Annual Report
EMSP Program at FSU on Redox and Speciation of Actinides
First Year (10/96 - 9/97)

The program at Florida State University was funded to collaborate with Dr. A. Felmy (PNNL) on speciation in high level wastes and with Dr. D. Rai (PNNL) on redox of Pu under high level waste conditions. The funding provided support for 3 research associates (postdoctoral researchers) under Professor G. R. Choppin as P.I. Dr. Kath Morris from U. Manchester (Great Britain), Dr. Dean Peterman and Dr. Amy Irwin (both from U. Cincinnati) joined the laboratory in the latter part of 1996. After an initial training period to become familiar with basic actinide chemistry and radiochemical techniques, they began their research. Dr. Peterman was assigned the task of measuring Th-EDTA complexation prior to measuring Pu(IV)-EDTA complexation. These studies are associated with the speciation program with Dr. Felmy. Drs. Morris and Irwin initiated research on redox of plutonium with agents present in the Hanford Tanks as a result of radiolysis or from use in separations. The preliminary results obtained thus far are described in this report. It is expected that the rate of progress will continue to increase significantly as the researchers gain more experience with plutonium chemistry.

An(IV)-EDTA and An(IV)-DTPA Stability Constants

Introduction

The actinides (An) are a major contaminant at many DOE installations, and are present in mixed wastes containing organic complexing agents such as ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DPTA) [Riley et al. 1992]. Reliable data on the stability constants for the formation of An-EDTA and An-DPTA complexes can be found in the literature [Martell and Smith 1974], however, stability constant data for the Pu(IV)-EDTA or Pu(IV)-DTPA complexes applicable to high ionic strength (> 1 M) solutions are generally not available. We are in the process of determining the stability constants for these complexes over a range of solution ionic strengths. This report gives a brief summary of experimental technique and the results obtained thus far. The future goals for this research program are also presented.

Experimental Method

Due to the complex oxidation-reduction chemistry of plutonium, the Pu(III), Pu(IV), P(V), and Pu(V1) oxidation states can co-exist in the same experiment. Therefore careful control of the redox speciation of the metal is necessary. In the initial part of this program, Th(IV) is used as an oxidation state analogue for Pu(IV). Since the tetravalent state is the only stable thorium oxidation state, redox speciation is not a concern.

The Th(IV)-EDTA stability constant is determined spectrophotometrically by competition with the colored dye arsenazo III (AAIII). AAIII forms metal complexes which strongly absorb ($\epsilon > 30000$ L $M^{-1}cm^{-1}$) at ~670 nm. The free arsenazo III molecule absorbs little ($\epsilon < 1000$ L M^{-1} cm^{-1}) in this region [Sherry et al. 1988, Budesinsky 1968]. The conditional stability constant for the Th(IV)-AAIII complex is determined by measuring the absorption spectra of solutions containing Th(IV) and AAIIIin 0.0 - 1.0 molar ratios and fitting the variation in the spectra using the SQUAD computer program [Leggett 1977]. Once the Th(IV)-AAIII conditional stability constant is known, the Th(IV)-EDTA conditional stability constant is determined by monitoring the absorption spectra of solutions, which contain constant Th(IV) and

