Radiochimica Acta 74, 129–134 (1996)
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Stability of Various Plutonium Valence States in the Presence of NTA and EDTA

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(Received September 15, 1995; accepted March 19, 1996)

Plutonium / Speciation / Nitrilotriacetic acid / Ethylenediaminetetraacetic acid / Complexation / Migration of radionuclides

Abstract

The migration of radionuclides in the subsurface depends strongly on their oxidation states and their solubility. Complexation with chelating agents generally stabilizes the radionuclide in a soluble form, which may increase migration. This study provides fundamental knowledge of the behavior of plutonium in the presence of nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). These complexing agents have been identified as contaminants in the mixed organic-radionuclide waste at U.S. Department of Energy (DOE) sites.

We studied the complexation behavior of the different oxidation states of plutonium: Pu(III), Pu(IV), Pu(V), and Pu(VI) in the presence of NTA and EDTA at various concentrations of plutonium and several Pu/organic-chelating ratios. We found that Pu(IV) is the predominant oxidation state at pH 5 to 8. Pu(III) was oxidized and Pu(V) and Pu(VI) were reduced. We found that the presence of NTA and EDTA in plutonium solution stabilizes plutonium in soluble form and therefore enhances its potential migration in the subsurface.

Introduction

Mixtures of radionuclides, metals, organic complexing agents, and organic solvents [1, 2] were identified at the different disposal sites within the U.S. Department of Energy (DOE) complex. Interactions between species present in these mixtures can enhance or suppress contaminant migration; e.g., if an interaction between a radionuclide and a complexing agent stabilizes the radionuclide in soluble or insoluble forms, the migration of the radionuclide in the geosphere may be enhanced or reduced. Therefore, it is important to understand the thermodynamics and kinetics of multispecies reactions to assist in the development and validation of models for transport that are used for designing protection measures of groundwater resources. Our current research examines the behavior of plutonium with nitrilotriacetic acide (NTA) and ethylenediaminetetraacetic acid (EDTA). We reported earlier the thermodynamic complexation behavior of Pu(IV), Pu(V), and Pu(VI) with NTA [3, 4] which provided supplementary stability constants to the review by Anderegg of the stability constants for Pu-NTA systems [5]. A wealth of thermodynamic information is available for the Pu-EDTA systems that was also thoroughly reviewed and summarized by Anderegg [6]. There are still significant discrepancies for some of the plutonium-EDTA stability constants. These discrepancies require elimination through future additional thermodynamic measurements.

To accurately describe the aqueous Pu-NTA and Pu-EDTA systems, however, additional information is needed on the kinetic stability of individual plutonium oxidation states in the presence of the organic acids. Choppin and Rao [7] showed that Np(VI) is reduced by several dicarboxylic acids and hydroxylic compounds. Shastri and Amis [8] and Zakharova *et al.* [9] reported reduction of Np(VI) and Pu(VI), respectively, with oxalic acid. The purpose of our study was to determine the stability of different oxidation states of plutonium (III, IV, V, and VI) in the presence of NTA and EDTA. Plutonium was studied at macroscopic concentrations (10^{-3} M) and at microscopic concentrations (10^{-7} M) to better simulate plutonium concentrations at contaminated sites. Also, the plutonium-to-ligand ratios were varied over a large range to cover possible site conditions where large excess of NTA and EDTA may be present.

Experimental

Reagents

Reagents used in our experiments are: $NaClO_4$, $HClO_4$ (G.F.S.); NTA, NaOH, xylene, HCl, HNO_3 (Baker); EDTA, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (PMBP), di(2-ethylhexyl)-phosphoric acid (HDEHP) (Aldrich); toluene (Mallinckrodt). UniverSol (ICN Biomedicals) was used as the scintillation solution for counting the α activities of ^{239}Pu. All reagents are AR and GR quality. All aqueous solutions were prepared with freshly distilled deionized water collected under argon atmosphere.

