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TITLE FORMATION, CHARACTERIZATION, AND STABILITY OF PLUTONIUM(IV) COLLOID: A PROGRESS REPORT

AUTHOR(S) David E. Hobart, David E. Morris, Phillip D. Palmer and Thomas W. Newton

Nuclear and Radiochemistry Group (INC-11)
Isotope and Nuclear Chemistry Division
Los Alamos National Laboratory

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FORMATION, CHARACTERIZATION, AND STABILITY OF PLUTONIUM(IV) COLLOID: A PROGRESS REPORT*

D. E. Hobart, D. E. Morris, P. D. Palmer,
and T. W. Newton

Isotope and Nuclear Chemistry Division
Los Alamos National Laboratory
Los Alamos, New Mexico, 87545 USA

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FORMATION, CHARACTERIZATION, AND STABILITY OF PLUTONIUM(IV) COLLOID: A PROGRESS REPORT

D. E. HOBART, D. E. MORRIS, P. D. PALMER, and T. W. NEWTON*
Isotope and Nuclear Chemistry Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545 USA
(505) 667-9313

ABSTRACT

Plutonium is expected to be a major component of the waste element package in any high-level nuclear waste repository. Plutonium(IV) is known to form colloids under chemical conditions similar to those found in typical groundwaters. In the event of a breach of a repository, these colloids represent a source of radionuclide transport to the far-field environment, in parallel with the transport of dissolved waste element species. In addition, the colloids may decompose or disaggregate into soluble ionic species. Thus, colloids represent an additional term in determining waste element solubility limits. A thorough characterization of the physical and chemical properties of these colloids under relevant conditions is essential to assess the concentration limits and transport mechanisms for the waste elements at the proposed Yucca Mountain Repository site. This report is concerned primarily with recent results obtained by the Yucca Mountain Project (YMP) Solubility Determination Task (WBS 1.2.3.4.1.4.A) pertaining to the characterization of the structural and chemical properties of Pu(IV) colloid. Important results will be presented which provides further evidence that colloidal plutonium(IV) is structurally similar to plutonium dioxide and that colloidal plutonium(IV) is electrochemically reactive.

INTRODUCTION

It has long been known that aqueous Pu(IV) forms colloids under appropriate chemical conditions.[1] This material is often called "polymeric" Pu(IV), but colloid or colloidal is the preferable label so as not to imply necessarily that the material has a chain like structure. The colloid can form solution like *sols* that are optically clear, display a characteristic absorption spectrum, and do not settle out on long standing.[1-4] In noncomplexing acid solutions with concentrations greater than about 0.05 M, Pu(IV) is predominantly aquated Pu^{4+}. This highly charged ion hydrolyzes readily. In 0.05 M acid and unit ionic strength, $Pu(OH)^{3+}$ and Pu^{4+} have about equal concentrations. At lower acid concentrations further hydrolysis is expected, giving the ions $Pu(OH)_2^{2+}$, $Pu(OH)_3^{+}$ and neutral species such as $Pu(OH)_4^0$. Formation constants have been estimated for these species,[4] but measurements have been made only for the $Pu(OH)^{3+}$ species.[5] An important reason for this lack of data is that colloidal Pu(IV) forms quite rapidly in the pH region where the more highly hydrolyzed species can be studied. In addition, aqueous Pu(IV) is unstable with respect to Pu(III) and Pu(V) as shown, for example, in the oxidation state stability field diagram published by Allard et al.[6]

Pu(IV)-colloid is of particular interest in nuclear waste management because it is one of the dominant forms of plutonium under chemical conditions similar to those found in the environment. There is an interest in this material with regard to its formation in process streams and in its utilization in the production of nuclear fuel elements by *sol-gel* processes.[7] We are currently involved in an ongoing program to investigate the formation and stability of Pu(IV)-colloid and to characterize the chemical and physical properties of the colloid. In this report, some recent results are discussed pertaining to the chemical and structural characterization of Pu(IV) colloid using electronic absorption and diffuse reflectance spectroscopies and electrochemical and redox titrametric methods.

One of the most important, yet relatively unexplored, aspects in the chemical characterization of Pu(IV) colloid is the determination of the structure of the colloid. Several direct structural probes have been utilized. However, in the published structural studies,[2,3] it has been necessary for experimental reasons to examine the Pu(IV) colloid in a dried form

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* Guest scientist of the Isotope and Nuclear Chemistry Division

Recently, attempts have been made in our laboratories to deduce structural information for Pu(IV)-colloid *suspended in solution* utilizing electronic spectroscopy as a probe by comparing spectral data for the colloid with that obtained for other Pu(IV) complexes.