$$K_{therm.} = K'_{cond.}[1 + K_1[H^+] + K_1K_2[H^+]^2 + ...] \tag{1}$$

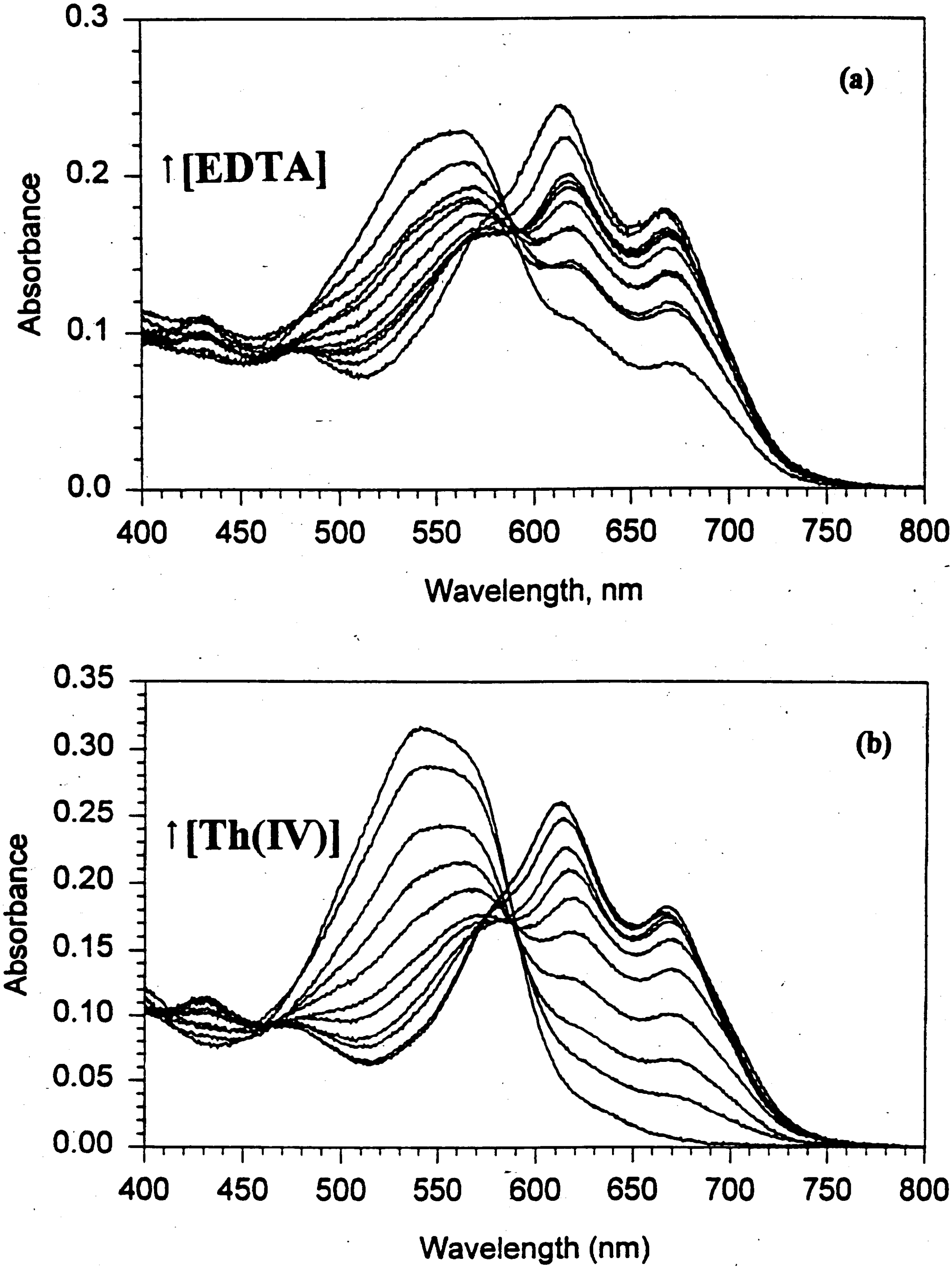
AAIII concentrations, as the EDTA concentration is increased. The conditional stability constants are determined at pcH = 3.0. The thermodynamic stability constant for the Th(IV)-EDTA complex is calculated by correcting the conditional values for protonation of the ligand. The stepwise protonation constants for EDTA are taken from the literature [Mizera et al. 1995].

Results and Discussion

Representative sets of absorption spectra used for the determination of the Th(IV)-EDTA and Th(IV)-AAIII conditional stability constants at I = 1.0 m NaCl and pcH = 3.0 are shown in Figures 1a and Figure 1b, respectively. As the concentration of Th(IV) ion is increased the absorption at 540nm (see Figure 1b) corresponding to the uncomplexed AAIII decreases and the absorption at 670 nm corresponding to bound AAIII increases. In Figure la, the concentration of Th(IV) and AAIII are held constant while the EDTA concentration is varied. The increase in the free AAIII absorption as the concentration of added EDTA is increased (see Figure la) is due to the competition of EDTA for Th(IV) metal ions which results in an increase in the free AAIII concentration.

The conditional stability, constants determined at I = 1.0 m NaCl and pcH = 3.0 for the Th(IV)-AAIII species and the Th(IV) EDTA species are $\log K'_{Th(IV)-AAIII} = 6.15 \pm 0.03$ and $\log K'_{Th(IV)-EDTA} = 3.31 \pm 0.03$, respectively. The thermodynamic stability constant for the Th(IV)-EDTA complex, calculated using Eq. 1, is $\log K_{Th(IV)-EDTA} = 12.07 \pm 0.03$. Literature values for the Th(IV)-EDTA stability constant [Martell and Smith 1974] are approximately ten orders of magnitude higher. The discrepancy between the determined and the literature value is too large to be-attributed to the formation of protonated metal-EDTA complexes. The conditional stability constant for formation of the Th(IV)-AAII complex of $\log K'_{Th(IV)-AAIII} = 5.88 \pm 0.04$ at I = 3.0 m NaCl and pcH = 3.0 has also been determined. Attempts to determine the Th(IV)-EDTA stability constant by competition experiments at I = 3.0 m NaCl have not been successful. This is most likely due to the interference by sodium binding to the EDTA in the concentrated electrolyte solutions. Obviously, additional experiments are needed to resolve this problem.

Figure 1



0.3
0.2
0.1
0.0
Absorbance
(a)
↑[EDTA]
400
450
500
550
600
650
700
750
800
Wavelength, nm
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Absorbance
(b)
↑[Th(IV)]
400
450
500
550
600
650
700
750
800
Wavelength (nm)

Summary and Future Work

To date the attempts to determine reasonable stability constant values for the Th-EDTA system in concentrated electrolytes have had limited success. Efforts in the immediate future will center around determining the difficulties with the experimental technique. In order to accomplish this, experiments will be conducted in dilute (0.3 m NaCl) solution and the possibility of the formation of hydrolyzed thoriumcomplexes will be investigated. When reliable values for the Th(IV)-EDTA stability constants are obtained, experiments will shift to the Pu(IV)-EDTA system.