Apparatus and methods

The spectrophotometer (Guided Wave Inc., model 260) used is described elsewhere [10]. The wavelength range is from 400 to

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Table 1. Characteristic absorption bands and molar absorptivities of the different plutonium oxidation states

Plutonium ion	Wavelength (nm)	Molar absorptivity (M^{-1} cm^{-1})
Pu(III)	561	36.9
Pu(IV)	470	57.4
Pu(V)	569	19
Pu(VI)	830	366.2

1000 nm. The spectrophotometer uses a 0.25-mm exit slit and a silicon detector that gives 1-nm wavelength resolution.

We used a LKB Wallac, 1219 Rackbeta liquid scintillation counter and a high-purity germanium counting system (designed at Lawrence Berkeley National Laboratory) to determine plutonium concentrations [11].

pH measurements were performed using a semimicro Ross combination pH electrode that was calibrated with NIST-traceable standard buffers solutions. The 3 M KCl reference solution was replaced with a filtered, carbonate-free 3 M NaCl reference solution to avoid precipitation of $KClO_4$. All experiments were performed at ambient temperature (25±1°C) and in an argon atmosphere. For the oxidation state determination we used the solvent extraction technique described by Nitsche *et al.* [12]. Solvent extraction methods are indirect techniques that may disturb the initial oxidation-state distribution. However, the technique that we used has been tested by comparing it with the direct technique of Laser Photoacoustic Spectroscopy [13]. Results of this test showed good agreement between the oxidation-state distribution obtained by chemical extraction and those obtained by Photoacoustic Spectroscopy.

Preparation of plutonium solutions

The isotopes ^{239}Pu and ^{242}Pu were used. The isotopic distribution of ^{239}Pu was described previously [4]. The isotopic purity of ^{242}Pu is 99.932%.

The dissolution of PuO_2 and the adjustment of the individual plutonium oxidation states were carried out electrochemically to avoid the use of HF and the introduction of any reducing agents such as iron(II), nitrite, or hydroxylamine. PuO_2 was dissolved in 1 M $HClO_4$ at 0.0 volts vs. Ag/AgCl). The electrochemical equipment and the preparation of individual oxidation states were described elsewhere [14, 15].

The purity of all oxidation states was verified by spectrophotometry. The characteristic absorption bands and molar absorptivities that we determined for our spectrophotometer are described in Table 1.

Results and discussion

We performed two series of experiments: one at macroscopic concentrations of plutonium (10^{-3} M), and a second one at lower concentrations ($\sim 10^{-7}$ M). In the first series of experiments we used conventional spectrophotometry to determine plutonium speciation; in the second series, we used the solvent extraction technique to determine plutonium oxidation state distribution because plutonium concentrations were below the detection limit of the conventional spectrophotometry.

Plutonium valence stability at macroscopic concentrations

a) Pu-NTA systems

In a series of experiments, plutonium solutions containing each a pure oxidation state, Pu(III), Pu(IV), Pu(V), or Pu(VI) were mixed with NTA. The pH was adjusted to about 5 by adding the corresponding amount of NaOH. We always started by adding NTA to an acidic solution of Pu and then we adjusted the pH to 5. This procedure will prevent precipitation of plutonium hydroxides. This procedure is especially necessary when adjusting the pH of the Pu(IV) solutions, to prevent the formation of Pu(IV) colloids, which will occur if the pH was adjusted before the addition of NTA. The final ionic strength was approximately 0.01 M. The solutions were analyzed as a function of time for oxidation-state changes.

