MASTER**THE RADIOLYTIC OXIDATION AND REDUCTION OF PLUTONIUM**

by

Sherman Fried, Arnold Friedman, J. C. Sullivan

Kenneth Nash, Donald Cohen, and Ruth Sjoblom

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared for

International Symposium

on the

Scientific Basis for Nuclear Waste Management

Materials Research Society

Boston, Massachusetts

November 27-30, 1979

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**Operated under Contract W-31-109-Eng-38 for the
U. S. DEPARTMENT OF ENERGY**

Scientific Basis for Nuclear Waste
Management

Paper to be given at the International
Symposium sponsored by the Materials
Research Society, Boston, Massachusetts
November 27 - 30, 1979

1

THE RADIOLYTIC OXIDATION AND REDUCTION OF PLUTONIUM

Sherman Fried, Arnold Friedman, J. C. Sullivan,
Kenneth Nash, Donald Cohen, and Ruth Sjoblom
Chemistry Division, Argonne National Laboratory,

9700 South Cass Avenue, Argonne, Illinois 60439 U.S.A.

It has been shown on several occasions that all other things being equal, the rate of migration of plutonium through an aquifer is greatly influenced by its oxidation state. It is a reasonable expectation that other actinides exhibiting multiple oxidation states will behave similarly. By and large the more highly charged ions in solution move through rock strata more slowly than those of lesser charge. Thus for comparative experiments on the relative migration rates of Pu(IV) and Am(III) we would expect Pu(III) to move about 10 times faster than Pu(IV)* and it has been shown PuO_2^{2+} moves about 250 times more rapidly than Pu(IV).¹

Since one of the more important parameters of safety assessment is radionuclide migration rate it can be seen that it becomes important to know the oxidation states of radionuclides (actinides for the purpose of this report) existing in possible leachates from the material originally emplaced in a repository.

It was with this in mind that a study of the "intrinsic stability" of plutonium oxidation states in ground water solutions was undertaken. One of the most prominent proposals for a waste repository in WIPP (Waste Isolation Pilot Project) which intends to utilize bedded salt strata as the isolating medium. Ground water in that context is saturated brine and is made up to specifi-

*Americium(III) was used instead of Pu(III) for the comparative experiments because of the difficulty of maintaining Pu(III) in that state in air at pH's of about 5-6. It was felt that the behavior of Am(III) would be sufficiently close to that of Pu(III) to serve as a reasonable stand-in.

cations issued by Sandia Laboratories and designated as "Solution A."

Concomitant with the studies of plutonium oxidation states in "Solution A" parallel studies were made in dilute brines (Copenhagen Seawater) since emplacement of radwastes in seabed sediments is also under consideration (Seabed). Studies were also carried out in distilled water to examine the stability of the oxidation states of plutonium unperturbed by the presence of large concentrations of extraneous ions. Some of these studies have been made under anoxic conditions (to avoid the perturbing effects of oxygen) and others were made in the presence of air since it was not known whether ground water in a WIPP-type repository will contain oxygen or not. In the case of Seabed, bottom waters in some areas of the oceans may contain amounts of oxygen in solution corresponding to 10% of that of surface waters and in other areas, e.g., the Black Sea, the water contains no free oxygen. In some cases the pH was controlled and in others it was allowed to vary as plutonium was converted from one oxidation state to another. It should be made clear that the latter case (of uncontrolled pH) was not one of choice but rather was imposed upon the experiment by virtue of the fact that some of the reaction vessels were sealed in vacuo and it was not possible to monitor the pH without losing the integrity of the experiment.

The plutonium solutions employed were relatively concentrated, approximately 0.02 M. This high concentration enabled the determination of the oxidation state by spectrophotometric observation of optical adsorption peaks corresponding to a specific oxidation state. Monitoring the progress of the change in oxidation state was accomplished by repeated spectrophotometric observations.

Plutonium was prepared in pure oxidation states as the chloride. Whenever possible the use of oxidizing or reducing reagents that would leave residues was avoided since the presence of extraneous cations or anions would only complicate the interpretation of the observations. Thus Pu(III) was prepared by electrolytic reduction of Pu(IV) and Pu(VI) was prepared by oxidation of Pu(IV) by ozone. The plutonium isotope used in these experiments was ^{242}Pu .