The plutonium work will be performed using ^{242}Pu isotope which has a lower specific activity that ^{239}Pu or ^{238}Pu. The Pu(IV) stock solutions will be prepared using published techniques [Lovett and Nelson 1981]. In order to minimize the quantity of ^{242}Pu used in any single experiment, long (5 cm) pathlength optical cells will be used. These cells have already been designed and manufactured.

After the Pu-EDTA stability constants are determined, the constants for the DTPA system will be measured. These experiments should be somewhat easier to perform since ‘published values for the Th(IV)-DTPA stability constants [Martell and Smith 1974] are 3-4 orders of magnitude larger than the corresponding Th(IV)-EDTA constants. The larger constants for the Th(IV)-DTPA complex implies that DTPA should be better able to compete with AAIII for Th(IV) metal ion.

Dr. Dean R. Peterman

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The Redox Chemistry of Pu(V) in NaCl Solutions

Introduction

The stable oxidation state of plutonium under saline conditions (specifically in sea water) is reported to be Pu (V) (Choppin 1991). The experimental program is designed to examine&e oxidation state distribution of Pu(V) in the presence of NaCl over a broad range of pH and ionic strengths, and in the presence and absence of simple redox agents which may be pertinent to both DOE wastes as well as general environmental systems. This report gives a brief summary of the experimental procedures of the project, progress thus far and also outlines future goals.

Experimental

In order to ascertain the redox speciation of Pu at trace levels (typically 10^{-9} - 10^{-10} M) intrusive oxidation state separation techniques must be employed (eg Nitsche et al 1988, Nash et al 1988, Saito & Choppin 1983). This study uses published separation techniques based on chemical selectivity for particular oxidation states to study the systems of interest. A summary of the separation techniques which have been identified as relevant is given in Table 1. Pu (III) is not considered as it is absent in pH $\geq$ 6 oxic waters.

For the batch experiments which have been performed, plutonium was prepared as the $^{238}PuO_2+$ species following the method of Saito et al 1985. This involved the production of Pu(VI) by oxidation with $KMnO_4$, and subsequent photolytic reduction to Pu (V) in a thenoyltrifluoracetone solution. Pu (V) produced in this way was back extracted into a saline aqueous phase at pH 4.5 and was then added to the NaCl solutionto give a final solution concentration of 10^{-10} M plutonium. At the appropriate time, a fraction of the solution was withdrawn for oxidation state separation by the chosen method. A number of repeat analyses were performed for each time point to ensure the quality of the experimental data.

Thus far, full data sets have been obtained for Pu(V) addition to 0.1, 0.7 and 3.0 m NaCl solutions at p_cH = 4.7 and 8.2 in the absence of any redox agents and in the dark. In addition to these, a number of scoping experiments have been performed investigating the effect of light, peroxide and hypochlorite.

