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Plutonium VI Solubility Studies in Savannah River Site High Level Waste (U)

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PLUTONIUM(VI) SOLUBILITY STUDIES IN SAVANNAH RIVER SITE HIGH-LEVEL WASTE SUPERNATE

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ABSTRACT

Pu(VI) was found to be stable in synthetic SRS waste supernate for periods of at least one month, and have a solubility of the order of 100 mg/L. Electromigration experiments found Pu(VI) migrating toward the anode. Irradiation of synthetic waste tank supernate to 5×10^6 R reduced Pu(VI) in solutions 6M NaOH and less, but had only a minor effect in higher NaOH concentrations. Irradiation did not affect Pu(VI) solubility in high-salt, high-NaOH solutions. Speciation studies found Pu(VI) the major valence of Pu in waste tank supernate solutions; some Pu(IV) is oxidized to Pu(VI) in strongly basic solutions to increase the Pu solubility. It is proposed that oxygen is the oxidizing agent for Pu(IV), with Pu(IV) disproportionation as less likely possibility.

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INTRODUCTION

Previous investigations have that found that Pu solubility is enhanced by high NaOH concentrations.[1-3] Other components of the waste supernate, nitrate, nitrite, aluminate, carbonate, sulfate, chloride, oxalate and phosphate have only a minor influence on Pu solubility. ^{60}Co irradiation increases Pu solubility in synthetic waste supernate[4], although in some circumstances nitrate and nitrite prevent an increase in Pu solubility by scavenging the radiation-produced species that might oxidize Pu(IV). However, the cause of the increase in Pu solubility at high NaOH concentrations and after irradiation has not yet been established.

Two explanations have been proposed for the solubility behavior of Pu in strongly basic solutions: formation of a hydroxide complex, and oxidation of some fraction of Pu(IV) to a more soluble Pu(V) or Pu(VI) species. While both explanations may be valid, the behavior of Pu(VI) in strongly basic solutions has not been studied. The completion of tests to determine if chloride influences the solubility of Pu in the waste supernate and studies on the behavior of Pu(VI) in strongly basic solutions are reported here.

EXPERIMENTAL SECTION

Solutions were prepared by dissolving reagent-grade chemicals in water and mixing with an equal volume of Pu tracer in 0.25M HNO_3. An HNO_3 solution of Pu was purified by anion exchange and diluted directly for Pu(IV) tracer; for Pu(VI) tracer, a dilute solution of $KMnO_4$ was added drop-wise until the tracer solution retained a permanent pink color. Attempts to oxidize Pu(IV) with Ce^{+4} were unsuccessful; tests found that MnO_4^- is reduced to MnO_4^{2-} in less than 5 minutes in strong base or instantly when NO_2^- is present.

Solutions were normally agitated for one hour before sampling. Samples were filtered with 0.2μ syringe filters, thus defining "solubility" as Pu species smaller than 0.2μ. For Pu analysis, samples were diluted with 9M HNO_3 and Pu separated by anion exchange. Pu was determined by alpha-counting and alpha pulse-height analysis of aliquots of the anion exchange effluents.

Pu speciation involved assuming that the only species present were Pu(IV), Pu(VI) and Pu polymer. Samples that were not valence-adjusted before anion exchange would adsorb only Pu(IV); Pu(VI) and Pu polymer would be collected by washing the column with 8M HNO_3. A second aliquot of the same sample was reduced with Fe^{2+}, then oxidized with $NaNO_2$ before anion exchange to convert Pu(VI) to Pu(IV). In this sample, both Pu(IV) and Pu(VI) are absorbed and Pu polymer washed from the column by 8M HNO_3. The combined results allow an estimate of the relative amount of each species. If Pu(V) is present, it would disproportionate to Pu(VI) and Pu(IV) when the sample is mixed with 9M HNO_3.[5,6]

Some samples were irradiated with ^{60}Co for ca. 5×10^6 Rad to simulate the effect of radiation on Pu valence. Two different ^{60}Co sources were used, one ca. 4×10^4 R/hr (approximately the field in SRS waste tanks) and a source that was ca. 10^6 R/hr. Total dose was a nominally 5×10^6 Rad for all irradiated samples.

Electromigration experiments were performed in a glass cell where the cathode, center and anode compartments were separated by fritted disks. The electrodes were 1 cm. x 8 cm. platinum strips. Electromigration conditions were 50 mA, 5 v. at room temperature.