In the case of anoxic preparations, a quantity of pure plutonium compound (as the chloride) was introduced into a glass ampoule. To this was added a known volume of "Solution A." The combined solutions were evaporated in a stream of nitrogen at room temperature in order to avoid possible decomposition or oxidation. The ampoule containing the dried mixture of salts was connected to a vacuum line and the system pumped until the pressure was of the order of 10^{-5} mm Hg.

At this point water was distilled onto the dried salt mixture (in the same high vacuum) until enough had been added to reach the original volume of the solution (Pu + Solution A). Thus the "Solution A" was reconstituted with the Pu in such a way that it was oxygen free. At this point the glass ampoule was sealed off and was ready for continued spectrophotometric observation.

The foregoing description applies to the preparation of all oxidation states of plutonium in the various solvents when it was desired to study them under highly anoxic conditions.

Another method for the preparation of anoxic solutions of plutonium was the use of a controlled atmosphere box. It was possible to lower the oxygen content of its atmosphere to 1-2 parts per million. The use of this box permitted the study of reactions in openable containers (in the box) so that changes in pH and E_h could be monitored by a pH and E_h electrode in the box or if desired, the pH could be controlled by addition of small amounts of the appropriate reagents. Withdrawal of aliquots from the main batch enables the monitoring of samples by the spectrophotometer.

Other solutions of plutonium were prepared in air using stoppered spectrophotometer cells as reaction vessels. These preparations could be monitored for pH from time to time by removing the stopper and insertion of a glass electrode.

To anticipate, it should be said at this point that all evidence indicates that the oxidation state of plutonium in solution is affected by radiolysis of the water. This appears to be true whether air is present or the solution is oxygen and whether the solution is acidic or basic or in concentrated brines or pure water. This result is surprising in view of the fact that previous work states that the most common effect of radiation is to decrease the oxidation number.²

The extent or the rate of the reactions may vary from solution to solution but in the main the same effects are observed. Indeed the observations seem to indicate that water radiolysis will be a major factor in determining the oxidation state of plutonium solutions in the near vicinity of the radiation field of a waste repository. In fact it can be postulated that even small quantities of plutonium carried away from the repository by some leaching and transport process and subsequently adsorbed on some mineral in a rock stratum will also be subjected to the oxidation effects of radiolysis from its own alpha activity.

The reasons for making the statement given above is as follows: an anoxic solution of Pu^{+3} in water made some two years ago was found to oxidize slowly to Pu(IV) and Pu(VI) . This was demonstrated

by observing the decrease in concentration of Pu(III) in solution spectrophotometrically and then isolating the Pu(IV) and Pu(VI) components by chemical separation procedures. Examination of the kinetics showed that the reaction could be expressed as pseudo first order with a "half life" of Pu^{+3} concentration of about 1.3×10^3 days.

It was considered possible that this oxidation was due to radiolysis. If radiolysis is a factor in these reactions, then the rate ought to correspond to the intensity of the radiation field. Accordingly very small amounts of ^{244}Cm were added, increasing the level of alpha activity from ten to one hundred times that of the plutonium alone. The amount of ^{244}Cm required was only a few micrograms and it is unlikely that any chemical effect of curium would be observed since the predominant if not sole oxidation state of curium is plus three. It was found that the oxidation of the Pu^{+3} was speeded up in amounts roughly proportional to the level of added alpha activity. Thus the question of intrinsic stability of plutonium oxidation states is probably moot since all plutonium is radioactive and indeed in a real repository where substantial radiation fields exist radiolysis effects on oxidation states will be of paramount importance.

In view of the foregoing it was decided to carry out all experiments in the presence of enough ^{244}Cm to raise the level of alpha activity one hundred fold over the original alpha activity of solution due to ^{242}Pu alone. In this way changes could be observed in reasonable time spans and the prior demonstration of proportionality of redox rate to alpha activity justified these experiments.