Table 1 - Separation Methods Used for Pu Speciation Analysis at Trace Levels

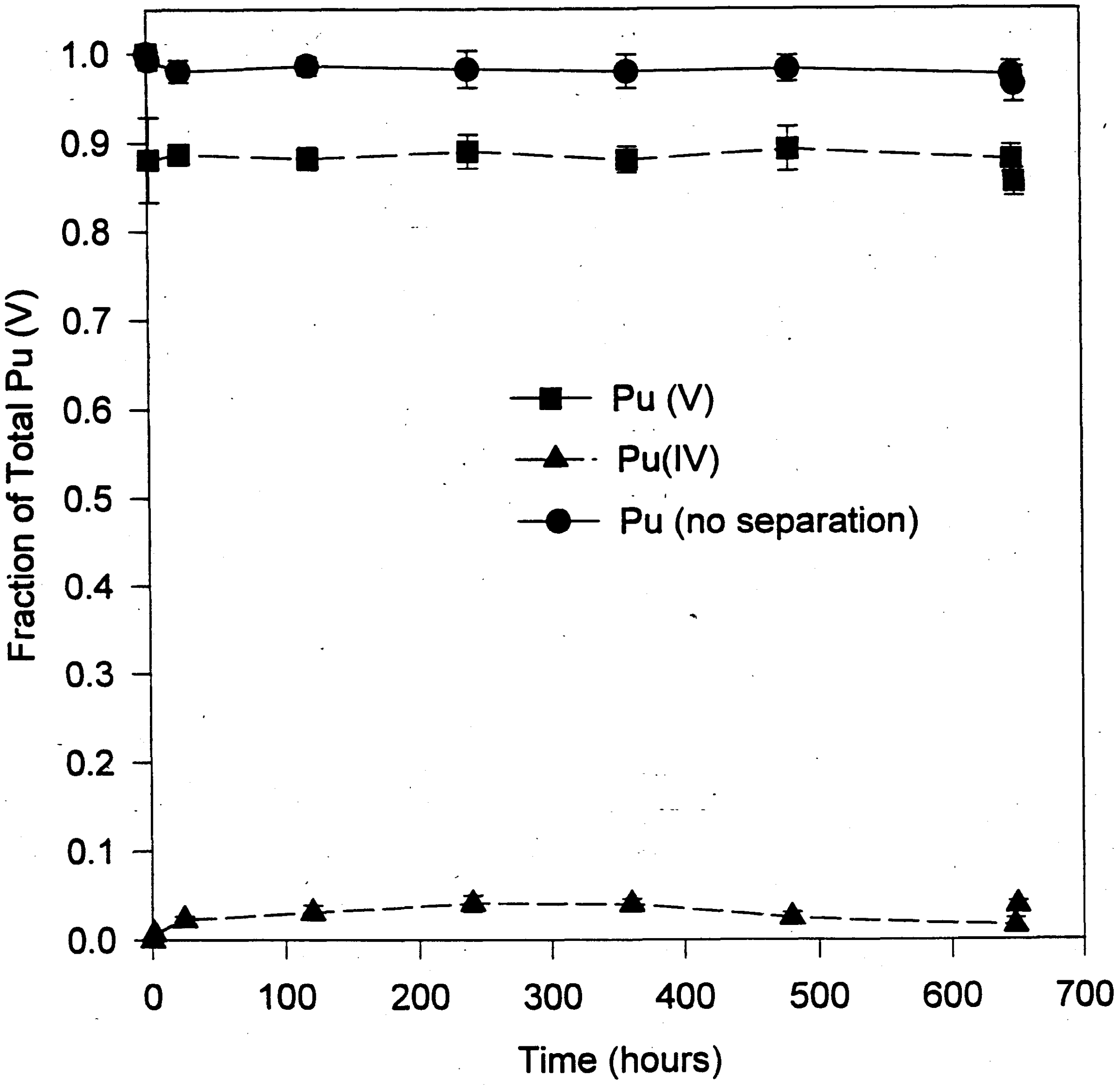
System pH	Separation Method	Pu Speciation Obtained	Reference
4.7	Thenoyltrifluoracetone Extraction	Pu(other) - Extracted Pu(V) - Aqueous	Bertrand & Choppin1982 Kobashi et al 1988
8.2	Dibenzoylmethane Extraction	Pu (IV) - Extracted Pu (V, VI) Aqueous	Saito & Choppin 1983 Kobashi et al 1988
8.2	Silicon Dioxide Sorption	Pu (V) - Solution Pu (VI) - Sorbed	Orlandini et al 1986 Kobashi et al 1988
8.2	Calcium Carbonate Sorption	Pu (V) - Sorbed Pu (VI) - Solution	Orlandini et al 1986 Kobashi et al 1988
10	Buffer to pH 8.2 Dibenzoylmethane Extraction	Pu (IV) - Extracted Pu (V, VI) Aqueous	Saito & Choppin 1983 Kobashi et al 1988

Results and Discussion

Initially data for Pu(V) addition to a range of NaCl solutions of varying pH and ionic strength were obtained. It should be noted that these experiments were run in the dark as plutonium has been observed to be photochemically active (e.g. McCubbin & Leonard 1997; Choppin 1990; Choppin & Kobashi 1990). The experiments were run for approximately three weeks to ensure that any slow reduction of Pu(V) which occurred may be observed.

Data for a 0.7m NaCl, pH 8.2 system which underwent a thenoyltrifluroacetone extraction by buffering the solution phase to pH 4.7 immediately prior to separation (Table' 1) is included in Figure 1. The long term stability of Pu(V) in this system is clearly illustrated with 88.1 ± 1.2% of the total plutonium remaining unextracted in the aqueous phase as Pu(V). In contrast the organic phase defined as the Pu (IV) fraction is more variable with 2.7 ± 1.2% of the plutonium being extracted from the aqueous phase. The variability in Pu (IV) concentration with time is probably a fuction of the low count rates associated with these samples rather than a true

