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## Crystallinity and Solubility of Pu(IV) Oxide and Hydrrous Oxide in Aged Aqueous Suspensions

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*Crystallinity/Solubility/Plutonium/Plutonium oxide/Plutonium hydrrous oxide*

### Summary

The solubility and crystallinity of  $^{238}\text{PuO}_2$  ( $c$ ,  $c$  = crystalline),  $^{239}\text{PuO}_2$  ( $c$ ), and  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$  ( $a$ ,  $a$  = amorphous) was monitored, over a period of 1300 days, to study the effect of aging these compounds in aqueous suspensions.  $^{238}\text{PuO}_2$  ( $c$ ) was found to convert to a steady-state solid that had properties, including solubility, similar to that of  $\text{Pu(IV)}$  polymer. Both the  $^{239}\text{PuO}_2$  ( $c$ ) and  $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}$  ( $a$ ) converted to  $\text{PuO}_2$  ( $lc$ ,  $lc$  = less crystalline) and hence had similar solubilities. The results indicated that regardless of whether one starts with  $\text{PuO}_2$  ( $c$ ) or  $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}$  ( $a$ ), the aging process, in which dehydration and crystallization is opposed by radiolytic effects, will convert these solids to a steady state material having properties between those of the true crystalline  $\text{PuO}_2$  and those of fresh hydrated oxide.

### Introduction

Determining the mobility of hazardous elements contained in nuclear wastes is central to assessing the long-term safety of various disposal methods. To assess the potential mobility of such elements, the solubility of their compounds under geologic environments must be known to determine the amount of an element available for transport. In this paper, the effect of aging on the solubility of  $\text{Pu(IV)}$  oxide and amorphous hydrrous oxide is discussed. These Pu compounds are the most likely to precipitate and to be present in the wastes.

With time, finely divided precipitates change so as to increase the crystallite size and effective crystallinity of the precipitates. This phenomenon, called "Ostwald ripening", is caused by higher solubility of materials in a very finely divided state [1]. The higher solubility is the result of a more positive free energy of the finely divided material due to incomplete lattice binding at the crystal surface, combined with the very large surface areas of fine precipitates. For very insoluble hydrrous oxides such as hydrrous ferric oxide, an increase in crystallite size or perfection does not result in crystals large enough to appreciably improve filterability; however, it does cause sharpening of the X-ray diffraction pattern with time [1]. It is well-known that aging of hydrrous oxides of higher oxidation-state metals including hydrrous plutonium oxide increases the difficulty of their dissolution in acids. The aging of precipitated trivalent lanthanide [2] and actinide [3] hydroxides and of thorium hydrrous oxide [4] have been studied by electron microscopy and X-ray and electron diffraction techniques and it has been found that initially amorphous materials age gradually at 25°C to form crystalline materials. In the case of thorium, the final product is crystalline  $\text{ThO}_2$ .

The quantitative information on the effect of aging on different  $\text{Pu(IV)}$  solid phases is very limited. It has been noted that  $^{238}\text{PuO}_2$  is more mobile in biological systems than  $^{239}\text{PuO}_2$  [5, 6] and that  $^{238}\text{PuO}_2$  ( $c$ ,  $c$  = crystalline) unlike  $^{239}\text{PuO}_2$  ( $c$ ) becomes amorphous upon standing in pure water for 9 months [5]. Other work has shown that  $^{238}\text{PuO}_2$  ( $c$ ) undergoes dissolution more rapidly than  $^{239}\text{PuO}_2$  ( $c$ ) and several hypotheses for this behavior have been presented [7–10]. Since extremely small chemical difference is to be expected between adjacent Pu isotopes, and since it is known that dry  $^{238}\text{PuO}_2$  ( $c$ ) reaches equilibrium lattice expansion of about 0.3% in two to three weeks but remains crystalline [11, 12], this behavior can only be attributed to the reaction of the  $^{238}\text{PuO}_2$  ( $c$ ) with the radiolysis products of water. Recently, it has been noted [13] that alpha radiolysis in air-saturated suspensions of actinide oxides produces nitric acid, which can markedly lower pH in unbuffered suspensions. Since  $\text{PuO}_2$  solubility increases with a decrease in pH [14], the increased ultra-filterability of  $^{238}\text{PuO}_2$  suspensions [5, 6] could be explained because of the decrease in pH due to radiolysis; it does not, however, explain the loss of crystallinity [5] of  $^{238}\text{PuO}_2$  which occurs in aqueous suspensions.