It is proper to point out at this time that the effect of radiolysis is obviously mainly on the water rather than the plutonium directly since the concentration of the water is so much greater than the plutonium. It is observed that the overall effect of radiolysis is to oxidize Pu(III) to Pu(IV) and thence to Pu(VI). After a time Pu(VI) appears to be reduced and a cycle of oxidation-reduction can be initiated.

The fact that the radiolytic oxidation of Pu exhibits pseudo first order reaction kinetics is not surprising. The reaction is probably between the Pu ion and OH radical. The OH radical is maintained at a constant concentration by its replenishment from the radiolysis of the water. The only other reactant is apparently the Pu. The rate will then depend only on the concentration of the Pu and hence the reaction appears to be first order.

As the Pu(III) is depleted, the OH radicals can accumulate more rapidly than they are consumed and they may combine to form H_2O_2 . In any event the concentration of OH radicals will now change

as the reaction proceeds and the rate will no longer be first order.

The apparent paradox of radiolysis acting both to oxidize and reduce plutonium can be explained if certain reactions are postulated. They are:

1. Water is decomposed by radiation into OH radicals and hydrogen atoms or hydrogen atoms plus hydrated electrons.
2. The hydroxyl radical is an oxidizing agent oxidizing Pu(III) and its products successively to Pu(VI).
3. The Pu(III)-hydroxyl radical oxidation reaction is fast. (the second order rate constant is of the order of 10^8). The Pu(IV) to Pu(V) is slow while the Pu(V) to Pu(VI) is fast.
4. When all the Pu(III) is oxidized, the OH radicals accumulate (for lack of substrate) and begin to react with each other to form hydrogen peroxide.
5. Hydrogen peroxide reacts with PuO_2^{++} [Pu(VI)] to reduce it according to the equation

Thus the Pu(VI) is reduced after all the Pu(III) is depleted.

The reaction is made plausible by observing that the addition of H_2O_2 to PuO_2^{++} results in a precipitate and an increase in pH as required by equation (1) and Pu(V) has been spectrophotometrically observed during the reaction of Pu(VI) with H_2O_2 at pH 8-8.5. Furthermore on standing for a time some of the Pu(VI) reappears. This is consistent with the known disproportionation of Pu(V) into Pu(VI) and Pu(IV) according to the equation

The results of our experimental observations are summarized in the following set of graphs. These graphs show the changes of pH, the oxidation of the various plutonium species in various solutions as well as the final reduction of Pu(VI). They display the reactions under anoxic conditions, and in the presence of air as well as in various media.

The data shown in the various graphs are only for comparison and cannot in themselves be used to predict the concentrations of various plutonium species in the indicated solutions in a real

repository. These calculations can only be made when the rate laws governing the reactions are completely elucidated.

Likewise the changes observed in E_h and pH in the laboratory sized samples cannot be directly translated into the corresponding changes in very dilute solutions such as would result from the leaching of the radioactive source emplaced in a repository. Clearly the reaction rates will change over many orders of magnitude from laboratory conditions to field conditions and possibly even the mechanism will change. It is to be expected that the rock strata themselves through which the radionuclide migrate will modify and "buffer" the pH and E_h of the solutions.

The net result of these series of reactions is that plutonium may undergo a cycle of oxidation and reduction. This is a composite effect since it is the sum of radiolytic oxidation and reduction and disproportionation and repropotionation reactions. The period of the cycle must depend on concentration of Pu, radiation field intensity, pH of solution, temperature, and formation of complexes. Thus the migration characteristics of all of the oxidation states of Pu (with the possible exception of Pu(VII)) will have to be considered.

It should also be pointed out that these radiolysis effects are probably not confined to plutonium. Neptunium, uranium, technetium and iodine are probably among the multivalent ions that will be affected and their various migration characteristics will have to be determined and will also have to be factored into the safety assessment of a repository.

1. S. Fried and A. Friedman, Retention of Plutonium(VI) on Los Alamos Tuff, Waste Management 76, P. 206, CONF-761020, Proceedings of the Symposium on Waste Management, Tucson, Arizona, Oct. 3-6, 1976. National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161.
2. J. M. Cleveland, The Chemistry of Plutonium, pp. 38-46, published by the American Nuclear Society, LaGrange Park, Illinois 60520, 1979.