We observed that at ligand-to-metal ratios of about 6 to 1, and at an initial plutonium concentration of about 10^{-3} M, the final stable species of plutonium, when mixed with NTA, is the Pu(IV)-NTA complex. Thus, Pu(V) and Pu(VI) are reduced while Pu(III) is oxidized. The Pu(IV)-NTA complex formed in the pH range of 5 to 7 has a characteristic absorption band at 496 nm. The form of this complex has not been identified yet. At lower pH (1.1), the formation of two complexes of Pu(IV) with NTA was suggested by Nitsche and Becraft [3]: $PuNTA^{+}$ and $PuHNTA^{2+}$. The characteristic absorption bands observed by Nitsche and Becraft are different from that observed in this work. This suggests that the complex formed at pH 5 to 7 is different from the one formed at pH 1.1.

Pu(III) becomes oxidized to Pu(IV), probably due to the increased stability of the Pu(IV)-NTA complex compared to the Pu(III)-NTA complex. The formation constants for ($Pu^{III}NTA$) and ($Pu^{IV}NTA)^{+}$ are 3.98×10^{10} [16] and 7.24×10^{12} [3], respectively. Fig. 1 shows three spectra taken at 15 min, three hours, and eight hours after the addition of NTA. The absorbance bands at 560 and 600 nm, characteristic of Pu(III), disappear and another absorbance band at 496 nm, characteristic of Pu(IV)-NTA complex, forms. The total conversion of Pu(III) to Pu(IV)-NTA complex occurred within about eight hours. The oxidation of Pu(III) to Pu(IV) was accompanied with a pH increase from 5.4 to 8.3. Pu(III) hydrolysis is negligible in this range of pH, therefore, there is no liberation of hydroxyl groups from a hydrolyzed form of Pu(III). At this moment, we do not have an interpretation for the pH increase. More investigations are needed to examine the radiolysis effect on the pH of Pu(III)-NTA system.

The addition of an excess amount of NTA to a solution that contained originally Pu(IV)-polymer and NTA with the ratio [NTA]/[Pu(IV)-polymer] = 6/1 led to the dissolution of the polymeric form. Fig. 2 shows that at a ratio of [NTA]/[Pu(IV)-polymer] = 45/1, Pu(IV)-polymer depolymerizes and transforms to Pu(IV)-NTA complex within 14 days of adding the ex-

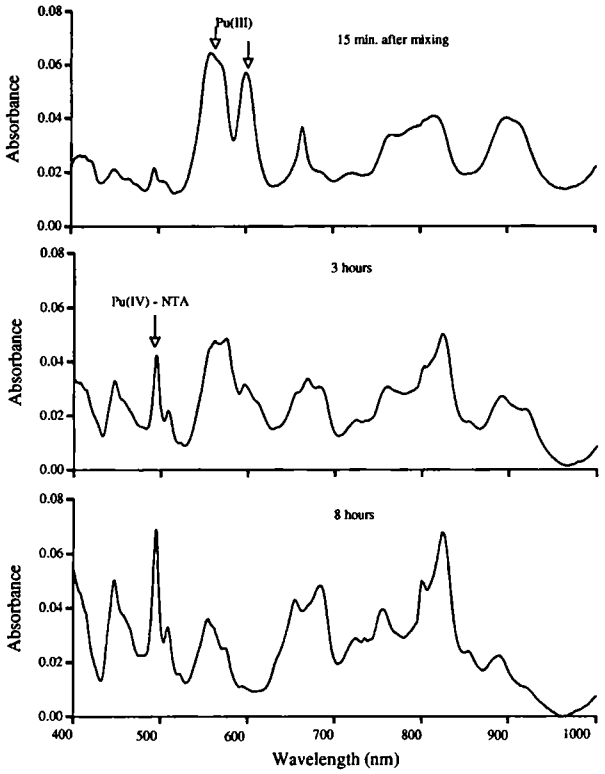


Fig. 1. Transformation of Pu(III) to Pu(IV) in the presence of NTA. [NTA]/[Pu(III)] = 6/1, [Pu] = 1.4×10^{-3} M, initial pH = 5.4, final pH = 8.3.

