



# Plutonium partitioning in three-phase systems with water, colloidal particles, and granites: New insights into distribution coefficients



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## HIGHLIGHTS

- The  $K_{s/d+c}$  developed in this study can describe the mobility of colloidal species.
- Traditional solid/liquid  $K_{s/d}$  is 2–3 orders of magnitude larger than the  $K_{s/d+c}$ .
- Colloidal particles can strongly compete with grains for Pu in three-phase systems.
- Distribution percentages of Pu in the three phases are experimentally determined.

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## ABSTRACT

The traditional sorption experiments commonly treated the colloid-associated species of low-solubility contaminants as immobile species resulted from the centrifugation or ultrafiltration, and then solid/liquid distribution coefficients ( $K_{s/d}$ ) were determined. This may lead to significantly underestimated mobility of the actinides in subsurface environments. Accordingly, we defined a new distribution coefficient ( $K_{s/d+c}$ ) to more adequately describe the mobile characteristics of colloidal species. The results show that under alkaline aqueous conditions the traditional  $K_{s/d}$  was 2–3 orders of magnitude larger than the  $K_{s/d+c}$  involving the colloidal species of  $^{239}\text{Pu}$ . The colloid/liquid distribution coefficients  $K_{c/d} \gg 0$  ( $\sim 10^5$  mL/g) revealed strong competition of the colloidal granite particles with the granite grains for Pu. The distribution percentages of Pu in the three-phase systems, depending on various conditions such as particle concentrations,  $\text{Na}^+$  concentrations, pH and time, were determined. Moreover, we developed the thermodynamic and kinetic complexation models to explore the interaction of Pu with the particle surfaces.

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## 1. Introduction

The groundwater aquifer, a three-phase system, consists of water, mobile colloidal particles, and stationary solids such as granites. The colloidal particles including mineral and organic particles with the 1 nm to 1  $\mu\text{m}$  in size typically have the concentrations of <5 mg/L (Schäfer et al., 2012) and sometimes several tens of mg/L in the water surrounding detonation cavities (Buddemeier and Hunt, 1988). The presence of colloids in groundwater is one primary condition to meet the colloid-facilitated actinide transport, and other conditions include that the colloid-associated actinides must be stable and can remain in suspension for sufficiently long times (Ryan and Elimelech, 1996; Honeyman, 1999). Unexpected large-scale migration of Pu in the subsurface environments at some nuclear sites has been found (Penrose et al., 1990;

Kersting et al., 1999; Novikov et al., 2006), generally ascribed to the colloids served as the carriers of the low-solubility Pu.

It is well known that the dissolved Pu(IV) in aqueous solutions readily hydrolyze to form polynuclear species even at low pH (Knopp et al., 1999; Rothe et al., 2004; Walther et al., 2009) and then these two species attain the thermodynamic equilibrium. On the other hand, the colloids and solids present in the solutions may compete for the dissolved Pu, leading to transformations from the free Pu in water to both colloid-associated species and immobile species retained on the solids. Moreover, the colloids having large specific surface areas can further compete with the solids for Pu. The competition between the three phases for Pu is closely related to the fate and transport of Pu in subsurface environments, and is a key concern necessarily involved in both the performance assessment of high-level radioactive waste repositories (McKinley and Scholtis, 1993) and the remediation of contaminated fields such as nuclear test sites (Larson et al., 2005; Yaron et al., 2008).

The traditional sorption/distribution experiments treated the colloid-associated species of low-solubility contaminants as

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immobile species, as a result of centrifugation or ultrafiltration procedures (Pathak and Choppin, 2006; Lujanienė et al., 2007; Vandenhove and Van Hees, 2007; Liua et al., 2011; Wang et al., 2011; Dong et al., 2012; Ivanov et al., 2012). The colloid-associated species centrifugally settled at the bottom of the tubes where the stationary solids such as rock grains existed, or retained on the ultrafiltration membranes, so that this species artificially made a contribution to the immobile fraction retained on the solids. A solid/liquid distribution coefficient, a ratio of the concentration of contaminants sorbed on the solid phase ( $\Gamma_s$ , mol/g) to the dissolved concentration in the liquid phase ( $C_d$ , mol/L), i.e.  $K_{s/d} = \Gamma_s/C_d$ , was then determined. This experimentally determined coefficient reflects, in fact, a competition of both the solids and the particles with the water for contaminants but not the real competition of the solids with the water for contaminants. Accordingly, the colloidal species ( $C_c$ , mol/L), usually accounting for the main fraction of the mobile species composed of  $C_d$  and  $C_c$  (Bates et al., 1992; Bednar et al., 2007; Xie et al., 2012), was completely ignored. Hence, risk of contaminants into the environments may be significantly underestimated.

Enough attention has not been paid to the colloids served as a third phase existing in the batch sorption experiments, as suggested by Honeyman (1999). So, challenges facing us arise. How to compete between water, particles, and solids for Pu under various aqueous conditions such as pH, ionic strengths, and colloid concentrations? What different distribution coefficient will be caused if the third phase as carriers of the low-solubility contaminants is involved? Here, we define a new distribution coefficient  $K_{s/d+c}$ , a ratio of the concentration of the immobile species  $\Gamma_s$  (mol/g) to the summed concentrations of the dissolved ( $C_d$ ) and colloidal species ( $C_c$ , mol/L), i.e.  $K_{s/d+c} = \Gamma_s/(C_d + C_c)$  where the  $C_d$  and  $C_c$  have the mobility. It is noted that this  $\Gamma_s$ , different from the  $\Gamma_s$  in the traditional  $K_{s/d} = \Gamma_s/C_d$ , does not include the contribution of colloidal species. In contrast to the traditional  $K_{s/d}$ , the expression for  $K_{s/d+c}$  can adequately describe the mobile characteristics of both the colloidal and dissolved species.