Information on the redox reactivity of Pu(IV) colloid, i.e., the potentials at which oxidation and reduction occur and the rates and mechanisms of these processes, is of fundamental importance to the characterization of this species because redox reactions may represent viable mechanisms of colloid degradation to give dissolved ionic species with enhanced environmental mobility. Further, results relating to redox reactivity will be of great value in defining the general reactivity patterns for the colloid so that other pertinent chemical kinetic phenomena can be interpreted more readily. Finally, it may be possible to utilize voltammetric redox techniques to obtain results relating to the physical properties of the colloid. Such data would be useful to corroborate the results obtained using other techniques.

EXPERIMENTAL

Colloidal sols of Pu(IV) and the solid complexes $Pu(C_2O_4)_2 \cdot 6H_2O$ and $Pu(SO_4)_2 \cdot 4H_2O$ were prepared and purified according to standard procedures described in detail elsewhere.[8] Samples of high-fired PuO_2 were obtained from the Materials and Science Technology Division of Los Alamos National Laboratory. The PuF_4 sample was generously provided by J. D. Farr of Los Alamos National Laboratory. The electronic spectroscopic studies were carried out using a Varian Cary Model 17D UV-Vis-NIR spectrophotometer. For the colloidal sols, the instrument was operated in the standard absorption mode. However, because of the insolubility of PuO_2 and $Pu(C_2O_4)_2$ and the opacity of these materials as finely divided solids, it was necessary to obtain the electronic spectra for these samples using diffuse reflectance methods. The electronic spectra of PuF_4 and $Pu(SO_4)_2$ were also obtained by diffuse reflectance. The custom designed diffuse reflectance attachment for the Varian Cary spectrophotometer was obtained on loan from Dr. Jack Young of the Analytical Chemistry Division of Oak Ridge National Laboratory. With the reflectance apparatus in place, the instrument was operated in the usual double beam absorption mode. Neutral density screen filters were placed in the reference beam of the spectrophotometer and the absorbance was adjusted electronically as necessary to keep the signal output within the absorbance range of the instrument.

The voltammetric investigations of Pu(IV) colloid were conducted in a microvolume electrolysis cell described in detail elsewhere.[9] The bulk electrolysis studies were done in either a long path-length spectroelectrochemical cell or a standard three-electrode electrolysis cell. Working electrodes were fabricated from platinum for the oxidation studies and mercury for the reduction studies. These experiments were controlled with an EG&G Princeton Applied Research Corporation Model 273 Potentiostat interfaced to an IBM PC/AT using the HEADSTART software package or with a Model 173 Potentiostat and Model 175 Universal Programmer. Titrimetric investigations were monitored spectrophotometrically using the Cary Model 17D in the standard absorption mode.

RESULTS AND DISCUSSION

A. Spectroscopic Characterization

When the electronic absorption spectrum of Pu(IV) colloid is compared with that obtained for the aquated Pu^{4+} ion (Figure 1), it is clear that there are numerous differences between these spectra.

