Sorption and Oxidation of Tetravalent Plutonium on Mn Oxide in the Presence of Citric Acid

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Sorption experiments of Pu^{IV} on synthetic Mn oxide were made in 0.1 M NaCl + 0.1 mM sodium citrate solutions under acidic to alkaline pH conditions. As the results of the sorption experiments, Pu was efficiently removed from the solutions under neutral pH conditions, where Pu forms the stable 1:2 Pu^{IV}–citrate complex. Furthermore, it was demonstrated that Pu^{IV} was oxidized to Pu^{V} and Pu^{VI} on Mn oxide.

Plutonium (Pu) is a radioactive element contained in radioactive wastes. If Pu is released from radioactive wastes, the fate of Pu in natural environments would be a serious problem for human activities. Therefore, it has been of great concern to predict the behavior of Pu in natural environments.[1–3] The behavior of Pu in natural water systems is governed by solubility, redox, complexation, and sorption. Since the oxidation state of Pu significantly affects solubility, complexation, and sorption properties, knowledge of the redox chemistry of Pu is essential for modeling the behavior of Pu in aqueous systems, which contributes to design of efficient remediation procedures for Pu contaminated areas.

Interaction of dissolved Pu species with solid materials such as Fe and Mn oxides is an important process which can change the chemical species of Pu.[4–9] In particular, Mn^{IV} oxide has received considerable attention because of its sorption and oxidizing properties.[10] In addition, Mn oxide is ubiquitous in natural environments. Nevertheless, little work on Pu oxidation by Mn oxide has been reported.[6,9] Previous studies on Pu^{IV} oxidation by Mn oxide were carried out using solutions with low initial Pu concentrations of 10^{-8}–10^{-11} M, in which Pu was dissolved mainly as free aquo ions, to prevent Pu^{IV} precipitation.[6,9] Although solubility of Pu^{IV} is lower than that of Pu^{V} and Pu^{VI}, Pu^{IV} forms strong complexes with organic acids such as citric acid, which are present in transuranic (TRU) wastes.[11–13] Complexation of Pu^{IV} with organic ligands results in the stabilization of Pu^{IV} in aqueous phase and further enhances the mobility of Pu. Therefore, it is necessary to evaluate the influence of organic ligands on sorption and oxidation processes at solid–water interfaces. In particular, citric acid forms fairly strong complexes with Pu^{IV}.[11–13] In this study, we investigated sorption and oxidation of Pu^{IV} on Mn oxide in the presence of citric acid, which was not considered in previous work on Pu^{IV} oxidation.[6,9]

Manganese(IV) oxide was synthesized as reported by Murray, using $KMnO_4$ and $MnCl_2$.[14] After drying at 40 °C, aggregated Mn oxides were crushed and pulverized with an agate mortar and subsequently sieved to collect the <125-µm size fraction. XRD analysis identified the synthetic product as poorly crystalline Mn oxide (Figure 1S).[15] The specific surface area of the synthetic Mn oxide ($27.8\,m^2\,g^{-1}$) was determined with a Brunauer–Emmett–Teller (BET) analyzer (BELSORP-mini, BEL JAPAN, INC) at Hiroshima University. We used ^{238}Pu (half-life: 87.7 year) as a radionuclide in this study. The stock solution of ^{238}Pu (1.0×10^{-8} M) was prepared in 1 M HNO_3. Plutonium in the stock solution was placed in the tetravalent state electrochemically. Sorption experiments of ^{238}Pu on Mn oxide were carried out using 0.1 M NaCl solutions with 0.1 mM sodium citrate and different pH conditions at room temperature. After addition of the ^{238}Pu stock solution and synthetic Mn oxide powders, pH of the solutions was adjusted with drops of HCl or NaOH solution. Initial ^{238}Pu concentration was 2×10^{-10} M in all the experiments. The concentration of the Mn oxide was $0.167\,g\,L^{-1}$, corresponding to $4.63\,m^2\,L^{-1}$ as the surface area.

After sorption experiments, the Mn oxide and solution were separated by centrifugation. The supernatant was used for determination of the remaining ^{238}Pu concentration in the solutions. The redox speciation of Pu sorbed on the Mn oxide was determined using solvent extraction with thenoyltrifluoroacetone (TTA) and di(2-ethylhexyl)phospharic acid (HDEHP) (Figure S2),[15] which have been frequently used in previous studies.[4–6,8,9] Sample solutions were added to liquid scintillation cocktails (Ultima-Gold AB and FG, Packard Instruments Company, Meriden, CT, USA), and then ^{238}Pu concentrations were measured by a combination of liquid scintillation with alpha/beta discrimination (Tri-Carb 2550TR/AB, Packard Instruments Company, Meriden, CT, USA).[16]

The results of the sorption experiments are shown in Figure 1. Sorption of Pu on Mn oxide increased with increasing reaction time at pH 5.6, and 85% of Pu added was removed from aqueous phase after 52 h (Figure 1a). At pH higher than 6.6, sorption was fairly rapid, and most Pu^{IV} added was sorbed on Mn oxide within several hours. The fractions of Pu sorbed on Mn oxide after 52 h were plotted as a function of pH in Figure 1b. Sorption of Pu increased with increasing pH, and the sorption edge was observed in the pH region between 4 and 6. Such sorption edge is typically observed in partitioning of Pu between oxide minerals and aqueous solutions.[4,7–9] At pH higher than 6.6, most of Pu was removed from the solutions.