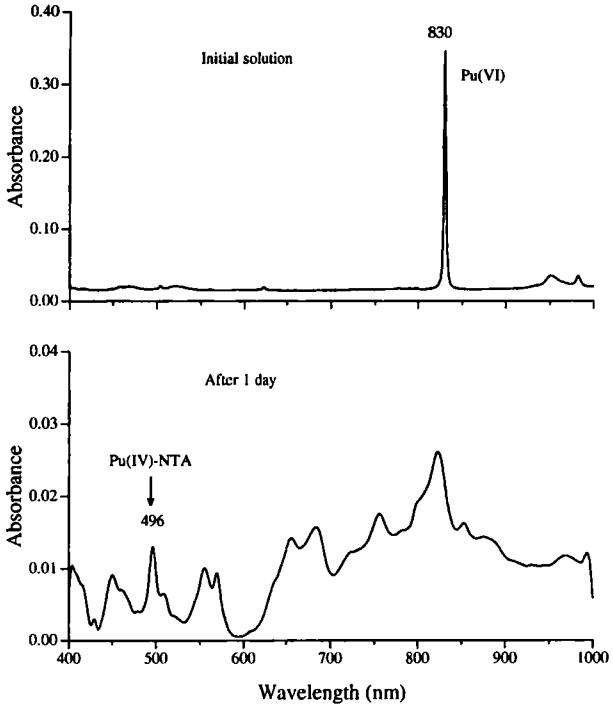


Fig. 3. Transformation of Pu(VI) to Pu(IV) in the presence of NTA. [NTA]/[Pu(VI)] = 6/1, [Pu] = 9×10^{-4} M, initial pH = 5.7, final pH = 7.8. (The top spectrum represents Pu(VI) in acid solution before addition of NTA.)

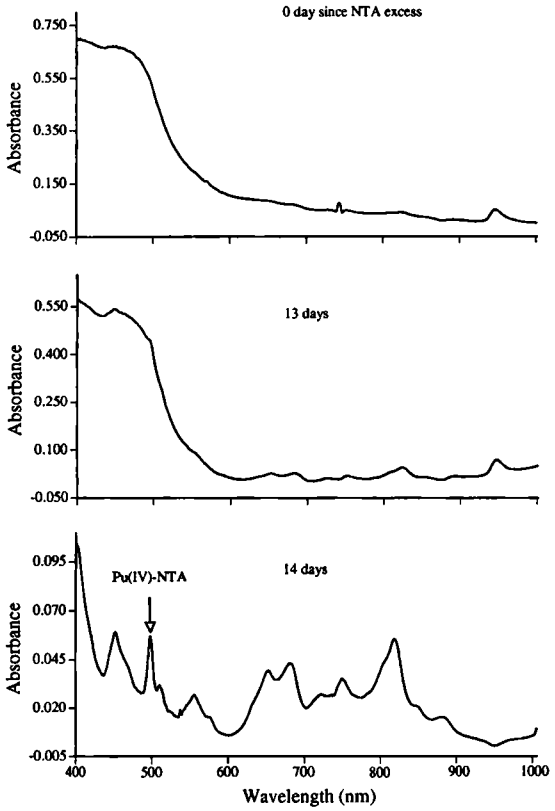


Fig. 2. Depolymerization of Pu(IV) colloid by excess of NTA. [NTA]/[Pu(IV)] = 45/1, [Pu] = 1×10^{-3} M, initial pH = 5.6, final pH = 7.1.

cess amount of NTA. During the depolymerization, the pH of the system changed from 5.6 to 7.1. This may be due to the liberation of hydroxyl ions from the dissolution of the Pu(IV)-polymer.

