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The speciation, transformation kinetics and fate of spiked Pu (IV) in highly saline groundwater

Xu Zhou*, Haijun Dang, Xiaoyuan Han, Weiping Li, Yu Wang, Weixian Wang, Nana Chai

Northwest Institute of Nuclear Technology, Xi'an 710024, China

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ABSTRACT

The mobility of plutonium (Pu) in groundwater is dependent of its speciation distribution and transformation. The speciation and transformation kinetics of Pu(IV) and its colloids in highly saline groundwater have, however, been rarely studied. In the present study, groundwater (Ionic strength 1 M) from Dunhuang region, NW China, was collected for investigating the speciation, transformation kinetics and fate of spiked Pu (IV) with aging time. The results showed that ~99% of the spiked Pu (IV) (over initial concentration c_0 range 2.5×10^{-10}–7.8×10^{-7} mol·L^{-1}) was easily associated with the natural colloids and transformed into relatively unstable Pu pseudo-colloids in 1 day, which then gradually deposited and/or adsorbed on the container walls with aging. The suspended Pu pseudo-colloids decreased in similar exponential models, with rate equations $r(t) = -3.1 \times 10^{-10} e^{-t/4}$ and $-1.3 \times 10^{-8} e^{-/3}$ for $c_0 = 1.25 \times 10^{-9}$ mol·L^{-1}and 4.17×10^{-8} mol·L^{-1}, respectively. The chemical speciation of the suspended colloidal Pu was dominated by "Fe/Mn Oxides" at the early time, while "Carbonates" with slower depositing rate ($r(t) = -6.9 \times 10^{-12} e^{-0.149t}$) dominated it (~82%) at equilibrium state. Whatever the c_0 was, the concentration of dissolved Pu (i.e., the apparent solubility of Pu) kept at 0.7×10^{-11} mol·L^{-1} over aging. The valence of dissolved Pu was dominated by Pu(IV) at early time, while Pu(V + VI) would become dominant (~95%) at equilibrium state with transformation rate of $r(t) = -92.9e^{-t/16.6} + 96.9$. The equilibrium times of Pu deposition (and/or adsorption), speciation transformation of the suspended colloidal Pu, and valence change of the dissolved Pu were 30 d, 80 d and 120 d, respectively. The kinetic process for each Pu species could be well fitted with exponential model. These results suggest that the majority of released Pu(IV) into highly saline groundwater will be easily associated with natural aquatic colloids and then become immobile in short time due to deposition (and/or adsorption) onto the environmental medium, but potential migration risk caused by stable suspended Pu colloids cannot be ignored.

1. Introduction

With the rapid development of nuclear energy industry, the disposal of high-level radioactive waste (HLW) has become a worldwide challenge (Rechard et al., 2014; Kurosawa and Ueta, 2001; Wang, 2010). Due to its hypertoxicity, the transport of plutonium (Pu) in the groundwater is an indispensable research subject (Xie et al., 2014; Kersting, 2013; Novikov et al., 2006; Salbu and Skipperud, 2009) for the siting and safety assessment of an HLW repository. Pu released into groundwater can exist in various physicochemical forms, ranging from simple Pu(IV)/Pu(V) cations and PuO_2(*am, hy*), to complex Pu polymers and Pu colloids (include Pu intrinsic-colloids and Pu pseudo-colloids) (Choppin, 2006; Salbu, 2007). The mobility of Pu strongly depends on its speciation in groundwater (Choppin, 2006). For example, aqueous Pu(IV) readily hydrolyzes and forms amorphous oxyhydroxides (polymeric species, i.e., Pu intrinsic colloid) which then associates easily with the migratory natural aquatic colloids (Walther et al., 2009; Zhao et al., 2016; Kersting and Reimus, 2003; Van De Weerd and Leijnse, 1997), while Pu(V) usually exists as dissolved species and can migrate along with the flow of groundwater (Powell et al., 2014; Runde et al., 2002; Orlandini et al., 1986). The speciation and fate of Pu are significantly affected by physicochemical parameters of groundwater, including Eh, pH, ion strength, especially the content and component of natural aquatic colloids (Kersting and Reimus, 2003; Hu et al., 2008; Kunze et al., 2008). Therefore, in case of a leakage of a repository, it is crucial to examine the speciation transformation and the fate of released Pu under specific hydrochemical environment.

Previous investigations were carried out mainly focusing on the physicochemical species, solubility and aquatic environment behavior of Pu in natural groundwaters but excluding the speciation

* Corresponding author.
E-mail address: zhouxu_2010@sina.cn (X. Zhou).

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transformation rate of Pu(IV) (Stepan et al., 2011; Buesseler et al., 2009; Efurd et al., 1998; Hu et al., 2008; Kersting et al., 1999), and in simulated groundwaters (T. I. Trofimov, et al., 2008 and 2009; Andrson et al., 2009) commonly under lower ionic strength and excluding natural aquatic colloids. However, the speciation transformation kinetics of Pu(IV) is important to assess its stability and mobility in groundwater systems (e.g, How did the concentration of total Pu vary and the Pu(IV) disproportionate with aging in contaminated groundwater). Moreover, a final nuclear waste repository may be located in a highly saline geology region usually accompanied by highly saline groundwater environment (Wang, 2010; Remi Marsac et al., 2017, and references therein), which can affect the fate of released Pu (Salbu and Skipperud, 2009; Choppin, 2006; Xie et al., 2012). Besides, knowledge of natural aquatic colloids is crucial for understanding the environmental mobility, sorptivity, redox processes of Pu in the groundwater, which perform a significant control on Pu transport in natural waters (Saito et al., 2013; Kersting et al., 1999). As Pu(IV) can easily associate with natural aquatic colloids, the chemical species of colloidal Pu and its transformation rateaffect its stability and mobility in aquatic system. However, they are also rarely investigated (N., Stepan et al., 2011).

In the present study, highly saline groundwater from Dunhuang region, NW China, was collected for investigating the speciation transformation kinetics and the fate of spiked Pu(IV). We mainly examined the transformation rates and equilibrium times of the suspended colloidal and dissolved Pu, oxidation states of the dissolved Pu, and chemical species of the colloidal Pu. Through nitrogen protection of the groundwater over the whole sampling, transportation and experiment process, the results are expected to be more unique and representative for a specific highly saline groundwater from the most potential site of Chinese waste repository.

