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DISSOLUTION OF URANIUM OXIDE
ARISING FROM SLUG FAILURE

by

F. J. Johnston, P. E. Wills, and J. J. Katz

CHEMISTRY DIVISION

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DISSOLUTION OF URANIUM OXIDE ARISING FROM SLUG FAILURE

by

F. Johnston,* P. Wills,** J. J. Katz

I. Introduction

The purpose of this work was to study reagents which might be effective in dissolving uranium oxide produced during slug failure in water-cooled reactor systems. An aspect of this problem which has subsequently become of primary importance is the solubility or transportability of the oxide in pure water.

Early in the experimental work, samples of the oxide produced by reaction of water on uranium metal were submitted for x-ray analysis and spectrochemical analysis. The x-ray analysis, performed by S. Siegel, showed the material to be essentially UO_2 but with a much more diffuse pattern than the commercially available material which is prepared at higher temperatures. The autoclave oxide is thus more finely divided. Spectrochemical analysis by J. Goleb showed traces (less than 0.1%) of Al, As, Cr, Na, P, and Zr, presumably picked up from the autoclave.

II. Survey of Dissolution Agents for UO_2

2. General - In order that a reagent be useful for dissolving the UO_2 formed in slug rupture, it was required that it be effective in concentrations of the order of one-thousandth molar and that it and the dissolved uranium be removable on the ion exchange resins normally used for purifying the D_2O . Preliminary experiments performed by the Reactor Engineering Division indicated that periodic acid fulfilled these requirements. The initial experiments in the search for suitable reagents were therefore performed using H_5IO_6 as a standard. Prospective reagents were tested, and their effectiveness in dissolving the uranium oxide was compared visually with that of periodic acid in comparable concentrations. Promising reagents were then tested quantitatively, solutions being analyzed for uranium in the analytical laboratory of the Chemical Engineering Division.

Both UO_2 prepared at high temperature and UO_2 produced under conditions simulating actual slug failure were used in the initial experiments. The rate of solution of the high temperature produced oxide was very much slower than that of the autoclave oxide. The latter was used exclusively in the later experiments. The reagents tested fell into three categories; O_3 and H_2O_2 each used in combination with other oxidants, acids or complexing

*du Pont trainee

**du Pont trainee, now at Savannah River

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agents, and miscellaneous reagents. Most of the reagents examined and all that were found to have some effectiveness are listed in the subsequent paragraphs.

2.1 Experiments with ozone - A large number of oxidizing agents and complexing agents were tested in combination with O_3 in the hope that the ozone would continuously regenerate the oxidizing agent (or serve as the oxidizing agent itself), enabling the use of oxidants in essentially catalytic concentrations. Some of the reagents tested with ozone are given in Table I.

In no instance was the effectiveness of a given reagent visibly enhanced by the presence of O_3 . An important factor in this lack of effectiveness of O_3 is doubtless its low solubility in aqueous solutions.

2.2 Experiments with H_2O_2 - Most of the reagents tested with H_2O_2 are listed in Table II.

Several combinations were found which were very effective in dissolving the UO_2 . These were:

- 1) $H_2O_2 + N_2H_4 \cdot H_2SO_4$
- 2) $H_2O_2 + H_2SO_4$
- 3) $H_2O_2 + NaOH$
- 4) $H_2O_2 + K_2CO_3$

Sodium peroxide may, of course, be substituted for H_2O_2 in the above couples. The alkaline peroxide systems 3) and 4), although very effective, were not studied further because the effect on aluminum of basic solutions would limit their usefulness.

Saturated solutions of UO_2 in 0.002 M H_2O_2 , 0.004 M $N_2H_4 \cdot H_2SO_4$ and in 0.002 M Na_2O_2 , 0.004 M H_2SO_4 were prepared and analyzed for uranium. The ratio $\frac{(U) \text{ at saturation}}{(H_2O_2) \text{ initial}}$ was found to be 0.89 and 0.87 respectively for the two systems, very nearly a 1-1 correspondence between peroxide and uranium. The necessity of maintaining the initial concentration ratio $\frac{(\text{peroxide})}{(\text{acid})}$ equal to or less than $1/2$ must be emphasized. At greater relative peroxide concentrations, some uranium peroxide will settle out upon standing. This was found to be true if either H_2O_2 or Na_2O_2 was used with the acid.

