

Research Group for Interfacial Reaction Field Chemistry

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The research objectives of this group are to explore novel chemical reactions of aqueous species of elements at liquid-solid and liquid-liquid interfaces to contribute to environmental chemistry, actinide chemistry, and waste treatment. As the progress of the year of 2017 we report novel findings: pseudocolloid formation of heavy element aqueous species with soluble glycoprotein on the cell surface of *Paramecium* [1] and removal of selenium anions by coprecipitation with BaSO_4 [2].

Pseudocolloid formation of heavy element aqueous species with soluble glycoprotein on the cell surface of *Paramecium*

To evaluate the potential transfer pathways of radionuclides from the aquatic environment to the human food chain, the role of microbes has received intense attention because microbial transformation of radionuclides is very different from abiotic transformation. Most known microbial transformation reactions of radionuclides such as sorption and biomineralization have been identified by using bacteria and unicellular fungi such as yeast. Although, in aquatic ecosystems, protozoa are key members of microbial communities and control bacterial populations, little is known about the microbial transformation of radionuclides by protozoa.

We investigated the interaction of inorganic aqueous Eu(III) , Pb(II) , and U(VI) with *Paramecium sp.*, a representative single-celled protozoan that lives in freshwater. Living and pre-killed *Paramecium* cells were tested. The pre-killed cells were killed with a fixative. After 24 h exposure of the cells to inorganic aqueous solutions containing Eu(III) , Pb(II) , or U(VI) , analyses by microparticle-induced X-ray emission with a focused beam ($<1 \mu\text{m}$) did not detect those elements in the living cells, whereas they were clearly detected in the pre-killed cells. A fraction of the Eu , Pb , and U in the aqueous phase bound to a large (*ca.* 250 kDa) *Paramecium* biomolecule and formed a metal-organic complex. The characteristics of the biomolecule were consistent with those of the soluble glycoproteins covering the surfaces of *Paramecium* cells. These results show that *Paramecium* cells transform inorganic aqueous Eu , Pb , and U to soluble organic complexes (Fig. 1). This complex formation may facilitate migration of those heavy elements in the environment.

Removal of selenium oxyanions from aqueous solution by coprecipitation with BaSO_4

Barite, BaSO_4 , is a common phase in many geological environments. It is easily synthesized by mixing aqueous solutions of barium salt (BaCl_2) and sulfate (Na_2SO_4) and its solubility is extremely low. It is known that barite serves as a sequestering phase for the removal of toxic or radioactive elements such as Ra^{2+} from polluted solutions. In the present study, we explored a novel application of barite as a sequestering phase for selenium anions, selenite (Se(IV)) and selenate (Se(VI)) ions, from aqueous solutions. ^{79}Se with an extremely long half-life plays a key role in safety assessments for radioactive waste disposal since under most of the geological environment selenium is present as highly soluble and consequently mobile selenite and selenate. However, effective

methods for containment of selenium anions have yet to be developed.

We investigated the uptake of Se(IV) and Se(VI) during coprecipitation with barite through batch experiments to understand the factors controlling effective removal of Se(IV) and Se(VI) from polluted water to barite. The factors include (i) chemical affinity related to the degree of surface complexation between barite surface and Se(IV)/Se(VI) ion and (ii) structural similarity related to the structural geometry of incorporated ions into the substituted site. The uptake of Se(IV) by barite was dependent on pH (slightly), coexistent calcium ion, and sulfate concentration in the initial solution, possibly due to their effects on the chemical affinity and structural similarity. On the other hand, the uptake of Se(VI) by barite was strongly dependent on sulfate concentration in the initial solution, which is only related to the structural similarity. By adjusting those factors, we succeeded in greatly increasing the uptake of Se(IV) and Se(VI) (Fig. 2).

We are planning to prepare simulated waste forms containing barite to investigate if the selenium in barite is immobilized in the waste forms.

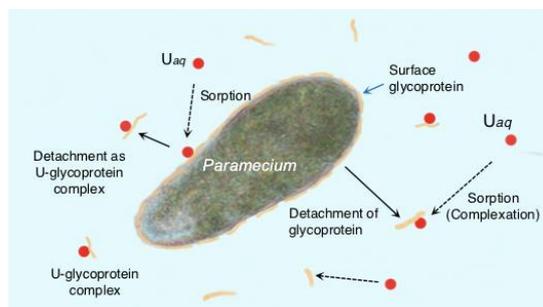


Fig. 1 Complexation of heavy elements with surface glycoprotein of *Paramecium* [1].

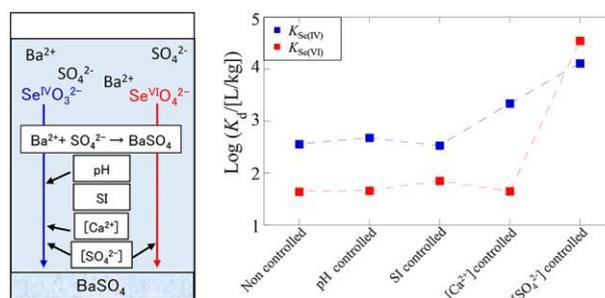


Fig. 2 Factors for controlling the uptake of selenium anions during coprecipitation with barite [2].

References

- [1] N. Kozai et al., *Chemosphere*, **196**, 135 (2018).
- [2] K. Tokunaga and Y. Takahashi., *Environ. Sci. Technol.*, **51**, 9194 (2017).