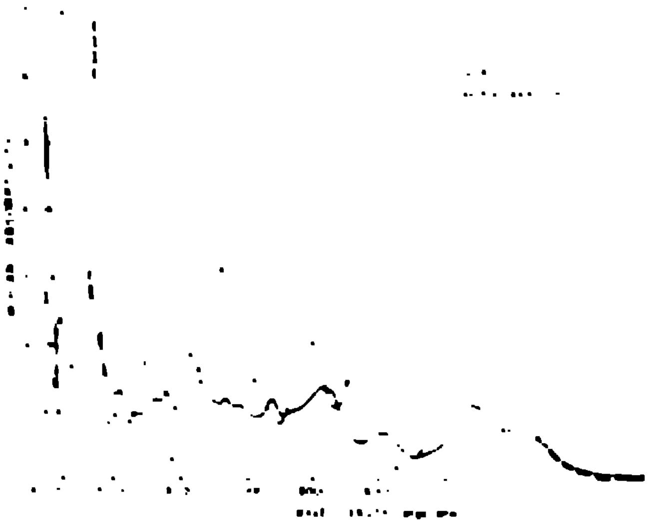

FIGURE 1. ABSORPTION SPECTRA OF AQUEOUS Pu(IV) AND Pu(IV) COLLOIDAL SOL

This suggests that there are significant differences in the environments of these two tetravalent plutonium species. In particular, the most prominent visible absorption bands for Pu(IV) colloid occur at [illegible], 615, and 740 nm, whereas the major visible absorption bands for aquated Pu^{4+} are at 4[illegible], 660 and [illegible] nm. In contrast to these major differences between the spectra for the colloid and aquated Pu^{4+}, the band maxima for Pu(IV) colloid are *strongly correlated* with the band maxima in the diffuse reflectance spectrum of high-fired PuO_2 in the visible and near-IR spectral regions (Figure [illegible]

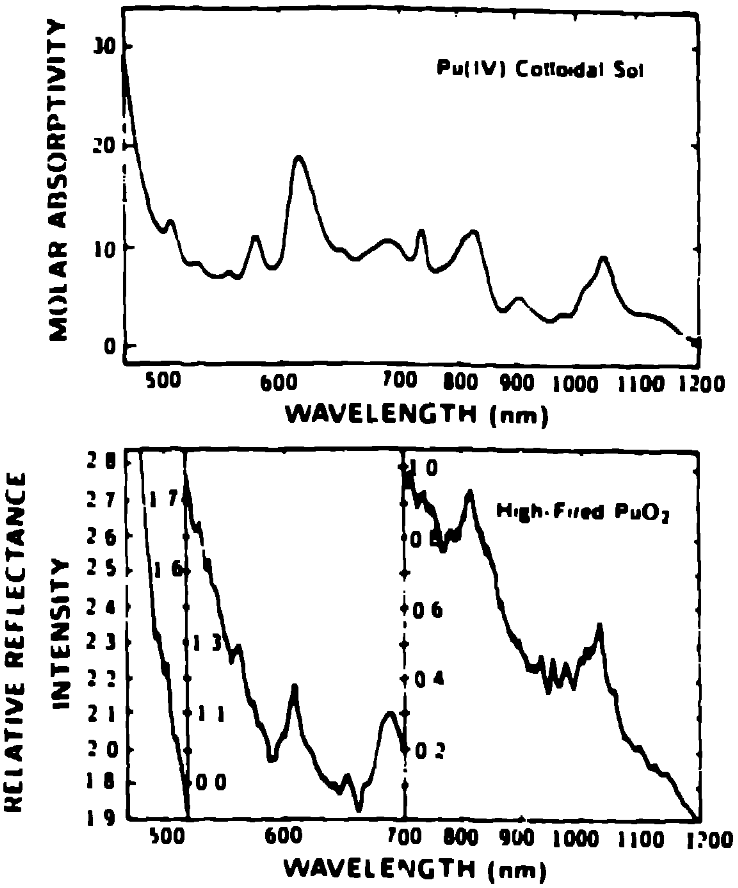

FIGURE 2 ABSORPTION SPECTRUM OF Pu(IV) COLLOIDAL SOL AND DIFFUSE REFLECTANCE SPECTRUM OF HIGH FIRED PLUTONIUM DIOXIDE

It should be emphasized that diffuse reflectance spectroscopy provides the same information as absorption spectroscopy with respect to the energies of the transitions between energy levels in the analyte. Thus, the *locations of the bands* in the UV visible near infrared spectral region arising from electronic transitions are expected to be the same for any given sample whether determined by absorption spectroscopy or diffuse reflectance spectroscopy. However, the mechanisms that determine the *intensities* in these spectral bands are quite different for diffuse reflectance than for absorption. Therefore, there will be no discussion of intensities in this report.

The number of bands in the electronic spectrum of an actinide complex and the positions of the band maxima depend to a large extent on the environment of the actinide ion. For this reason, electronic spectroscopy can be used as a sensitive structural probe. Tetravalent plutonium has a ground state electronic configuration [Radon core] $5f^4$ and the electronic spectrum of this ion is dominated by f-f transitions. In the free ion case (i.e. no complexation of Pu(IV)), these transitions are strictly parity forbidden. Similarly, for complexed Pu(IV) in a sufficiently high symmetry environment, the electronic transitions from the ground vibrational level of the ground electronic state to the ground vibrational level of the excited electronic state (the so called electronic origin transitions) will also be forbidden. In this case the observed spectral bands (neglecting any crystal field splittings) are due to transitions to other excited vibrational levels in the excited electronic state or from other excited vibrational levels of the ground electronic state. Such transitions are referred to as vibronic transitions. For Pu(IV) in a low symmetry environment, the electronic spectrum can contain both electronic origin transitions and vibronic transitions.