It is known that strong, kinetically fast oxidizing agents such as  $\text{Ce(IV)}$ ,  $\text{Ag(II)}$ , and  $\text{Co(III)}$  [15, 16] readily dissolve  $\text{PuO}_2$  in acid solutions. Radiolysis of water rapidly produces the OH radical, which is a powerful and rapid oxidizing agent [17, 18]. Other strongly oxidizing radicals are also formed as primary and/or secondary radiolysis products. We, therefore, hypothesize that the conversion of crystalline  $^{238}\text{PuO}_2$  to amorphous in water [5] is due to oxidative and temporary dissolution of the crystalline  $\text{PuO}_2$  through oxidation to the more soluble  $\text{Pu(V)}$  and/or  $\text{Pu(VI)}$  by oxidizing radicals produced by alpha radiolysis followed by reduction and precipitation of amorphous hydrrous  $\text{Pu(IV)}$  oxide. Possibly reducing radiolysis products of water, such as a hydrated electron and the hydrogen atom, may also cause momentary dissolution and re-precipitation of amorphous  $\text{PuO}_2$ .

This paper examines more fully the effect of long-term aging in water on the crystallinity and solubility of  $^{239}\text{PuO}_2$  ( $c$ ) and discusses further the  $^{238}\text{PuO}_2$  ( $c$ ) behavior in water.

### Experimental

The  $^{239}\text{PuO}_2$  ( $c$ ) and  $^{239}\text{Pu(IV)}$  hydrrous oxide ("hydroxide") and the method of measuring their solubilities were

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the same as reported in RAI *et al.* [14]. The  $^{238}\text{PuO}_2$  (*c*) (84.8%  $^{238}\text{Pu}$  with the remainder higher Pu isotopes) was prepared by precipitation of Pu(III) oxalate from ascorbic acid-hydrazine reduced Pu-nitrate anion exchange product which was followed by washing, drying, and ignition of the oxalate for 2 hr at  $750^\circ\text{C}$ . About 35 mg of this  $^{238}\text{PuO}_2$  (*c*), after grinding to a fine powder, was placed in a loosely capped small glass bottle containing 30 ml of triple-distilled water and allowed to stand for 1266 days with occasional mixing. Occasionally more triple-distilled water was added to make up for that lost by radiolysis. Although the liquid volume varied between 10 and 30 ml, radiolysis was not allowed to take the system to dryness at any time. The liquid volume was about 12 ml at the time of sampling.

All sample filtration was through  $0.015\ \mu\text{m}$  Nuclepore<sup>®</sup> filters unless otherwise noted; in such cases, Amicon type CF25 Centriflo<sup>®</sup> membrane filter cones having  $0.0018\ \mu\text{m}$  pore size were used. All absorption spectra were measured using a Cary Model 14 recording spectrophotometer. X-ray diffraction patterns were obtained with Gammadiff Camera [19] using  $\text{CuK}\alpha$  radiation. Plutonium oxidation state analyses were as described previously by RAI and SWANSON [20]. Plutonium concentrations were determined by alpha spectroscopy and liquid scintillation techniques.

## Results and discussions

To better identify the effects of aging of  $^{238}\text{PuO}_2$  oxide in water, a sample of  $^{238}\text{PuO}_2$  (*c*) which had been in triple-distilled water for 1266 days was examined. An earlier more concentrated suspension (0.5 g,  $^{238}\text{PuO}_2$  (*c*) in 30 ml  $\text{H}_2\text{O}$ ) had appeared to develop into a blackish olive-green colloidal suspension within about 6 months. The aqueous phase in the current sample also became an olive-brown to olive-green after several months and showed a pronounced Tyndall Effect. The aqueous phase after 1266 days equilibration was decanted off the residual solids and centrifuged at 1500 g for 5 minutes. The absorption spectrum of the liquid showed Pu(IV) polymer at about  $5.5 \times 10^{-3}\ \text{M}$  based on its known spectrum [21]. This solution also contained Pu(VI) at  $2.6 \times 10^{-4}\ \text{M}$  based on molar extinction coefficient value of 550 [21] for the sharp intense peak at 831 nm. The solution had a pH of 1.52 and  $\log[\text{NO}_3^- \text{ molarity}]$  of  $-1.38$  attributed [13] to radiolytic production of nitric acid from dissolved air.