The reduction of Pu(VI) and Pu(V) to Pu(IV) by NTA may be induced by an electron transfer reaction from the NTA. As mentioned above, several investigations have shown the reduction of actinide ions by organic compounds [7–9, 17]. The stability of Pu(V) in the absence and presence of NTA at pH 3 was investigated previously [4]. The reduction of Pu(V) to Pu(IV) in the presence of NTA appears to be faster at pH ~5 than at pH 3 but is still slower than the transformation of Pu(III) to Pu(IV). This is due to the fact that the reduction of Pu(V) involves the rupture of the Pu–O bonds. Fifteen days after adding NTA to Pu(V) solution, only 43% of Pu(V)-NTA complex transformed to Pu(IV)-NTA. The pH of the system increased from 5.4 to 7.7 during this transformation. The change in Pu(V) spectrum upon addition of NTA was reported previously [4]. The reduction of Pu(VI) by NTA appears at first to be faster than the reduction of Pu(V). About 80% of Pu(VI) transforms to Pu(IV)-NTA within six hours. However, the remaining 20% are present as a Pu(V)-NTA complex that reduces slowly to the Pu(IV)-NTA complex. After 21 days, 17% of plutonium is still in the form of Pu(V)-NTA. The pH of the system increased from 5.7 to 7.8 within 21 days (Fig. 3). The pH increase in Pu(V)-NTA and Pu(VI)-NTA systems is probably linked with the rupture of Pu–O bonds.

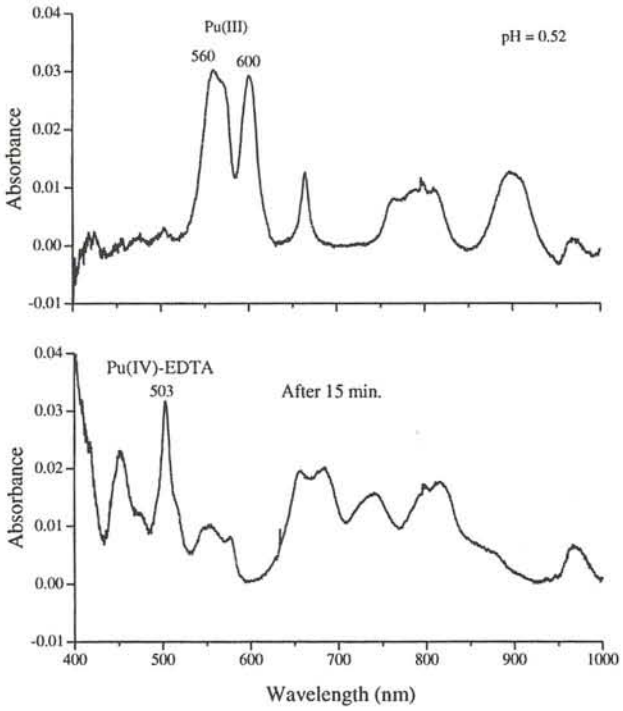


Fig. 4. Transformation of Pu(III) to Pu(IV) in the presence of EDTA. [EDTA]/[Pu(III)] = 6/1, [Pu] = 7.9×10^{-4} M, pH = 6.

b) Pu-EDTA System

At macroscopic concentration of plutonium, we only examined the interaction of EDTA with Pu(III). Literature describing the decomposition of Pu(VI)-EDTA complex over a period of several days to yield a Pu(IV)-EDTA complex has been published [18]. Similarly, Pu(V)-EDTA complex is expected to be reduced. However, for Pu(III)-EDTA system, the available literature suggests that Pu(III)-EDTA complex is stable [18]. From our studies of NTA systems, we expected that Pu(III)-EDTA complex will transform to Pu(IV)-EDTA. Therefore, we decided to examine the Pu(III)-EDTA system.

EDTA was added to a Pu(III) solution to obtain a ratio of [EDTA]/[Pu(III)] = 6/1. The concentration of Pu(III) was 7.9×10^{-4} M. After the addition of EDTA, the pH of the solution was adjusted to 6 with NaOH. The absorbance spectrum taken 19 minutes after adjusting the pH indicates, as expected, the formation of a Pu(IV)-EDTA complex. The characteristic peak of Pu(IV) at 470 nm was shifted to 503.5 nm. The spectrum looked very similar to the Pu(IV)-NTA spectrum. The calculated molar absorptivity of the Pu(IV)-EDTA peak at 503.5 nm is (44.1 ± 1.0) cm^{-1} M^{-1}.