2. Materials and methods

2.1. Sampling and characterization of the groundwater

Five-liter groundwater (100 m depth) was collected into a protective container with a self-designed Nitrogen-Assistant Sampling Equipment from a monitoring well in Dunhuang region under sampling flow rate of 0.5 L/min, and kept in an Anaerobic Glove Box in Lab (shown as Fig. 1). The sampling operation with small flow rate would not disturb the groundwater system because the water level was not found to be lowered after the sampling. The groundwater have a TDS (Total Dissolved Solids) content of 9.2 ± 0.4 $g{\cdot}L^{-1}$, ionic strength of 1 M, Eh of −75 ± 5 mV, and pH of 7.4 ± 0.1 (See Table S1 in the *Supporting Information*). The salt content in the sample in significantly higher than for simulated groundwater samples (Trofimov T. I. et al., 2008 and 2009; Andrson E.B. et al., 2009) and the samples collected at the "Mayak" site (N. Stepan et al., 2011) and other sites (Efurd et al., 1998; Hu et al., 2008; Kersting et al., 1999). The samples were kept in the glove box over the whole experiment period (up to 180 d) to ensure that the small changes of pH (from 7.5 to7.8) and Eh (from −70 to - 50 mV) have less impact on the speciation of Pu (see Fig. S1, Fig. S2 and Fig. S3 in the *Supporting Information*).

The concentration and particle size distribution of natural colloids in the groundwater were measured by direct filtration method combined with DLS (dynamic light scattering, Zeta Sizer Nano ZS, Malvern Instruments) analysis, giving a colloid concentration of 9.4 ± 2.0 $mg{\cdot}L^{-1}$ and a two-component size distribution with the major one (~65%) of 450 nm–800 nm and a minor one (~35%) of 220 nm ~ 450 nm. The mineral composition of natural colloids was characterized by X-Ray Diffraction (XRD) measurements, showing that the colloids were mainly consisting of carbonate, sulfate and silicate

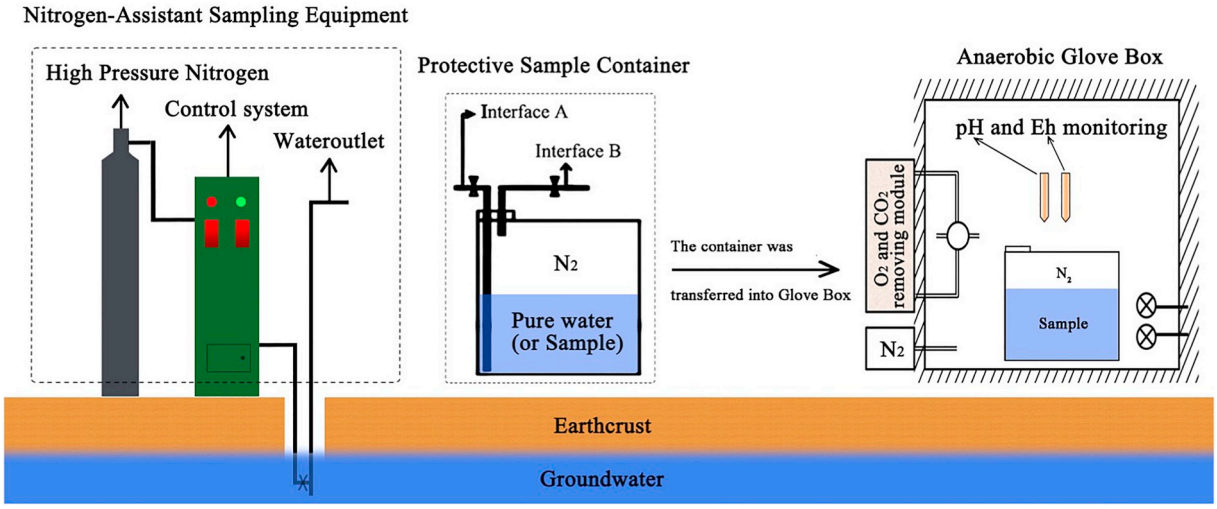
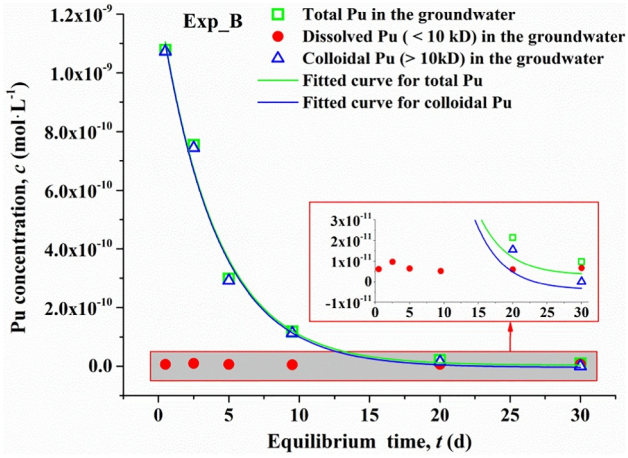


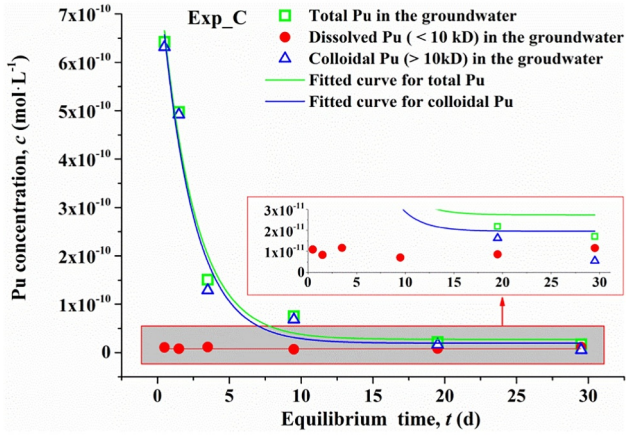
Fig. 1. Nitrogen protected sampling process.

Table 1
A brief introduction of the experiments.