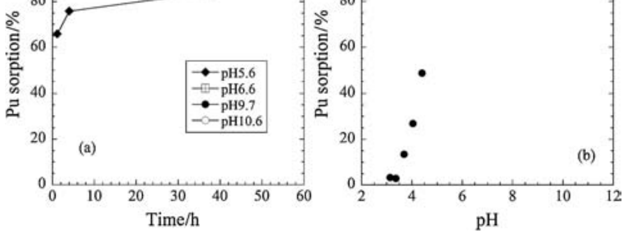

Figure 1. (a) Sorption kinetics of Pu^{IV} on Mn oxide in 0.1 M NaCl solution with 0.1 mM sodium citrate and (b) sorption of Pu^{IV} on Mn oxide as a function of pH after 52 h.

Since we used solutions with the initial citrate/Pu ratio of 5×10^5, Pu possibly formed citrate complexes in the solutions.[11–13] According to speciation calculation, 1:2 Pu^{IV}–citrate complex ($Pu^{4+} + 2cit^{3-} \rightarrow Pucit_2{}^{2-}$) is dominant in the solution at pH 2–7.5 (Figure S3).[15] At pH 8–9, hydrolysis of Pu to form $Pu(OH)_4$aq is important. The carbonate complexes of $Pu(CO_3)_4{}^{4-}$aq and $Pu(CO_3)_5{}^{6-}$aq are dominant under alkaline conditions at pH higher than 9.5.

The extent of Pu sorption on Mn oxide depends on the protonation of surface functional groups, Pu species in solution and sorbed Pu–surface complexes. It has been shown that the protonation on surfaces of Mn oxide is due to hydroxy groups as well as those of other oxide minerals.[17] At low pH values, the surface has a net positive charge due to the protonation of the hydroxy groups, whereas the deprotonation of the hydroxy groups results in a net negative surface charge at higher pH. Therefore, sorption of cation is favored by higher pH values, whereas that of anion is favored by lower pH values.[17] The surface charge of Mn oxide is negative at pH higher than 3. Sorption of negatively charged metal–citrate complexes on negatively charged oxide minerals was suppressed.[18] Our results show that sorption of Pu on Mn oxide increased with increasing pH from 3 to 7 where $Pucit_2{}^{2-}$ is dominant (Figures 1 and S3[15]). These facts suggest that sorption of Pu on Mn oxide was accompanied with dissociation of Pu from $Pucit_2{}^{2-}$ and that positively charged Pu aquo ions were sorbed on Mn oxide. Similarly, dissociation of Pu^{IV} carbonate complexes may have occurred at pH between 9.5 and 11 where $Pu(CO_3)_4{}^{4-}$aq and $Pu(CO_3)_5{}^{6-}$aq are dominant (Figures 1 and S3[15]).

The fractions of Pu^{IV}, Pu^{V}, and Pu^{VI} sorbed on the Mn oxide were determined in solutions with pH 5.6, 6.6, and 9.7, respectively, using solvent extraction with TTA and HDEHP (Figures S2).[15] The results of the solvent extraction show that Pu^{IV} oxidation is favored under higher pH conditions (Figure 2). Redox potentials of Pu^{VI}/Pu^{IV} and Pu^{V}/Pu^{IV} lower from acidic to alkaline conditions, indicating that Pu^{VI} is more stable in alkaline solutions.[12] This agrees with the results in Figure 2. In the pH range where we investigated, the fraction of Pu^{V} was smaller than those of Pu^{IV} and Pu^{VI} and relatively constant around 10–15% of total Pu sorbed on Mn oxide through experimental time. The fractions of the three oxidation states at pH 3.7 and 4.0 were not quantitatively determined because the amounts of Pu sorbed on Mn oxide were small (Figure 1b). Fortunately, we detected qualitatively the existence of Pu^{VI} sorbed on Mn oxide at pH 3.7 and 4.0, indicating that oxidation of Pu^{IV} to Pu^{VI} proceeded at pH lower than 5.

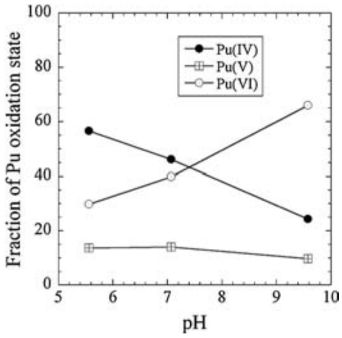

Figure 2. Fractions of Pu^{IV}, Pu^{V}, and Pu^{VI} on Mn oxide as a function of pH after 52 h.

Khasanova et al. reported Pu^{IV} oxidation by Mn oxide, but unfortunately they did not show any quantitative data on the Pu^{IV} oxidation.[9] Morgenstern and Choppin conducted sorption experiments of Pu^{IV} on synthetic Mn^{IV} oxide in 1 M NaCl solutions without organic acids as chelating agents.[6] Their experimental results indicated that the oxidation of Pu^{IV} occurred on Mn oxide under pH conditions between 2 and 8.1. Consequently, it is consistent with the previous work that Pu^{IV} oxidation was observed in the pH range between 5.6 and 9.7 in our sorption experiments (Figure 2).

This work is the first report that shows that Mn oxide can remove Pu efficiently from aqueous phase even in the presence of citrate under neutral pH conditions, where 1:2 Pu^{IV}–citrate complex is dominant (Figure 1). Furthermore, we demonstrated that Pu^{IV} oxidation occurs on Mn oxide surface in the presence of citrate (Figure 2). This suggests that Mn oxide can change the chemical species of Pu because of its strong oxidizing properties, even if Pu^{IV} forms strong complexes with organic acids in natural water systems. The results of this study are important in terms of modeling the behavior of Pu in natural environments and give fundamental information to future work on interaction of Pu between solid and aqueous phases in the presence of strong chelating agents.

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