Plutonium valence stability at microscopic concentrations

In this section we describe the study of the Pu-NTA and Pu-EDTA systems at lower plutonium concentrations that may better simulate plutonium concentrations at contaminated sites. We added either NTA or EDTA solutions to individual Pu(III), Pu(IV), Pu(V), and Pu(VI) solutions. Plutonium concentrations ranged from 3.8×10^{-7} to 6.3×10^{-7} M. The ratios of NTA and EDTA to plutonium were selected to cover a wide range of possible contaminant concentrations. No information is available about the real ratios of organic chelating agents to plutonium in the radioactive wastes at DOE sites. The following Pu to ligand ratios were used: 1/1, 1/10, 1/20, 1/100, and 1/20,000. The highest 1/20,000 ratio was chosen by taking into consideration the solubility limits of NTA and EDTA. The ionic strengths of the solutions varied from 5×10^{-2} M to 10^{-5} M. The solutions were placed in Teflon vials and maintained under argon atmosphere. The pH of each solution was adjusted to 7−8 with NaOH. A second series of experiments, consisting of Pu(III), Pu(IV), Pu(V), and Pu(VI) solutions without NTA or EDTA, was carried out concurrently with the same conditions. A significant decrease in plutonium concentrations was observed in the samples that did not contain NTA or EDTA due to the formation of Pu(IV) polymer. Before the analysis of plutonium oxidation-state distribution by the solvent extraction technique, samples were filtered through 4.1-nm Amicon filters to separate any solid particles larger than or equal to 4.1 nm (smallest pore size filters available). The filters were presaturated to avoid any sorption of the experimental solution on the filter. From the filtration study, we found that plutonium is present in a solid form, probably Pu(IV)-polymer, that can be filtered from all solutions that did not contain NTA or EDTA. The presence of NTA or EDTA, however, inhibits this process and stabilizes plutonium in solution.

Tables 2 and 3 summarize the experimental results for plutonium oxidation-state distribution in the presence of NTA and EDTA at different plutonium to organic acid ratios.

Table 2. Plutonium oxidation-state distribution in the presence of NTA. [Pu] = 5×10^{-7} M, pH = 7−8

Initial sample content	Oxidation-states distribution after 10 days of adding NTA[a]			
	% Pu(III)	% Pu(IV)	% Pu(V)	% Pu(VI)
Pu(III)/NTA				
1/10	20	80	0	0
1/100	14	86	0	0
Pu(IV)/NTA				
1/20	18	76	0	0
1/100	12	83	5	0
1/20,000	1	97	2	0
Pu(V)/NTA				
1/100	0	28	66	6
1/20,000	0	36	62	2
Pu(VI)/NTA				
1/100	0	48	31	21
1/20,000	0	38	61	1

[a] Uncertainty ranges between 5 and 7%.

Table 3. Plutonium oxidation-state distribution in the presence of EDTA. [Pu] = 5×10^{-7} M, pH = 7–8

Initial sample content	Oxidation-states distribution after 10 days of adding EDTA[a]			
	% Pu(III)	% Pu(IV)	% Pu(V)	% Pu(VI)
Pu(III)/EDTA				
1/1	29	71	0	0
1/100	12	87	0	0
Pu(IV)/EDTA				
1/20	11	83	0	0
1/100	15	85	0	0
Pu(V)/EDTA				
1/1	0	51	49	0
1/100	0	44	52	4
Pu(VI)/EDTA				
1/1	0	35	61	4
1/100	0	79	21	0

[a] Uncertainty ranges between 5 and 7%.

