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Study of Uranium(IV) as Reducing Agent for Plutonium
IIa - Stability of Uranium(IV) in Solution

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STUDY OF URANIUM(IV) NITRATE AS REDUCING AGENT FOR PLUTONIUMIIa - STABILITY OF URANIUM(IV) IN SOLUTION

by

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ABSTRACT
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The stability of uranium(IV) nitrate has been studied in the aqueous acidic phase, in the organic phase (30% TBP in SST) and in an emulsion of an aqueous phase with an organic phase. The study was related to the data for the use of uranium(IV) as reducing agent for plutonium(IV) in a U-Pu partition cycle of the Eurochemic separation flowsheet.

It is shown that aqueous nitric acid solutions of uranium(IV), by themselves very unstable, can be made very stable by the addition of hydrazine in a suitable quantity. On the other hand, in the organic phase the oxidation which takes place there and which is 100 to 1000 times faster than that in the aqueous phase stabilised with hydrazine, remains just as fast - and is often even faster - when this organic phase is put into contact with an aqueous phase containing hydrazine. An important result of this study is the remarkable stabilisation of uranium(IV) nitrate in the organic phase or in an emulsion, when an inert atmosphere is used. Finally, it is shown that absence of light is very favourable to the stability.

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1. INTRODUCTION

A knowledge, at least an empirical knowledge, of the laws governing the oxidation of U(IV).

- in aqueous nitric acid solutions,
- in solution in an organic solvent containing 30% TBP and equilibrated with aqueous nitric acid solutions,
- in emulsions of these 30% TBP-hydrocarbon solutions with aqueous nitric acid solutions,

is essential for the solution of three problems of practical interest for the Eurochemic plant, namely :

- 1) the permissible storage time for aqueous solutions of U(IV) between their preparation and their use in the appropriate unit,
- 2) conversely, the possibility of reoxidising the U(IV) present in organic solutions which must be recycled to units in which a reducing agent is undesirable,
- 3) the excess of U(IV) necessary in the feed to the appropriate unit in steady conditions to give the right concentration profile of U(IV) in the organic and aqueous phases for a good reduction of Pu(IV).

Hence, the compositions of the solutions studied were of three types :

- 1) aqueous solutions leaving the electrolytic cell for the preparation of U(IV), and having compositions around :

- 2) U(IV) solutions required for feeding to the 1BX and 2D units and with compositions in the following range :

- 3) organic 1BSU solutions (30% TBP in Shellsol-T) with the composition :

obtained by equilibration with an aqueous phase having the 1BXP composition :

2. DATA FROM THE LITERATURE

The stability of the tetravalent state of uranium is low; reoxidation to U(VI) takes place, probably for several reasons.

2.1. OXIDATION BY AIR (1)

- a) U(IV) solutions oxidise spontaneously in air according to the relation established by Halpern and Smith (2) for perchloric acid solutions :

$$-\frac{d[U^{4+}]}{dt} = K \frac{[U^{4+}][O_2]}{[H^+]} \quad (1)$$

where $K = 10^{-3} \text{ sec}^{-1}$ in 1 M $HClO_4$

These workers think that there is a chain reaction of the type :

- b) Gordon and Taube (3), using oxygen labelled with O-18, showed that only one of the oxygen atoms of UO_2^{2+} is derived from the oxidising agent (O_2), and Rona (4) observed that the oxidation is favoured by an increase of $[UOH^{3+}]$, i.e. by the presence of a hydrogen bond. These two observations seem to support the hypothesis of Halpern and Smith.

2.2 NITRIC ACID SOLUTIONS

In this case, reoxidation is very rapid after an induction period (5,6,7,8), and according to Ermolaev and Krot (6) the rate of oxidation, after this induction period, follows a first order reaction equation :

$$-\frac{d[U(IV)]}{dt} = K[U(IV)]$$

where the constant K depends on factors such as temperature, $[NO_3^-]$, $[H^+]$. Ermolaev and Krot (6) conclude from this that the oxidation rate of U(IV) in nitric acid solution is determined by the reaction :

Slade (5) arrives at the same conclusions as to the importance of the role of HNO_2 , and suggests that the following reactions take place :

Bhat and Mathur (8) showed that the induction period shortens at strong acidities ; at $[HNO_3] \geq 4N$, there is no longer an induction period, the reaction immediately obeys a first order rate law and reoxidation rate increases with higher $[HNO_3]$. Similarly, for a constant acidity, the reoxidation rate increases with $[NO_3^-]$. Finally these workers observed a reoxidation rate in organic TBP solution comparable to (but slightly higher than) that observed in the aqueous phase, and also with an induction period. (The work of Bhat and Mathur was carried out with an inert atmosphere). This result is contradicted by Slade (5) who found a rate in organic TBP solution very much lower than in aqueous solutions.