A thorough interpretation of the electronic spectra of Pu(IV) complexes would require a complete group theoretical treatment and additional experimental data. Such a treatment is beyond the scope of the present work. However, the implication of the above discussion is that significant differences in the electronic spectra of Pu(IV) complexes are expected if the complexes have different site symmetry for the Pu(IV) ion and/or if they have different vibrational energy level spacings, as would result from different complexing ligands or differing bond strengths for bonds to the same ligand.

The diffuse reflectance spectra of the other Pu(IV) complexes, which possess various symmetries and differing vibrational energies, were obtained to explore further this correlation between the electronic spectra and the structure in Pu(IV) complexes. The crystallographic symmetry of the oxide complex is face-centered cubic, that of the oxalate complex is triclinic and that of the sulfate complex is orthorhombic. The symmetry of the fluoride complex depends on the hydration number and is unknown for the sample employed in this study. However, it is most likely the anhydrous salt which is monoclinic. It should be emphasized that the site symmetry of the Pu(IV) ion in these complexes is not necessarily the same as the crystallographic symmetry, but the crystallographic symmetry is a useful initial point for comparison. The spectra of these complexes are shown in Figures 3 and 4 with the spectrum of PuO_2 serving as a reference for comparison. These spectral data clearly reveal the variations in the electronic spectra that result from differences in the symmetry environment and vibrational energies.

