



# Colloid-associated plutonium aged at room temperature: evaluating its transport velocity in saturated coarse-grained granites

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## ABSTRACT

The fate and transport of colloidal contaminants in natural media are complicated by physicochemical properties of the contaminants and heterogeneous characteristics of the media. Size and charge exclusion are two key microscopic mechanisms dominating macroscopic transport velocities. Faster velocities of colloid-associated actinides than that of  $^3\text{H}_2\text{O}$  were consistently indicated in many studies. However, dissociation/dissolution of these sorbed actinides (e.g., Pu and Np), caused by their redox reactions on mineral surfaces, possibly occurred under certain chemical conditions. How this dissolution is related to transport velocities remains unanswered. In this study, aging of the colloid-associated Pu (pseudo-colloid) at room temperature and transport through the saturated coarse-grained granites were performed to study whether Pu could exhibit slower velocity than that of  $^3\text{H}_2\text{O}$  ( $U_{\text{Pu}}/U_{\text{T}} < 1$ ). The results show that oxidative dissolution of Pu(IV) associated with the surfaces of colloidal granite particles took place during the aging period. The relative velocity of  $U_{\text{Pu}}/U_{\text{T}}$  declined from 1.06 (unaged) to 0.745 (135 d) over time. Size exclusion limited to the uncharged nano-sized particles could not explain such observed  $U_{\text{Pu}}/U_{\text{T}} < 1$ . Therefore, the decline in  $U_{\text{Pu}}/U_{\text{T}}$  was ascribed to the presence of electrostatic attraction between the negatively charged wall of granite pore channels and the  $\text{Pu(V)O}_2^+$ , as evidenced by increasing  $\text{Pu(V)O}_2^+$  concentrations in the suspensions aged in sealed vessels. As a result of this attraction,  $\text{Pu(V)O}_2^+$  was excluded from the domain closer to the centerline of pore channels. This reveals that charge exclusion played a more important role in dominating  $U_{\text{Pu}}$  than the size exclusion under the specific conditions, where oxidative dissolution of colloid-associated Pu(IV) was observed in the aged suspensions.

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## 1. Introduction

The transport velocity is an important quantity describing how fast contaminants transport through subsurface media. Low-solubility metal and organic contaminants often existed as colloidal species in natural aquatic environments (Plathe et al., 2013; Zänker and Hennig, 2014). In field experiments of the aquifers, model colloids were observed to travel much faster

than solute tracers, e.g., bacteria travelled 1.25–2.5 times faster than  $\text{Br}^-$  (Harvey et al., 1989; McKay et al., 1993a,b) and 1–2 times faster than the groundwater (Sinton et al., 2000). Also, faster velocities of colloid-associated actinides such as Pu, Am, and Np than that of  $^3\text{H}_2\text{O}$  were widely reported in lab-scale experiments (Artinger et al., 1998, 2000; Delos et al., 2008; Schäfer et al., 2003, 2004). To accurately assess environmental risk of the contaminants, especially the colloidal actinides with long half-life and high radiotoxicity, insights into their transport velocity are needed.

Transport velocities of colloidal contaminants are impacted by their size and surface charge. Nano-sized contaminants can

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travel shorter pathways in pore channels than the bulk water does and thus exhibit faster velocities (i.e., an effect of size exclusion) (Keller and Auset, 2007; Sinton et al., 2010). It is well known that the natural media such as granites and soils are generally characterized by negatively charged surfaces under environmentally relevant pH conditions (Drelich and Wang, 2011). For the contaminants having the negatively charged surfaces, they are therefore concentrated around the channel centerline where the local water velocity is at its maximum, due to the electrostatic repulsion exerted by the channel wall. In this case, their transport velocities can be enhanced (i.e., an effect of charge exclusion). On the contrary, electrostatic attraction between the positively charged contaminants and the wall may decrease their velocities because this attractive interaction makes the contaminants closer to the pore wall where the water velocity is at its minimum. Size exclusion was usually invoked to explain the velocity-enhanced phenomenon (Keller et al., 2004; Small, 1974). However, this mechanism, which does not involve charge effect on the transport of charged contaminants, is limited to the uncharged nano-sized particles and thus cannot account for the decrease in transport velocity. Accordingly, it seems likely that electrostatic interaction (charge exclusion) may sometimes play an important role, to which attention is paid in this study. Here, the charge exclusion describes the case that the positively charged contaminants are excluded from the domain closer to the pore centerline. This contrasts with the other case that the negatively charged contaminants are excluded from the domain closer to the pore wall.