a) Pu-NTA systems

The general behavior of plutonium-NTA solutions at low concentrations of Pu is close to that observed at macroscopic concentrations. But as expected, the kinetics at low concentrations are slower than at high concentrations. We are continuing to analyze all solutions as a function of time to ensure that the reactions between species have reached steady state. In the solutions that initially contained Pu(III), the predominant form after 10 days from adding NTA was Pu(IV). At [Pu(III)]/[NTA] = 1/10, 80% of Pu(III) was oxidized to Pu(IV); at the higher ratio of [Pu(III)]/[NTA] = 1/100, 86% of Pu(III) was oxidized. In the solutions that initially contained Pu(IV) and at [Pu(IV)]/[NTA] = 1/20 and 1/100, the results are somewhat surprising: about 15% of plutonium was present as Pu(III). This reduction of Pu(IV) is unexpected because of the higher thermodynamic stability of Pu(IV)-NTA compared with Pu(III)-NTA, as mentioned earlier. This reduction is not observed at higher NTA concentrations; at [Pu(IV)]/[NTA] = 1/20,000, about 97% of Pu stays in form of Pu(IV). We expect that the remaining 15% Pu(III) will oxidize with time to the more stable form Pu(IV)-NTA. In the solutions that initially contained Pu(V) and at [Pu(V)]/[NTA] = 1/100, 28% of Pu(V) was reduced to Pu(IV). The remaining 66% were still present as Pu(V). At [Pu(V)]/[NTA] = 1/20,000, 36% of Pu(V) was reduced to Pu(IV).

We used the Hydraql speciation model developed by Papelis *et al.* [19] to calculate the species distribution for the system Pu-NTA as a function of pH for the different ratios of NTA/Pu. The thermodynamic complexation constant for Pu(V)-NTA that we used to calculate the species distribution is $\log\beta = 6.75$ [4]; for Pu(V) hydrolysis we used $\log\beta = -9.73$ [20]. At [Pu(V)]/[NTA] = 1/20,000, Pu(V) is expected to be totally complexed with NTA, and therefore the reduction to Pu(IV) is expected to be complete in the presence of NTA. We expect that the reduction to Pu(IV) will proceed with time. In the solutions that initially contained Pu(VI), the predominant form of plutonium is Pu(IV) and Pu(V). At [Pu(VI)]/[NTA] = 1/100, 21% of Pu still present as Pu(VI); at [Pu(VI)]/[NTA] = 1/20,000, all Pu(VI) was reduced to either Pu(V) or Pu(IV).

b) Pu-EDTA systems

The behavior of plutonium-EDTA solutions was similar to that of Pu-NTA solutions. However, at the same ratio of Pu/organic acid, the transformation to Pu(IV) seems to be faster in the EDTA systems, especially for the solutions that originally contained Pu(V) and Pu(VI). At [Pu]/[EDTA] = 1/100, 44% of Pu(V) transformed to Pu(IV) (only 28% had been transformed to Pu(IV) in the NTA system), and 79% of Pu(VI) transformed to Pu(IV) (only 48% had been transformed to Pu(IV) in the NTA system). This higher tendency of EDTA to reduce Pu(V) and Pu(VI) by comparison with NTA is probably due to the higher stability constant of Pu(IV)-EDTA complex compared to Pu(IV)-NTA. The presence of Pu(III) in the solutions that contained originally Pu(IV) in both NTA and EDTA systems indicates that a reduction of Pu(IV) has taken place. We did not observe this behavior at macroscopic concentrations of plutonium. The reduction of Pu(IV) to Pu(III) in the presence of carboxylic acids, when Pu(IV) is at microscopic concentrations, has already been observed by Madic [21] and Métivier [22].

Acknowledgments

The authors thank gratefully Professor Charles Madic, Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires, France, for his suggestions.

This work was suported by the Director, Environmental Sciences Division, Office of Health and Environmental Research, as part of the U.S. Department of Energy's Subsurface Science Program, under Contract No. DE-AC03-76SF00098.

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