Filtration of the above solution through a  $0.0018\ \mu\text{m}$  membrane filter removed all color, and the adsorption spectrum showed only the intense 831 nm peak of Pu(VI). The amount of Pu(VI) decreased slowly and markedly over 24 hr at which point the solution was made  $1\ \text{M}$   $\text{HNO}_3$  and  $0.001\ \text{M}$   $\text{MnO}_4^-$ . The spectrum obtained within 1 minute of  $\text{MnO}_4^-$  addition indicated the same amount of Pu(VI) as initially, with no change over 20 hr. From these results, the soluble Pu was determined to be initially entirely Pu(VI) and the slow reduction after filtration was to Pu(V). These

conclusions are based on: 1) only Pu(V) is oxidized so rapidly by  $\text{MnO}_4^-$  as indicated in this experiment, and 2) no change occurred between 1 minute and 20 hr [22]. Radiometric analysis on the solution (filtered) gave  $3.45 \times 10^{-4}\ \text{M}$  Pu, and chemical oxidation state determination showed 0.5% Pu(III) plus Pu(IV) and 88% Pu(V) plus Pu(VI) (because of inherent errors in oxidation state determination methods, the total percentage of all oxidation states does not add up to 100). This long-term solubility of  $^{238}\text{PuO}_2$  (Fig. 1) fits almost exactly that predicted by extrapolation (from pH 3.5 to 1.5) of the linear solubility relationship reported for  $^{239}\text{Pu}(\text{IV})$  polymer by RAI and SWANSON [20].

The above results indicate that crystalline  $^{238}\text{PuO}_2$  is rather rapidly converted not just to an amorphous oxide but also to colloidal hydrous oxide (polymer). The conversion of  $^{238}\text{PuO}_2$  (*c*) to polymer and the rapid decrease in pH because of radiolytic production of nitric acid explain the apparent high solubility of aged  $^{238}\text{PuO}_2$  (*c*) suspensions and the high mobility in biological systems. However, this behavior raises the question of whether radiation chemistry affects the solubility and mobility of  $^{239}\text{PuO}_2$  (*c*) but on a longer time scale.

Fig. 1 shows the effect of aging on the pH and solubility of both  $^{239}\text{PuO}_2$  (*c*) and  $^{239}\text{Pu}(\text{IV})$  hydrous oxide [ $^{239}\text{PuO}_2 \cdot x\ \text{H}_2\text{O}$  (*a*, *a* = amorphous)]. As the suspensions age, the solubilities of  $^{239}\text{PuO}_2$  and  $^{239}\text{PuO}_2 \cdot x\ \text{H}_2\text{O}$  tend to merge; most, if not all, of the effect is due to decreased solubility of  $\text{PuO}_2 \cdot x\ \text{H}_2\text{O}$  with time. Since this comparison depends on extrapolation of both the  $\text{PuO}_2$  and  $\text{PuO}_2 \cdot x\ \text{H}_2\text{O}$  lines to below the pH range actually measured [14], the aged solids were removed by centrifugation, washed,