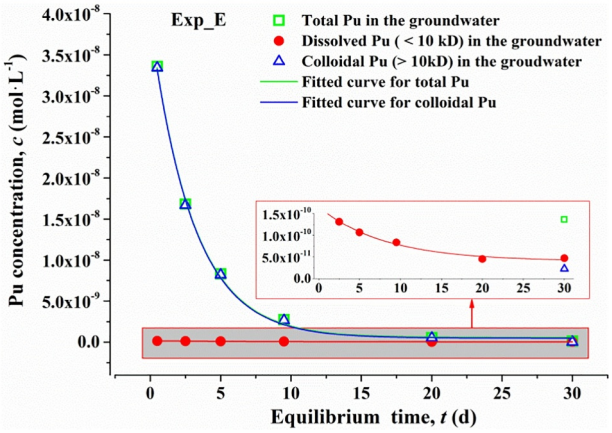
Exp.	Sample types	Sample volume (mL)	Initial ^{239}Pu concentration, c_0 ($mol{\cdot}L^{-1}$)	Standing time(d)
A	Original groundwater	80	$(2.52 \pm 0.04) \times 10^{-10}$	180
B	Original groundwater	500	$(1.26 \pm 0.02) \times 10^{-9}$	1, 2, 4,8,20, 30,90,180
C	Original groundwater	500	$(1.22 \pm 0.02) \times 10^{-9}$	1, 2, 4, 8,20, 30,90,180
D	Original groundwater	80	$(4.87 \pm 0.08) \times 10^{-9}$	180
E	Original groundwater	500	$(4.17 \pm 0.07) \times 10^{-8}$	1, 2, 4, 8,20, 30,90,180
F	Original groundwater	80	$(7.80 \pm 0.12) \times 10^{-7}$	180
G	Original groundwater	80	$(1.26 \pm 0.02) \times 10^{-9}$	180
H	Colloid- removed groundwater	500	$(1.14 \pm 0.02) \times 10^{-9}$	180
I	Colloid- removed groundwater	80	$(1.14 \pm 0.02) \times 10^{-9}$	180
J	ultrapure water	80	$(1.68 \pm 0.03) \times 10^{-9}$	180



(a: Pu Initial concentration c_0= 1.26×10^{-9} mol·L^{-1}, without shaking)



(b: Pu Initial concentration c_0=1.26×10^{-9} mol·L^{-1}, with shaking)



(c: Pu Initial concentration c_0=4.17×10^{-8} mol·L^{-1}, without shaking)

Fig. 2. Concentration change trends of total Pu, colloidal Pu and dissolved Pu in the groundwater solutions.

(see Fig. S4 in the *Supporting Information*).

2.2. Experimental methods

2.2.1. Experimental design

^{239}Pu stock solution (1 μg·g^{-1}, ~95% of ^{239}Pu (IV), checked by solvent extraction (Schramke et al., 1989; Wang et al., 2014)) was purified using DOWEX 1 × 4 anion exchange resin to remove the decay products and other impurities and adjusted to Pu(IV). Groundwater sample was divided into several subsamples, into which various amounts of Pu (IV) were added as soon as possible. The details of the experiments are listed in Table 1. Briefly, Exp_A to Exp_F were designed to study the speciation transformation kinetics of Pu(IV) in the groundwater with aging time under different initial concentrations. Exp_H and Exp_J with natural colloids removed by untrafiltration using 10 kD ultra-filter were contrast experiments to examine the effect of natural colloids on the speciation of Pu. In addition, the changes of pH and Eh were monitored in the Exp_C and Exp_E to confirm the effectiveness of the protective measures on the groundwater. Exp_G and Exp_I were performed as parallel experiments for Exp_B and Exp_H to confirm the accuracy of the experimentation. The distribution and kinetic processes of multiple Pu speciation were examined at various aging times during the experiment, mainly including the transformation rates and equilibrium times of the suspended colloidal Pu and dissolved Pu, oxidation states of the dissolved Pu and chemical species of the colloidal Pu.

The adsorption of Pu on the membrane and Ultrafiltration Tube and the uniformity of Pu concentration in water samples were checked before experiment. The results show that these factors have negligible influences on the investigation results of ^{239}Pu speciation transformation (See Table S2, Fig. S5 and Table S3 in the *Supporting Information*).

2.2.2. Measurement of particle size distribution of suspended colloidal Pu

The particle size distribution of suspended colloidal Pu was measured by Filter Membrane Fractionation Technique. 4 mL sample solution was filtrated with 0.45 μm and 0.22 μm Millipore filters, 100 kD and 10 kD ultrafiltration tubes (Amicon Ultra-4 mL, Millipore) in order. The concentration of ^{239}Pu in each filtrate was analyzed using isotope dilution inductivity coupled plasma mass spectrometric method (ID-ICP-MS) to calculate the particle size distribution of the colloidal Pu.

2.2.3. Analysis of chemical species of suspended colloidal Pu

A modified sequential extraction procedure (see Table S4 in the *Supporting Information*) based on Tessier procedure (Tessier et al., 1979; Huang et al., 2012) was employed to extract Pu in various speciation from the suspended colloidal Pu, by which colloid-associated Pu was categorized into five fractions: Exchangeable(F1), Carbonate(F2), Fe/Mn Oxides(F3), Organic(F4) and Residual(F5). In this work, the Pu retained by 10 kD ultrafiltration tube was regarded as colloidal Pu, but it could not be separated from the 10 kD ultrafiltration tube due to the very low content (~0.06 mg natural colloids in 4 mL original groundwater and even lower after aging). So the extraction was conducted by directly adding extraction agent into the inner pipe of the 10 kD Ultrafiltration tube.

2.2.4. Analysis of oxidation states of dissolved Pu

Oxidation states of dissolved Pu is an important topic of Pu speciation study since it significantly affects the migration of Pu in groundwater (Kaplan et al., 2004). In this study, the Pu permeated through the 10 kD ultrafiltration tube was regarded as dissolved Pu, the oxidation states of which were investigated using solvent extraction method as described in the literatures (Schramke et al., 1989; Wang et al., 2014). Briefly, samples containing Pu were adjusted to 1 M HCl solution, from which Pu(IV) and Pu(IV + VI) were extracted by TTA-Xylene and HDEHP-Xylene solutions, respectively. The concentrations of Pu(IV), Pu(IV) and Pu(VI) were calculated by determination of plutonium remained in the aqueous phase after extraction.

2.2.5. Sample pretreatment for ^{239}Pu determination of samples containing Pu colloids

The samples containing Pu colloids was first acid digested. Three digestion methods were investigated and the digestion method using 8 M HNO_3 for 2 h was selected due to its simplicity and short digestion

Table 2
The kinetic process fitting for concentration changes of Total Pu, Colloidal Pu and Dissolved Pu in the groundwater solutions of Exp_B, Exp_C and Exp_E.

