wet condition for two days.

Figure 2 shows how the intensity of the pre-edge peak at 5989 eV in Cr K-edge XANES spectra changes during the repeated measurements. The intensity of the pre-edge peak (μt_{peak}) was subtracted off the pre-edge background absorption (μt_{BK}) and further normalized by the absorbance on the first measurement;

$$\mu t_{\text{peak}}' = (\mu t_{\text{peak}} - \mu t_{\text{BK}}) / (\mu t_{\text{peak}} - \mu t_{\text{BK}})_{\text{the 1st measurement}} \quad (1)$$

The Cr(VI)/Total Cr (Cr(VI)/T-Cr) ratios expressed on the legends in Fig. 2 are cited from Tsuno et al. [3]. The intensity of the sharp pre-edge peak in the samples under the wet condition decreases dramatically with repeated measurements (Fig. 2). The decrease of the intensity ($\mu t_{\text{peak}}'$) is same among all samples except for the samples

reacting for 20 days. The μ_{peak} for the wet samples is reduced by half within three repeated measurements. The decrease of μ_{peak} seems not to relate with Cr(VI) reduction properties. On the other hands, the changes at pre-edge peak for the dry samples are not pronouncedly. A decrease of 30% over time is found for μ_{peak} at the highest different from wet samples. The decrease ratio of μ_{peak} becomes small with increasing the reacting times (from 2 days to 240 days), although there is no significant difference between reactions times of 120 days and 240 days.

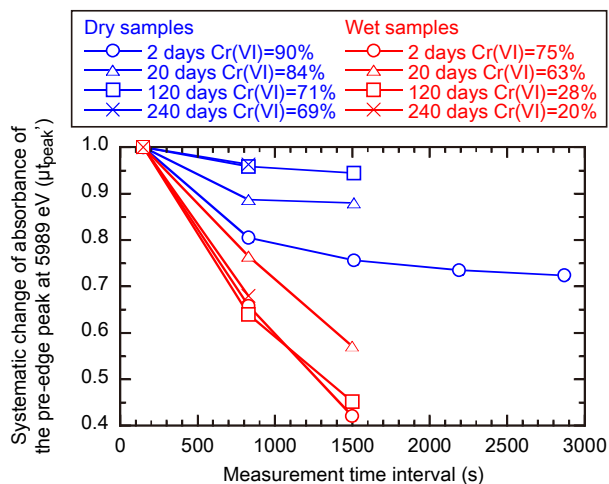


Fig. 2: The Systematic change of absorbance of the pre-edge peak at 5989 eV with the multi-scans. The measurement time interval for the pre-edge peak is calculated by $150s + 670s \times (n-1)$, where $n = 1-5$.

Figure 3 shows that the Cr(VI)/T-Cr ratios determined using a linear combination fitting of standard Cr(III) and Cr(VI) materials. Because the whole XANES region was used for the fitting, the Cr(VI)/T-Cr data were plotted against the averaged time of the measurement ($670s/2$). The estimated ratio decreases gradually at each measurement. Especially, the percentages of Cr(VI) of the wet samples reacting with Cr(VI) for 2 days and 20 days decrease dramatically within three repeated measurements.

Table 1 summarizes the Cr(VI)/T-Cr ratios determined for samples. The "LCF" indicates a linear combination fitting result of XANES spectra measured on the first time using the spectra of Cr(VI/III) references. We fitted a linear regression line ($y=a+bx$) or a regression curve ($y=a+bx+cx^2$) to the data in Fig. 3. The estimated intercepts (a) indicate the Cr(VI)/T-Cr ratios that are free from reduction by X-ray irradiation. They are listed on Table 1 as "Regression". The re-evaluated Cr(VI)/T-Cr values for the dry samples do not differ from the LCF values significantly. The LCF values obtained for the wet samples reacting with Cr(VI) for 2 days and 20 days are 9–16% smaller than the re-evaluated Cr(VI)/T-Cr values. However, there are small differences for samples reacting with Cr(VI) over 120 days. The error in a linear

combination fitting of XANES spectra is empirically $\pm 5\%$. As long as the Cr(VI)/T-Cr ratio is determined using LCF, there seems not to be severe problem for the most samples. However, we must pay attention that the Cr(VI)/T-Cr ratios in soil samples determined using XAFS spectroscopy method are always lower than the real values because of the reduction process by X-ray irradiation.

Finally, it is reasonable that the reduction of Cr(VI) in the wet samples by X-ray irradiation is accelerated more than that in dry samples. However, it is unclear why the Cr(VI) in dry samples is reduced by X-ray irradiation. The JSO-1 used for experiments was not dried under the high temperature. The amount of H_2O in JSO-1 is 8.36 wt. %, which is determined by drying at $110^\circ C$ [5]. The hygroscopic minerals in JSO-1 would absorb variable amounts of moisture [5]. The Cr(VI) reduction of dry samples by X-ray irradiation would not be caused without such inherent waters.

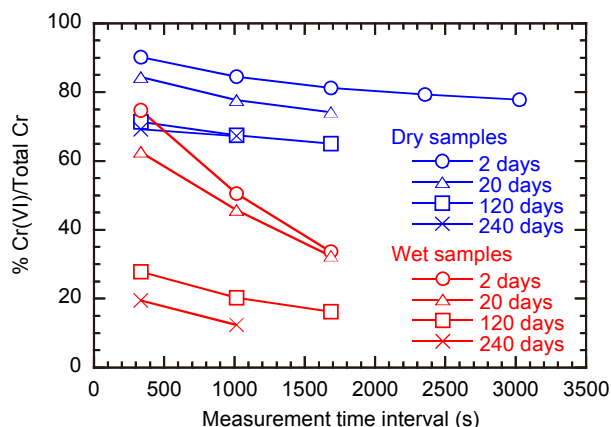


Fig. 3: The Cr(VI)/T-Cr ratios determined using a linear combination fitting of standard Cr(III) and Cr(VI) materials. The measurement time interval is calculated by $670s/2 + 670s \times (n-1)$, where $n = 1-5$.

Table 1: Cr(VI)/T-Cr ratio determined for JSO-1 reacting with $K_2Cr_2O_7$

Reaction time	Dry condition		Wet condition	
	LCF	Regression	LCF	Regression
2 days	90%	93%	75%	89%
20 days	84%	89%	63%	72%
120 days	71%	74%	28%	33%
240 days	69%	70%	20%	23%

References

- [1] P. R. Wittbrodt and C. D. Palmer, Environ. Sci. Technol. **30** (1996) 2470.
- [2] N. Kožuh *et al.*, Environ. Sci. Technol. **34** (2000) 112.
- [3] H. Tsuno *et al.* Geostand Geoanalyst Res. **30** (2006) 55.
- [4] A. Ohta *et al.* Bull. Geol. Surv. Japan **62** (2011) 347.
- [5] A. Terashima *et al.* Geostand. Newsl. **26** (2002) 85.

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