Figure 1 - 0.7m NaCl, pcH 8.2, TTA Separation, Pu (V) - 3 repeats



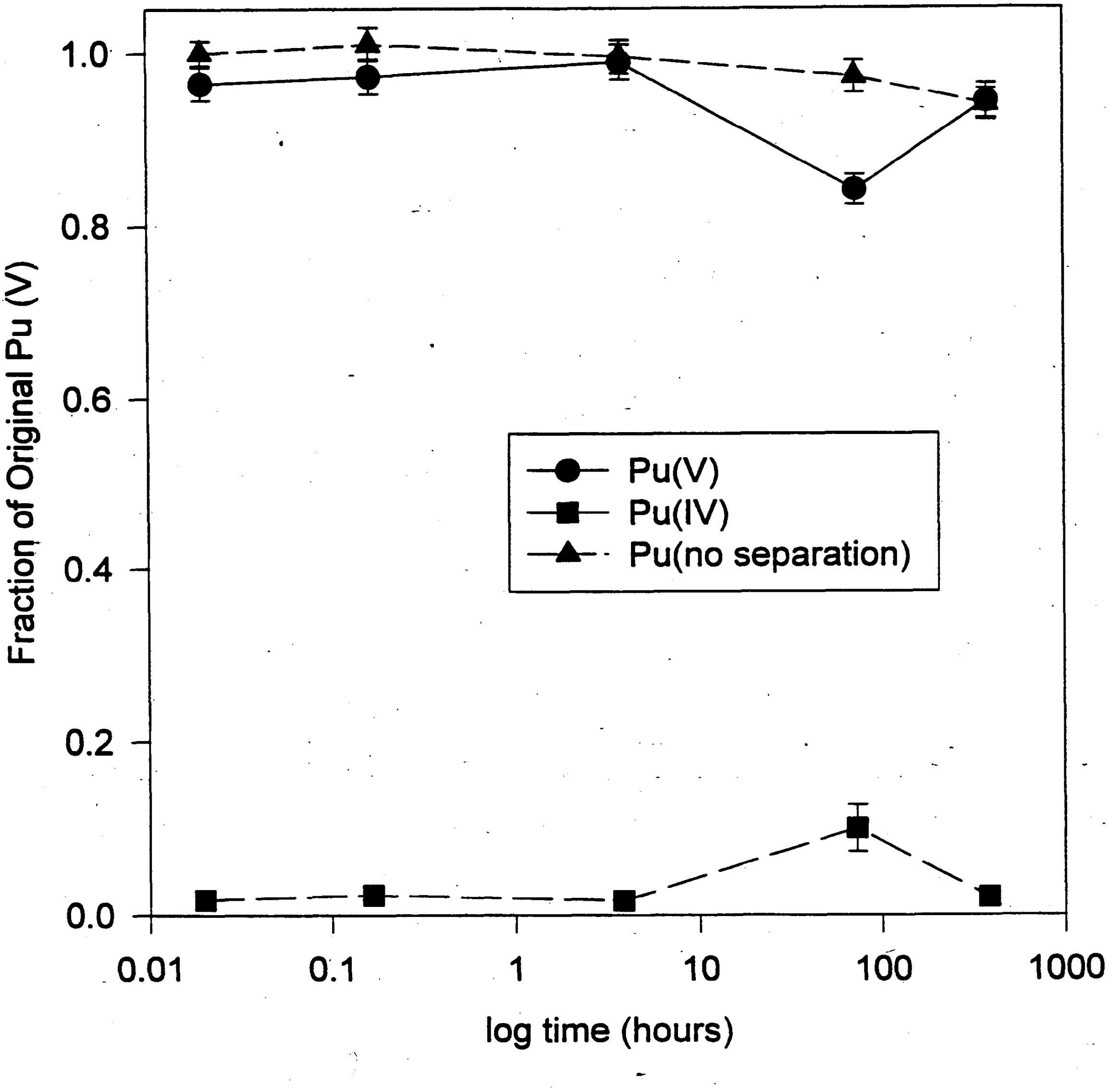
reflection of variations in the Pu (IV) concentration.

It should be noted that the organic phase from a TTA extraction at pH 4.5 -5.0 contains all other plutonium species except Pu (V) (Kobashi et al 1988). However, dibenzoylmethane extractions run at the same pH and ionic strength had already shown that all the plutonium was present as Pu (IV,V) species in the unextracted phase (see Table 1). Therefore, the TTA extraction run on pH 8.2 samples which were buffered to pH 4.7 immediately prior to extraction allowed Pu (V) and Pu (IV) to be independently identified. The data for systems run at pH 4.7 and 8.2, and I = 0.1,0.7 and 3.0 m NaCl using combinations of TTA and DBM extractions show a similar pattern to that in Figure 1 in that Pu (V) remains as the dominant species in solution over a period of weeks.

In addition to the experiments run in the absence of redox agents, a number of scoping experiments have been carried out examining the effect on Pu (V) speciation of the redox active agents hydrogen peroxide, sodium hypochlorite and light. Data for the addition of hydrogen peroxide to Pu (V) in a 0.7 m NaCl, pH 8.2 system kept in the dark are illustrated in Figure 2. The level of hydrogen peroxide in this experiment was 1 x 10^{-5} M, a concentration that is at the higher limit of peroxide concentrations found in seawater (Zika et al 1985). The data show no significant difference to the system in the absence of any redox active agents (Figure 1) with 94.2 ± 6.8% of the Pu present as Pu (V) and 3.6 ± 3.6% as Pu (IV). This suggests that, for similar pH and ionic strength systems, hydrogen peroxide will not have a significant effect on Pu (V) redox chemistry.

Data for Pu (V), 0.7 m NaCl, pH 8.2 systems which have been exposed to light (both U.V. and artificial sunlight) and hypochlorite show little or no change from the pattern seen for Pu (V) in the dark, and in the absence of redox agents (Figure 1). There is no dramatic change in the redox speciation of Pu (V) in these systems at shorter time points, and little if any discernable difference in the prevalence of the Pu (V) species at longer time points. Preliminary data for pH 4.7 systems in the presence of peroxide and hypochlorite also show little or no change in plutonium speciation after addition of hydrogen peroxide or exposure to light.