Exp.	c_{Pu}	Fitting equation	R^2	$r\ (t) = dc/dt$	$k(d^{-1})$
B	c_T	$c_T = 1.25 \times 10^{-9} e^{-t/4} + 3.1 \times 10^{-12}$	0.980	$r_T = -3.1 \times 10^{-10} e^{-t/4}$	0.25
	c_C	$c_C = 1.25 \times 10^{-9} e^{-t/4} - 4.0 \times 10^{-12}$	0.981	$r_C = -3.1 \times 10^{-10} e^{-t/4}$	0.25
	c_D	$c_D = 0.7 \pm 0.1$			
C	c_T	$c_T = 7.9 \times 10^{-10} e^{-t/2.32} + 2.7 \times 10^{-11}$	0.965	$r_T = -3.4 \times 10^{-10} e^{-t/2.32}$	0.43
	c_C	$c_C = 7.9 \times 10^{-10} e^{-t/2.25} + 2.0 \times 10^{-11}$	0.955	$r_C = -3.5 \times 10^{-10} e^{-t/2.25}$	0.44
	c_D	$c_D = 1.0 \pm 0.2$			
E	c_T	$c_T = 3.9 \times 10^{-8} e^{-t/3} + 5.8 \times 10^{-10}$	0.998	$r_T = -1.3 \times 10^{-8} e^{-t/3}$	0.33
	c_C	$c_C = 3.9 \times 10^{-8} e^{-t/3} + 5.0 \times 10^{-10}$	0.998	$r_C = -1.3 \times 10^{-8} e^{-t/3}$	0.33
	c_D	$c_D = 1.3 \times 10^{-10} e^{-t/8} + 4.1 \times 10^{-11}$	0.989	$r_D = -1.6 \times 10^{-11} e^{-t/8}$	0.13

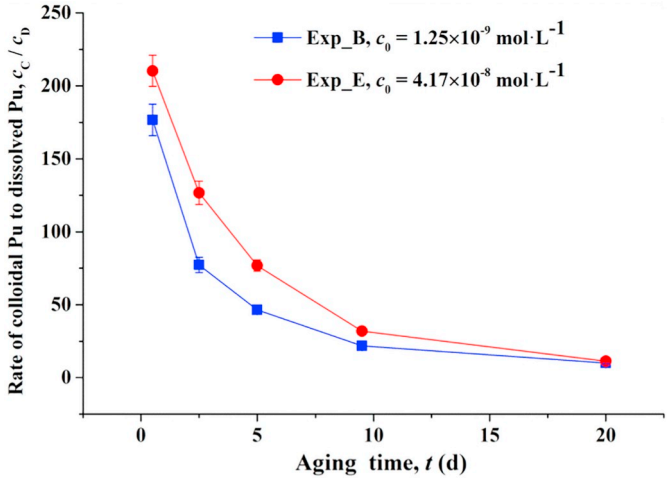


Fig. 3. The profile of c_C/c_D as function of aging time for Exp_B and Exp_E.

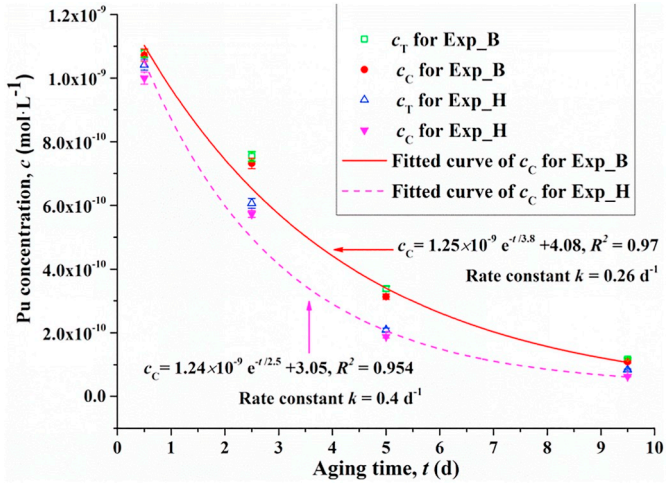


Fig. 4. c_T and c_C as functions of aging time under the groundwater with (Exp_B) and without (Exp_E) natural aquatic colloids ($c_0 = 1.25 \times 10^{-9}$ mol·L^{-1}).

time (see Fig. S6 and related details in the *Supporting Information*).

3. Results and discussions

3.1. Transformation and its kinetics of total, colloidal and dissolved Pu in the groundwater solutions with aging time

Concentrations of total, colloidal and dissolved Pu in the groundwater were determined at various aging times for Exp_B, Exp_C and Exp_E as shown in Fig. 2. The kinetic processes were fitted with a first order mechanism (exponential decay profile) for the concentration change (including total Pu (c_T), colloidal Pu (c_C) and dissolved Pu (c_D) in the solutions), and the kinetic rate equation $r(t)$ were presented in Table 2. Fig. 2(a) (for Exp_B) shows a continuous decrease of c_T from 1.26×10^{-9} mol·L^{-1} to 4.18×10^{-11} mol·L^{-1} with a rate constant k of 0.25 d^{-1} during 30 d, and a steady dissolved Pu concentration level around 0.8×10^{-11} mol·L^{-1}. Meanwhile, most of Pu in the solution is in colloidal form with c_C decreased as decreasing c_T accordingly, with nearly asame decrease rate (r_T and r_C). Fig. 2(b) and (c) show similar change trends, suggesting that shaking and Pu initial concentration c_0 do not greatly affect the concentration change trends, but the dynamic process has been obviously accelerated by shaking (Exp_C), which was evidenced by a greater rate constant (0.44 d^{-1}) compared to that for Exp_B (0.25 d^{-1}). Besides, a higher c_0 (4.17×10^{-8} mol·L^{-1}) for Exp_E could result in greater c_C/c_D and k than those for Exp_B ($c_0 = 1.25 \times 10^{-9}$ mol·L^{-1}), which means that colloidal Pu can be formed easily for higher initial Pu concentration (see Fig. 3). Meanwhile, Fig. 4 shows that although both Exp_B (in the presence of natural colloids) and Exp_H (in absence of natural colloids) for same initial Pu concentration have decreasing c_T and c_C, the rate constant k of c_C for Exp_B (0.26 d^{-1}) was less than that for Exp_H (0.4 d^{-1}). This indicated that Pu would suspend a longer time in groundwater containing colloids, and thus might migrate for a relative long distance in the favor of the colloids. It can be seen from Table 2 that if the aging time t went to infinity, c_D in Exp_B, Exp_C and Exp_E would be 0.7×10^{-11} mol·L^{-1}, 0.7×10^{-11} mol·L^{-1} and 4.1×10^{-11} mol·L^{-1}, respectively. This indicated an apparent solubility of 0.7×10^{-11}–4.1×10^{-11} mol·L^{-1} for Pu in the investigated groundwater, and 0.7×10^{-11} mol·L^{-1} may be more closer to the intrinsic solubility taking into consideration of the formation of very fine intrinsic Pu colloids under higher Pu concentration (see Fig. 5, the fraction of colloidal Pu in groundwater increased with initial Pu concentration c_0). The solubility obtained is obviously lower than that of Pu(IV) hydroxide calculated by Xie et al. (2015) for ionic strength $I = 0$, and Pu(IV), Pu(V + VI) and $Pu(IV)_{coll}$ calculated and experimentally determined by Neck et al. (2007) under Ar atmosphere and oversaturated PuO_2 (am, hyd) at pH 7.5 (I = 0.1 M). Based on the above experiments, the equilibrium time of ~30 d of deposited (and/or adsorbed) of the suspended colloidal Pu was obtained.