Solid samples for x-ray diffraction were filtered from solution.

RESULTS

Chloride Effect on Solubility

Previous results[4] on the solubility of Pu(IV) in basic solutions can be summarized by Figure 1, where the increase in Pu solubility as the NaOH concentration increases is shown along with the increase in solubility after irradiation. In general, the presence of molar amounts of $NaNO_3$ and $NaNO_2$, as in SRS and Hanford waste tank supernates, suppresses the effect of the free radicals formed by radiation. Electromigration experiments found that Pu(IV) migrated to the anode in 3M NaOH solution.

The effect of chloride ion during irradiation was investigated because other workers[7] found chloride oxidized to the ClO^- ion, which subsequently oxidized Pu(IV) to Pu(VI), by

$$Pu(OH)_4 + ClO^- \longrightarrow PuO_2(OH)_2 + Cl^- + H_2O$$

The results from irradiating Pu(IV)-spiked NaOH-NaCl solutions showed that chloride had no effect on Pu solubility. The data are shown in Table 1.

Table 1.

Pu Solubility in NaOH-NaCl Solutions

Concentration, M			Pu, mg/L	
NaOH	NaCl	$NaNO_3$	Irradiated	Control
4	0.05		2.47	0.39
4	0.05		3.28	0.15
4	0.05	0.90	0.64	0.53
4	0.10	0.90	0.70	0.53
2	0.10	0.90	0.38	0.04
2	0.10		0.12	0.23
6	0.10		2.47	0.59
6	0.10		2.60	0.82
6			2.84	0.65

Pu(VI) Stability

Initial experiments with Pu(VI) found solubilities of the order of 100 mg/L, possibily limited by not adding sufficient tracer. The stability of Pu(VI) in strong base was tested by repeatedly sampling NaOH solutions. Over a 25-day period, the concentration of Pu in 2-10M NaOH did not change. $NaNO_3$ and $NaNO_2$ also showed no effect on the Pu(VI) solubility; the data are shown in Table 2.

Table 2

Pu(VI) Stability in NaOH Solutions

Concentration, M			Pu, mg/L		
NaOH	$NaNO_3$	$NaNO_2$	0 days	4 days	25 days
2			73	58	66
4			57	71	81
6			69	64	71
8			68	67	78
10			72	69	81
4	1	0.5	56	76	75
4	1	0.5	61	76	66
4	1	1	80	75	68
4	1	1.8	68	73	66

An electromigration experiment in 3M NaOH found that Pu(VI) migrated to the anode. Figure 2 shows the increase in Pu concentration in the anode compartment with time.

Irradiation Effects

Irradiation of Pu(VI) solutions found that radiation reduces Pu(VI) at lower base concentration, but has no effect at high NaOH (Figure 3). The presence of $NaNO_3$ and $NaNO_2$ has a minor effect on Pu(VI) solubility under irradiation; data are shown in Table 3.

Table 3

Pu(VI) Solubility under Irradiation in NaOH-$NaNO_3$-$NaNO_2$ Solutions

Solution Conc., M			Pu, mg/L	
NaOH	$NaNO_3$	$NaNO_2$	Control	Irradiated(a)
1	2.8	0.7	79	1.90
2	2.0	0.45	126	63
2	4.0	1.5	111	79
4	2.5	2.5	114	143

(a) Total Dose 6 x 10^6 R

Evaporation Tests

To simulate the operation of a waste farm evaporator, a solution of synthetic waste supernate was spiked with Pu(VI) tracer, evaporated and sampled as the volume was reduced. The results are shown in Table 4.

Table 4

Pu(VI) Solubility During Evaporation

Concentration, M			Pu, mg/L
NaOH	$NaAlO_2$	Na_2CO_3	
1.68	0.64	0.09	81
2.05	0.84	0.03	62
2.58	1.23	---	83
2.79	1.0	0.37	160
6.79	0.68	0.17	114

Speciation Experiments

NaOH solutions (2M-10M) were spiked with Pu(IV) and Pu(VI) tracer, irradiated in a ^{60}Co source to 5 x 10^6 R, and the Pu species in the irradiated and control samples determined by an anion exchange procedure. As outlined above, aliquots of each solution were anion-exchanged without adjusting the Pu valence, and again with the valence adjusted to Pu(IV). A comparison between the two column runs allows an estimate of Pu(IV), Pu(VI) and Pu(IV) polymer in the sample. Pu(III) and Pu(V) are assumed to be unstable and therefore not present in the strongly basic solutions.