Ermolaev and Krot (6) propose the following mechanism for the decomposition of nitric acid :

The induction period comes to an end when the following equilibrium is set up :

2.3. STABILISED NITRIC ACID SOLUTIONS

The oxidation of U(IV) in nitric acid solutions can be very much reduced by the addition of stabilising agents such as ferrous sulphamate or hydrazine. The action of these agents depends on the amine group, which destroys the nitric ions (9):

For hydrazine, Schlea et al. (7) refer to Jost and Russel (10), who assume a two-stage reaction :

the hydrazoic acid HN_3 in fact being formed through an intermediate compound (11) :

Schleier et al. point out that some reactions take place which are too rapid for their rate to be determined. These workers showed that the yield of hydrazoic acid is highest when $\frac{[\text{NO}_2^-]}{[\text{N}_2\text{H}_4]}$ init. = 1. It reaches an amount equivalent to 12% of the initial hydrazine, or 0.024 M HN_3 from hydrazine initially 0.2 M, and this hydrazoic acid is extracted by the TBP the more strongly the less the TBP is complexed. Now the lower explosion limit for aqueous solutions of hydrazoic acid is 17% (4.7M); this concentration can be reached in the condensate distilled from solutions at least 0.05M in HN_3 . On the other hand, with an initial hydrazine concentration of 0.05M, HN_3 does not accumulate to this potentially dangerous concentration.

In this way, Streeton and Jenkins (9) stabilised 0.45M uranium (IV) nitrate solutions with 0.05 to 0.1M of hydrazine and observed only 5% reoxidation per week. They showed further that, although it is not extracted into the organic TBP phase, hydrazine in an emulsion quickly destroys the nitrites which are present in the organic phase. (Nitrous acid in 0.01M solution in the organic TBP phase is almost completely destroyed in 0.5 minutes when the organic phase is contacted with aqueous 1.8M nitric acid containing 0.1M hydrazine).

Ondrejcin (12) observed that light has a fairly large effect on the reoxidation of U(IV) stabilised by hydrazine (U(IV) solutions 0.13 and 0.22M, total U 0.16 and 0.25M, N_2H_4 0.1 and 0.2M, HNO_3 0.8 and 0.5M), except for low hydrazine concentrations (0.02M) and 0.9M HNO_3 . This worker found that the reoxidation rate followed a linear law and with a 30g/l solution containing 0.63M HNO_3 and 0.1M hydrazine, he observed 0.5% reoxidation per day (or 3.5% per week).

3. EXPERIMENTAL DATA

The stability of U(IV) in aqueous solutions, organic solutions and emulsions was studied in the absence of radiation. The effects of various radiations, which are not dealt with here, are the subject of a supplementary report (13).

3.1 TECHNIQUES USED

3.1.1 Reagents

1. U(IV) nitrate

Solutions of $U(NO_3)_4$ were obtained by electrolysis of solutions of uranyl nitrate $UO_2(NO_3)_2$ (UCB analytical grade), in two different types of electrolytic cell.

a) industrial type cell with Pt-Hg electrodes. The composition of the initial solution was :

(	$UO_2(NO_3)_2$	:	1.6M
(	HNO_3	:	2.0M
(	$N_2H_5NO_3$	:	0.2M

and the operating conditions were :

$$V = 7.5 \text{ v} \quad I = 50 \text{ A}$$

Nitric acid was added to the anode compartment so that the solution was kept 0.5M in free nitric acid. The yield of the reduction was 72%. The electrolysed solutions had roughly the composition :

(	$U(NO_3)_4$	:	1M
(	$UO_2(NO_3)_2$	:	0.4M
(	HNO_3	:	0.4M
(	$N_2H_5NO_3$	:	0.2M

This type of cell was used for preparing solutions which gave the results of Figs. 3.2.1 - 9 to 15.

b) laboratory type cell with Pt-Pt electrodes. The composition of the initial solution was :

($\text{UO}_2(\text{NO}_3)_2$: 0.4M
(HNO_3 : 0.8M

and the applied potential was 2.5 V. When an 80% yield had been reached, 0.5 M HNO_3 was added to prevent any hydrolysis of the $\text{U}(\text{NO}_3)_4$. Solutions from this type of cell were used in most of the experiments.

In addition, an industrial type cell with Pt-Pt electrodes was used, which was similar to the Pt-Hg cell but in which the bath of Hg was replaced by a platinum mesh.

2. U(IV) chloride

This was obtained by electrolysis of UO_2Cl_2 (laboratory cell with Pt-Pt electrodes), which was either the BDH product (for Fig. 3.2.1-4) or obtained from the CEN (for Figs. 3.2.1-5 to 8).

3. Sodium nitrite

Solutions were prepared from Merck analytical grade NaNO_2 .

4. Hydrazine nitrate

Solutions were obtained by neutralising hydrazine hydroxide concentrated to 5M (Pleuger).

5. Nitric acid

These solutions were prepared from HNO_3 of density 1.4 (14.3M), UCB analytical grade.

In the particular case of Fig. 3.2.1-12, air was bubbled through the solutions after they had been diluted to the required concentration. After this, the solutions were stored in the dark in a thermostat.