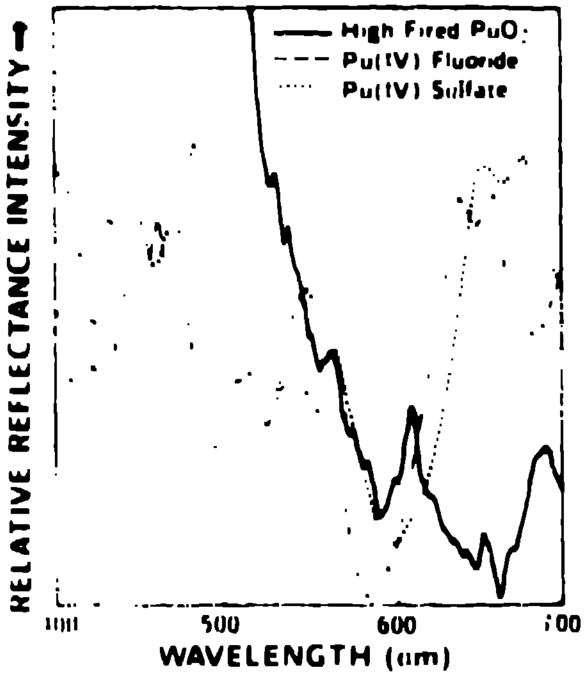

FIGURE 3 DIFFUSE REFLECTANCE SPECTRA OF PLUTONIUM DIOXIDE, Pu(IV) FLUORIDE AND Pu(IV) SULFATE

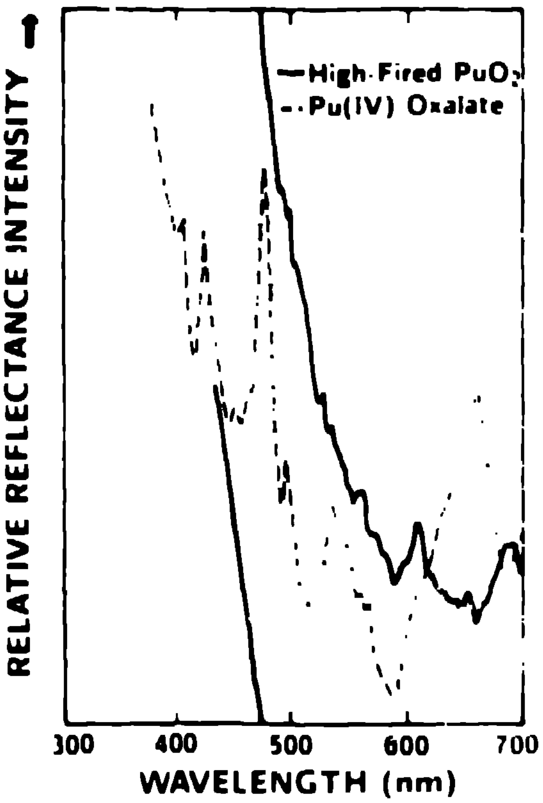

FIGURE 4 DIFFUSE REFLECTANCE SPECTRA OF PLUTONIUM DIOXIDE AND Pu(IV) OXALATE

The excellent correlation between the spectrum of Pu(IV) colloid and that of high fired plutonium dioxide (Fig. 2) can be compared to the variations between the spectra shown in Figures 3 and 4. This large degree of coincidence between the colloid spectrum and the oxide spectrum is strong evidence that the structure of the colloid is very similar to that of high fired PuO_2. This conclusion has been suggested previously by others on the basis of x-ray[1] and electron[2] diffraction studies. Furthermore, because high fired PuO_2 is a high symmetry complex, the observed electronic bands are predominantly due to vibronic transitions. This implies that conclusions regarding the structural similarity of the colloid and PuO_2 can be extended to include similarities in the vibrational energies in addition to similarities in the site symmetry of the Pu(IV) ion. This conclusion is also supported by previous infrared spectral studies wherein it was shown that the two prominent vibrational modes of PuO_2 are also seen at the same energy in the colloid.[10] Thus, these electronic spectral results indicate that Pu(IV) colloid, when suspended in solutions, is structurally quite similar to solid high fired PuO_2.

A photoacoustic spectrum of PuO_2 has been published by Heinrich et al.,[11] however, it lacks sufficient resolution and detail to allow observation of its resemblance to the spectrum of Pu(IV) colloid.

B Electrochemical Characterization

The electrochemical behavior of *dissolved* plutonium in its four readily accessible oxidation states is well characterized[12] and can be interpreted within the framework of existing simple theories of solution phase thermodynamics and kinetics. In contrast, there are very few reports concerning the application of electrochemical methods to the study of Pu(IV) colloid. Presumably, this paucity of data can be attributed in large part to the inherent complexity in investigating redox reactivity in distinctly heterogeneous media such as colloidal suspensions. Despite the anticipated complexity in the redox reactions of Pu(IV) colloid, the dominant electrochemical processes are still expected to be reduction to a dissolved Pu(III) species and oxidation to a dissolved Pu(VI)O_2^{2+} species. This latter process may also involve a Pu(V) species as an intermediate.

The initial experiments were designed to test these hypotheses. To determine the product of the reduction of Pu(IV) colloid, Zn(Hg) amalgam, with a potential of −0.76 V versus the normal hydrogen electrode (NHE), was chosen as a reducing agent. Using a specially designed spectroelectrochemical cell,[7] a solution of Pu(IV) colloidal suspension in dilute perchloric acid was stirred in the presence of excess Zn(Hg). The course of the reaction was monitored spectrophotometrically by detecting the diminution of the spectrum of Pu(IV) colloid and the growth of the spectrum of the reduction product. The product spectrum was readily identified as that of dissolved aquated Pu^{3+}. This reduction reaction was determined to follow simple first order kinetics with a half time of ~40 min. In a related experiment, the Zn(Hg) amalgam was replaced with a potentiostatically controlled mercury cathode and the rate of reduction of the colloid was monitored spectrophotometrically as a function of applied potential. In this case, it was determined that a significant reduction rate occurs even at ~ −0.40 V versus NHE. The reaction appears to reach a maximum rate at ~ −0.76 V versus NHE and this rate is maintained at more negative potentials. To determine the product of the oxidation of Pu(IV) colloid, the reaction of a stirred solution of colloid in contact with a potentiostatically controlled platinum gauze anode was studied. Here too, the progress of the reaction was followed spectrophotometrically. In this case, it was found that no significant rate of colloid oxidation takes place until the potential reaches ~ +1.6 V versus NHE. The product of the oxidation was identified as Pu(VI)O_2^{2+}. No Pu(V)O_2^{+} was detected, but the existence of this species as a short lived intermediate in this reaction cannot be excluded because the time scale of the assay was rather long.