In general, the valence of Pu in the control solutions spiked with Pu(IV) showed an increasing percentage Pu(VI) with increasing NaOH concentration. In 2M NaOH, Pu remained Pu(IV); in 6M NaOH, Pu(IV) and Pu(VI) were about equal (46%, 43%) and in 10M NaOH, Pu(VI) was 76% of the total Pu. Irradiation of these solutions did not affect the valence in 2M NaOH, but the 6M and 10M NaOH solutions were all Pu(VI). The solubility was increased from 0.80 mg/L to 5.3 mg/L during irradiation of he 10M solution.

The NaOH solutions spiked with Pu(VI) did not show any change in valence; irradiation reduced the solubility over a factor of 10 in the 2M and 6M NaOH solutions, but only a factor of 2 in the 10M NaOH solution. Mixed Pu(IV) and Pu(VI) tracers were an attempt to simulate a Pu(V) spike; actually, solutions spiked with the mixture showed solubilities that could be predicted from the results of solutions spiked with Pu(IV) and Pu(VI). No sample showed more than 10% Pu(IV) polymer. The data are shown in Table 5.

Table 5

Pu Speciation Experiments

NaOH, M	Tracer Pu Valence	Pu, mg/L irradiated	Valence	Pu, mg/L control	Valence
2	IV	0.089	IV	0.42	IV
6	IV	0.41	VI	0.43	90% VI
10	IV	5.25	VI	0.80	75% VI
2	VI	0.46	VI	22	90% VI
6	VI	1.71	50% VI	42	90% VI
10	VI	30	95% VI	59	84% VI
2	IV/VI	0.21	VI	7.1	90% VI
6	IV/VI	1.71	90% VI	10	90% VI
10	IV/VI	57	95% VI	8.7	VI

DISCUSSION

The high solubilities and stability of Pu added to as a Pu(VI) spike to NaOH, NaOH-$NaNO_3$ and synthetic waste supernate solutions indicate that only a fraction of Pu(IV) oxidized to Pu(VI) would explain the increases in solubility observed as waste supernate is concentrated. Attempts to determine the solid phase in equilibrium with Pu(VI) by x-ray found only amorphous material. Since electromigration indicates that the Pu(VI) is an anion in solution, a possible solid phase might be $Na_2PuO_2(OH)_4$.

The speciation experiments show that Pu(IV) is oxidized to Pu(VI) in concentrated NaOH, possibly by oxygen. Oxidation might either go by (a) a one-electron followed by Pu(V) disproportionation or (b) a two-electron process, as

(a) $4PuO_2 \cdot 2H_2O + O_2 \dashrightarrow 4PuO_2(OH) + 6H_2O$

$2PuO_2(OH) + 2H_2O \dashrightarrow Pu(OH)_4 + PuO_2(OH)_2$

(b) $2PuO_2 \cdot 2H_2O + O_2 \dashrightarrow 2PuO_2(OH)_2 + 2H_2O$

Since the concentration of Pu in solution is of the order 10^{-5} to 10^{-6}M, the two-electron process seems more probable.

A second possible route for oxidizing Pu(IV) to Pu(VI) is by the disproportation of Pu(IV), although this has not known to occur in basic solutions. Possible reactions are:

$3PuO_2 \cdot 2H_2O \dashrightarrow 2Pu(OH)_3 + PuO_2(OH)_2 + 2H_2O$

Pu(III) is rapidly air-oxidized to Pu(IV), as

$4Pu(OH)_3 + O_2 + 2H_2O \dashrightarrow 4PuO_2 \cdot 2H_2O$

The low concentration of Pu(IV) in solution suggests that these reactions would slow.

The major species formed by radiolysis of water --H_2, H_2O_2, H, OH and HO_2 --are capable of being either oxidizing or reducing agents, depending on the conditions, so oxidation by one of these species depends on the stability of Pu(VI) toward reduction by another radiation-produced species. Evidently high concentrations of NaOH and other salts either stabilize Pu(VI) or prevent reducing radicals from reacting.

The speciation experiments performed in this work can not completely distinguish Pu(V) and Pu(VI) in samples where the Pu(IV)/Pu(VI) ratio is near 1, since disproportionation of Pu(V) would lead to equal amounts of Pu(IV) and Pu(VI). However, Nitsche, et al.[8] found mainly Pu(VI) in the speciation of Pu in pH 7 salt brines, a system much more favorable to Pu(V) stability than the strong base solutions studied here.

