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Radiolysis of Solutions Containing Pu(VI)

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The reduction of Pu(VI) in nitric acid solutions containing uranium and various fission product elements occurring either as a result of its inherent alpha radiation or irradiation using an external gamma source at dose rates similar to those typically experienced by dissolved fuel solutions during reprocessing has been investigated. The presence of the additional metals has been shown to eliminate the induction periods required prior to the reduction of Pu(VI) in nitric acid. G values for the autoradiolytic reduction of Pu(VI) have been found to be between 0.6 and 1.1 for 3 g/l Pu solutions containing between 0.12 and 9.2 % ^{238}Pu (balance ^{239}Pu). Uranium and palladium have been found to accelerate the reduction of Pu(VI) during gamma irradiation at dose rates of between 0.41 and 1.64 kGy/hour.

KEYWORDS: radiolysis, plutonium, reduction, G-value

1. Introduction

The effect of the inherent radioactivity on the oxidation state of plutonium ions in solution was recognised very shortly after the first macroscopic amounts of plutonium became available and early studies were conducted as part of the Manhattan Project[1)]. However, the behaviour of plutonium ions, in nitric acid especially, has been found to be somewhat complex, so much so that a relatively modern review paper included the comment that "The vast amount of work carried out in nitric acid solutions can not be adequately summarised. Suffice it to say results in these solutions are plagued with irreproducibility and induction periods..."[2)]. Needless to say, the presence of other ions in solution, as occurs when irradiated nuclear fuel is dissolved, further complicates matters. The purpose of the work described below was to add to the rather small amount of quantitative data available relating to the radiolytic behaviour of plutonium in solutions of irradiated nuclear fuel.

Previous work using upwards of 20 elements in solution showed that uranium and palladium in particular had very significant effects on the rate of reduction of Pu(VI) by radiolysis at very high dose rates[3)]. Consequently Pd and U together with other elements either implicated in other works to have more minor effects or not previously tested, were added to nitric acid solutions containing hexavalent plutonium for radiolysis studies. These studies investigated both the inherent alpha radiolysis and also external irradiation using a ^{60}Co gamma source.

2. Alpha radiolysis

Three solutions containing uranium – 300g/l, plutonium – 3.0 g/l, neptunium – 0.1 g/l, cerium – 1.0 g/l, palladium – 0.6 g/l, iron – 1.0 g/l, technetium – 0.3 g/l were made up in 3.5 M nitric acid. The plutonium used in each of the three solutions had a different proportion of the 238 isotope in order to enable dose rate effects to be studied. ^{238}Pu contents of 0.12, 2.94 and 9.20 % were used, the balance being essentially all ^{239}Pu. The α dose rate of these solutions was thus $4.6 \cdot 10^{13}$, $3.3 \cdot 10^{14}$ and $1.03 \cdot 10^{15}$ $eVml^{-1}s^{-1}$. Prior to the start of each experiment, plutonium was converted to the hexavalent form by ozonolysis. The change in the proportion of hexavalent and tetravalent plutonium was then determined over a two month period by extraction of Pu(IV) using TTA from samples of each solution. The method consisted of diluting each 0.1 ml aliquot by a factor of 1000 using 1 M nitric acid followed by extraction of Pu(IV) by a 0.5 M solution of thenoyl trifluoroacetone (TTA) in toluene at a solvent to aqueous ratio of 5:1. Phase separation was achieved by centrifugation and a 0.025 cm^3 sample of the organic phase was dried on a steel target and the Pu content was then measured by α counting.

