Standard Experimental Report
(All fields are mandatory)

Proposal title: Selenate uptake by green rust probed by anomalous X-ray scattering
Proposal number: 20211123
Beamline:D2AM
Shifts: 12
Date(s) of experiment: from: 09/6/2022 to: 13/6/2022
Date of report: 5/10/2022

- Objective & expected results (less than 10 lines): **-**

The objective of this study is to clarify the short- and intermediate-range atomic order structures in selenium(VI)(Se(VI))-bearing green rust (GR; $3Fe^{II}_4Fe^{III}_2(OH)_{10}(SO_4)_2$) using anomalous X-ray scattering. The expected result is that detail information about the partial structural short- and intermediate-range order of the Se(VI)-bearing GR is obtained from the experimentally obtained ΔkS(Q)'s and S(Q)'s and the subsequent Reverse Monte Carlo(RMC) simulation. The partial structure factors Sij(Q), partial pair-correlation functions gij(r), and the three-dimensional atomic configurations can clarify the selenate removal mechanism by GR. We expected to discuss the relation between the structure of GR and pH and/or absorbed Se(VI) with the viewpoint of the partial structures factors.

- Results and the conclusions of the study (main part): **-**

Figure 1 shows the differential intensity profile of Se(VI)-bearing GR obtained from the intensity data at Se K-edge (12.658 keV). The measured energy was set below the edge at -10 and -200 eV. The Se(VI)-bearing GR was made by reacting Se(VI) to GR during 10 min at pH 9 in the glove box. The atmosphere of glove box was kept under nitrogen(N_2) atmosphere to prevent oxidation of GR by oxidation during experiments. The Se(VI)-bearing GR sample encapsulated in a 0.5 mm diameter capillary and measured at beamline D2AM. To prevent oxidation during measurement in beamline D2AM, the atmosphere of a glass capillary was also kept under N_2 atmosphere. The measurement data of an empty 0.5 mm glass capillary was used as background data.

The Figure 1 displays the normalized S(Q) using the PdfGetx software. We observe a weak energy dependence of Se(VI)-bearing GR sample. This trend is also obtained in the previous study about the GeO_2-Bi_2O_3 glass[1-2].

Figure 2 shows the radial distribution function of selenium(VI)-bearing green rust obtained from (a) the intensity data measured close to Se K-edge(12.648 keV) and (b) difference intensity between far(12.468 keV) and near(12.648 keV) Se K-edge. In the figure 2, several peaks, showing atomic pairs, were observed. In a previous paper using x-ray absorption fine structure (XAFS) analysis[3], it was reported that a part of Se(VI) was reduced to Se(IV), and Se(0) and a part of GR was oxidized goethite(FeOOH) according to below equations during experiments.

$$3Fe^{II}_4Fe^{III}_3(OH)_{12}SO_4 + 2SeO_4^{2-} + 2OH^- \rightarrow 18FeOOH(s) + 3SO_4^{2-} + 2Se^0 + 10H_2O$$
$$Fe^{II}_4Fe^{III}_3(OH)_{12}SO_4 + 2SeO_4^{2-} + 2OH^- \rightarrow 6FeOOH(s) + SO_4^{2-} + 2SeO_3^{2-} + 4H_2O$$

Based on this, it is possible to contain not only Se(VI) but also Se(IV) and Se(0) atomic pairs in the peak (Figure 2).

Based on the known model of GR, several characteristic distances can be identified and are shown in Figure 2-a.

After that, detail information about the partial structural short- and intermediate-range order of the Se(VI)-bearing GR will be analyzed using RMC simulation.