2.3 Experiments with miscellaneous reagents - Many tests were made in which various oxidizing agents alone and in combination with acids and various complexing agents were examined for dissolution effect on the UO_2 . Typical of these are reagents listed in Table III.

REAGENTS TESTED WITH OZONE FOR DISSOLUTION OF UO_2

A Stream of Oxygen Consisting of 1.5% O_3 was Bubbled Through
These Solutions at a Rate of Roughly 300 cc./min.

Reagent	Concentration	Effect.	Reagent	Concentration	Effect.
1) H_2SO_4	0.010 M (0.1%)	-	12) $\text{K}_2\text{S}_2\text{O}_8$	0.005 M (0.13%)	+ *
2) HNO_3	0.015 M (0.1%)	-	AgNO_3	0.006 M (0.11%)	
3) H_5IO_6	0.005 M (0.14%)	++ *	13) KMnO_4	0.005 M (0.08%)	+++*
4) HI	0.010 M (0.14%)	-	H_2SO_4	0.010 M (0.1%)	
5) KI	0.010 M (0.13%)	-	14) KMnO_4	0.0015M (0.08%)	-
6) CoCl_2	0.005 M (0.14%)	-	15) H_2O_2	0.015 M (0.05%)	-
7) AgNO_3	0.006 M (0.11%)	+ *	16) $\text{Na}_3\text{C}_2\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$	0.029 M (1%)	-
a) + HNO_3	0.01 M (0.1%)	+ *	17) $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	0.043 M (1%)	-
8) $\text{HC}_2\text{H}_3\text{O}_2$	0.010 M (0.06%)	-	18) $\text{Na}_2\text{C}_2\text{O}_4$	0.074 M (1%)	-
9) NiCl_2	0.008 M (0.11%)	-	a) + H_2SO_4	0.010 M (0.1%)	-
10) $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$	0.008 M (0.11%)	-	19) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	0.018 M (0.5%)	-
11) $\text{K}_2\text{S}_2\text{O}_8$	0.005 M (0.13%)	-	a) + H_2SO_4	0.010 M (0.1%)	-
			20) $\text{Na}_3\text{VO}_4 \cdot 16\text{H}_2\text{O}$	0.010 M (0.5%)	-
			a) + H_2SO_4	0.010 M (0.1%)	-

* The addition of O_3 , however, resulted in no increase in effectiveness over the reagent alone.

++ Means the reagent was apparently less effective than 0.005M H_5IO_6 .

++ Means the reagent was apparently as effective as 0.005M H_5IO_6 .

+++Means the reagent was apparently more effective than 0.005M H_5IO_6 .

- The reagent had no visible effect in dissolving the UO_2 .

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Table II

REAGENTS TESTED WITH H_2O_2 FOR DISSOLUTION OF UO_2
 $(\text{H}_2\text{O}_2) = 0.005 \text{ M (0.017\%)} \text{ UNLESS OTHERWISE STATED}$

Reagent	Concentration	Effect.	Reagent	Concentration	Effect.
1) HNO_3	0.010 M (0.07%)	+	13) Urea	$\sim 0.17 \text{ M (1\%)}$ $(\text{H}_2\text{O}_2) \sim 0.029 \text{ M (1\%)}$	-
2) H_2SO_4	0.010 M (0.1%)	+++	14) $(\text{NH}_4)_2\text{C}_2\text{O}_4$	0.005 M (0.06%)	+
3) $\text{HC}_2\text{H}_3\text{O}_2$	$\sim 0.1 \text{ M (0.6\%)}$	-	15) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	0.005 M (0.16%)	+
4) K_2CO_3	0.010 M (0.14%)	+++	16) NH_4CrO_4	$\sim 0.12 \text{ M (1.6\%)}$ $(\text{H}_2\text{O}_2) \sim 0.03 \text{ M (1\%)}$	-
5) NaOH	0.010 M (0.04%)	+++	17) Na_2MoO_4	$\sim 0.2 \text{ M (5\%)}$ $(\text{H}_2\text{O}_2) \sim 0.03 \text{ M (1\%)}$	-
6) Na_2SO_4	$\sim 0.02 \text{ M (0.3\%)}$	+	18) $(\text{NH}_4)_2\text{S}_2\text{O}_8$	$\sim 0.2 \text{ M (5\%)}$ $(\text{H}_2\text{O}_2) \sim 0.03 \text{ M (1\%)}$	-
7) $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	0.04 M (1%)	-	19) NaOCl	0.010 M (0.07%)	-
8) $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$	0.010 M (0.13%)	+++	20) $\text{N}_2\text{H}_4 \cdot \text{HCl}$	0.005 M (0.03%)	-
9) $\text{N}_2\text{H}_5\text{OH}$	$\sim 0.05 \text{ M (0.3\%)}$	-	21) $\text{NH}_2\text{SO}_3\text{H}$	0.010 M (0.1%)	++
10) Glycerine	$\sim 0.01 \text{ M (1\%)}$	-	22) $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$	$\sim 0.03 \text{ M (1\%)}$	-
11) $\text{NH}_2\text{OH} \cdot \text{HCl}$	$\sim 0.14 \text{ M (1\%)}$	-	23) Urea Peroxide	$\sim 1\%$	-
12) FeCl_2	$\sim 0.08 \text{ M (1\%)}$	-	24) Versene	$\sim 1\%$	-