Figure 2 - 0.7m NaCl, pHc 8.2, TTA Separation, Pu(V) - 2 repeats
NO ILLUMINATION, 1 x 10^{-5} M H_2O_2



Summary and Future Work

Experimental observations show that Pu (V) remains as the stable state of plutonium in NaCl solutions for a number of weeks in the absence of light at I = 0.7 m NaCl and pH 4.7 and 8.2. In addition, initial experiments assessing the-effect of redox agents hypochlorite, hydrogen peroxide and light show little or no effect in altering the plutonium oxidation state in solution.

Future work includes examining pH 10 systems, initially at I = 0.7 m NaCl, to assess the stability of Pu(V) in the absence and the presence of hydrogen peroxide, hypochlorite and light. Indeed, Choppin (199 1) suggests that in neutral brine solutions Pu (VI) may be the more stable plutonium species. As little work has been reported in the literature for pH 10 systems, a number of areas must be addressed before scoping experiments can begin. These include selection of an appropriate buffer. For redox speciation studies it is neccesary to choose a buffer with minimal tendancy to form complexes and to change the oxidation states of the actinide ions (Saito & Choppin 1983). CAPS0 (3-[Cyclohexylamino]-2-hydroxy-l-propanesulphonic acid) has been identified as an appropriate buffer to undergo testing. In addition, none of the reported Pu separation methods can be directly applied to solutions at pH 10. It is necessary to alter the pH to either 8.2 (for DBM and sorption separations) or 4.7 (for TTA separation) before the system can undergo redox separation (Figure 1). Again this area is being examined to chose the least invasive method of separation. One final experimental consideration is the effect of carbonate on both pH 8.2 and pH 10 systems. Indeed, the presence of carbonate in solutions has been shown to alter the charge and composition of actinide ions in (neutral) solution (Clark et al 1995). Future work therefore includes undertaking carbonate controlled experiments for the pH 8.2 and 10 systems.

Another area of interest is the effect of high ionic strength on the redox speciation of plutonium Current Pu oxidation state separation methods were adapted from studies focusing primarily on fast oxidation state separation in seawaters (i.e. pH 8.0, 0.7m NaCl). In order to assess the behaviour of these extractions at higher ionic strengths, a series of experiments using oxidation state analogues U (VI) and Np (V) undergoing both DBM and TTA extractions and $CaCO_3$ and SiO_2 sorption separations in brine solutions will be performed. The separation methods will be performed at ionic strengths of 0.lm and 3.0m NaCl, and at pH 4.7, 8.2 and 10.

This will examine the efficiency of these separation methods under such ionic strength conditions.

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Oxidation of Plutonium in Basic Media

Introduction

One aspect of the project which has begun involves the synthesis and characterization of, MnO_2. For this study, vital information was gathered from the work of Keeney-Kennicutt and Morse (1985) who studied the adsorption of Pu (V) on one form of MnO_2. The effects of time, solid to solution ratios, ionic strength (indirectly), and other factors not necessarily relevant here were studied. These authors used solutions which initially were Pu (V); however, under some conditions, they found three oxidation states present-IV, V, VI. Based on this information, a mixture of all three oxidation states may be present in these studies. They also found, that upon adsorption to the surface of the MnO_2, Pu (V) was converted to a mixture of Pu (VI) and Pu (IV). Although variations in ionic strength were not explicitly studied, they compared solutions of deionized water and seawater; in solutions of seawater, adsorption to the surface was less than that in distilled water. A majority of adsorption occured within the first 2 hours, but that adsorption was not complete, or; in some cases, did not reach equilibrium until as much as 10 days.

For natural water systems, where sodium chloride is present, radiolysis reactions lead to the production of HClO. Radiolysis of the water present in these systems leads to the formation of various radicals and ions according to the equation from Büppelmann et al. (1988):

$$H_2O \rightarrow e^-_{aq}\ ,\ OH^{\cdot}\ ,\ H^{\cdot}\ ,\ H_2O_2\ ,\ H_2\ ,\ H^+ \qquad (1)$$

In addition to the formation of hydrogen peroxide (which is a significant oxidant), other significant radicals are formed. Reactions of the type given by Magirius et al. (1985) then become factors in the determination of the preferred oxidation state of plutonium in these systems.

$$OH^{\cdot} + Cl^- \rightleftharpoons Cl^{\cdot} + OH^- \qquad (2)$$

$$2\ Cl^{\cdot} + H_2O \rightarrow H^+ + Cl^- + HClO \qquad (3)$$

Dissociation of HClO may lead to the formation of ClO^- with both species being strong oxidizing agents. Such reactions then lead to changesin plutonium oxidation state due to the presence of the oxidants HClO, ClO^- and H_2O_2. Therefore, studies of the effect of both NaOCl and H_2O_2 are essential.