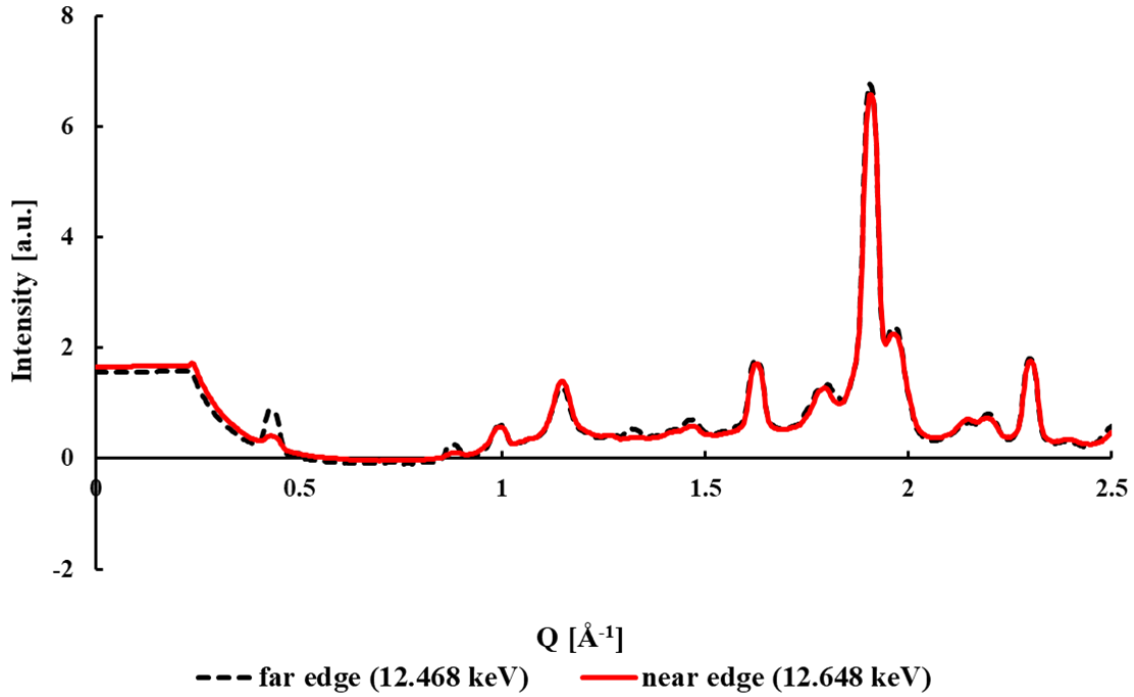

Figure 1. The differential intensity profile of selenium(VI)-bearing green rust obtained from the intensity data measured at Se K-edge (12.468 keV and 12.648 keV).

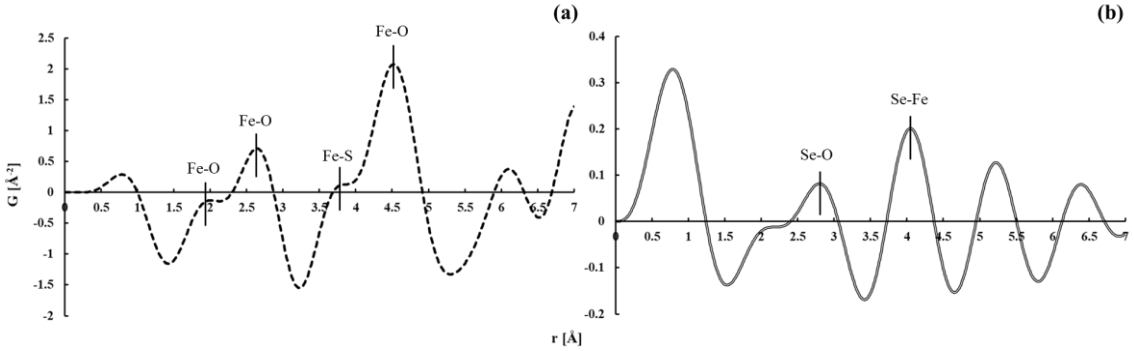

Figure 2. The radial distribution function of selenium(VI)-bearing green rust obtained from (a) the intensity data measured 12.468 keV and (b) difference intensity between far(12.468 keV) and near(12.648 keV) Se K-edge. The straight line indicate the interatomic distance in the structure of green rust.

[1] K. Sugiyama. Structural analysis of inorganic substances by the anomalous x-ray scattering (AXS). J. Mineral. Soc. Jpn. 1994, 23(2), pp. 69 - 76.
[2] Y. Waseda, K. Sugiyama, Y. Sunamori, K. Omote, M. Ashizuka. Structural analysis of $70GeO_2 30Bi_2O_3$ glass by x-ray diffraction. Sci. Rep. RITU. 1994, A38, pp. 175 - 182.
[3] A. Onoguchi, G. Granata, D. Haraguchi, H. Hayashi, and C. Tokoro. Kinetics and mechanism of selenate and selenite removal in solution by green rust-sulfate. R. Soc. Open Sci. 2019, 6, 182147.

- Justification and comments about the use of beam time (5 lines max.): **-**

We plan to measure AXS close to the Fe K and Se K edges (-20 and -200 eV) on the GR sulfate obtained from Se removal experiments at the beamline BM02. The number of analysis samples is two samples. The difference between the two samples is the concentration of Se in the GR sulfate.

- Publication(s): **-**

These results should be published in a journal.