Results are shown in **Fig. 1** and the data in **Table 1.** These results are interesting in that the rate of reduction of Pu(VI) to Pu(IV) appears to have been accelerated by the presence of the other ions. Vladimirova[4)] indicates that in 4 molar nitric acid in the absence of other species, a 10^{-2} molar

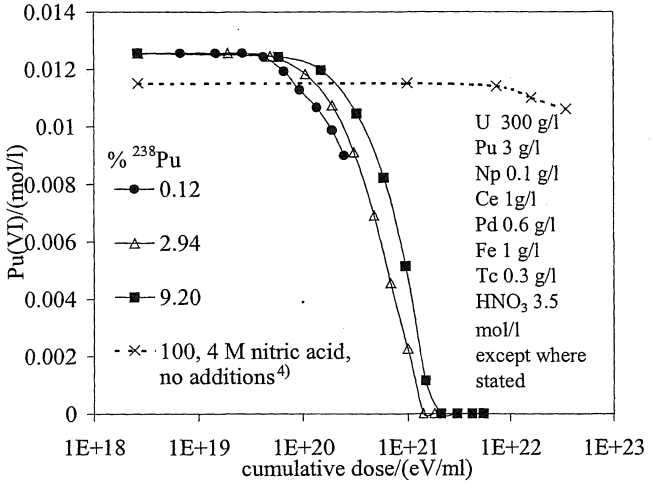

Fig. 1 Autoradiolytic reduction of Pu(VI)

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solution of hexavalent ^{238}Pu reduces with a G value of approximately 0.01 or 0.1 if one-fifth of the Pu is present as Pu(IV) initially, at doses up to $3 \cdot 10^{22}$ eV/ml.

Table 1 Rate of autoradiolytic reduction

Exposure time/days	Percentage Pu(IV) in each solution		
	1*	2*	3*
0.66	0	0	1.0
1.7	0	0	4.7
3.7	0	5.8	16.8
6.7	0	14.5	34.5
10.7	1.05	27.5	59.0
16.7	5.0	44.9	90.8
23.7	10.2	63.7	100
34.7	15.1	81.9	100
48.8	21.4	100	100
62.8	28.4	100	100

*solutions 1, 2, 3 contained 0.12, 2.94 and 9.20 % ^{238}Pu respectively

Our results given in **Table 2** indicate G values of approximately 1.1 and 0.6 for solutions containing 0.1 and 9.2 % ^{238}Pu respectively. Vladimirova's results would be expected to show slightly smaller G values due to the higher dose rates (100% ^{238}Pu) used but this effect is not large enough to explain the 60 to 80-fold increase in G values shown by this work for solutions of similar acidity and plutonium concentration.

Table 2 Autoradiolytic G-values

$\%^{238}Pu$	dose rate/ (eV/ml/hr)	%reduction/ day	$G_{(-Pu(VI))}$
0.12	$1.65 \cdot 10^{17}$	0.57	1.09
2.94	$1.20 \cdot 10^{18}$	2.93	0.79
9.20	$3.20 \cdot 10^{18}$	6.56	0.61

It is therefore apparent that the acceleration of the rate of reduction of hexavalent plutonium reported to occur under high dose rate electron bombardment[5] in the presence of uranium and palladium also occurs during autoradiolysis. Moreover, no reduction of a 10^{-2} mol/l Pu(VI) solution up to a dose approaching 10^{22}eV/ml was observed by Vladimirova[4] whereas our results show complete reduction to Pu(IV) of a solution of similar concentration at doses of less than $2.5 \cdot 10^{21}$ eV/ml albeit at a dose rate approximately a factor of 10 lower.

The induction period prior to any Pu(VI) reduction observed for all three ^{238}Pu contents in this work was approximately $5 \cdot 10^{19}$ eV/ml after which the steady state reduction rate was established most quickly (in absorbed dose terms) at the slowest dose rate (lowest ^{238}Pu content).

3. Gamma Radiolysis

Solutions of similar composition to those used for the alpha radiolysis experiments were made up, with the exception that only ^{239}Pu was used and that the acidity and uranium concentration was varied. Samples were irradiated using a ^{60}Co source for up to 30 days at different dose rates (determined by ferrous sulfate dossimetry). Reduction of Pu(VI) to Pu(IV) was again determined using TTA extraction and alpha counting of evaporated samples as described above. Results are shown in **Figs. 2-6**.