3.1.2 Determination Methods

1. Determination of U(IV)

a) Potassium dichromate method

- Reagents : 15% H_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ (whose normality is fixed according to the concentration of uranium (IV) to be determined), 0.2% sodium diphenylamine sulphonate in water (end-point indicator).
- Operation : Five drops of the indicator and an aliquot of the sample to be determined are added to 40 cm^3 of the H_2SO_4 solution. The U(IV) is reoxidised with $\text{K}_2\text{Cr}_2\text{O}_7$, which is added from a graduated burette until the indicator just turns violet.
- Application : For organic phases where the cerimetric method cannot be used (Figs . 3.2.2-1 to 4, and 3.2.3-1 to 4).

b) Spectrophotometric measurements

U(IV) has several absorption peaks in the visible range between 400 and 700 m/μ (Fig. 3.1.2-1). The peak at 650 m/μ with a molar extinction coefficient $\epsilon = 22.8$ for the nitrate in organic TBP solution and 51.2 for the chloride in aqueous solution (HCl 1.5N) enables the concentration to be measured directly for solutions containing 0 to 8 g/l U(IV).

c) Cerimetric Determination

- Reagents : 1N H_2SO_4 , 1N HNO_3 , ceric sulphate solution (of normality fixed by the concentration of U(IV) to be determined), 0.0025N ferrous o-phenanthroline (as indicator) and 0.1N $\text{Fe}_2(\text{SO}_4)_3$ to stabilise the indicator.

- Operation : An aliquot of the sample to be determined, and two or three drops of indicator and of $\text{Fe}_2(\text{SO}_4)_3$ are added to 40 cm³ of a mixture of 1M HNO_3 and H_2SO_4 . The U(IV) is reoxidised with the $\text{Ce}(\text{SO}_4)_2$, which is added from a graduated burette until the indicator just changes from red to pale blue.
- Application : For aqueous phases for which spectrophotometry is ruled out by the need for dilution ; used for Figs. 3.2.1 - 9 to 15.

2. Determination of Hydrazine Nitrate

a) Titration against potassium bromate

- Reagents : Standard KBrO_3 solution, solution of 25 g/l KBr in water, concentrated HCl , 0.1% solution of methyl red in methanol (indicator).
- Operation : An aliquot of the sample to be determined, 0.5 cm³ of conc. HCl , and a few drops of the indicator are added to 30 cm³ of KBr solution. The mixture is titrated against the KBrO_3 solution, the end point being shown by the decolorising of the indicator.

b) The Method of Pesetz and Petit (21)

This method involves the formation of orange yellow dimethylaminobenzaldazine by the reaction of dimethylaminobenzaldehyde chlorohydrate with hydrazine in alcoholic solution. The absorption of light at 4,650 Å follows Beer's law and enables very precise spectrophotometric measurements to be made down to 10^{-6} M.

3. Determination of U(IV)

U(IV) was calculated by the difference between the total uranium (determined by X-ray absorption) and the U(IV) content.

3.1.3 Operating Conditions

a) Temperature

The tests were all carried out at ambient temperature without any special control, except for Figs 3.2.1-1 to 12 (in a thermostat at 23°C), Figs. 3.2.2-2 and 3 (organic phase in a thermostat at 30°C and 55°C) and Fig. 3.2.3-4 (emulsion in thermostat at 55°C).

b) Atmosphere

1. The tests in the aqueous phase were carried out in air without any special precaution, except for Figs. 3.2.1-14 and 15 (study of the influence of the atmosphere : nitrogen or air bubbling), and Fig. 3.2.1-6 when the work was carried out under vacuum at 10^{-4} Torr (re-oxidation of UCl_4 by NO_2^- , studied with the glass apparatus of Fig. 3.1.3-1).
2. The organic phases were studied with air or oxygen bubbling, and in one case (Fig. 3.2.2-5) with nitrogen bubbling.

c) Light

1. In the aqueous phase the work was often done in the absence of light, e.g. for Fig. 3.2.1-11 (study of the influence of hydrazine concentration) or for Fig. 3.2.1-12 (influence of acidity), and in all the cases where U(IV) could be determined by spectrophotometry (Figs. 3.2.1-1 to 8).
2. In emulsion, the tests were carried out in the light, except for Fig. 3.2.3-1, which shows its influence.
3. In the organic phase, the tests were carried out in the absence of light so that the influence of the atmosphere (Fig. 3.2.2-1) and the temperature (Fig. 3.2.2-2 and 3) could be studied.

3.2 EXPERIMENTAL RESULTS

The stability of U(IV) was studied successively in the aqueous phase, in the organic phase and in emulsions with or without stabiliser.

