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Speciation and interactions of plutonium with humic substances and kaolinite in aquifer systems

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Abstract

The speciation of plutonium (Pu) in contact with humic substances (HS) and kaolinite has been performed in aquifer systems. Mainly the redox behavior, complexation, and sorption of plutonium are discussed here. The redox behavior of Pu(VI) in contact with HS was studied and it was found that Pu(VI) is reduced to Pu(III) and Pu(IV) within a couple of weeks. The complexation constants (log β_{LC}) of Pu(III) and Pu(IV) with HS have been determined by means of the ultrafiltration method. Furthermore, the sorption of Pu(III) and Pu(IV) onto kaolinite has been investigated as a function of pH by batch experiments under aerobic and anaerobic conditions.

Keywords: Plutonium; Speciation; Humic substances; Kaolinite

1. Introduction

For the safety assessment and conception of nuclear waste repositories, studies of the speciation of long-lived radionuclides in aqueous systems under natural conditions are mandatory. A dominant contribution to the radiotoxicity over storage times of up to one million years is delivered by plutonium [1]. Its migration behavior in the environment is not well understood at present. Therefore, the chemical species of plutonium in aqueous systems have to be studied and three important chemical processes must be investigated: redox reactions, complexation, and sorption of plutonium onto mineral surfaces.

In this work, kaolinite is used as a model clay mineral, which contains mainly hydroxylated sites of Si and Al [2]. Humic substances (HS), a mixture of organic macromolecules, are distributed ubiquitously in the ecosphere and play an important role in the interaction processes with actinide ions [3–5,12–16].

The complexation of the tri-, penta- and hexavalent actinide ions with HS has been reported in the literature [3–5] whereas the complexation constants of tetravalent actinide ions with HS are scarcely found in the literature.

The sorption of actinide ions onto kaolinite and other mineral surfaces has been investigated in the last decades [6–8]. The results show that the sorption depends significantly on the oxidation state, pH, ionic strength, temperature, aerobic or anaerobic conditions, and the type of mineral surface. Sorption studies of plutonium and other tetravalent actinides onto mineral surfaces, e.g. goethite [9], calcite [6], or other soils [10], were carried out. In this paper, we report the results from the sorption experiments of tri- and tetravalent plutonium onto kaolinite.

2. Experimental

For the present experiments, ^{239}Pu, ^{234}Th, and ^{241}Am were used. The tri-, tetravalent oxidation state of Pu was obtained by potentiostatic electrolysis and their purity was verified by UV/Vis spectroscopy. Pu(III) solutions were stabilized with a reducing agent, NH_2OHHCl, in the absence of air (inert gas) up to a pH ≈ 5.5 [11]. The purity and activity of ^{234}Th and ^{241}Am was checked by gamma spectroscopy and liquid scintillation counting (LSC).

The commercially available Aldrich humic acid (AHA) (sodium salt, charge no. 01816-054) and the Gorleben fulvic acid (GFA) (GoHy-573) were purified and isolated as described in [12,13]. Kaolinite standard KGa-1b was obtained from the Clay Mineral Society (CMS) Source Clays Repository (Washington County, Georgia, USA) [2].

For the Pu(VI) reduction experiments, Pu(VI) solutions were brought in contact with GFA and AHA at different pH values. The concentration of the final

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Table 1
Experimental parameters and conditions for the sorption studies of Pu(III), Pu(IV), Am(III), and Th(IV) onto kaolinite

Parameter	Conditions
Kaolinite, [KGa-1b]	4 g/L
[^{239}Pu(IV)], [^{239}Pu(III)]	3.5×10^{-7}–6.9×10^{-9} M, 1×10^{-6}–1×10^{-8} M
[^{234}Th(IV)], [^{241}Am(III)]	6.6×10^{-13} M, 1.0×10^{-9} M
Ionic strength, I	0.1 M $NaClO_4$
pH	1–11
Preconditioning time	48–64 h
Contact time of kaolinite with plutonium	48–120 h
pCO$_2$	$10^{-3.5}$ atm
Phase separation (centrifugation)	1 h (∼2500 rpm)
Detection	LSC, DNAA, γ-spectroscopy
Anaerobic conditions	≈100% argon, 4 ppm O_2