Table 3 listed the c_T, c_D, c_D/c_T and c_C/c_T in the groundwater solutions after aging for 1 year. Despite of quite different initial Pu concentration, ~99% of spiked Pu were removed by deposition and adsorption (except Exp_J), which means that Pu was easily adsorbed or precipitated on the container walls (rock walls for real underground cases). The minor remnant Pu (~1%) in the water phase was mostly in dissolved form (> 77%) except Exp_E, Exp_F and Exp_J, while the rest was in colloidal form(< 23%). The decrease of c_T in the solutions during aging may be also partly accounted by coprecipitation of Pu(IV) with other elements and/or sorption to container walls. The coprecipitation may occur because the ground water collected is over saturated. The activity products of some natural compounds which might precipitate in the groundwater were calculated for pH = 7.5 and pH = 8.5 (the pH of groundwater changed from 7.5 to 7.8 during the

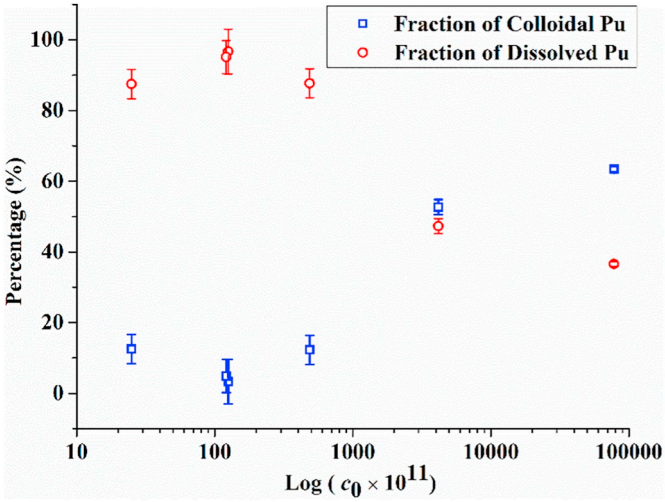


Fig. 5. Fractions of Colloidal and Dissolved Pu at equilibrium for various initial Pu concentrations.

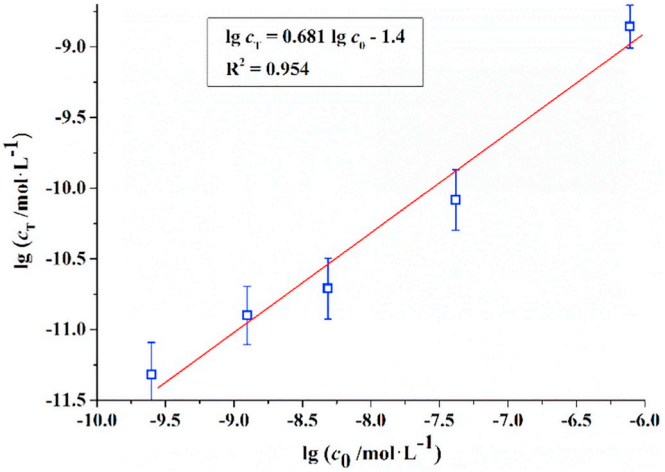


Fig. 6. The relationship between equilibrium Pu concentration c_T and initial Pu concentration c_0.

experiments) and summarized in Table S5 in the *Supporting Information*. It show that $CaSO_4$, $CaCO_3$ and $Fe(OH)_3$ were all in saturated state and a part of which may precipitate and remove Pu from the solutions when the groundwater was kept away from its habitat environment.

It should be noted that colloidal Pu (63.4%) would dominate in Pu solution for very high initial Pu concentration for Exp_E and Exp_F. This may be due to the forming of Pu intrinsic colloid quickly before Pu was adsorbed onto the natural colloids when high concentration Pu(IV) spike solution was added into the groundwater. For Exp_J, meanwhile, fine intrinsic Pu colloid dominated (~96%) because ultrapure water contains no natural colloids, which are larger and tend to adsorb or precipitate Pu into solid form. So Exp_F gave a much higher apparent solubility of Pu (~5×10^{-10} mol·L^{-1}).

The effect of c_0 on the final equilibrium Pu concentration c_T may give hints on the mechanism of Pu removal from groundwater. If Pu was mainly removed via adsorption on precipitation (or sedimented natural colloids), a linear partition between the solid phase and the solution should be demonstrated. On the other side, if Pu was removed via intrinsic colloidization or precipitation, the equilibrium concentration of Pu should be limited by the apparent solubility in the solution and kept nearly constant whatever the initial Pu concentration was. Fig. 6 shows the relation between c_T and c_0 for experiments A, B, C, D, E and F. It can be seen that c_T increased with the increasing c_0, and an approximate linear relation was observed in the logarithmic graph. However, most of Pu in the groundwater solutions was in colloidal form with concentration decreasing as aging, and dissolved Pu (or colloidal Pu with particle size of < 3 nm) dominated the Pu in the groundwater at equilibrium state (see Fig. 3). So we deduced that increasing c_T with initial concentration presented in Fig. 6 was mainly consisting of colloidal Pu with particle size of < 3 nm formed under high initial Pu concentration, which was also demonstrated by the increasing c_C/c_T with increasing c_0 from Exp_B to Exp_F as presented in Fig. 5.