3.2.1 Aqueous phase

a) Unstabilised solutions of $U(NO_3)_4$ in nitric acid

- A dilute solution of U(IV) nitrate ($2g/l$), $1M$ in HNO_3 was first studied at ambient temperature by spectrophotometry (therefore in the dark) (Fig. 3.2.1-1). After a short induction period, the reoxidation was very rapid, half-reoxidation being achieved in a time $\tau = 3\frac{1}{2}$ hours. Addition of NO_2^- in the form of $NaNO_2$ at a concentration $[NO_2^-] \approx 2[U(IV)]$ accelerated the reoxidation since τ was reduced to 45 minutes.

- A more concentrated solution of U(IV), $0.4M$, containing in addition $0.1M$ U(VI) and total nitrate of $2.6M$ (i.e. a solution with the composition of those coming from the electrolytic cell) was reoxidised a little less quickly ($\tau = 10$ hours): Fig. 3.2.1-2.

b) U(IV) chloride solutions

Determining the mechanism of U(IV) reoxidation was based on the tetrachloride UCl_4 , which in HCl solution, even dilute ($0.05M$), and in the absence of all other stabilisers, is remarkably stable (Fig. 3.2.1-3). Addition of $NaNO_3$, like that of HNO_3 , at twice the U(IV) concentration, did not affect the stability within 20 days, the time of the test. On the other hand, the addition of NO_2^- ions started a rapid reoxidation (Fig. 3.2.1-4). This took place even in a solution with a high concentration of HCl ($1M$) and therefore in spite of the stabilising effect expected of the Cl^- ions (Fig. 3.2.1-5).

By keeping $[U(IV)] / [NO_2^-]$ constant at $\frac{1}{2}$ and $[Cl^-]$ at $1M$, and by varying the acidity, it was confirmed that from 0.2 to $1.0M$ the stability increases. In the absence of oxygen (NO_2^- and $U(IV)$ solutions degassed before being put in contact), the effect under vacuum hardly differed from the effect in air at high acidity (Figs. 3.2.1-6 to 8), but on the other hand at low acidity, the reoxidation was very much less under vacuum. It appears, therefore, that under vacuum, the effect of acidity is relatively smaller than in air.

c) $U(NO_3)_4$ solutions stabilised with hydrazine nitrate

1. Influence of hydrazine concentration :

- For a weak solution (10 g/l), $3M$ in HNO_3 at ambient temperature and in the light, the presence of hydrazine nitrate between 0.1 and $2M$ had such a large stabilising effect that, in the worst case, τ was still longer than $1,000$ hours (Fig. 3.2.1-9). The effect of the hydrazine concentration is shown in Fig. 3.2.1-10.
- For more concentrated solutions (between 65 and 85 g/l) kept in darkness in a thermostat, the stability was even greater ($\tau = 4,000$ hours, or almost 6 months): Fig. 3.2.1-11).

2. Influence of acidity

This study concerned solutions 10 g/l in $U(IV)$ and $0.1M$ in hydrazine :

- when $[NO_3^-]$ was kept constant at $3M$, and in darkness, it was observed that the degree of reoxidation remained comparable in the whole concentration range from 0.25 to $3M$ in HNO_3 (Fig. 3.2.1-12) but suddenly became very high as soon as the acidity was zero (τ fell from $4,000$ hours to 500 hours).
- when $[NO_3^-]$ was kept constant at $6M$ and in the presence of light, it was observed (Fig. 3.2.1-12) that the stability was maximum for an acidity of approximately $1M$, and that it slowly decreased as the $[HNO_3]$ was increased from 1 to $6M$.

3. Effect of the nature of the nitrate ions :

The presence of uranyl nitrate up to the concentrations studied (1.5M) did not appear to change the oxidation rate of U(IV) (Fig. 3.2.1-13).

4. Effect of atmosphere :

The part played by atmospheric oxygen in the reoxidation of U(IV) is demonstrated by Fig. 3.2.1-15 which shows that $\tau(\text{air}) = 340$ hours and $\tau(\text{N}_2) = 650$ hours.

3.2.2 Organic Phase

The organic phase studied, which was 30% TBP in Shellsol-T, had the 1 BSU composition, i.e. 1 g/l U(IV), 0.145M in U(VI) and 0.26M in HNO_3 . The aqueous phase which was used for equilibration had the following composition : 10 g/l U(IV), 0.16M in U(VI) and 1.65M in HNO_3 .

1. Influence of atmosphere on the reoxidation

Under a nitrogen atmosphere a wider variety of solutions was studied especially at acidities of 1, 2, and 3M. These solutions did not contain uranyl ions. The concentration of U(IV) was always 1 g/l. Fig. 3.2.2-0 shows that in the presence of light, whatever the acidity, the U(IV) concentration was practically unchanged after 25 hours but that it began to decrease rapidly when the nitrogen bubbling was stopped.

In the tests carried out on solutions of the 1 BSU type in the absence of light and at ambient temperature, no appreciable reoxidation was found with a nitrogen atmosphere. In the same conditions but with an air atmosphere, reoxidation became appreciable with $\tau = 30$ hours. When air was bubbled at $104 \text{ cm}^3/\text{minute}$ through the organic solutions, the reoxidation became faster with $\tau \approx 5$ hours. When air was replaced by oxygen, the reoxidation rate increased further with $\tau = 3$ hours (Fig. 3.2.2-1).