Pu(VI) solution in contact with GFA (0.5 mg/L) was ≈2.5×10^{-6} mol/L Pu at ionic strength $I \approx 1$ mol/L (1 M $HClO_4$) and pH 1, 2.5, 5, and 9 under inert gas atmosphere. The reduction of the oxidation states of Pu in solution was measured by CE-ICP-MS and UV/Vis spectroscopy at different time intervals. For the redox kinetic experiments, a plutonium cocktail (Pu(III) ≈ 5%, Pu(IV) ≈ 39%, Pu(V) ≈ 22%, and Pu(VI) ≈ 34%) was brought into contact with GFA at ionic strength $I \approx 1$ mol/L and pH ≈ 1.

For the complexation experiments, AHA and Pu(III), Pu(IV), and Am(III) were brought into contact at different pH values and the mixture was shaken continuously. After an equilibration time of one week, aliquots of the solution were filtrated using ultrafiltration (1 kDa pore size), and the free Pu, Am ion concentration was determined by LSC. The loading capacity LC was determined from plots of [MHA(z)]/[HA(z)]$_t$ versus [M^{z+}]$_t$/[HA(z)]$_t$ for the different pH values as discussed in detail by Kim et al. [14].

The sorption experiments were carried out in 15 mL scaled polypropylene screw cap centrifuge tubes at room temperature and in the presence of light. A suspension of 4 g/L kaolinite was preconditioned in 0.1 M $NaClO_4$ and shaken continuously for 48 h. After mixing Pu (Am, Th) solutions with the preconditioned kaolinite, the pH values between 1 and 11 were readjusted by adding 0.1 M $HClO_4$ or 0.1 M NaOH. The solid and liquid phases were separated by centrifugation. After centrifugation, the supernatants were analyzed in order to determine the content of free Pu (Am, Th) ions in the liquid phase by LSC. The sorbed amount of Pu (air-dried kaolinite, solid phase) was also measured for some samples by beta delayed neutron activation analysis (DNAA). The experimental conditions for the sorption studies are summarized in Table 1.

3. Results and discussion

3.1. Redox reactions

The redox speciation of Pu(VI) under natural conditions in contact with AHA and GFA has been investigated by online coupling of capillary electrophoresis to inductively coupled plasma mass spectrometry (CE-ICP-MS) and UV/Vis spectroscopy [15]. The reduction of Pu(VI) with GFA occurs faster with increasing pH values (1, 2.5, 5, 9) [16], in good agreement with results obtained for a mixture of Pu with AHA [15]. The enhanced reduction of Pu(VI) with increasing pH can be explained by the increasing fraction of dissociated groups of the HS [17]. It has been shown that Pu(VI) is reduced by AHA and GFA to Pu(IV) and Pu(III) within a couple of weeks, see Fig. 1. Similar reduction behavior has been found for humic-rich Gorleben ground water [15,18]. It has been demonstrated that the reduction of Pu(VI) to Pu(V) is fast compared to the reduction of Pu(V) to Pu(IV) and Pu(III) [16]. Thus, in aqueous systems, plutonium in contact with HS is present mainly in the tri- and tetravalent state. Therefore, we have focused our work on the investigation of Pu(III) and Pu(IV) under natural conditions.