3.2. Particle size distribution of the suspended colloidal Pu

The particle size distribution of the suspended colloidal Pu after 180 days' aging for Exp_B was measured as shown in Fig. 7. It is seen

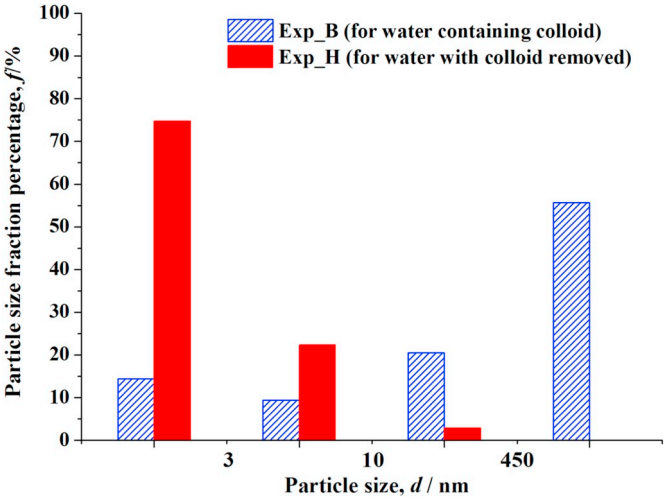


Fig. 7. Particle size distribution comparison of the suspended colloidal Pu in highly saline groundwater with and without natural aquatic colloids as spiked Pu(IV) was aging for 180d.

Table 3
Fractions of Pu in different speciation in the groundwater after aging for 1 year.

Exp.	c_0 (mol·L^{-1})	c_T ($\times 10^{-11}$ mol·L^{-1})	c_D ($\times 10^{-11}$ mol·L^{-1})	Fraction of dissolved Pu(%)	Fraction of colloidal Pu(%)	Pu removal from water phase (%)
A	(2.52 ± 0.04) × 10^{-10}	0.48 ± 0.01	0.42 ± 0.01	87.5 ± 1.9	12.5 ± 1.9	98.1 ± 0.1
B	(1.26 ± 0.02) × 10^{-9}	1.26 ± 0.02	1.21 ± 0.02	96.7 ± 2.1	3.3 ± 2.1	98.9 ± 0.1
C	(1.22 ± 0.02) × 10^{-9}	1.72 ± 0.03	1.63 ± 0.03	95.1 ± 2.1	4.9 ± 2.1	98.6 ± 0.1
D	(4.87 ± 0.08) × 10^{-9}	1.95 ± 0.03	1.71 ± 0.03	87.7 ± 1.9	12.3 ± 1.9	99.6 ± 0.1
E	(4.17 ± 0.07) × 10^{-8}	6.13 ± 0.09	2.90 ± 0.05	47.3 ± 1.0	52.7 ± 1.0	99.8 ± 0.1
F	(7.80 ± 0.12) × 10^{-7}	139 ± 2	50.0 ± 0.8	36.6 ± 0.8	63.4 ± 0.8	99.8 ± 0.1
G	(1.26 ± 0.02) × 10^{-9}	1.24 ± 0.02	1.18 ± 0.02	95.2 ± 2.1	4.8 ± 2.1	99.0 ± 0.1
H	(1.14 ± 0.02) × 10^{-9}	0.38 ± 0.01	0.36 ± 0.01	94.5 ± 2.0	5.5 ± 2.0	99.6 ± 0.1
I	(1.14 ± 0.02) × 10^{-9}	0.33 ± 0.01	0.29 ± 0.01	90.2 ± 1.9	9.8 ± 1.9	99.7 ± 0.1
J	(1.68 ± 0.03) × 10^{-9}	19.7 ± 0.3	0.88 ± 0.02	4.3 ± 0.1	95.7 ± 0.1	88.2 ± 0.3

c_0, c_T, c_D and c_C are initial Pu concentration, concentrations of total Pu, dissolved Pu and colloidal Pu, respectively.

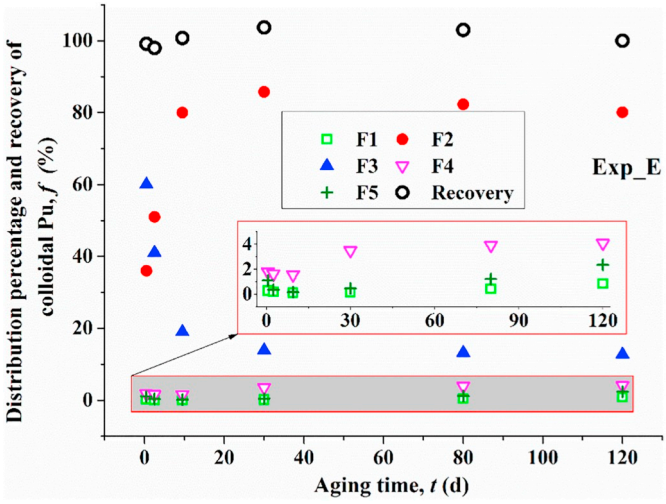


Fig. 8. The change trends of the relative mass fractions of the five speciation fractions of the suspended colloidal Pu with aging time for Exp_E.

that the majority of the colloidal Pu (particle size > 10 kD or 3 nm) in the groundwater has particle size > 450 nm while the minority of it with particle size ranging from 10 nm (100 kD) to 450 nm. The particle size distribution of colloidal Pu was very similar to that of natural colloids in the groundwater examined. So it is deduced that spiked Pu was first adsorbed onto natural colloids and then deposited at the bottom of the container (and/or adsorbed by the container walls). The results obtained matched the particle distribution of Pu associated colloids in the groundwater at "Mayak" site with anoxic condition examined by Stepan et al. (2011).

It is well recognized that natural aquatic colloids in groundwater is one of the main factors affecting the speciation distribution and migration of Pu (Kersting and Reimus, 2003; Van De Weerd and Leijnse, 1997; Degueldre et al., 1996). But the difference in Pu partition in granitic groundwater with natural colloids present or removed is not very clear. So we compared the particle size distributions of the suspended colloidal Pu with and without natural colloids as shown in Fig. 7 (Exp_B vs Exp_H). It can be seen that most of the spiked Pu transformed into colloidal Pu with particle size of > 10 nm in groundwater containing natural colloids, while it mainly kept as dissolved species and formed Pu intrinsic-colloids with particle size mainly of < 10 nm in the groundwater free of natural colloids. This implied that natural aquatic colloids can easily adsorb Pu and thus carries Pu to wherever it goes.

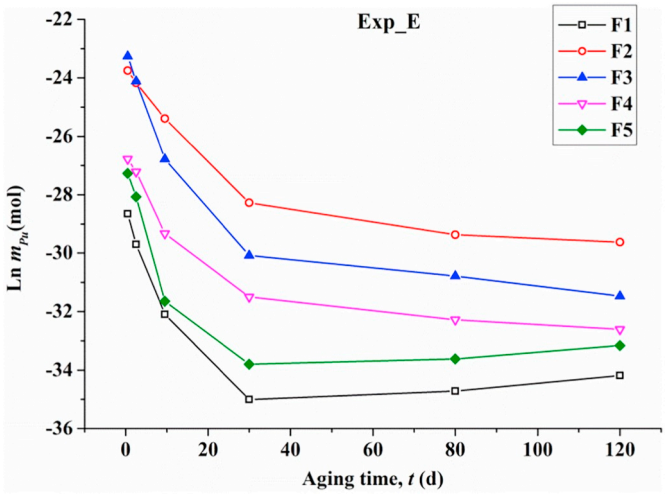


Fig. 9. The change trends of the absolute amount of the five speciation fractions of the suspended colloidal Pu with aging time for Exp_E.