2. Influence of temperature

In the tests carried out in thermostats at 30 and 50°C in the absence of light with oxygen bubbling at 104 cm³/min. through the solutions, an exponential variation was found for the increase of reoxidation rate with temperature (Figs. 3.2.2-2 and 3).

3. Reoxidation by nitrites

The reaction is too rapid in emulsion for it to be easily studied in a separated organic phase.

3.2.3 Emulsions

The organic phase was 30% TBP in Shellsol-T equilibrated with 3, 2 or 0.5M HNO₃. The aqueous phase contained 10 or 20 g/l of U(IV) and 0.1M hydrazine. The hydrazine was practically not extracted into the organic phase (22) ; the equilibrium of U(IV) between the two phases was achieved instantaneously in the 30% TBP/Shellsol-T system.

In a general way, the reoxidation was slightly faster in the separate organic phase, and a fortiori much faster than in the aqueous phase containing hydrazine.

1. Effect of light

For a solution containing 10 g/l U(IV), 2M HNO₃ and 0.1M N₂H₅NO₂ in a 1:1 emulsion with an organic phase of 30%TBP in SST, the reoxidation rate of the U(IV) extracted into the organic phase (τ = 4 hours in the presence of light) became very much slower when light was excluded (Fig.3.2.3-1).

2. Effect of acidity

The stability increased with acidity. The results were identical with solutions of 20 g/l (Fig. 3.2.3-2) and 10 g/l (Fig. 3.2.3-3). See also Fig. 3.2.3-8.

3. Effect of temperature

At 55°C the stability was still comparable to that observed at 25°C as long as high acidity was maintained (2 to 3M in HNO_3). In contrast, at low acidity (0.5M) the reoxidation accelerated considerably with $\tau = \frac{1}{2}$ hour (Fig. 3.2.3-4).

4. Effect of atmosphere

Whatever the acidity between 0.6 and 3M (Figs. 3.2.3-5 to 7), the stability remained almost perfect under a nitrogen atmosphere ; in the presence of air the reoxidation was very rapid, increasing with decreasing acidity. (τ is 12 hours at 3M, 4 hours at 2M and 3 hours at 0.6M).

5. Reoxidation by nitrites

The conditions of nitrite reoxidation of the residual U(IV) in 1 BSU recycled to column HA were studied. As this reoxidation must take place at the top of the HA column, the study was made on an emulsion which simulated the composition of the last stage of this column. As a result of the dilution of 1 BSU in HA, the U(IV) concentration is so low that it approaches the limit of sensitivity of the spectrophotometric determination.

The compositions of the two phases contacted in a 1:1 ratio were :

- organic phase :	30% TBP	(	HNO_3	:	0.160M
	in SST	(	U(VI)	:	0.338M
		(	U(IV)	:	1 g/l
- aqueous phase :	HNO_3	-	2.95M		
	U(VI)	-	0.09M		

Table 1
REOXIDATION BY NITRITES

Time (seconds)		5	10	20	30	120
$\frac{[U(IV)]}{[NO_2]} = 1$		27.8	26.7		27.8	
" = 2		28.3	28.3		24.5	
" = 4	% U(IV)	6.5	7.3	8.7	5.9	4.1
" = 6	remaining	16.7	18.5	17.4	16.7	18.1
" = 10		21.7	22.3			26.8

As shown in Table 1, whatever the quantity of nitrite introduced, the resulting reoxidation took place practically instantaneously. The percentages were calculated from the optical density "before" and "after". As the optical density "after" was at the limit of precision, it is not possible to conclude from these results whether the reoxidation was complete or not.

4. DISCUSSION

This study of the stability of uranium (IV) nitrate has shown that its aqueous acid solutions are very unstable (but with instability decreasing with increasing acidity) and that in the presence of a sufficient quantity of hydrazine, the stability is improved by a factor of 100 to 1000. In contrast, in the organic phase the reoxidation of U(IV) which is very slightly less than that in an unstabilised aqueous phase, remains as high - and is often still higher - when the organic phase, is put into contact with an aqueous phase containing hydrazine. (See Table 2).

Whilst the virtual completeness of the reoxidation in the aqueous phase appears to be due to nitrites alone, in the organic phase or in emulsion it is first the atmosphere which plays the biggest role, then light. The maximum stability is obtained in the absence of air and of light.

In short, the group of results obtained confirms the previous results of different authors (1 to 9 and 12) with regard to :

- the principal role of nitrites in the reoxidation of uranium (IV) nitrate in the aqueous phase;
- the effect of acidity, which reduces the instability in all cases;
- the intervention of oxygen in the auto-oxidation which follows hydrolysis at low acidities.

On the other hand, the often quite long induction period reported by some authors occurred only rarely. But in addition, it was observed that the stability in the organic phase is perfect when an inert atmosphere is used, whilst in the presence of air, even in the dark, the oxidation is very great. The same is true when the organic phase is in contact with an aqueous phase containing hydrazine, i.e. strong oxidation in air, remarkable stability in the absence of oxygen.