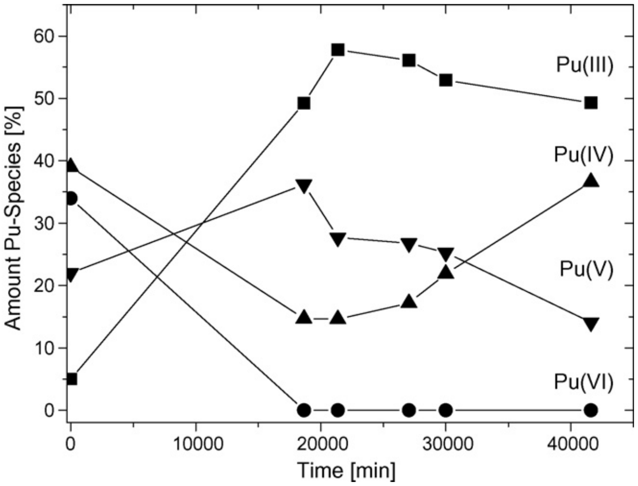

Fig. 1. Interaction of a plutonium cocktail (2.5 × $10^{-}5$ M) with Gorleben fulvic acid (Gohy-573, 36 mg/L) at ionic strength $I \approx 1$ M and different pH values as a function of time determined by CE-ICP-MS.

3.2. Complexation

The time dependence of the plutonium complexation with AHA has been investigated and the complexation constants of Pu(III) and Pu(IV) at various pH values have been determined. Different concentrations of Pu(IV) (6.6×10^{-6} to 6.6×10^{-8} M), Pu(III), Am(III) [11] and AHA (0.01 to 25 mg/L) have been used. The experiments show that a period of about one week is necessary to reach equilibrium for the complexation of both Pu(III) and Pu(IV) with AHA. The stability constants (log β_{LC}) [14] were determined by means of ultrafiltration. The stability constants (log β_{LC}) [14] were determined by considering the maximum accessible functional sites for complexation with a metal ion, the loading capacity (LC) [14]. For the LC values of 3.3% at pH 1.8, 4.5% at pH 2.5, (see Fig. 2) and 9.2% at pH 3 for Pu(IV) were obtained. It has been observed that Pu(IV) exists as $[Pu(OH)_2]^{2+}$ at pH values from 0.3 to 2.0 in the aqueous solution [19], so $z = 2$ was considered for the LC calculation [14]. Using these LC data, log β_{LC} values between 6.4 and 8.4 are found for Pu(IV). With the LC values specified by Buda et al. [11] log β_{LC} between 6.2 and 6.8 were obtained for Pu(III). These results are in good agreement with log β_{LC} values determined for Am(III) [11]. The scattering of the log β_{LC} values for Pu(IV) might be influenced by the precipitation of humic acid at low pH and colloid formation of plutonium.

3.3. Sorption

The sorption studies have been performed by batch experiments under aerobic and anaerobic conditions (≈100% argon, 4 ppm O_2) at pH values of 0–11, at different concentration of plutonium, and a solid phase concentration of 4 g/L kaolinite

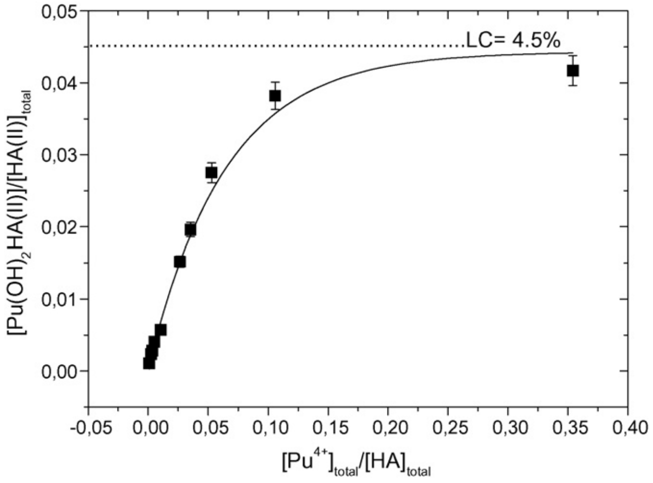

Fig. 2. Determination of the loading capacity (LC) for the complexation of Pu(IV) with humic acid at pH 2.5, $[Pu(IV)] = 6.6 \times 10^{-7}$ M, [HA] = 0–25 mg/L and ionic strength 0.1 M $NaClO_4$.