Experimental

The equation for the preparation of MnO_2 by the oxidation of manganous ion by permanganate is:

$$3\ Mn^{2+} + 2\ MnO_4^- + 2\ H_2O \rightarrow 5\ MnO_2 + 4\ H^+ \tag{4}$$

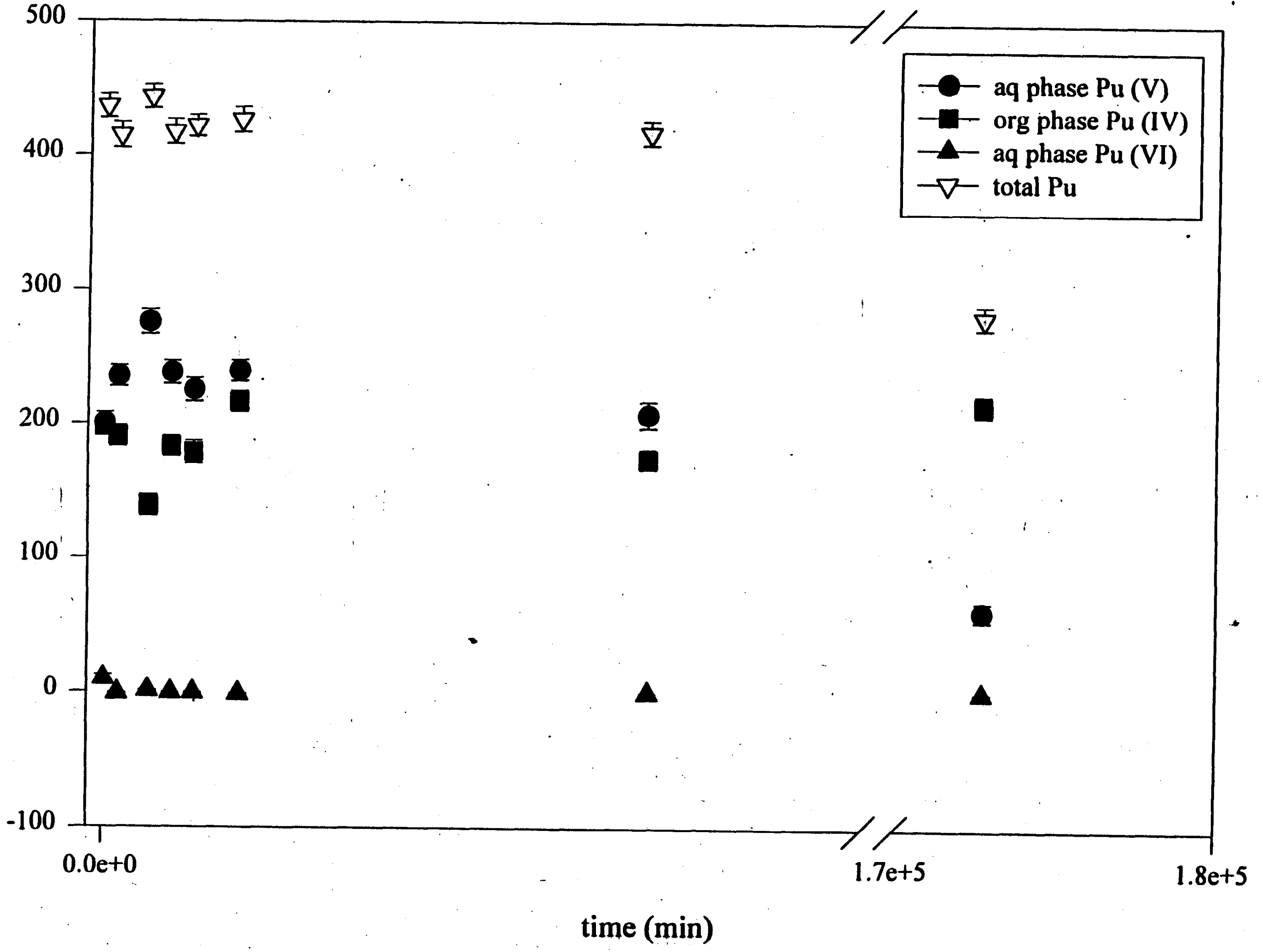
For these. experiments multiple batches were combined into one stock solution which was then used for experimentation. For characterization, the sample's surface area and Mn:O ratio was to be measured. The surface area measurements involved dehydration, rehydration and, finally, dehydration of the sample prior to measurement of the BET surface area. The sample was placed on a Micromeritics® ASAP 2010 and the BET surface area of 170.1292 ± 1.0880 m^2/g was measured. The Mn:O ratio will be measured using atomic emission spectroscopy since atomic absorption spectroscopy is not possible as the light source available is not of the proper wavelength.