- TABLE 2 -

SUMMARY OF THE MAIN RESULTS FOR THE TIME OF HALF REOXIDATION

Medium	Composition of Solution				Operating Conditions			Figure reference	τ time of half-reoxidation	Comments
	$[N_2H_5^+]$ - M -	$[U(IV)]$ - M -	$[U(VI)]$ - M -	$[HNO_3]$ - M -	Atmosphere	Light	Temperature			
<u>Aqueous Phase</u>	0.0	2 to 100	0 to 0.1	1.0	air	without	ambient	3.2.1-1 & 2	4 to 10 h	[increases with $[U(IV)]$ id.
	0.1	10 to 80	-	0.5 to 3.0	"	with or without	"	3.2.1-9 & 11	1000 to 4000 h (1, 3 to 6 months)	
	2.0	10	-	3.0	"	with	"	3.2.1-9	> 4000 h	[increases with $[N_2H_5^+]$ HNO_3 total = 3.0M
	0.1	10	-	0.0	"	without	"	3.2.1-12	500 h	
<u>Organic Phase</u> TBP 30%/SST	-	-	-	1 to 3 (Aq.)	H ₂	with	ambient	3.2.2-0	> 250 h	No reoxidation under H ₂ except for $[U(VI)] = 0$
	-	"	0.145	0.26	air	without	"	3.2.2-1	30 h	
	-	"	"	"	air bubb.	"	"	"	5 h	
	-	"	"	"	O ₂ bubb.	"	"	"	3 h	
	-	"	"	"	"	"	50°C	"	1 h	
	-	"	"	"	"	U.V.	ambient	(13)	1 min.	
<u>Emulsion</u> O/A = 1	0.1	10	-	2.0 (Aq.)	air	with or without	ambient	3.2.3-1	3h30 to 15 h	[decreases very much with illumination [increases with $[HNO_3]$
	0.1	"	-	3.0 (Aq.)	"	with	"	3.2.3-8	15 h	
	0.1	"	-	"	O ₂	"	"	3.2.3-5	4 h	
	0.1	"	-	"	H ₂	"	"	"	> 200 h	

4.1 IN AQUEOUS PHASE

Uranium (IV) nitrate in solution in 1M acid and in the absence of a stabiliser reoxidises completely in 8 to 20 hours (depending on the U(IV) concentration and the presence of other ions) (Figs. 3.2.1-1 and 2). On the other hand UCl_4 in solution in 1M acid has not undergone more than 10% reoxidation after 500 hours (Fig. 3.2.1-3), but if nitrite ions are added to it in the form of NaNO_2 , reoxidation may be complete in a few tens of minutes. Furthermore if hydrazine is added to solutions of U(IV) nitrate, the reoxidation rate is very much reduced and becomes the same as for UCl_4 (Figs. 3.2.1-9 and 10).

These facts demonstrate the important role of nitrites in the reoxidation of U(IV), and the effectiveness of hydrazine as stabiliser opposing the action of nitrites.

The rate constant (see Annex) for the oxidation of U(IV) by nitrites was determined under vacuum, in the absence of light and in hydrochloric acid solution (see § 3.2.1-b). In these conditions the value $K = 75\text{M}^{-1} \text{min}^{-1}$ for $[\text{H}^+] = 1\text{M}$, or a rate constant approximately 1000 times greater than that for the auto-oxidation in HClO_4 determined by Halpern and Smith (2) (for the same acidity).

The supposed participation of the two following mechanisms for the reoxidation of U(IV) nitrate :

- 1) hydrolysis and auto-oxidation,
- 2) action of nitrites,

is fairly well illustrated by Fig. 3.2.1-12, which shows that:

- a) for $[\text{HNO}_3] < 1\text{M}$, reoxidation increases very rapidly as a result of the first type of reaction, the action of nitrites being then negligible as a result of the presence of 0.1M hydrazine;

- b) for $[\text{HNO}_3] > 1\text{M}$, the first type of reaction disappearing with the absence of hydrolysis, there only remains a very weak oxidation due to nitrites, which is practically negligible in the case where $[\text{NO}_3^-]_{\text{total}} = 3\text{M}$.

4.1.1 The Participation of Nitrites in the Reoxidation is demonstrated in figs. 3.2.1-1 and 2 which show the behaviour of solutions in nitric acid without stabiliser. By applying the equation of the pseudo-reaction of the second order with respect to NO_2^- - equation (A-19) of the Annex - an estimation can be made of the average quantity of nitrite present during the course of the reaction. For a solution containing 2 g/l (Fig. 3.2.1-1), $[\text{NO}_2^-]$ is found to be approximately 0.06M (between 2h and 5h), whereas the solution 0.4M in U(IV) (Fig. 3.2.1-2) would titrate at $[\text{NO}_2^-] \approx 0.05\text{M}$. These figures are very high compared with the fact that radiolysis of nitric acid solutions by energies of 20 to 75 Mrads (14) results in a maximum of 0.01M NO_2^- . Therefore, either the electrolytic preparation of U(IV) must produce a large amount of nitrite - and this seems to be confirmed by the fact that there is never an induction period, whereas most of the workers who use other methods for preparing U(IV) observe this phenomenon - or the U(IV) must catalyse the decomposition of the nitric acid.

