Pu Sorption to Activated Conglomerate Anaerobic Bacteria

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The sorption of Pu to the anaerobic bacteria activated under specific conditions of temperature, pH and depleted nutrients after long dormant period was investigated. After 4 h at neutral pH, the distribution coefficient (K_d) between bacteria and aqueous phase at 308 and 278 K had around 10^3 to 10^4. After over 5 days, however, the K_d at only 308 K had increased to over 10^5. Sterilized (dead) and dormant anaerobic bacteria adsorbed Pu to the same extent.

While considering safety assessments in the geological disposal of radioactive wastes, microorganism interaction with the radioactive waste has been neglected or its role for safety assessments and in radionuclide migration research underestimated.[1,2] In anaerobic environments at repositories, some species of microorganisms, brought into the repository by disruptive events such as human intrusion, can flourish in the presence of sufficient moisture and nutrients, such as residues of explosives used in the excavation of the repositories.[3]

Active bacteria affect the mobility of metals. Chemical and biological activities of microorganisms are dependent on their chemical environment such as pH and E_h. The rapidity of response of a bacterial population will also depend on its activity level. However, the effect of the viability and biological activity of bacteria on the sorption process in a repository environment has not been fully understood. The present work was designed to study plutonium–anaerobic bacteria interaction in the period immediately following reactivation of the bacteria. Since it was reasonable to assume an environment low in nutrients, a very depleted nutritional regimen was provided. The time dependence of Pu sorption is discussed in relation to bacterial activity, and to chemical conditions in the solution such as high (e.g., concrete-modified seepage water) or low pHs and E_h.

A mixture of anaerobic bacteria (MAB), originally used for the treatment of pulp and paper waste-water, was selected, since we have not yet specified the anaerobic bacteria capable of colonizing the proposed repository sites. The mixture, in conglomerate form (0.5 to 2 mm diam), included iron-reducing and sulfate-reducing bacteria. After expelling the dissolved oxygen with pure nitrogen gas, MAB was stocked in the refrigerator (278 K) in distilled deionized water without any special treatment over a few years. For the present study the dormant MAB was reactivated as follows. The stock solution was brought to room temperature for 24 h and then diluted with 0.5% sucrose to obtain a bacterial content of 0.1% dry weight (w/w) in the MAB working solution. MAB was then cultured at 308 K for 48 h. The distribution experiment was carried out in 8 mL stoppered glass-vessels with the aid of a mechanical shaker. The MAB solution (5 mL) was anaerobically adjusted to the desired pH with nitric acid and sodium hydroxide and ^{240}Pu(IV) as a nitrate form was added, adjusting the Pu content to ca. 10^{-11} mol dm^{-3}.

After shaking at 308 ± 0.1 K for 4 h, 5 days (5 d), 10 days (10 d), and 60 days (60 d), pH was taken as the equilibrium pH. E_h in the MAB suspension was monitored with a platinum electrode. The residue, collected on a 0.22-μm membrane filter, was defined as the solid phase and the filtrate as the liquid phase. The concentration ratio of ^{240}Pu between the two phases was determined by alpha spectrometry with the aid of ^{236}Pu as a chemical yield tracer.[4–7] For comparison the authors also investigated the distribution behavior of the nuclide at 278 ± 0.1 K using the same procedure as at 308 K.

Information on the activity of MAB and the chemical conditions, pH and E_h, of dissolved species of Pu is needed while considering reasons for K_d change with time (Figure 1). For the duration of the experiment the pH remained stable over the entire pH range at both temperatures. The E_h stayed almost constant for pH 2 and 12, while it changed for pH 7. At 308 K the E_h decreased to 100 mV (vs NHE) over the first 5 d at neutral pH, and increased then to 200 mV with time. The E_h at 278 K, on the other hand, decreased slowly to the same level (200 mV) over 60 d. The decrease of E_h supports that MAB could be active and that the chemical condition became more reducing. MAB show significant activity only around pH 7.

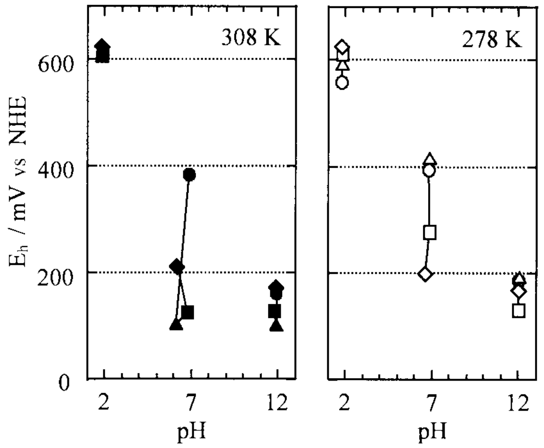

Figure 1. Time dependence of E_h as a function of pH in suspended MAB after equilibration. Circle, triangle, square, and diamond marks represent the results for 4 h, 5 d, 10 d, and 60 d, respectively.