3.3. Speciation transformation ant its kinetics of the suspended colloidal Pu with aging time

The speciation distribution of the suspended colloidal Pu was investigated as function of aging time for Exp_E by the modified Tessier Method, which categorizes the colloidal Pu into five fractions: **F1**-Exchangeable, **F2**-Carbonate, **F3**-Fe/Mn Oxide, **F4**-Organic and **F5**-Residual. The change trends of the relative percentage and absolute amount of the five fractions with aging time are presented in Fig. 8 and Fig. 9, respectively. The kinetic processes of the five fractions were well fitted by exponential model and the results are summarized in Table 4. The approximate 100% of extraction recoveries at various aging times as shown in Fig. 8 demonstrated the validness of the sequential extraction process. It can be seen from Figs. 8 and 9, the equilibrium time of speciation transformation of the suspended colloidal Pu was ~80 d. The absolute amount of each fraction decreased with aging time in 30 days and then changed little (note that the measurement uncertainty may be great for very low Pu concentration). The Fe/Mn Oxide fraction **(F3)** and Carbonate fraction **(F2)** account for the most part of colloidal Pu at the early time, but "Carbonates" with slower deposited rate (see Table 4, $r(t) = -6.9 \times 10^{-12} e^{-0.149t}$) became dominant (~82%) at equilibrium state with the other relative fractions coming as F3(12.7%) > F4(4.1%) > F5(2.4%) > F1(0.8%).

The chemical speciation of the suspended colloidal Pu for different c_0 (Exp_E, Exp_F and additional Exp_1 and Exp_2) are compared in Fig. 10. It is seen that c_0 has little effect on the chemical speciation distribution of the colloidal Pu. However, high initial Pu concentration tends to have a higher percentage of **F3** fraction which may suggest the formation of Pu intrinsic colloids under high c_0. To clarify this perception, the chemical speciation of the colloidal Pu in original groundwater (Exp_G) and that in ultra-pure water (Exp_J) after 1 year's aging were compared in Fig. 11. The results show that **F2** dominated the colloidal Pu in the groundwater while **F3** is the main speciation of colloidal Pu in the ultra-pure water. As we know, there were no carbonates and Fe/Mn oxides in ultra-pure water, so it can be deduced that dissolvability of **F3** fraction for Exp_J should be similar with the Pu intrinsic colloids. In other words, Pu intrinsic colloids have similar dissolvability to the colloidal Fe/Mn oxides in the extraction.

It should be noted that chemical speciation of the colloidal Pu for Exp_1 and Exp_2 (giving a relative high percentage of F4 fraction) were measured after 200 days aging instead of 120 d for Exp_E and Exp_F. Furthermore, Exp_1 and Exp_2 are parallel experiments and the consistent results also demonstrated that the chemical speciation analysis procedure is valid and applicable for this study.

Table 4
The kinetic process fitting for absolute amount changes of the five chemical speciation of the suspended colloidal Pu for Exp_E in 30 days.

Fractions	Fitting equation	R^2	$r(t) = dm_{Pu}/dt$	Rate constant $k(d^{-1})$
F1	$m_{Pu} = 3.8 \times 10^{-13} e^{-0.302t}$	0.992	$r(t) = -1.1 \times 10^{-13} e^{-0.302t}$	0.302
F2	$m_{Pu} = 4.7 \times 10^{-11} e^{-0.149t}$	0.996	$r(t) = -6.9 \times 10^{-12} e^{-0.149t}$	0.149
F3	$m_{Pu} = 5.1 \times 10^{-11} e^{-0.221t}$	0.952	$r(t) = -1.1 \times 10^{-11} e^{-0.221t}$	0.221
F4	$m_{Pu} = 1.8 \times 10^{-12} e^{-0.154t}$	0.939	$r(t) = -2.8 \times 10^{-13} e^{-0.154t}$	0.154
F5	$m_{Pu} = 1.9 \times 10^{-12} e^{-0.493t}$	0.998	$r(t) = -9.6 \times 10^{-13} e^{-0.493t}$	0.493

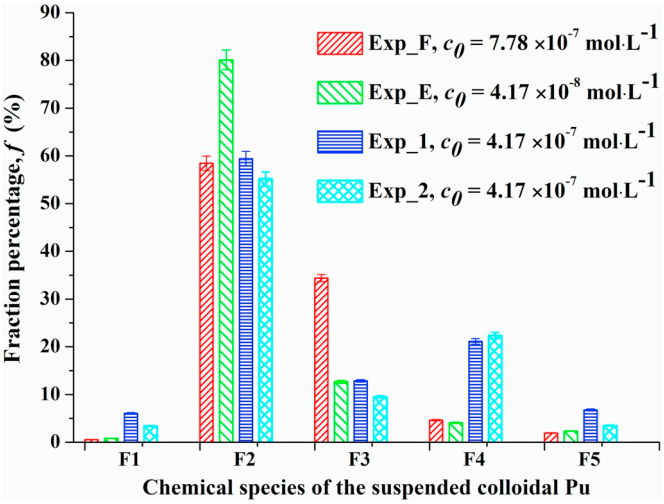


Fig. 10. Speciation distribution of the suspended colloidal-Pu at equilibrium state for the groundwater solutions under different Pu initial concentrations.

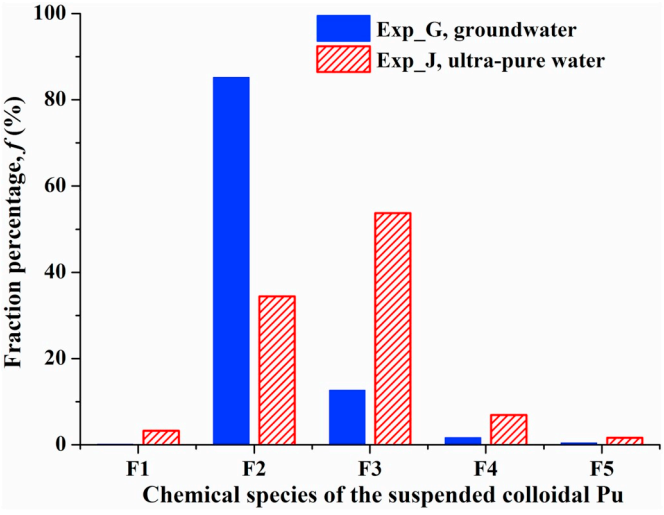


Fig. 11. Chemical speciation distribution of the suspended colloidal Pu in the groundwater and ultra-pure water under same Pu initial concentrations.