+ Means the reagent was apparently less effective than 0.005M H_5IO_6 .

++ Means the reagent was apparently as effective as 0.005M H_5IO_6 .

+++ Means the reagent was apparently more effective than 0.005M H_5IO_6 .

- The reagent had no visible effect in dissolving the UO_2 .

Table III

MISCELLANEOUS REAGENTS TESTED FOR DISSOLUTION OF UO_2

Reagent	Concentration	Effect.	Reagent	Concentration	Effect.
1) O_3 (see 2.1)		-	6) $\text{K}_2\text{S}_2\text{O}_8$	0.005 M (0.13%)	-
2) H_2O_2 (see 2.2)		-	a) + H_2SO_4	0.050 M (0.5%)	-
3) Na_2O_2	0.010 M (0.08%)	+++	b) + HNO_3	0.075 M (0.5%)	-
4) $\text{Co}(\text{HSO}_4)_4$	0.005 M (0.11%)		c) + citrate	~0.03 M (1%)	-
a) + H_2SO_4	0.010 M (0.1%)	+	d) + tartaric acid	0.04 M (1%)	-
b) + HNO_3	0.015 M (0.1%)	+	e) + oxalate	~0.07 M (1%)	-
(1) + 0.5% citrate		+	7) KMnO_4	0.005 M (0.08%)	-
(2) + ~0.5% tartrate		+	a) + HNO_3	0.015 M (0.1%)	+
(3) + ~0.5% oxalate		+	b) + H_2SO_4	0.010 M (0.1%)	+++
5) $\text{K}_2\text{Cr}_2\text{O}_7$	0.005 M (0.15%)	-	8) KClO_3	0.009 M (0.1%)	-
a) + H_2SO_4	0.010 M (0.1%)	+	9) HOCl	0.024 M (0.1%)	-
b) + HNO_3	0.015 M (0.1%)	+	10) $\text{K}_2\text{S}_2\text{O}_8$ }	0.005 M (0.13%) }	+
c) + citrate	0.029 M (1%)	-	AgNO_3 }	0.005 M (0.1%) }	
d) + tartaric acid	0.043 M (1%)	-	11) NaClO_2	0.005 M (0.04%)	-
e) + oxalate	0.07 M (1%)	-	a) + H_2SO_4	0.005 M (0.05%)	++

+ Means the reagent was apparently less effective than 0.005M H_5IO_6 .

++ Means the reagent was apparently as effective as 0.005M H_5IO_6 .

+++Means the reagent was apparently more effective than 0.005M H_5IO_6 .

- The reagent had no visible effect in dissolving the UO_2 .

It was found that most of the oxidizing agents tested, when coupled with an acid, had a visible dissolution effect upon the UO_2 . Several reagents were found which were visibly more effective than, or at least comparable to, H_5IO_6 in their action. These were:

- 1) $\text{KMnO}_4 - \text{H}_2\text{SO}_4$
- 2) $\text{NaClO}_2 - \text{H}_2\text{SO}_4$
- 3) Na_2O_2

Analyses of solutions of known initial reagent concentration which had been saturated with UO_2 at room temperature showed that the ratio: $\frac{(\text{U saturated})}{(\text{oxidant}) \text{ initial}}$ was between 1 and 1.5 for KMnO_4 and 0.5 for NaClO_2 . Results of analyses of corresponding H_5IO_6 solutions gave somewhat conflicting values for this ratio. Values obtained were 0.3 and 0.2, in either case, suggesting a comparatively low effectiveness.