In short, the part played by nitrites in the reoxidation must be according to the following mechanism :

Complementary information about these reactions is contained in the Annex.

4.1.2 The part played by auto-oxidation can be found again with weakly acid solutions stabilised by hydrazine against the action of nitrites. This is so, for example, for the solutions studied at different $N_2H_5^+$ concentrations ; the results of the study are given in Figs. 3.2.1-11 and 13. In the same way as for the action of nitrites, the quantities of O_2 present in the solutions during the reaction can be checked by applying the auto-oxidation equation like that established by Halpern and Smith (2). For the solutions referred to in Fig. 3.2.1-11, an extremely low concentration is found, the calculation giving approximately $0.5 \times 10^{-4} M$. Now it is known that an aerated aqueous solution contains roughly $10^{-3} M$ of dissolved oxygen. For the solution of Fig. 3.2.1-13, which is the nearest to $1M$ in HNO_3 , and which contains $0.75M$ HNO_3 , $0.75M$ $NaNO_3$, $0.75M$ $UO_2(NO_3)_2$ and $0.1M$ $N_2H_5^+$, the same calculation gives $0.5 \times 10^{-3} M$ O_2 .

For the mechanism, the following chain reaction can be proposed :

initiation :

propagation :

termination :

(*) This is a U(V) disproportionation mechanism as suggested by Kern and Orlenman (19):

It must be noted, however, that the hydrolysis (2) is important only at low acidities, since thermodynamic determinations (15) show that at an acidity of 0.5M only 10% of the U^{4+} is in the hydrolysed form.

4.2 IN SEPARATE ORGANIC PHASE AND IN EMULSION

The separate organic phases studied contained approximately 1 g/l of U(IV), 0.145M U(VI) and 0.26M HNO_3 . With a nitrogen atmosphere, no appreciable reoxidation was observed in 50 hours even with U.V. irradiation; on the other hand, in the presence of air, reoxidation was very rapid ($\tau \approx 30$ hours).

The fact that reoxidation does not take place under nitrogen seems to indicate a reduced role of nitrite in this case. It must not be forgotten that there is less than 0.6M of nitrate ions. The acidity is also very low, however, compared to that of the aqueous solutions studied, which makes hydrolysis possible (there are approximately 10 g of water per litre in the organic solution) (16,17) and therefore auto-oxidation also. This agrees with the fact that there is no action under nitrogen and that the oxidation increases when the air is renewed by bubbling and when the air is replaced by oxygen.

Another fact which puts the effect of nitrites in second place and which confirms the dominant role of oxygen in the reoxidation in the organic phase is the reoxidation which takes place in an emulsion of an organic phase with an aqueous phase stabilised by hydrazine. Streeton and Jenkins (9), as mentioned above, showed that hydrazine in the aqueous phase destroys the nitrites which form in an organic phase in emulsion. Now the separated aqueous phase is very stable ($\tau = 1000$ hours), but in emulsions rates comparable to those in the separated organic phases are found, and the reoxidation in emulsion disappears, as in the separated organic phase, as soon as an inert atmosphere is used (Figs. 3.2.3-5 to 7).

5. CONCLUSIONS

The conclusions which can be drawn from this study can be presented as answers to the problems posed in the Introduction.

- 5.1 Aqueous Solutions of Uranium (IV) Nitrate can be stored for 100 hours with less than 5% reoxidation, on condition that:
- the HNO_3 acidity is greater than or equal to 1M ,
 - the hydrazine concentration is greater than or equal to 0.1M .
- As shown in Fig. 5.1-1, a 0.5M concentration of hydrazine allows storage times of 200 hours to be achieved with the same level of reoxidation.

- 5.2 The Residence Times of the Organic Phases in emulsion in the 1BX (~ 10 minutes) and 1BS (~ 16 minutes) units are such that the following level of reoxidation may be assumed :
- from 2% (1BX) to 3% (1BS) in an air atmosphere not renewed;
 - from 5% (1BX) to 8% (1BS) in a renewed atmosphere of air or oxygen (from 15 to 20% in the regions where the acidity is below 1M), taking the effect of light into account in both cases.

On the other hand, levels of reoxidation greater than 0.2% and 0.4% respectively must not be expected if :

- there is an inert atmosphere (nitrogen),
- light is absent.

- 5.3 The reoxidation of the U(IV) remaining in 1BSU by nitrite added to HAS in quantities leading to concentrations of the order of 0.01M in the scrubbing zone of the HA unit must be completely ensurable.