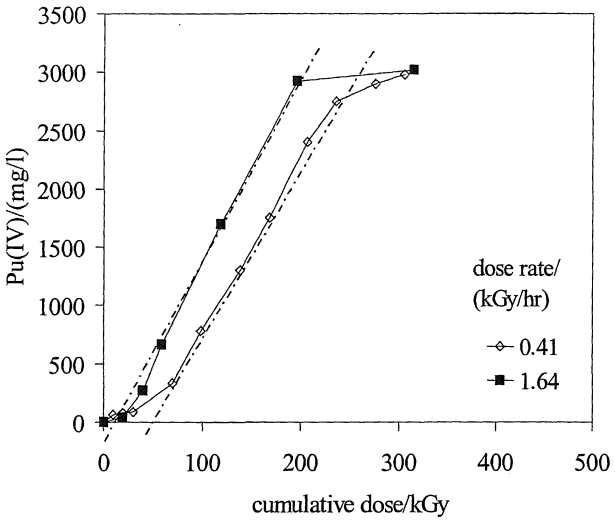

Fig.2 Effect of dose rate on rate of reduction of Pu(VI)

The G value for the reduction of Pu(VI) under both the standard conditions (300 g/l uranium, 3.5 mol/l nitric acid, 1.64 kGy/h) and reduced dose rate (0.41 kGy/h) shown in figure 2 is 0.65±0.04 although there is a slightly greater induction period in the case of the lower dose rate. The G value is reduced to approximately 0.26 by increasing the nitric acid concentration to 5 mol/l or reducing the uranium concentration from 300 to 100 g/l. Decreasing the nitric acid concentration to 2.5 mol/l or reducing the uranium concentration to 200 g/l increase and decrease respectively the G value measured under standard conditions by about 15%, see Figs. 3 and 4.

Other elements such as technetium and zirconium had no discernible effect on the rate of Pu reduction and likewise no change was observed when using de-aerated solutions, see Fig. 5.

These results agree with and augment those from previous experiments[3,5] conducted at dose rates three orders of magnitude higher than those used in this present study and show that the accelerated reduction of Pu(VI) by uranium and palladium ions occurs over a wide range of dose rates.

Radiolysis of 10^{-2} mol/l Pu(VI) in 0.3 to 8 mol/l nitric acid without additional ions shows no reduction of Pu(VI) at doses up to 170 kGy[6] whereas in the presence of 300 g/l uranium and other ions we observe complete reduction at a dose of between 200 and 500 kGy in 2.5-5 mol/l nitric acid.

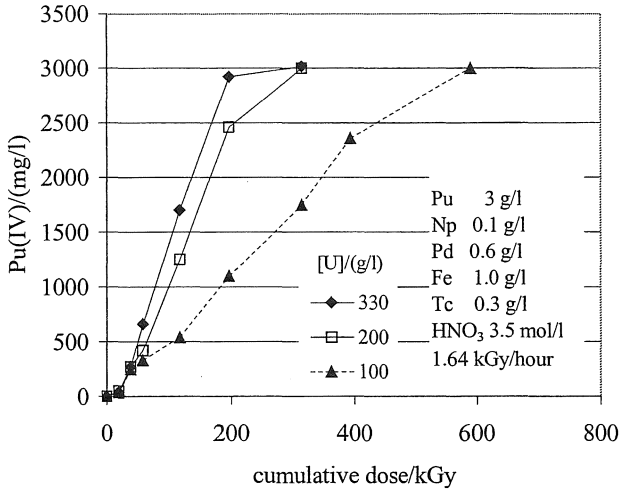

Fig. 3 The Effect of uranium concentration on the rate of reduction of Pu(VI)

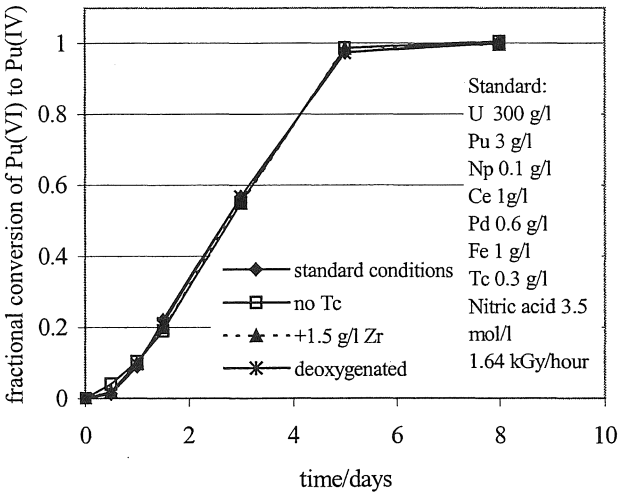

Fig. 5 Effect of Tc, Zr and de-aeration on reduction of Pu(VI)

