



Decreased solubilization of Pu(IV) polymers by humic acids under anoxic conditions

Jinchuan Xie^{*}, Jianfeng Lin, Wei Liang, Mei Li, Xiaohua Zhou

Northwest Institute of Nuclear Technology, P.O. Box 69-14, Xi'an City, Shanxi Province 710024, PR China

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Abstract

Pu(IV) polymer has a very low solubility ($\log[\text{Pu(IV)}_{\text{aq}}]_{\text{total}} = -10.4$ at pH 7.2 and $I = 0$). However, some aspects of their environmental fate remain unclear. Humic acids are able to complex with Pu^{4+} ions and their dissolved species (<10 kD) in the groundwater (neutral to alkaline pH) may cause solubilization of the polymers. Also, humic acids have the native reducing capacity and potentially reduce the polymeric Pu(IV) to $\text{Pu(III)}_{\text{aq}}$ ($\log[\text{Pu(III)}_{\text{aq}}]_{\text{total}} = -5.3$ at pH 7.2 and $I = 0$). Solubilization and reduction of the polymers can enhance their mobility in subsurface environments. Nevertheless, humic acids readily coat the surfaces of metal oxides via electrostatic interaction and ligand exchange mechanisms. The humic coatings are expected to prevent both solubilization and reduction of the polymers. Experiments were conducted under anoxic and slightly alkaline (pH 7.2) conditions in order to study whether humic acids have effects on stability of the polymers. The results show that the polymeric Pu(IV) was almost completely transformed into aqueous Pu(IV) in the presence of EDTA ligands. In contrast, the dissolved humic acids did not solubilize the polymers but in fact decreased their solubility by one order of magnitude. The humic coatings were responsible for the decreased solubilization. Such coatings limited the contact between the polymers and EDTA ligands, especially at the relatively high concentrations of humic acids (>0.57 mg/L). Solubilization of the humic-coated polymers was thus inhibited to a significant extent although EDTA, having the great complexation ability, was present in the humic solutions. Reduction of Pu(IV) polymers by the humic acids was also not observed in the absence of EDTA. In the presence of EDTA, the polymers were partially reduced to $\text{Pu(III)}_{\text{aq}}$ by the humic acids of 0.57 mg/L and the percentage of $\text{Pu(III)}_{\text{aq}}$ accounted for 51.7% of the total aqueous Pu. This demonstrates that the humic acids were able to reduce the aqueous Pu(IV), instead of the polymeric Pu(IV). Such a demonstration is supported by the very positive redox potential of aqueous Pu(IV)-EDTA complex: $E_{\text{h}}^{\circ}(\text{PuL}_2^{4+}/\text{PuL}_2^{5-}) = 154.3 \text{ mV} \gg E_{\text{h}}(\text{PuO}_2(\text{am})/\text{Pu}^{3+}) = -182.7 \text{ mV}$ calculated at $10^{-10} \text{ mol/L Pu}^{3+}$ and pH 7.2. At the higher humic concentrations (>0.57 mg/L), the polymers were reduced to a lesser extent because the much denser humic coatings resulted in lower concentrations of the aqueous Pu(IV). Consequently, humic acids make Pu(IV) polymers pretty stable unless the artificial ligands such as EDTA are present in the groundwater. © 2016 Elsevier Ltd. All rights reserved.

Keywords: Plutonium; Humic acid; Colloid; Solubility; Stability

1. INTRODUCTION

The aqueous Pu(IV) readily hydrolyzes and forms intrinsic colloids (i.e., Pu(IV) polymers) even under the acidic conditions. The Pu(IV) polymer as an amorphous

oxyhydroxide is oxygen-deficient and its structure resembles the poorly crystalline PuO_2 (Soderholm et al., 2008; Wilson et al., 2011). Sometimes this polymer is also called crystalline nanoparticle (Delegard, 2013; Romanchuk et al., 2013). The polymeric Pu(IV) with the low solubility ($\log[\text{Pu(IV)}_{\text{aq}}]_{\text{total}} = -10.4$ at pH 7.2 and $I = 0$) can resist solubilization even in strongly acidic solutions. Nevertheless, little is known about its environmental fate in

^{*} Corresponding author. Fax: +86 29 83366333.
E-mail address: xiejinchuan@nint.ac.cn (J. Xie).

subsurface environments. Either solubilization of polymeric Pu(IV) by various ligands in the groundwater or reduction to Pu(III)_{aq} ($\log[\text{Pu(III)}_{\text{aq}}]_{\text{total}} = -5.3$ at pH 7.2 and $I = 0$) by redox minerals such as Fe(II), increases its mobility in the geosphere and thus poses higher risks to human health. The solubility of Pu(IV) and Pu(III) hydroxide at pH 7.2 and $I = 0$ are calculated based on their solubility product of $\log K_{\text{sp}}^{\circ} = -58.5 \pm 0.7$ for Pu(IV) hydroxide (Neck et al., 2007) and $\log K_{\text{sp}}^{\circ} = -26.2 \pm 1.5$ for Pu(III) hydroxide (Lemire et al., 2001) (see the calculations in the Supplementary Data). Whether or not such sparingly soluble polymers exist as a stable species in the anoxic environments remains uncertain. A consensus on their stability was lacking in recent reviews (Altmaier et al., 2013; Geckeis et al., 2013; Kersting, 2013; Maher et al., 2013). Solubilization and reduction of Pu(IV) polymers, thereby controlling their fate and transport in the groundwater, depend on various chemical conditions, some of which are emphasized in this study.