The distribution coefficient (K_d) of plutonium was defined as follows,

$$K_d\ (\mathrm{mL/g}) = [\mathrm{Pu}]_{\mathrm{solid}} / [\mathrm{Pu}]_{\mathrm{liquid}}$$

where the subscripts 'solid' and 'liquid' denote the species in the solid and liquid phases, respectively, and the brackets signify the Pu concentration (Bq g^{-1} for the solid phase and Bq mL^{-1} for the liquid phase). The results from the Pu distribution experiment are shown in Figure 2. In the acid pH region (pH

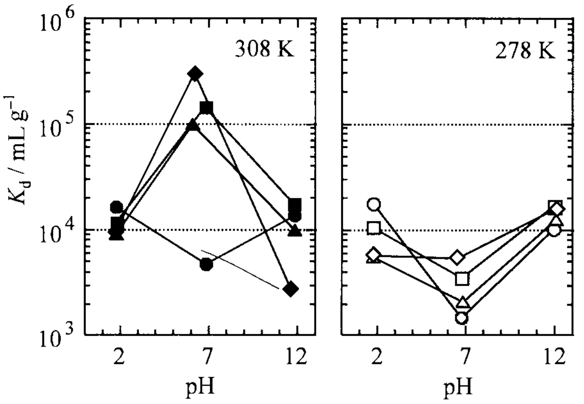

Figure 2. Distribution coefficients for Pu as a function of pH at 308 and 278 K. Circle, triangle, square, and diamond marks represent the results for 4 h, 5 d, 10 d, and 60 d, respectively.

2), K_d did not change with time. On the other hand, in the neutral pH, K_d changed with time, both at 308 and 278 K. After 4 h at 308 K the K_ds were 10^3 to 10^4. The K_d value at pH 7 was lower than the one at pH 2; at pH 2 the total activity of MAB would be quite low as there was no significant change in pH or E_h. This could be because the trivalent ion, Pu(III), might be a dominant species at pH 2 and 600 mV, while at pH 7 the hydroxide complex of Pu(IV) would dominate. Since the effective charge of these Pu(IV)-hydroxides is lower than that of Pu^{3+}, the complexation ability to anionic ligands would be lower. In alkaline pH, the K_ds indicated slightly higher than in the neutral. After 5 d the K_d at pH 7 was over 20 times higher than after 4 h, and did not fall below 10^5 over the remaining 55 d. The reduction to Pu(III) with its higher complexing ability may occur gradually during 60 d in the solution. Chemical conditions such as oxidation states and complexation of Pu with MAB are under estimation.

Similar changes in K_d were not found at 278 K as shown in Figure 2. There can be at least two factors contributing to this difference. The first of these involves an activation of the anaerobic bacteria. The data strongly suggest that the increase of K_d after 5 days at 308 K is due to a higher activity of MAB. The MAB for the experiments, both at 278 and 308 K, was activated for 72 h. It is possible that MAB was not completely activated during only 72 h. The second factor is based on a change of chemical properties of the metal ions. The sudden increase of K_d at pH 7 over 5 days at 308 K could have been caused by the production of Pu(III) by way of biological and/or chemical reduction. At 278 K and neutral conditions, the slight increase of K_d with time (from 1×10^{-3} to 6×10^{-3}) could be the result of the same reduction process. E_h in these conditions decreased from 400 to 200 mV (Figure 1). This is of especial interest, as Pu(III) has a large effective charge for binding to ligands. In higher pH regions there is an additional possibility that some precipitates such as a pseudocolloid which could be filtered onto a 0.22 μm membrane filter may form with MAB and with other metal complexes. If colloids were formed, the same result should have been obtained at 278 K. At neutral pH and 278 K, K_d was slightly increased with time from 4 h to 60 d. At this moment, it is difficult to suggest that colloid formation did not take place, or, that even at low temperature, some species of MAB might be active and could adsorb Pu species gradually.

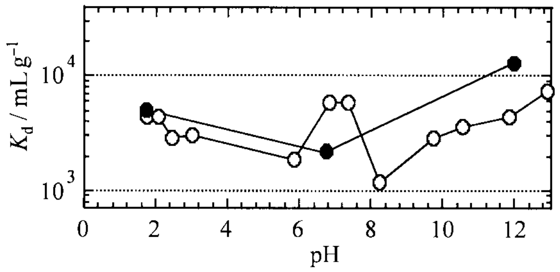

Figure 3. Comparison of K_d values between dormant (black) and sterilized (white) MAB.

In our previous work, the distribution of Pu regarding sterilized MAB, which was autoclaved at 393 K at 15 psi for 20 min before the distribution reaction, has been investigated.[8] After sterilization, most of the MAB components should have been decomposed and lost their activity. The K_d values for sterilized and dormant (this work at 278 K) MAB experimental series are summarized in Figure 3. Surprisingly the values from both experiments fall in the same range, 10^3 to 10^4. However, the biological condition of MAB used in the experiment with sterilization could have been different from the condition of the dormant MAB used in the present work. The temperature around waste packages in the repository site has been estimated to remain over 373 K for a long period.[9] The effect of bacteria, exposed to these high temperatures and high pressure, on radionuclide interactions should be evaluated for the safety assessment.

References and Notes

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