(Table 1). The sorption experiments have been conducted with different contact times (2–7 days), but no significant dependence on the contact time has been observed. A sorption edge at pH ≈ 1 and a maximum of the sorption at pH ≈ 8 for Pu(IV) (see Fig. 3) was observed and the pH edge for Pu(III) was found at pH ≈ 5.5. A more detailed description of the sorption experiments of Pu(III) onto kaolinite is discussed by Buda et al. [11]. In the case of Pu(IV), for intermediate pH 4 to pH 6, a decrease in the sorption is observed. To investigate the possible reasons for this minimum, the oxidation state of plutonium in solution (after sorption of Pu(IV) onto kaolinite) has been determined by liquid–liquid extraction and it has been found that Pu(V) is the dominant species ((≈85%)) in the solution at pH 4. Thus, the initially added Pu(IV) at pH 4 to pH 6 has been oxidized in solution partially to Pu(V) and the sorption of Pu(V) onto kaolinite is supposed to be weaker than that of Pu(IV) for that pH values in analogy with the known behavior of Np(V) [20]. In the presence of CO_2 at pH > 9, the sorption of plutonium decreases due to the formation of soluble carbonato complexes. To compare the sorption behavior of Pu(IV) and Pu(III) onto kaolinite with other actinides, the sorption of the oxidation state analogs Th(IV) and Am(III) has been studied. The sorption behavior of tetravalent Pu and Th, and trivalent Pu and Am, respectively, are comparable. The interaction of the tetravalent states with kaolinite is stronger than that of the trivalent states. Recently, the speciation of the sorbed Pu(IV) (pH 1, 4, 9) and Pu(III) (pH 6) onto kaolinite has been studied by extended X-ray absorption fine structure spectroscopy (EXAFS) [20]. The results show that Pu(IV) is the predominant sorbed species even for the Pu(III) experiments.

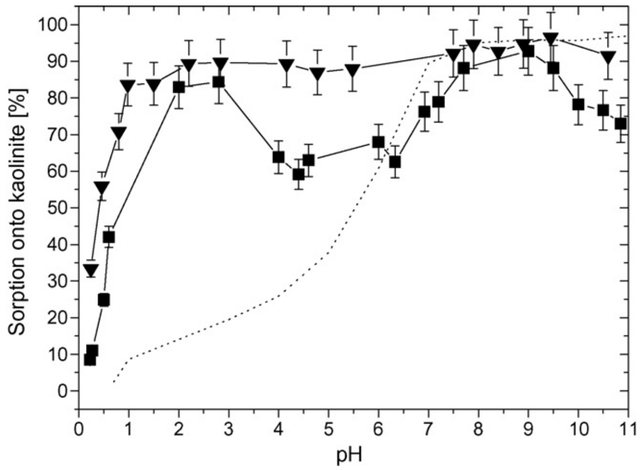

Fig. 3. Comparison of the sorption of tetravalent $Pu = 6.3 \times 10^{-9}$ M (square) and $Th = 6.6 \times 10^{-13}$ M (triangle) onto kaolinite as a function of pH, $pCO_2 = 10^{-3.5}$ atm, [KGa-1b] = 4 g/L, contact time = 120 h. The dashed curve shows schematically the sorption of the trivalent actinides onto kaolinite.

Three different chemical processes (redox reactions, complexation, and sorption) of tri- and tetravalent plutonium in the aqueous system have been investigated. So far, the binary systems Pu(IV)/Pu(III)-HS, Pu(IV)/Pu(III)-kaolinite, and HS-kaolinite have been studied. Work is in progress to investigate the ternary systems Pu(IV)/Pu(III)-HS-kaolinite.

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