Initial experiments to study oxidation state changes to plutonium induced by NaOCl have been performed. A buffered stock solution, containing sodium acetate as the buffer, was used as the solvent to prepare a new solution for each batch run containing the appropriate amount of NaCl to achieve the desired ionic strength. In the initial study this was 0.7 m. The pH was then adjusted to 4.7 (using either NaOH or HCl). To this solution was added the Pu spike to achieve a final Pu concentration of 1 x 10^{-10} M. An initial time point, t_0, was taken. Following this time point, the analyte being studied, NaOCl, was added to a final concentration of 1 x 10^{-3} M. For each time point, 600 µL of the Pu solution was removed and placed directly in a vial for counting for mass balance. An additional 2.0 mL of solution was placed in a vial for solvent extraction. For solvent extraction, a 2.0 mL aliquot of 0.50 M thenoyl-trifluor-acetone (TTA) in cyclohexane was added; the vial was shaken for 5 minutes followed by 1 minute of centrifugation. After separation of the two phases by centrifugation, 600 µL of the aqueous phase was removed and placed in a vial for counting; 400 µL of the aqueous phase was removedand placed in a tube for pH measurement. From this same solution, 1.5 mL of organic phase was removed and placed into a vial containing 1.5 mL aqueous solution (0.7 m, pH < 1); the vial was shaken for 5 minutes, followed by 1 minute of centrifugation. After separation of these two phases by centrifugation, 600 µL of the organic phase and 600 µL of the aqueous phase were removed and placed in a vial for countingl; 400 µL of the aqueous phase was removed and placed in a tube for **pH** measurement. The first sample was taken one minute after addition of NaOCI. Additional time points of 10, 30, 45, 60, and 90 minutes, 3, and 48 hours were taken.

Results and Discussion

The results of the experiment to determine the effect of 1 x 10^{-3} M NaOCl on Pu (IV) in 0.7 m NaCl at pH 4.7 are given below. The activities obtained for the various time points, for the mass balance and for the 3 phases or oxidation states, are given graphically in Figure 1. This figure shows that there is no significant amount of Pu (VI) present, even after 48 hours of contact with the NaOCl: However, the predominant oxidation state of the remaining plutonium is uncertain. Approximately 90% of the plutonium present in the mass balance is accounted for as being either in the (IV) or (V) oxidation state. There appears to be an initial increase in the Pu(V) concentration followed by a decrease in the Pu (V) concentration over the time period studied. However, this is somewhat unexpected. Plutonium is initially added to the system in the (IV) oxidation state. The t_0 time point, where the plutonium is present in a pH 4.7 solution with 0.7 m NaCl, indicates that approximately half of the plutonium is quickly oxidized to Pu (V). There is also a slight increase in concentration up to 10 min. This increase in concentration of Pu(V) is most likely explained by the fact that Pu(V) is the favored oxidation state of 0.7 m ionic strength solutions (sea water). Following addition of NaOCl, a portion of that Pu (V) is then reduced to Pu (IV) between 3 and 48 hours.

Figure 1
1 x 10^{-3} NaOCl
pH 4.7, 0.7 m NaCl, 1 x 10^{-10} Pu



Future Work

Characterization of the MnO_2 will be continued. Briefly, the experiments with MnO_2 will involve the studying of variations of pH, I and time. The pH's to be studied initially will be: 4.7, 8, and 10. The ionic strengths studied at each pH will initially be 0.1, 0.7 m NaCl. Time intervals of 15 min, 30 min, 45 min, 60 min, 90 min, 120 min, 3h, 6h, and 1, 2, 3, 4, 5, 6, 7, and 8 days will be studied. Initially, a 5.0 m^2/ L solution of MnO_2 will be prepared at a pH of 4.7 with sodium acetate buffer and 0.7 m NaCl. To this solution will be added a spike of Pu-238 to give a final Pu concentration of 10^{-10} M (~9000 cpm in 10 mL sample). The pH of 4.7 was chosen based on the separation technique described by Bertrand and Choppin (1982) in which various oxidation states of Pu were separated by solvent extraction using TTA. The ionic strength chosen is arbitrary and serves as a good starting point. This study-will be basically done as follows. The experiments will be done in batches to allow for time studies. Sixteen samples will be prepared at the same time, using the same procedure to prepare the MnO_2 solution. The same stock solution of Pu (IV) spike will be used. After adding the spike, the vial will be shaken for the allotted time to allow for oxidation/adsorption. The solid will then be removed from the solution by centrifuging the sample and decanting the supernatant. The solid will be diluted in a solution of the same ionic strength and pH to desorb the Pu for determining the oxidation state and the amount of Pu. This will immediately be centrifuged and the supernatant removed. This solution along with the previous supernatant solution will then be subjected to solvent extraction. The extraction procedure will follow that described previously.

It may also be worthwhile to study various solid to solution ratios. Keeney-Kennicutt and Morse found that at solid:solution ratios of 100 m^2/L, the amount of time for adsorption varied (with a general decrease in the amount of time for adsorption for higher ratios for the initial adsorption of Pu) as well as the oxidation states adsorbed. They also found that increasing ionic strength caused an adverse reaction in the amount of Pu adsorbed. This means that it may not be useful to do studies with ionic strength greater than 0.7 m NaCl.

Studies of the effect of H_20_2 on Pu (III) and Pu(IV) will be done along with continuing the NaOCl studies and will be carried out like the NaOCl studies already begun. The variables studied will be pH, I, and time. The pH's to be studied initially will be: 4.7, 8, and 10. The ionic strengths studied at each pH will be: 0.1,0.7, and perhaps 10 m NaCl. Time intervals of 15 min, 30 min, 45 min, 60 min, 90 min, 120 min, 3 h, and 6 h, and continuing to 1, 2, 3, 4, 5, 6, 7, and 8 days as warranted.

Dr. Amy E. Irwin

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