OXIDATION OF Pu^{+3} BY γ 's

1 MIN = 33,000 RADS

Pu CONC. = .017 M

RADIOLYTIC REDUCTION OF Pu^{+6} BY γ 's

ANAEROBIC - Pu CONC. = .017 M

1 MIN Co^{60} = 33,000 RADS

GROWTH OF Pu^{+6} BY RADIOLYTIC OXIDATION
OF Pu^{+4} IN WATER

ANAEROBIC - PU CONC. = .017 M

OPTICAL DENSITY AT 832 NM

0.4

0.3

0.2

0.1

0

30

60

90

120

150

180

210

240

270

300

330

360

TIME IN DAYS

$\propto$ RADIOLYSIS TO Pu^{+4} FROM Pu^{+3} (ANAEROBIC IN WATER)

Pu CONC. = .017 M

CM CONC. = 1.8×10^9 D/MIN/ML.

CHANGE IN PH OF Pu^{+3} IN AIR DURING
 α RADIOLYTIC OXIDATION IN SEA WATER

$\text{Pu CONC.} = .017 \text{ M}$

$\text{CM CONC.} = 1.8 \times 10^9 \text{ D/MIN/ML.}$

CHANGE IN pH OF Pu^{+3} IN AIR
DURING α RADIOLYTIC OXIDATION IN WATER

$\text{Pu CONC.} = .017 \text{ M}$

$\text{CM CONC.} = 1.8 \times 10^9 \text{ D/MIN/ML.}$

CHANGE IN pH OF Pu^{+3} IN AIR IN SOLUTION A
DURING α RADIOLYTIC OXIDATION

$\text{Pu CONC.} = .017 \text{ M}$

$\text{CM CONC.} = 1.8 \times 10^9 \text{ D/MIN/ML.}$

OXIDATION OF Pu^{+3} BY α RADIATION
IN COPENHAGEN SEA WATER

Pu CONC. = .017 M

CM CONC. = 1.8×10^9 D/MIN/ML.

OXIDATION OF Pu^{+3} BY ALPHA RADIATION
IN WATER

$\text{Pu CONC.} = .017 \text{ M}$

$\text{CM CONC.} = 1.8 \times 10^9 \text{ D/MIN/ML.}$

OXIDATION OF Pu^{+3} BY ALPHA RADIATION
IN SOLUTION A

$\text{Pu CONC.} = .017 \text{ M}$

$\text{CM CONC.} = 1.8 \times 10^9 \text{ D/MIN/ML.}$

SUCCESSIVE APPEARANCE OF Pu PEAKS
DURING α RADIOLYSIS

Pu CONC. = .017 M

.900

.600

.300

Pu⁺³ SPECTRA (STARTING MATERIAL)

.900

.600

.300

Pu⁺⁴ COLLOID SPECTRA
(20 DAYS)

.750

.450

.150

+ PuO₂²⁺ PEAK
(34 DAYS)

4600

5500

6400

Å

7300

8200

9400

10,000

OPTICAL DENSITY

RATE OF DISAPPEARANCE OF ^{242}Pu FROM DISTILLED WATER SPIKED WITH
 1.5×10^9 DPM/ML ^{244}CM UNDER ANAEROBIC CONDITIONS

RATE OF DISAPPEARANCE OF ^{242}Pu FROM SOLUTION A SPIKED WITH
 1.5×10^9 DPM/ML ^{244}Pu UNDER ANAEROBIC CONDITIONS

RATE OF DISAPPEARANCE OF ^{242}Pu FROM COPENHAGEN SEAWATER SPIKED WITH
 1.5×10^9 DPM/ML ^{244}CM UNDER ANAEROBIC CONDITIONS

OXIDATION OF Pu^{+3} BY β RADIATION

$\text{Pu}^{+3} + \text{Ca}^{45}$ IN H_2O

$T_{1/2} = 384$ days

$\text{Pu}^{+3} + \text{Ca}^{45}$ IN SOL. A

$T_{1/2} = 270$ days

$\text{Pu}^{+3} + \text{Ca}^{45}$ IN SEAWATER

$T_{1/2} = 320$ days