Some MnO_2 was usually formed in the $\text{KMnO}_4 - \text{H}_2\text{SO}_4 - \text{UO}_2$ systems despite the fact that the acid was present in considerable excess. This, however, is easily transportable in agitated water or readily dissolved by the addition of H_2O_2 or Na_2O_2 .

Because of the corrosive nature of the ClO_2^- , it is unlikely that this will prove a useful reagent.

Na_2O_2 alone is very effective, but the objection mentioned in 2.2 concerning the alkaline peroxide systems limits its potential usefulness.

2.4 Experiments using the laboratory loop - A series of experiments was performed in which the various reagents were tested with UO_2 in a small stainless steel laboratory loop of 1.5 l. volume. A given amount of UO_2 was added to the solution, which was kept in continuous circulation by a mechanical pump. Samples were removed at various intervals and analyzed for uranium content. We are indebted to the Chemical Engineering Division for these analyses. The reagents tested and the rate at which they dissolved UO_2 are given in Table IV.

A 50% HNO_3 rinse of the system following circulation of the reagent showed that the uranium had, in every case, been essentially completely taken up by the reagent tested.

2.5 Conclusions - The results obtained on the laboratory loop show that all of these reagents dissolve roughly 75% of the UO_2 within 20 minutes. In extrapolating these results to actual reactor cleanup conditions, it should be remembered that a decrease in reagent concentration must be accompanied by a corresponding decrease in the rate of dissolution. If we arbitrarily assume a first-power dependence of the rate upon the oxidant concentration, then a concentration decrease from 10^{-3} M to 10^{-5} M will be accompanied by a hundredfold decrease in the rate of dissolution.

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Table IV

RATE OF DISSOLUTION OF UO_2 BY VARIOUS REAGENTS

Initial Reagent Concentration	Fraction of Total Uranium Dissolved at Time t:				
	0.33 hr.	1.0 hr.	1.5 hr.	2.0 hr.	3.0 hr.
0.001 M KMnO_4 } 0.024 M H_2SO_4 }	0.87	0.93	0.93	0.98	1.00
0.001 M H_2O_2 } 0.002 M $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ }	0.71	0.95	1.00		
0.001 M H_2O_2 } 0.002 M H_2SO_4 }	0.70	0.86		1.00	
0.003 M NaClO_2 } 0.003 M H_2SO_4 }	0.72	0.90		1.00	
0.003 M H_5IO_6 }	0.79	0.92	0.97		1.00

The results obtained indicate that almost any strong oxidant, in combination with an acid, will be to some extent effective in dissolving the UO_2 .

III. Dissolution or Transportability of UO_2 by Pure H_2O .

Because of the objectionable aspects of adding any chemical reagents to the closed heavy water system, it is of primary importance to study the possibility of dissolution, or at least transport, of the oxide particles by pure water.

A series of semiquantitative experiments was therefore undertaken to determine solubilities of UO_2 in H_2O . In these experiments autoclave-prepared UO_2 was exposed to water under varying conditions of oxygenation, H_2O pretreatment, and temperature of exposure. Exposures were carried out in glass-stoppered Pyrex vessels with agitation afforded by magnetic stirrers. Aliquots were removed at various intervals, centrifuged, filtered, and subjected to fluorometric analysis. It immediately became evident that the numbers obtained varied widely and seemed to be a function of the length of centrifugation, type of filter paper used, and the number of filtrations. These observations together with the appearance of a very strong Tyndall effect in some of the filtered solutions suggested that we were dealing with a colloidal phenomenon.

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"Solubility" numbers obtained ranged from $U \approx 10^{-6} M$ to $U > 10^{-5} M$, considerably greater than had been anticipated.

