Pu oxidation state distributions in suspensions of the Mont Terri Opalinus Clay isolate *Sporomusa* sp. MT-2.99

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The time-dependent ^{242}Pu oxidation state distribution in the presence of *Sporomusa* sp. cells as a function of pH with or without Na-pyruvate was analyzed. In all cases, the presence of bacterial cells enhanced removal of Pu from solution and accelerated Pu interaction reactions, e.g. biosorption and bioreduction.

Clay is one potential host rock for a safe storage of nuclear waste in a deep geological repository. The indigenous bacterium *Sporomusa* sp. MT-2.99 was isolated from Mont Terri Opalinus Clay, which can serve as such a potential host rock.[1] In order to describe the fate of accidentally released plutonium in such an environment, knowledge is necessary on how these bacteria are interacting with plutonium. Our report aims to summarize the knowledge regarding Pu-*Sporomusa* interactions.[2, 3]

EXPERIMENTAL. The experimental details are summarized in literature.[2, 3] New experiments were performed anaerobically at [dry biomass] of 0.33 ± 0.01 $g_{dry\ weight}$/L in the presence of 10 mM Na-pyruvate at pH 4 at 25 °C in 0.1 M $NaClO_4$. Details about the Eh-pH calculations using geochemical speciation "Geochemist's Workbench"® 11.0.3 can be found in.[4]

RESULTS. Figure 1 depicts a generalized Eh–pH diagram of the dominant Pu species that exist for a range of Eh and pH values calculated under anaerobic conditions. As a result of the batch experiments, in the blanks with no electron donor, the decrease of Pu(VI) at pH 6.1 was 3.2 times faster than at pH 4. The increase of Pu(V) at pH 6.1 was 3.3 times faster than at pH 4.

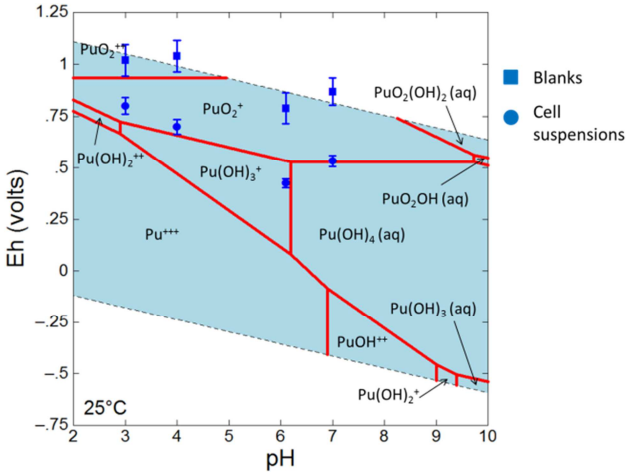

Fig. 1: Eh–pH diagram of Pu calculated for a 0.1 M $NaClO_4$ solution with 180 µM Pu in the absence of CO_2 at 25 °C. The diagram includes the measured Eh and pH values from selected experiments at pH 3, 4, 6.1, and 7 (blanks and corresponding cell suspensions).[4]

At pH 4, Pu(VI) was more stabilized in the blanks. This observation and the dominance of Pu(V) is in agreement with the Eh-pH calculations shown in Fig. 1. A significant change of the Pu oxidation state distributions was observed in the supernatants compared with the blanks if no electron donor was added. At both pH values, a fast decrease of Pu(VI) combined with a fast increase of Pu(V) was observed. These processes were accelerated due to the influence of the cells. The observed cell mediated reduction process of Pu(VI) to Pu(V) is not yet fully understood. The dominance of Pu(V) in the supernatants/cell suspensions is also in agreement with the Eh-pH calculations shown in Fig. 1 (for pH 3, 4, and 7). For the cell suspension at pH 6.1 predominantly Pu(IV) was predicted (cf. Fig. 1). This could not be confirmed experimentally due to the dominance of Pu(V).
The cells displayed a strong pH dependent affinity for Pu. In the absence of Na-pyruvate, a strong enrichment of stable Pu(V) in the supernatants was discovered, whereas Pu(IV)-polymers dominated the Pu oxidation state distribution on the biomass at pH 6.1 (cf. Fig. 2). A pH-dependent enrichment of the lower Pu oxidation states (e.g. Pu(III) at pH 6.1 which is considered to be more mobile than Pu(IV) formed at pH 4) was observed in the presence of up to 10 mM Na-pyruvate (cf. Fig. 2).

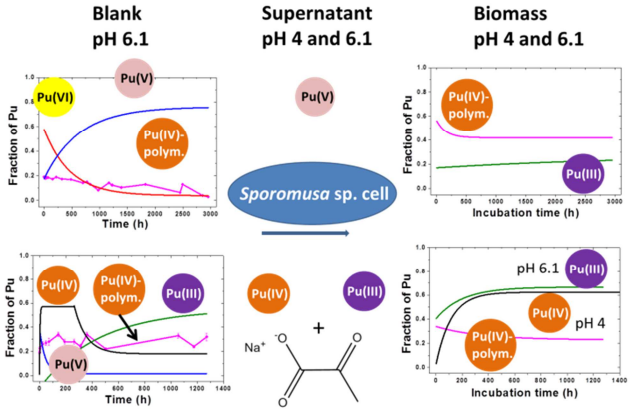

Fig. 2: Summary of Pu oxidation state distributions measured in the batch experiments with *Sporomusa* sp. MT-2.99 cells.

To conclude, a moderate to strong impact of *Sporomusa* sp. cells on the Pu speciation was observed. Parameters influencing the Pu interaction process were the pH, the initial Pu concentration, the Pu speciation and the presence or absence of an electron donor, in this case Na-pyruvate. The results presented contribute for a better mechanistic understanding for Pu biogeochemistry at the molecular level in the presence of host rock indigenous bacterial cells.

ACKNOWLEDGEMENTS. The authors thank the BMWi for financial support (contract no.: 02E10618 and 02E10971), Velina Bachvarova and Sonja Selenska-Pobell for isolation and Monika Dudek for cultivation of the bacteria, as well as the BGR for providing the clay samples.

[1] Bachvarova, V. *et al.* (2010) *Report FZD-530*, p. 18.
[2] Moll, H. *et al.* (2015) *Report HZDR-059*, p. 15.
[3] Moll, H. *et al.* (2016) *Report HZDR-067*, p. 47.
[4] Moll, H. *et al.* (2017) *Environ. Sci. Pollut Res.*, submitted.