The aims of this study are to determine the relative fraction of dissolved, colloidal, and immobile  $^{239}\text{Pu}$  in the three-phase systems with water, colloidal granite particles, and granite grains under various aqueous conditions, to obtain the distribution coefficient  $K_{s/d+c}$ , and to assess the discrepancy in  $K_{s/d+c}$  and traditional  $K_{s/d}$ . The granite particles (<1  $\mu\text{m}$  in diameter) having the negatively charged surfaces and granite grains are used as the colloidal particles and the solids in the sorption experiments, respectively. The term of colloidal Pu is referred to the sum of colloid-associated Pu and polymeric Pu (intrinsic colloids).

## 2. Materials and methods

### 2.1. Granite

The granite drill cores returned from Lop Nor (a nuclear test site) in northwestern China were crushed and then sieved with stainless steel sieves. The mineral phases detected by X-ray diffraction (D/MAX-2500) are 61% quartz, 13% anorthose, 7% chlorite, 6% potassium feldspar, 9% biotite, 2% isinglass, 1% calcite, and minor hematite. The major chemical constituents detected by X-ray fluorescence spectroscopy (Axios) are 65.2%  $\text{SiO}_2$ , 15.6%  $\text{Al}_2\text{O}_3$ , 3.7%  $\text{FeO}$  ( $\text{Fe}_2\text{O}_3$  0.6%), 3.6%  $\text{K}_2\text{O}$ . The minor constituents of 1.85 ppm U and 0.7 ppm Ta were detected by ICP-MS (X-Series II). The more detailed results are reported in Table S1. The groundwater at Lop Nor has the pH of about 8.5 and its ionic composition is presented in Table S2. The fine particles attached onto the crushed granite grains of the 1–2 mm in diameter were completely removed with pure water (18.2 M $\Omega$ , Millipore) in order to avoid introducing

unknown amounts of colloidal particles in the sorption experiments. Then these 1–2 mm grains after gradually oven-drying at 50 °C were used as the stationary solids in the water–colloid–solid systems.

### 2.2. Granite particles

The granite particles of <1  $\mu\text{m}$  in diameter were fractionated from the crushed granites of <30  $\mu\text{m}$  in diameter, as the following. The crushed granites of  $\sim 80$  g were added to a glass beaker (4 L pure water), and then the particle suspensions with Stoke's diameter of <1  $\mu\text{m}$  were siphoned from the upper suspensions into a polypropylene vessel. The prepared suspensions were stored in the refrigerator (4 °C) and used as the colloidal particle source materials. Since these particles are derived from the granite drill cores, their chemical constituents are identical to the results in Table S1.

To determine the mass concentration of the parent suspensions, six 25 mL aliquots of the suspensions were transferred to concave Teflon membranes, respectively, and then dried at 50 °C by infrared light. The determined mass concentration was  $168.0 \pm 12.2$  mg/L. The suspensions could be diluted with pure water to obtain the desired particle concentrations. A higher concentration of 774.4 mg/L could result from vacuum evaporation at room temperature.

### 2.3. Particle surface characterization

Electrokinetic potentials ( $\zeta$ ) of the colloidal particles, as a function of the  $\text{Na}^+$  concentration from 0 to 0.6 M, were measured using Nano ZS (Malvern) under the pH 8.5 conditions. Also, the  $\zeta$ -potentials were measured at the various pH from 1.8 to 11.2. The results are presented in Fig. S1. These experiments were performed to examine the charge properties of granite surfaces (positive or negative) under environmentally relevant conditions, and to determine the isoelectric point.

### 2.4. Sorption/distribution experiments

The granite grains (1–2 mm in diameter) of 6.25 g, onto which the fine particles were removed, were added in the polypropylene tube with 25 mL particle suspensions, so that the ratio of liquid to solid was 4:1 mL/g. This ratio generally employed in the batch sorption experiments was recommended by ASTM (1990). A small amount of  $^{239}\text{Pu}$  (IV) stock solution ( $14.03 \pm 0.25$  ng/g in 1.5%  $\text{HNO}_3$ ) was added to the suspensions to obtain the initial trace level concentration of  $C_0 = \sim 10^{-10}$  M. To determine the concentrations of the suspended Pu ( $C_t$ ), one aliquot (0.5 mL) of the suspensions was sampled from the tube that was placed in one mechanical shaker and continually shaken for setting time. Also, one aliquot (1 mL) of the suspensions was transferred to a 10 kD ultrafiltration tube (Amicon Ultra-4, Millipore) to determine the concentrations of the dissolved Pu ( $C_d$ ) that was the filtrate fraction passing through the 10 kD membranes.

The particle concentrations ( $c_c$ ),  $\text{Na}^+$  (NaCl) concentrations, and pH (by  $\text{HNO}_3$  or NaOH) in the three-phase systems, and the shaking time ( $t$ ) could be adjusted according to the desired experimental conditions. For example,  $c_c$  ranged from 5.1 to 774.4 mg/L for studying the effects of the particle concentration on the Pu distribution in the three phases; pH ranged from 1.6 to 11.6 (Eh  $\sim 750$  to  $\sim -153$  mV) for the effects of pH;  $\text{Na}^+$  ranged from 0.002 to 0.5 M for the effects of  $\text{Na}^+$  concentrations;  $t$  ranged from 0 to 240 h for the kinetic effects. Other conditions not mentioned above in the corresponding experiments were  $\text{Na}^+$  concentrations = 0.002 M, pH = 8.5,  $t = 5$  h, and  $c_c = 168$  mg/L. Also, blank experiments without the particles and grains in the Pu solution were carried out to

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