The application of this work to treatment of basic waste solutions is that the addition of strong oxidizing agents should be avoided, since oxidation of Pu(IV) in the solid phase in the tank is likely to add Pu(VI) to the supernate. An example is $KMnO_4$ solution used for decontamination or resin destruction; these solutions should be reduced with $NaNO_2$ before discharge to waste tanks.

High concentrations of NaOH are inevitable in the evaporation of waste supernate solutions, but it should be recognized that evaporation will increase the solubility of Pu in these solutions. There is little, if any, risk of Pu precipitation in an evaporator, but the higher solubility of Pu in the evaporated supernate may lead to decontamination problems during In-Tank Processing.

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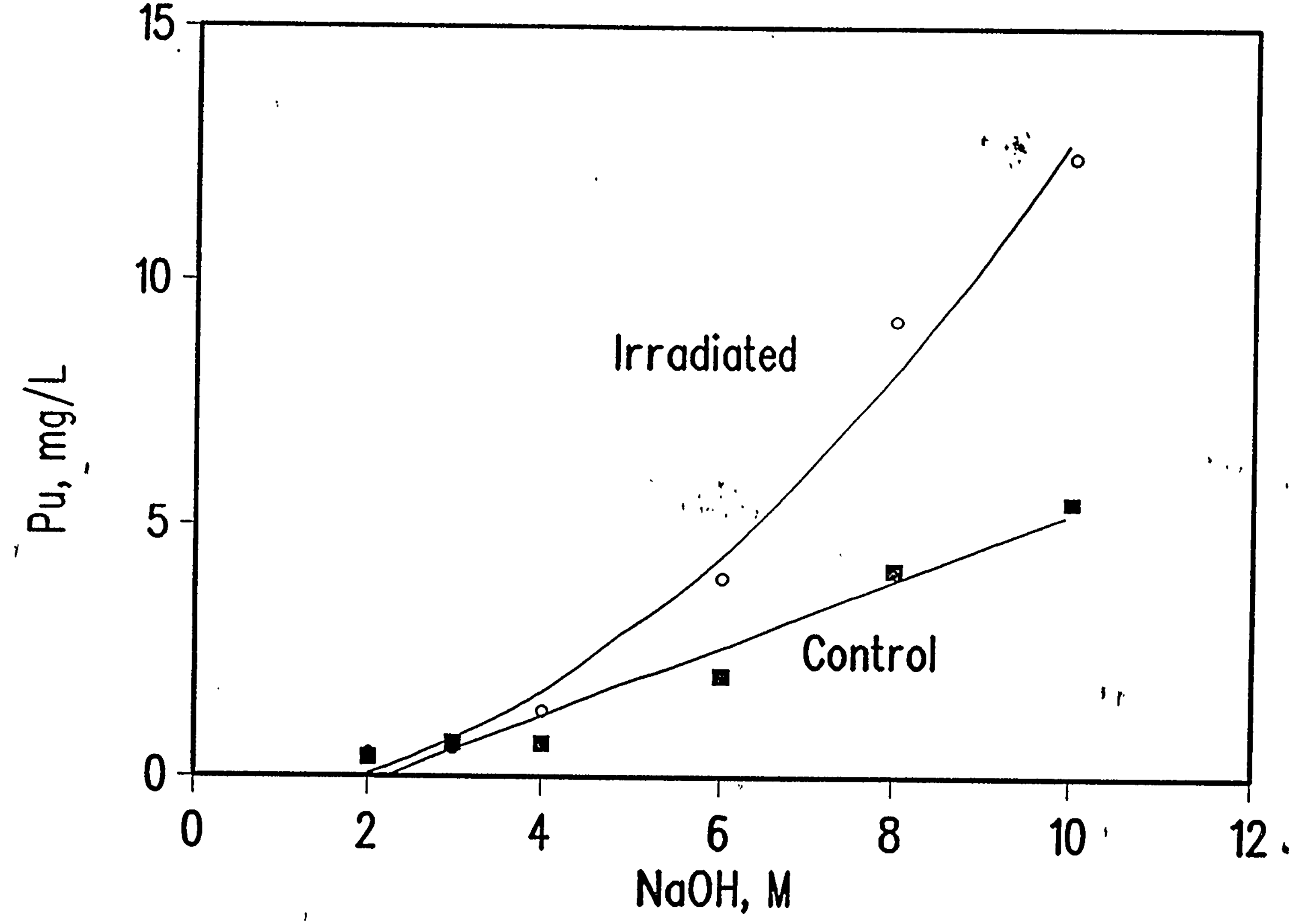
Figure Captions