Investigations of the oxidation of Pu(IV) colloid by cerium(IV) in perchloric acid were initiated several years ago in our laboratories. The reaction was found to be quite complicated and was not pursued. A recent report of similar studies in nitric acid[14] led to a reinvestigation of these studies. Experiments have now been conducted in both nitric and perchloric acids for several colloid preparations which differ in particle size. The potential of the Ce(IV/III) couple is ~+1.6 V in nitric acid and ~+1.7 V in perchloric acid versus NHE. The course of the oxidation reaction was followed by measuring the spectrophotometric absorbance of the product Pu(VI)O_2^{2+} peak near 830 nm. The results indicate that the initial rate of colloid oxidation is quite fast in all cases with the rate being faster in nitric acid than in perchloric acid. However, the reaction goes to completion only in nitric acid. In perchloric acid, the reaction becomes arrested after between 30 and 70% of the total Pu(IV) has reacted. This variation in the extent of completion appears to depend on particle size, acid concentration, and Ce(IV) concentration in a complicated way. No obvious trends in these reactivity patterns have been determined as yet. Representative kinetic data for these experiments, in the form of a Powell plot, are shown in Figure 5. The open circles are experimental data for a Pu(IV) colloid sample in dilute nitric acid with a most probable particle diameter of 2.1 nm. The filled circles are data for a Pu(IV) colloid sample in dilute perchloric acid with a most probable particle diameter of 25.5 nm. The dashed line is the theoretical curve for a first-order reaction and the solid line is the theoretical curve for a second order

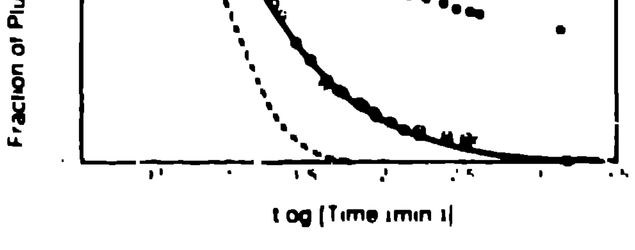

FIGURE 5 POWELL PLOTS FOR THE OXIDATION REACTION OF Ce(IV) WITH Pu(IV) COLLOID

reaction. Note that the data in nitric acid appear to follow theoretical second order kinetic behavior. This is a very surprising result because it suggests that the rate law is second-order in Pu(IV) colloid concentration. A simple mechanism consistent with this finding cannot be formulated. The data from experiments in perchloric acid do not appear to follow any simple rate law. These results are dramatically different from those reported previously[12] in which a first order dependence on colloid concentration was found in nitric acid. The present results also indicate that the small particle-size colloid samples react more rapidly than the large particle-size samples in nitric acid. These studies are continuing in hopes of unraveling these puzzling kinetic phenomena.

The voltammetric studies have used two standard techniques: cyclic voltammetry and chronoamperometry. Both techniques provide a much shorter time scale interrogation of the redox reactions than the methods discussed above. All of these experiments have been done in dilute hydrochloric acid and in the absence of stirring so that diffusion and migration are the only means of delivery of the colloid to the electrode. No oxidative voltammetric activity was detected for Pu(IV) colloid by either technique for applied potentials as positive as +1.6 V versus NHE. This suggests that the rate of colloid oxidation, even at potentials approaching values at which water is oxidized, is quite slow. Reductive voltammetric activity is observed for the colloid by both techniques in the potential range from ~ −0.9 to −1.2 V versus NHE. This voltammetric behavior is distinctly different from the usual behavior exhibited by dissolved species. A series of chronoamperograms as a function of potential is shown in Figure 6. This sample has a most probable particle diameter of 2.1 nm. The potentials for curves 1-4 are −1.20, −1.25, −1.30, and −1.35 V versus a Ag/AgCl reference electrode respectively. Note that these curves exhibit a current peak at times greater than $t=0$ instead of the usual $t^{-1/2}$ decay for $t>0$. This novel behavior may be attributable to the diffusion of a partially reduced colloid particle back to the electrode surface for further reduction.

The chronoamperometric data have been used to construct the current versus potential curves shown in Figure 7. Curve 1 is for a colloid sample with a most probable particle diameter of 2.1 nm and curve 2 is for a sample with a most probable particle diameter of 25.5 nm. These curves show that the rate of Pu(IV) colloid reduction increases as the potential is made more negative as expected. However, the characteristic plateau in these curves at the more negative potentials is not observed. This suggests that the electron transfer step itself is kinetically quite slow.