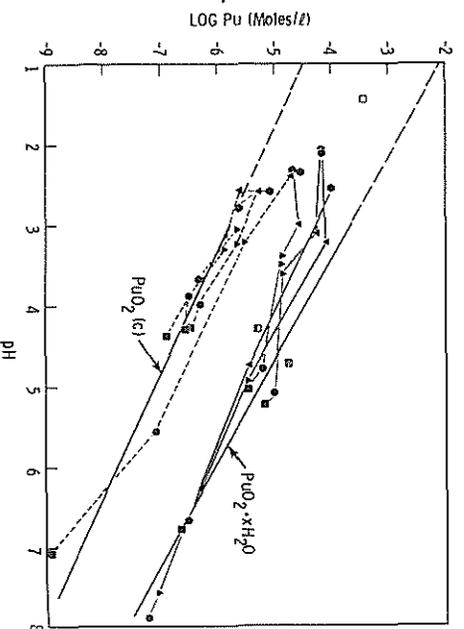


Fig. 1. Concentration of Pu in filtered solutions ( $0.1\ \mu\text{m}$  for most  $^{239}\text{Pu}$  and  $0.0018\ \mu\text{m}$  for the rest and  $^{238}\text{Pu}$  samples). Approximately, 90 days;  $\circ$ , 130 days;  $\blacktriangle$ , 250 days;  $\nabla$ , 600 days, and  $\bullet$ , 1300 days contact of material initially  $^{239}\text{PuO}_2$  (*c*) and  $\text{PuO}_2 \cdot x\ \text{H}_2\text{O}$  (*a*) with  $0.0015\ \text{M}$   $\text{CaCl}_2$ .  $\square$ , contact of initially  $^{238}\text{PuO}_2$  (*c*) with triple-distilled water for 1266 days;  $\square$ , four days contact of the preceding suspension after adjustment to pH 4.8 with  $\text{NaOH}$ ; and  $\square$ , eight days contact of coagulated and washed solids from the preceding suspension with distilled water adjusted to desired pH with  $\text{HCl}$ . Heavy solid lines are from Ref. [14] and heavy dashed lines from extrapolation of Ref. [14] data. Light solid lines trace individual  $^{239}\text{PuO}_2 \cdot x\ \text{H}_2\text{O}$  samples with time and light dashed lines trace  $^{239}\text{PuO}_2$  (*c*) samples with time.

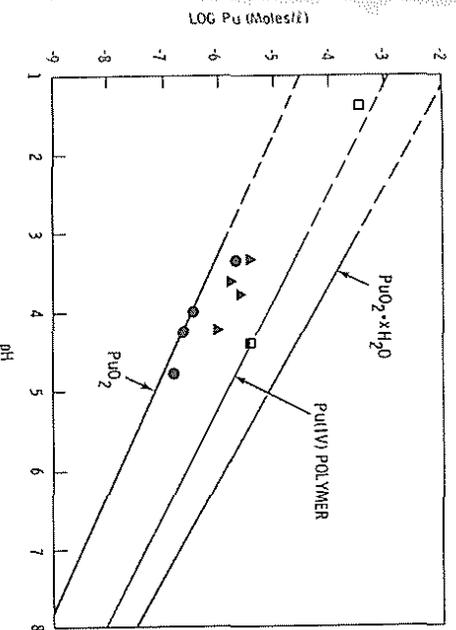


Fig. 2. Concentration of Pu in filtered (0.0018  $\mu\text{m}$ ) solutions,  $\bullet$ , originally  $^{239}\text{PuO}_2$  (*c*) and  $\blacktriangle$ , originally  $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}$  (*a*), contacted for approximately 1300 days with 0.0015 M  $\text{CaCl}_2$ , removed by centrifugation, washed and recontacted for 4 days with new 0.0015 M  $\text{CaCl}_2$ ,  $\square$ , originally  $^{238}\text{PuO}_2$  (*c*) contacted for 1266 days with triple-distilled water and  $\square$ , preceding material coagulated by increasing pH to 4.8, washed, and contacted with pH adjusted distilled water for 8 days. The solubility lines are from Ref. [14] and [20].

and equilibrated at higher pH values for up to 11 days. The solids were then washed a second time and reequilibrated for up to 27 days. Since the solubility results were similar for the 4 and 11 day equilibrations after the initial washing and for 27 day equilibration after the second washing, only the results for 4 day equilibration are being reported in Fig. 2. The  $^{238}\text{Pu}$  and  $^{239}\text{Pu}$  compounds aged in water show different solubility behavior (Fig. 2). The principal result of the aging of  $^{239}\text{Pu}$  compounds is a decrease in solubility of the  $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}$  to near that of the  $^{239}\text{PuO}_2$ , which changed very little, if any, in solubility between 90 and 1300 days. Apparently,  $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}$  ages much as would be expected for hydrated oxides in general to a material having a solubility similar to that of  $\text{PuO}_2$ . In both the 600 and 1300 day samples the solution species were found to be principally Pu(III) plus Pu(IV) below pH values of about 3.0 and 3.5 and to be principally Pu(V) above this pH. Spectrophotometric

techniques [22, 23] were used to further identify the species in solutions containing high enough Pu concentrations; Pu(IV) was found to be the reduced species and Pu(V) to be the oxidized species.

X-ray diffraction patterns of both  $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}$  at 1300 day and  $^{239}\text{PuO}_2$  at 1300 day were obtained (Table 1). These results showed that although  $^{239}\text{Pu(IV)}$  hydrated oxide developed some crystallinity [only a sharp peak corresponding to about 2.04 d ( $\text{\AA}$ )], it did not completely change to  $\text{PuO}_2$  (*c*). This is in contrast to amorphous thorium hydrated oxide that gradually ages at 25  $^\circ\text{C}$  to  $\text{ThO}_2$  (*c*) [4]. This result could be understood when it was found that two out of three samples of the originally fully crystalline  $\text{PuO}_2$  contained  $\text{PuO}_2$  (*lc*, *lc* = less crystalline) that also showed only a sharp peak corresponding to about 2.04 d ( $\text{\AA}$ ) after 1300 days in water. The fourth sample still showed some crystallinity, but since only crystalline  $\text{PuO}_2$  is detected by X-ray diffraction, the sample may still contain large amounts of  $\text{PuO}_2$  (*lc*).