3.4. Valence transformation ant its kinetics of the dissolved Pu with aging time

The valence transformation ant its kinetics of the dissolved Pu with aging time were examined and the results are presented in Fig. 12. It shows that Pu (IV) dominated the dissolved Pu in early time (< 10 d, see Fig. 12a) as the spiked Pu was originally tetravalent. However, the percent of Pu (IV) for dissolved Pu decreased gradually over aging while Pu (V + VI) increased accordingly as shown in Fig. 12b. It means that the weakly reductive atmosphere of the groundwater (Eh = -75 mV) cannot maintain the dissolved Pu of less than ~1% at Pu (IV) state, which would still be oxidized to Pu (V + VI) slowly during aging. The transformation marched with a half conversion time of 12.4 days and reached equilibrium after 120 d, with Pu (V + VI) percentage of 95% which is more soluble, while Pu(IV) could not be found due to adsorption and coprecipitation with natural aquatic colloids in the groundwater. The rate constant k (~0.056 d^{-1}) of valence transformation is much less than those of total or colloidal Pu concentration changes (e.g., for Exp_B, k for both total Pu and colloidal Pu was 0.25 d^{-1}), implying that slow oxidation of Pu (IV) did occur during aging and the Pu (IV) fraction decrease was not simply due to the readily adsorption or precipitation of Pu(IV). However, the reason of oxidation of Pu(IV) in the groundwater under weakly reductive condition is not clear yet and needs further study.

4. Conclusion

Highly saline granitic groundwater with ionic strength 1 M from Dunhuang region, NW China, was collected for investigating the speciation, transformation kinetics and fate of spiked Pu (IV) with initial concentration c_0 range 2.5 × 10^{-10}-7.8 × 10^{-7} mol·L^{-1}. The results show that ~99% of the spiked Pu (IV) was easily associated with the natural aquatic colloids and transformed into relatively unstable Pu pseudo-colloids in 1 day, and then gradually deposited and/or adsorbed by the container walls with aging. The suspended Pu pseudo-colloids decreased in similar exponential models with the rate equations of $r(t) = -3.1 \times 10^{-10} e^{-t/4}$ and $r(t) = -1.3 \times 10^{-8} e^{-t/3}$ for c_0 of 1.25 × 10^{-9} mol·L^{-1} and 4.17 × 10^{-8} mol·L^{-1}, respectively. The colloidal Pu was dominated by "Fe/Mn Oxides" at the early time, but "Carbonates" with slower depositing rate ($r(t) = -6.9 \times 10^{-12} e^{-0.149t}$) dominated it (~82%) at equilibrium state. Whatever the c_0 is, the dissolved Pu kept at 0.7 × 10^{-11} mol·L^{-1} over aging and was dominated by Pu(IV) at early time but by Pu(V + VI)(~95%) at equilibrium

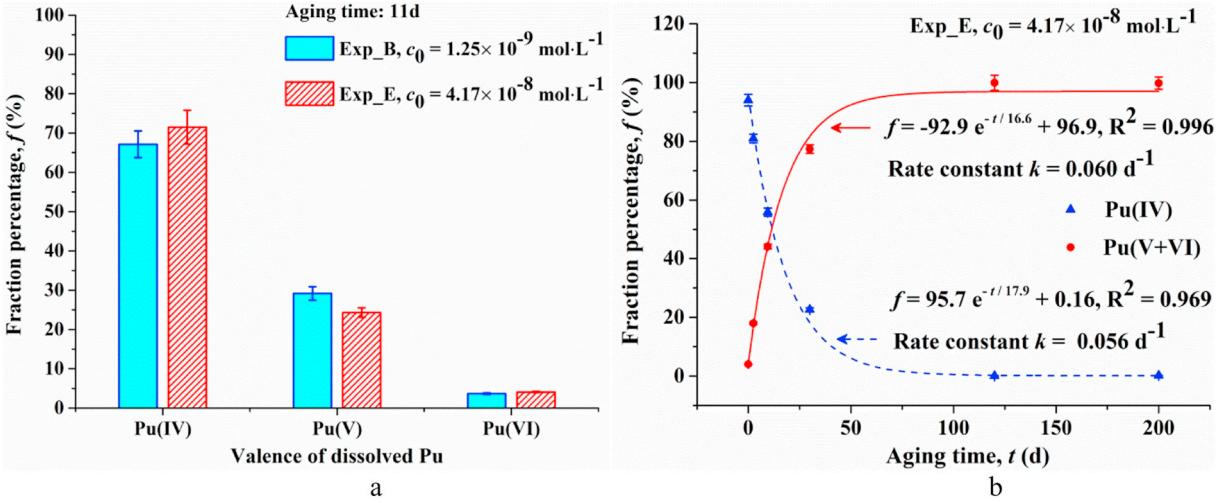


Fig. 12. Valence distribution of the dissolved Pu after 11 days aging (a) and its transformation profiles (b).

state with $r(t) = -92.9e^{-t/16.6} + 96.9$. The equilibrium times of the deposition and/or adsorption and the speciation transformation of the colloidal and dissolved Pu were 30 d, 80 d and 120 d, respectively. The kinetic processes for each of the Pu species could well be fitted by exponential model. Besides, the dissolved Pu increased with increasing c_0 due to the increase of the amount of $PuO_2(c)$ with particle size of < 3 nm (not separable with the dissolved Pu in this study) under higher c_0. By comparison of the observations for ultrapure water and groundwater with natural colloids removed, it was sure that natural aquatic colloids could easily associate and facilitate Pu to suspend a long time in the groundwater. The mobile Pu was dominated by Pu pseudo-colloids with main particle size of > 100 kD for groundwater with natural colloids, while it was dominated by Pu intrinsic colloids with particle size of < 100 kD in ultrapure water, which had similar solubility to "Fe/Mn oxides".

The results imply that majority of released Pu(IV) in highly saline groundwater will be easily associated with natural aquatic colloids and then become immobile in short time due to deposition and/or adsorption of the environmental medium, but potential migration risk caused by stable suspended Pu colloids cannot be ignored.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jconhyd.2019.103505.

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