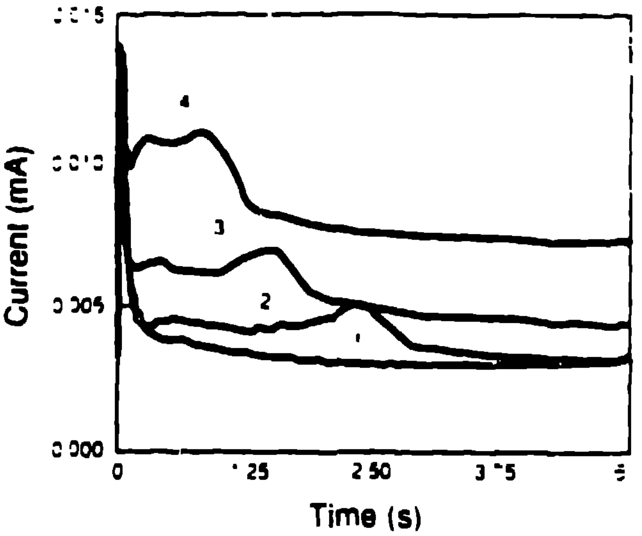

FIGURE 6 CHRONOAMPEROGRAMS FOR THE REDUCTION OF Pu(IV) COLLOID IN DILUTE HYDROCHLORIC ACID AT A MERCURY CATHODE

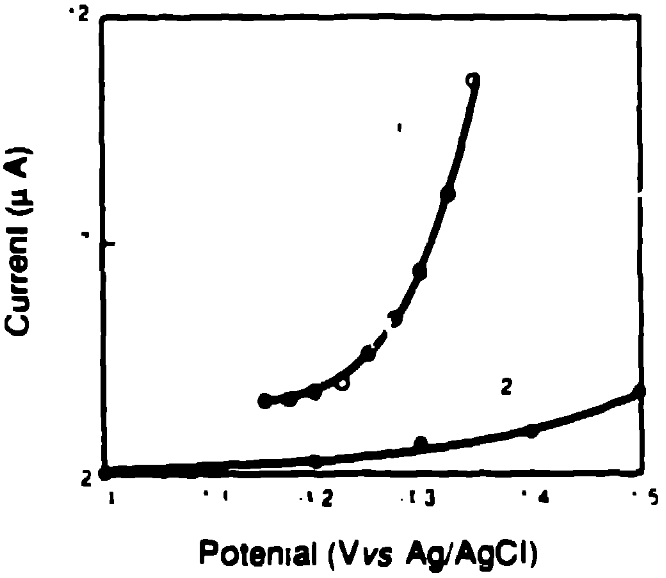

FIGURE 7 CURRENT VOLTAGE CURVES CONSTRUCTED FROM CHRONOAMPEROMETRIC DATA FOR THE REDUCTION OF Pu(IV) COLLOID IN DILUTE HYDROCHLORIC ACID AT A MERCURY ELECTRODE

Further, at any given potential, the rate of reduction of small particle size colloid samples is much greater than that of large particle size samples. This behavior can be attributed in part to the greater diffusivity of the smaller particles.

CONCLUSIONS

Additional structural investigations of Pu(IV) colloid, both suspended in solution and isolated from solution, are planned to support the electronic spectral data presented here. X ray diffraction and absorption methods and Raman spectroscopy will be exploited for these studies. The x ray diffraction and Raman spectroscopic probes will be used to provide specific structural information. The Raman technique will be used to probe the lattice vibrational modes of the colloid in order to gain information on crystallinity and long range order in the colloid. In addition, the Raman spectral results will be used to obtain molecular structural information (e.g., the strength of oxygen bonding to plutonium) for the colloid through examination of the internal vibrational modes. To fully understand both x ray diffraction and Raman spectral results, it will be necessary to examine certain other Pu(IV) model compounds as was done with the electronic spectral results reported here.

The preliminary results pertaining to the redox reactivity of Pu(IV) colloid reveal the anticipated complexity in the reactions of this important species. The potentials at which the colloid is oxidized and reduced are well removed from those for dissolved Pu(IV) and reflect the stability of the colloidal form of Pu(IV). Although these potentials are outside the range expected under normal environmental conditions, oxidation state stabilities of dissolved plutonium species are strongly influenced by coordination to environmentally ubiquitous complexants (such as carbonate ions), and similar effects may exist for colloidal Pu(IV). The unusual kinetic results for the Ce(IV) oxidation reaction and the novel voltammetric behavior for the colloid reduction suggest that particle size and solution composition play strong roles in determining reactivity. The results presented here have merely scratched the surface of this challenging problem and much additional work will be required to gain the necessary understanding of this system.

ACKNOWLEDGEMENTS

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