The solubility of  $^{239}\text{PuO}_2$  does not appear to increase over 1300 days despite its conversion to  $\text{PuO}_2$  (*lc*) in most cases. One explanation is that the  $^{239}\text{PuO}_2$  (*lc*) formed has the same solubility as crystalline  $\text{PuO}_2$ . The second, and more likely explanation, is that regardless of whether one starts with  $\text{PuO}_2$  (*c*) or  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$  (*a*), the aging process in which dehydration and crystallization is opposed by radiolytic effects will bring the material to a steady intermediate state. The  $\text{PuO}_2$  (*c*) solubility line shown in Fig. 1 and 2 is based on 90 and 130 days equilibration [14]. The fraction of the  $\text{PuO}_2$  (*lc*) present which would have had to dissolve to produce the highest solubility measured was only one part in  $10^6$ . If the radiolytic process which converts  $\text{PuO}_2$  (*c*) to  $\text{PuO}_2$  (*lc*) is a surface attack mechanism, sufficient  $\text{PuO}_2$  (*lc*) will be formed in even one day to control the measured solubility and the true  $\text{PuO}_2$  (*c*) solubility will be lower than the reported [14] values. The dissolution rate of laboratory aged  $\text{PuO}_2$  (*c*) in 4 M  $\text{HNO}_3$  occurs rapidly up to the point corresponding to dissolution of a surface monolayer after which the dissolution rate very markedly decreases [15]

Table 1. X-ray diffraction data for Pu solids from suspensions originally containing  $^{239}\text{Pu(IV)}$  crystalline oxide (oxide) and amorphous hydrated oxide

d ( $\text{\AA}$ ) Spacing (a)	at different approximate equilibration periods (days)					
	0		90		1300	
Standard $\text{PuO}_2$ ( <i>c</i> )	Oxide	Hydrated Oxide	Oxide	Hydrated Oxide	Oxide	Hydrated Oxide
3.08	3.118	ND	3.115	ND	ND	ND
1.894	1.909	ND	1.914	ND	2.04	2.04
1.617	1.627	ND	1.635	ND	ND	ND
0.911	ND	ND	0.919	ND	ND	ND

(a) Standard  $\text{PuO}_2$  (*c*) data from Joint Committee on Powder Diffraction Standards (1601 Park Lane, Swarthmore, Pennsylvania 19081, card No. 6-0306), only the four most intense diffraction lines are shown; diffraction patterns from Pu oxide sample showed absence of detectable crystalline impurities; ND = none detected; at 1300-day equilibration period only one of three original oxide samples showed all the most intense peaks (3.126, 1.917, 1.634, 0.913) the other oxide and hydrated oxide samples only showed a sharp peak corresponding to 2.03 or 2.04 d ( $\text{\AA}$ ).

which supports a surface attack mechanism. Freshly fired (900°C) oxide did not show this initial fast dissolution.

### Conclusions

The results presented here along with earlier observations [5, 6, 15] indicate that  $\text{PuO}_2(c)$  gradually converts to a  $\text{PuO}_2(lc)$  or hydrated amorphous material because of interaction with the radiolysis products of water. Because the normal aging process in hydrated oxides gradually converts them toward anhydrous crystalline material, a steady state material will be obtained in the case of plutonium having properties between those of the true crystalline  $\text{PuO}_2$  and those of fresh hydrated oxide ("hydroxide").

This rate of conversion and the position of steady-state material will, however, depend on the radiation field in the vicinity of the plutonium oxide surface. Thus, with  $^{239}\text{Pu}$ , the steady-state material is  $\text{PuO}_2(lc)$  having the solubility shown in Fig. 2 and reported earlier [14] as that for  $\text{PuO}_2(c)$ . The true solubility of  $\text{PuO}_2(c)$  is presumably somewhat lower. With  $^{238}\text{Pu}$  the steady-state material has the properties, including solubility, as shown in Fig. 2, corresponding to that of  $\text{Pu(IV)}$  polymer prepared by conventional methods.

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