The effect of changing the initial ratio of Pu(IV):Pu(VI) in the solution being irradiated is shown in figure 6. This shows that at a total Pu concentration of 3 g/l complete reduction of Pu(VI) to Pu(IV) is achieved in approximately 6 days (~250 kGy) irrespective of the proportion of Pu initially present as Pu(IV). This is in contrast to previous work which showed that much faster rates of reduction were observed with a Pu(VI):Pu(IV) ratio of 1:3 compared to that at a ratio of 3:1[5]. This difference is probably due to the differences in Pu and uranium concentrations and the dose used in this work compared to those of Tkhorzhnitskii [5]. Similarly, these differences may also account for the fact that Tkhorzhnitskii reports a dramatic reduction in the accelerative effect of palladium at cumulative doses above 100 kGy whereas no such effect was observed in this study.

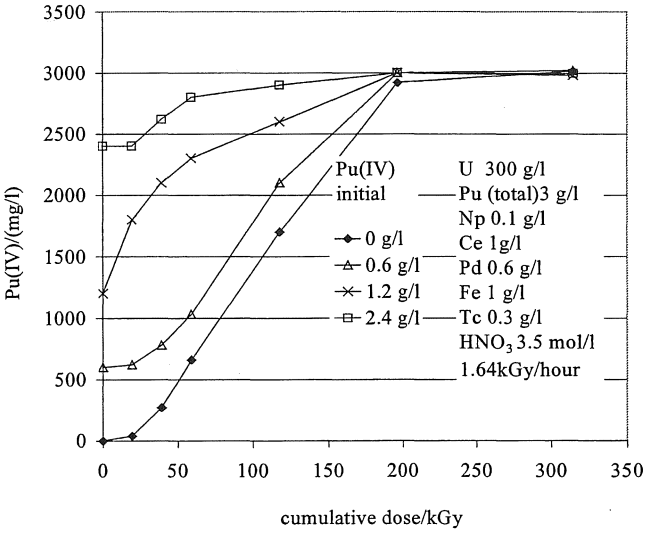

Fig. 6 Effect of initial Pu(VI):Pu(IV) ratio on rate of reduction of Pu(VI)

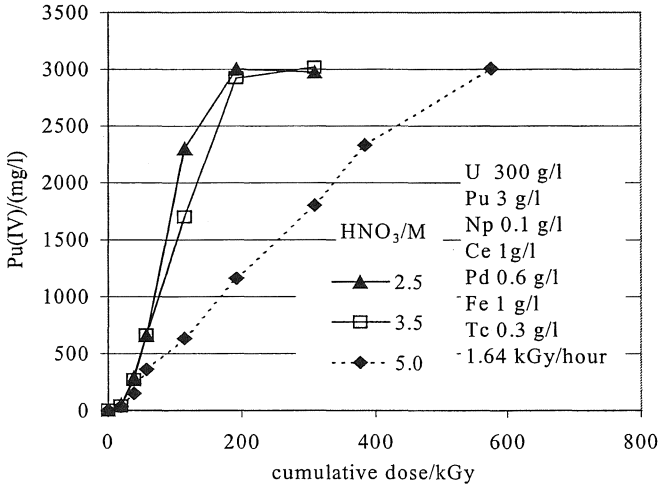

Fig. 4 The effect of nitric acid concentration on the rate of reduction of Pu(VI)

4. Discusion

In the absence of other ions, the reduction of Pu(VI) has been shown to be autocatalytic and to exhibit significant induction periods. In the presence of uranium or palladium these induction periods are not observed.