In our recent study, an expression for the relative transport velocity of colloid-associated Pu and  $^3\text{H}_2\text{O}$  ( $U_{\text{Pu}}/U_{\text{T}}$ ) was established based on a newly developed model of electrostatic interactions coupled with a parabolic water velocity profile (Xie et al., 2014a). The quantitative relationship between  $U_{\text{Pu}}$  and  $U_{\text{T}}$  was thus determined as  $U_{\text{Pu}}/U_{\text{T}} = 1.1$  to 1.5, depending on the water flow rates and ionic strengths. A further study on the effects of aging time on  $U_{\text{Pu}}/U_{\text{T}}$  has been now performed. This study was motivated by the following considerations. The Pu(IV) readily form relatively stable colloid-associated species, due to its high affinity for the mineral surfaces (Xie et al., 2012, 2013a). However, dissociation/dissolution of Pu(IV) from the surfaces was expected to occur with aged colloid-associated Pu. Typically, the associated Pu(IV) was partially dissolved in the presence of oxygen and then oxidized to more soluble Pu(V)<sub>aq</sub>. Whether, and to what extent, this dissolution may affect  $U_{\text{Pu}}/U_{\text{T}}$  is not yet clear. In contrast to commonly observed faster velocities of colloidal actinides than that of  $^3\text{H}_2\text{O}$ , emphasis is now given to a possibility of  $U_{\text{Pu}}/U_{\text{T}} < 1$  in specific conditions. Both the present and previous studies are considered as a complete report on relative movement of Pu and the bulk water in the pore channels. The mobility of colloid-associated Pu, as affected by its aging, is not studied here. The relationship between Pu species and its mobility (the percent recovery of Pu) was studied in detail in Xie et al., 2013a.

The colloidal granite particles with the size smaller than 1  $\mu\text{m}$  were fractionated from the granites collected at Lop Nor in northwestern China. The colloid-associated Pu was formed by sorption of Pu(IV) on these colloidal particles and then aged at room temperature up to 135 d. The coarse-grained granites packed into the columns were used as the stationary phase in transport experiments.

## 2. Material and methods

### 2.1. Coarse-grained granites

The granite drill cores returned from Lop Nor were crushed and sieved with stainless steel sieves (0.7 to 1.0 mm in pore diameter). Their elemental and mineralogical compositions were analyzed by X-ray fluorescence spectroscopy (Axios) and X-ray diffraction (D/MAX-2500), respectively. The fine particles attached onto the surfaces of the coarse-grained granites having 0.7 to 1.0 mm in size were completely removed with pure water (18.2 M $\Omega$ , Millipore) in order to avoid introducing unknown amounts of mineral colloidal particles in transport experiments. After gradually oven-drying at 50 °C, these granite grains whose specific surface areas (BET) were determined by ASAP 2020 (Micromeritics) were used as the stationary media packed into the columns.

### 2.2. Colloidal granite particles

The granite particles of <1  $\mu\text{m}$  in size were fractionated from crushed granites of <30  $\mu\text{m}$  in size, as the following: The crushed granites of ~80 g were added to a glass beaker (4 L pure water), and then the colloidal suspension with a calculated Stoke's diameter of <1  $\mu\text{m}$  was siphoned from the upper suspension into a polypropylene vessel. The prepared suspension was stored in a refrigerator (4 °C) and used as the colloidal source materials. To determine the mass concentration of the parent suspension, six 25 mL aliquots of the suspension were transferred separately to concave Teflon membranes and then dried at 50 °C by infrared light. The mass concentration was determined as  $195.2 \pm 5.9$  mg/L. The suspension was diluted to obtain the desired particle concentrations.

Electrokinetic potential ( $\zeta$ ) of the colloidal particles, as a function of the pH from 1.8 to 11.2, was measured using Nano ZS (Malvern). According to Smoluchowski's equation, electrophoretic mobility was converted to the  $\zeta$ -potential in this study. This experiment was performed to examine surface charge properties of the granites under natural alkaline conditions. The specific surface areas of the dried colloidal particles were also determined by the ASAP 2020.

### 2.3. Colloid-associated Pu

The prepared suspension was diluted with tritiated water to 35 mg/L (the concentration of colloidal granite particles) in a Teflon bottle. A small amount of  $^{239}\text{Pu}$  stock solution (~1.6  $\mu\text{g/g}$  in 0.5 mol/L  $\text{HNO}_3$ ) was drop by drop added to the suspension stirred continually with a magnetic stirrer, resulting in final Pu concentration of about  $10^{-9}$  mol/L. The atom ratios in the  $^{239}\text{Pu}$  stock solution were  $^{240}\text{Pu}/^{239}\text{Pu} = 0.0346$ ,  $^{241}\text{Pu}/^{239}\text{Pu} = 0.000355$  and  $^{242}\text{Pu}/^{239}\text{Pu} = 0.0000323$ . After 10 min, the pH was adjusted to 8.0 by 1.0 mol/L NaOH. The pH was measured by Orion 720A meter after calibrated by pH 4.00, 6.86, and 9.18 standard buffer solutions. The  $\text{Na}^+$  concentration caused by the NaOH solution was ~0.002 mol/L. This Pu suspension consisted of colloid-associated Pu and dissolved Pu (i.e., aqueous Pu).

Four 65 mL aliquots of the suspension were pipetted separately into 0.1 L Teflon bottles. The suspensions in the first three bottles were sealed with lutes and then aged at room

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