

Mechanism of selenite sequestration by low-soluble phosphate minerals

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Selenium-79 (the half-life of 6.5×10^4 yrs) is included in high-level radioactive waste derived from reprocessing, which will be disposed in deep geological repository. However, selenium has low affinity against various sorbents because the selenium speciation in the typical groundwater condition is anion such as selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}).

Apatite was previously proposed as an efficient sorbent for anion species as well as heavy metals like lead. On the other hand, lead salt of selenium oxoacid has low solubility and thus, Se-Pb-phosphate ternary system is of great interest for Se sequestration. In order to understand the mechanism of selenite sequestration by apatite or pyromorphite and the role of lead in the reaction, we have demonstrated sorption experiments under four conditions: (i.) hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) was reacted in 0.5 mM sodium selenite solution at initial pH of 5.0 and 9.5; (ii.) hydroxypyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$) was reacted in 0.5 mM sodium selenite solution at initial pH of 5.0; (iii.) hydroxyapatite was reacted in the solution content of 0.5 mM sodium selenite and 0.5 mM lead nitrate at initial pH of 5.3. All experiments were carried out at room temperature for 30 minutes to 30 days.

In the experiment (i.), powder X-ray diffraction analysis (XRD) shows no peaks of secondary mineral in both experiments. These XRD results indicate that selenium sorption takes place by surface adsorption including anion exchange and complex formation process. In the experiment (ii.), lead selenite (molybdomenite, PbSeO_3 , $\text{P}2_1/m$, $z = 2$) precipitates during reaction. In case of (iii.), XRD patterns show peaks of $\text{P}2_1/c$ ($z = 8$) lead selenite through the reaction, whereas peaks of $\text{P}2_1/m$ lead selenite disappeared after 1 hour.

Our results suggest that structure of precipitating lead selenite changes depending on the form of lead added to the experimental system and that even metal phosphate minerals with low solubility can quickly dissolve due to the affinity of metal ion for selenite. It is also worth to note that solubility of lead selenite in this experiment appears to be lower than that predicted from thermodynamic data.

Keywords: apatite, TEM, lead, selenium