Figure 1. Pu Solubility in NaOH in a Radiation Field

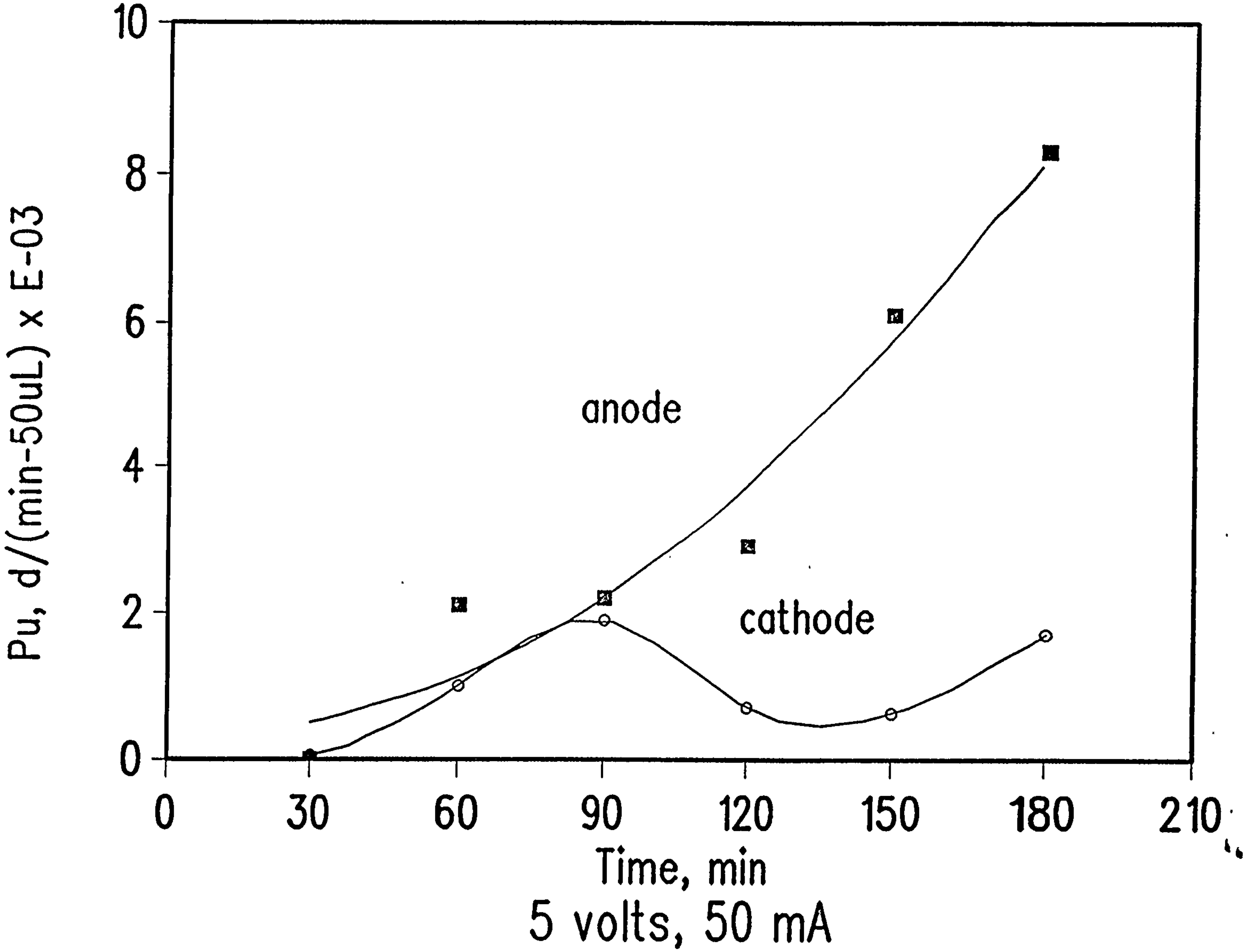
Figure 2. Electromigration of Pu(VI)

Figure 3. Irradiation of Pu(VI) in NaOH

Pu Solubility in NaOH in Rad Field



ELECTROMIGRATION OF Pu(VI)



Irradiation of Pu(VI) in NaOH