The direct reduction of Pu(VI) by the predominant radiolytic reducing agent, the aquated electron, (reaction (1)) is limited by the low concentration of Pu(VI) used in this study. Instead, the major reaction of the aquated electron will be with hexavalent uranium (2), present at a concentration two orders of magnitude higher than Pu(VI). The product, pentavalent uranium, can then either disproportionate (3) or react by reducing hexavalent plutonium(4). In the conditions used in this study the latter reaction is significantly faster than the disproportionation reaction. The pentavalent plutonium thus formed can then itself disproportionate (5) or react with Pu(IV) to give Pu(VI) and (III) (6). This latter reaction (6) is significantly

faster than (5) and it is this, in combination with reaction (7), that is responsible for the autocatalytic nature of the process.

$$PuO_2^{2+} + e_{aq}^- \rightarrow PuO_2^+ + H_2O \quad \ldots(1)$$

$$UO_2^{2+} + e_{aq}^- \rightarrow UO_2^+ + H_2O \quad \ldots(2)$$

$$2UO_2^+ \rightarrow U^{4+} + UO_2^{2+} + 2H_2O \quad \ldots(3)$$

$$UO_2^+ + PuO_2^{2+} \rightarrow UO_2^{2+} + PuO_2^+ \quad \ldots(4)$$

$$2PuO_2^+ \rightarrow Pu^{4+} + PuO_2^{2+} + 2H_2O \quad \ldots(5)$$

$$PuO_2^+ + Pu^{4+} \longleftrightarrow PuO_2^{2+} + Pu^{3+} \quad \ldots(6)$$

$$Pu^{3+} + PuO_2^+ + 4H^+ \rightarrow 2Pu^{4+} + 2H_2O \quad \ldots(7)$$

The very much reduced induction period observed in this work and in the work of Tkhorzhnitskii[5] implies a much faster build up of Pu(IV). This is attributed to palladium which acts as an efficient scavenger of oxidising ragicals such as $OH^{\cdot}$ (8) and $NO_3^{\cdot}$ (9) which would otherwise oxidise the tetravalent Pu(IV) thus preventing reaction (6) from occurring. The oxidised palladium can then disproportionate (10) or be reduced by pentavalent uranium (11) and similarly, tetravalent palladium formed in (10) can be reduced by reactions such as (12) as well as be aquated electrons and other reducing species.

$$Pd^{2+} + OH^{\cdot} \rightarrow Pd^{3+} + OH^- \quad \ldots(8)$$

$$Pd^{2+} + NO_3^{\cdot} \rightarrow Pd^{3+} + NO_3^- \quad \ldots(9)$$

$$2Pd^{3+} + H_2O \rightarrow Pd^{2+} + PdO^{2+} + 2H^+ \quad \ldots(10)$$

$$Pd^{3+} + UO_2^+ \rightarrow Pd^{2+} + UO_2^{2+} \quad \ldots(11)$$

$$PdO^{2+} + UO_2^+ + 2H^+ \rightarrow Pd^{3+} + UO_2^{2+} + H_2O \quad \ldots(12)$$

5. Conclusions

This work has confirmed that uranium and palladium accelerate the radiolytic reduction of Pu(VI) in nitric acid solutions under external gamma radiation and has shown that this effect is apparent at much lower dose rates than those previously investigated. Plutonium at a concentration of 3 g/l in solutions of 3.5 mol/l nitric acid containing 300 g/l U and 0.6 g/l Pd was reduced with a G value of 0.65 at dose rates between 0.41 and 1.64 kGy/h. Reducing the uranium concentration to 100 g/l or increasing the nitric acid concentration to 5 mol/l both reduce the G value to approximately 0.26.

Furthermore the effect of accelerated reduction due to the presence of uranium and palladium has also been shown to occur during autoradiolysis. Reduction of 10^{-2} molar Pu(VI) solutions to Pu(IV) in 3.5 mol/l nitric acid was observed at alpha doses of about 10^{21} eV/ml. No Pu(VI) is reduced under similar dose conditions and plutonium and nitric acid concentration in the absence of these other species.

6. References

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