By adopting a standard procedure for treating aliquots of the water which had been exposed to the UO_2 it was possible to obtain results which, although still not completely consistent, are, we feel, significant with respect to the amount of uranium taken up by the water. This procedure involved centrifugation of the aliquot for 5.0 minutes at high speed followed by filtration through Whatman #42 paper using a small Büchner funnel and suction flask.

3.1 Results - Below are listed, in flow sheet form, the results of several of the latest and most consistent series of experiments, and of several isolated experiments. Although no difference between the "solubility" of commercial UO_2 and of autoclave UO_2 could be observed, the latter was used exclusively in obtaining the results listed below.

Experiment A

UO_2 exposed to tap dist. water which had been passed through a mixed resin column (pH6.1). The temperature of exposure was $40^\circ C.$, and the analyses were performed at room temperature.

//

Experiment B

UO₂ exposed to tap dist. H₂O (pH6.5) at room temperature (28°C.).

	1	hr.
1)	U =	<u>7.77×10^{-6}</u> M
	4.5	hr.
2)	U =	<u>9.20×10^{-6}</u>
	17	hr.
3)	U =	<u>4.83×10^{-6}</u>
	23	hr.
4)	U =	<u>2.94×10^{-6}</u>
	25	hr. (temp. of exposure raised to 48°C.)
5)	U =	<u>7.60×10^{-6}</u>
	42	hr.
6)	U =	<u>8.36×10^{-6}</u>
	48	hr.
7)	U =	<u>8.78×10^{-6}</u>
	Passed through cation resin	
8)	U =	<u>7.14×10^{-6}</u>
	Passed through cation resin	
9)	<u>7.39×10^{-6}</u>	middle fraction
10)	<u>5.63×10^{-6}</u>	last fraction

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Experiment C

UO₂, tsp dist. H₂O (pH6.5), temp. of exposure 40°C.

Several individual experiments are worthy of mention and are listed in Table V.

Table VEXPERIMENTS ON "SOLUBILITY OF UO₂"(1)(2)

Reagent	pH	Time of exposure	U Conc.
1) Tap dist. H ₂ O	6.5	7 days (without agitation)	1.13×10^{-6} M
2) Tap dist. H ₂ O + drop of H ₂ SO ₄	3.95	21.5 hr. at 45°C.	8.40×10^{-6} M
3) Redistilled H ₂ O (Pyrex still)	6.2	17 hr. at 28°C.	2.04×10^{-6} M
		120 hr. at 28°C.	8.40×10^{-6} M
		360 hr. at 28°C.	22.0×10^{-6} M

(1) Prolonged bubbling of O₂ through a UO₂ - H₂O slurry resulted in no significant increase in solubility.

(2) The saturation of a solution with CO₂ during an exposure caused a slight but probably significant increase in the uranium "dissolved."

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3.2 Conclusions - The minimum value obtained for the concentration of uranium in H_2O was 10^{-6} M. This corresponds to a value of 0.2 part per million or slightly more than 0.2 gm of uranium per ton of D_2O . This figure is sufficiently high that transport and solution by the D_2O itself may be considered an important factor in removing the UO_2 formed from slug rupture. If sufficient time is allowed, the transportability of uranium in pure water will suffice for the removal of uranium from the reactor.

It must be mentioned, however, that the oxide used for the solubility measurements consisted, to all appearances, of uniform, finely divided particles of UO_2 . It has been observed that the oxide from a slug rupture consists to some extent of very large particles the rate of solution of which will be very much lower than that of the material used in these experiments.

The experimental evidence suggests that dissolution of UO_2 in pure water leads to the formation of colloidal aggregates; the behavior on the ion-exchange resins suggests that these aggregates are primarily negatively charged. The occurrence of colloidal aggregates is entirely consistent with the known chemical behavior of uranium ions in solution.

The results of this study to date apply only to the uranium oxide which is produced during slug failure. They may not apply to the behavior of the fission products, the substances which must be removed if radioactive decontamination is to be achieved. It is practically certain that all of the fission product species will not follow the behavior of uranium, and that dissolution or removal of the uranium will in general not necessarily lead to removal of the fission product species. Whether decontamination achieved through dissolution of the formed uranium oxides is adequate must be determined independently. It must be emphasized that far-reaching inferences about uranium cannot be obtained by examination of the gross fission product behavior, and that conversely, the fate of the fission product species is not readily derivable from data on the behavior of uranium.