Humic acids, which are an important component of natural organic matter, are ubiquitous in territorial and aquatic environments. In general, concentrations of the dissolved organic carbon in the groundwater fall within the range of 0.2 to 40 mg/L (Buckau et al., 2000a,b; Schäfer et al., 2012). The organic functional groups, such as carboxyl and phenolic groups, are abundant in humic acids and their complexation with Pu⁴⁺ ions seemingly increases the solubility of Pu(IV) polymers. Many researchers studied the chemical interaction between Pu and humic acids exclusively in acidic solutions (pH < 4) in order to determine the binding parameters (Torres, 1982; Guzzi et al., 2007; Reiller et al., 2008; Szabó et al., 2010; Marsac et al., 2014; Zimmerman et al., 2014; Sasaki et al., 2015). In their studies, Pu(IV) and humic acids were considered as aqueous and particulate (solid) species, respectively. On the contrary, Pu(IV)_{aq} may readily form the polymeric species in natural groundwater (generally neutral to alkaline pH), where humic acids exhibit the relatively high solubility. In this case, do the dissolved humic acids have yet the ability to enhance solubilization of Pu(IV) polymers? A study is needed to define the trend in their solubilization.

Humic acids contain redox active function groups, including quinone moieties. The quinone moieties, which act as the electron shuttle, may accept electrons from the dissimilatory metal-reducing bacteria (DMRB) and donate to the sparingly soluble metal oxides (Lovley et al., 1996; Roden et al., 2010; Klüpfel et al., 2014). For example, the humic acids accelerated biotic reduction of Fe(III) to Fe(II) under the anoxic conditions (Jiang and Kappler, 2008; Wolf et al., 2009; Amstaetter et al., 2012; Piepenbrock et al., 2014). The promoted biotic reduction of Pu(IV) to Pu(III) by the anthraquinone-2,6-disulphonate (AQDS), which is a model compound for quinone moieties in humic acids, was also reported (Rai et al., 2002; Plymale et al., 2012). Although humic acids as a mediator for microbially catalyzing metal reduction were intensively studied, their ability to directly transfer electrons to Pu(IV) polymers in the absence of DMRB was never investigated. Struyk and Sposito (2001) and Peretyazhko and Sposito (2006) experimentally determined the native reducing capacity (NRC) for humic acids. It thus

seems that humic acids have the potential to abiotically reduce the polymeric Pu(IV) to Pu(III). Note that the native reducing capacity of humic acids contrasts to their electron accepting and donating capacities in biotic environments and therefore is involved exclusively in abiotic environments.

However, humic acids have the high affinity for the surfaces of mineral particles and metal oxides (Ochs et al., 1994; Takahashi et al., 1999; Banik et al., 2007a; Yang et al., 2009; Bian et al., 2011; Bouby et al., 2011; Tinnacher et al., 2015) and form surface coatings via the electrostatic interaction and ligand exchange mechanisms (Kang and Xing, 2008). The humic coatings on the mineral and oxide surfaces may alter their redox chemistry, solubility, and surface charge. For example, the colloidal stability of mineral suspensions was greatly improved because the humic coatings caused steric and electrostatic stabilization of the particles (Niu et al., 2011; Tang et al., 2014). Either solubilization or reduction of Pu(IV) polymers by the dissolved humic acids may be limited to a certain extent if we now consider the polymers when masked by the humic acids. It is therefore interesting to find whether Pu(IV) polymers become more stable or not (i.e., solubilized or reduced) in the presence of humic acids. In this study, we attempt to determine the rate and extent of solubilization and reduction of Pu(IV) polymers in the presence of humic acids and to define the role of humic acids in affecting environmental fate of Pu(IV) polymers in subsurface environments.

The field groundwater (about 252 m depth) at Lop Nor has 7.0–8.5 pH and contains 0.5–1.3 mg/L TOC (total organic carbon). The solubilization and reduction experiments were conducted under anoxic and pH 7.2 conditions. To evaluate the ability of humic acids to reduce polymeric as well as aqueous Pu(IV), EDTA ligands were also introduced in some of Pu(IV) polymer solutions. The Pu in the 10 kD filtrate was an aqueous/dissolved species, and its change in concentrations with the reaction time was an indication of solubilization kinetics of the polymers. Due to the trace level concentrations of Pu (initial $\sim 10^{-9}$ mol/L ²³⁹Pu) in the present study, the Pu valence states, including Pu(III), Pu(IV), Pu(V), and Pu(VI), were experimentally determined with the solvent extraction method.

2. MATERIALS AND METHODS

2.1. Humic acid

The Pahokee peat humic acid standard (PPHA), which was purchased from the international humic substances society (IHSS), was well-characterized elsewhere. The total and aromatic C, the carboxyl and phenolic groups, the native reducing capacity, and the total Fe are reported in Table 1. The more detailed characterizations, such as C, H, and N contents, the amino acid composition, and the electron spin resonance data, are provided in the IHSS website.

The humic solution (1.0 g/L PPHA), buffered at pH 7.2 with $\sim 5 \times 10^{-3}$ mol/L MOPS (4-Morpholinepropanesulfonic acid, Sigma–Aldrich) and 2.0 mol/L NaOH, was

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