U.V. light (13), for its part, reoxidises U(IV) with a very good yield (quantum yield approximately 1) but the action is not catalytic and does not provoke a chain reaction.

In these conditions, the amount of energy necessary cannot be permitted from the point of view of solvent stability, and this excludes the direct reoxidation of U(IV) in the 1BSU organic phase.

Note : If, however, the recycling of 1BSU to the HA unit proves not to be absolutely essential, this recycling is not advisable as it implies the non-utilisation of 15 to 20% of the U(IV) in the 1BX unit (18).

ANNEX
=====

Rate constant for the oxidation of U(IV) by nitrite ions

- Thermodynamic data on various possible reactions

a) Thermodynamic data

The principal redox couples involved in this work are given in the table below in the direction of oxidation. The sign of E_0 is such that the value of E_0 increases with increasing tendency in the direction of the arrow.

Reduced form $\longrightarrow$	oxidised form	E_0 (in volts)
$U^{4+} + 2H_2O$	$UO_2^+ + 4H^+ + 1e^-$	- 0.58
UO_2^+	$UO_2^{2+} + 1e^-$	- 0.06
$U^{4+} + 2H_2O$	$UO_2^{2+} + 4H^+ + 2e^-$	- 0.32
Pu^{3+}	$Pu^{4+} + 1e^-$	- 0.98
$N_2H_5^+$	$N_2 + 5H^+ + 4e^-$	+ 0.17
$NO + H_2O$	$HNO_2 + H^+ + 1e^-$	- 0.99
$HNO_2 + H_2O$	$NO_3^- + 3H^+ + 2e^-$	- 0.94
$HO_2^\cdot$	$O_2 + H^+ + 1e^-$	+ 0.13
H_2O_2	$O_2 + 2H^+ + 2e^-$	- 0.68
$2H_2O$	$H_2O_2 + 2H^+ + 2e^-$	- 1.77
H_2O_2	$HO_2^\cdot + H^+ + 1e^-$	- 1.49
$2H_2O$	$C_2 + 4H^+ + 2e^-$	- 1.23
C_2^-	$O_2 + 1e^-$	- 0.56

With the aid of these data, the reactions which in normal conditions are possible and those which are impossible can be determined a priori, since in these conditions it is necessary that $\Delta E_c = [E_{o1} - E_{o2}] > 0$ where E_{o1} is the value of the normal reduction-to-oxidation potential of the couple providing the reducing agent in question and E_{o2} is that of the normal potential, also reduction-to-oxidation, of the couple providing the oxidising agent in question.

In the case of the oxidation of U^{4+} by O_2 , the only possible reactions (in the absence of hydrolysis) are :

With UO_2^+ , oxidation by O_2 is much easier :

Two reactions which are probably very rapid should be noted :

Finally, as far as the nitrite and nitrate ions are concerned, the four following reactions are thermodynamically possible in the direction of the arrow :

(*) Theoretically there can also be :

b) Estimation of the rate constant for the reaction between

If a first order rate is assumed with respect to U(IV) and to NO_2^- , i.e. if it is assumed that the oxidation rate of U(IV) is controlled by reaction (A8), and if the effect of acidity variation is neglected, the rate can be written :

$$- \frac{dC_A}{dt} = K_1 C_A C_B \quad (A10)$$

where T = Time

C_A = instantaneous concentration of U(IV)

C_B = " " " NO_2^-

K_1 = rate constant with respect to U(IV)

The instantaneous concentration C_B can be expressed as a function of C_A :

$$C_B = C_{B0} - (C_{A0} - C_A) = C_A + (C_{B0} - C_{A0}) = C_A + \Delta$$

where C_{A0} = initial concentration of U(IV)

C_{B0} = " " " NO_2^-

$\Delta = C_{B0} - C_{A0}$ expresses the stoichiometric excess of NO_2^- with respect to U(IV).

$$- \frac{dC_A}{dt} = K C_A (C_A + \Delta) \quad (A11)$$

Integration leads to the function :

$$\log \frac{\Delta + C_A}{C_A} = - K_1 t + \log \frac{\Delta + C_{A0}}{C_{A0}} \quad (A12)$$

In fact, even if the oxidation proceeds according to reaction (A8), the apparent concentrations, i.e. those of the experimental results, cannot be confused with those of equation (A12), because the U(V) formed during reaction (A8) is very unstable and disproportionates very rapidly into U(IV) and U(VI); according to Kern and Orlicman (19), $K_2 = 8.10^3 M^{-1} min^{-1}$ (at 25°C in perchloric acid solution) :

a disproportionation which is of the second order with respect to U(V) and of the first order with respect to H^+ . Nelson and Kraus (20), consequently, suggest the value $K = 1.7 \times 10^6$.

Therefore the most probable process for the reoxidation of U^{4+} by nitrites can be written :

and in these conditions, for a given acidity, the rate equation can be written :

$$-\frac{dC_A}{dt} = K_1 C_A C_B - K_2 C_x^2 \quad (\text{A17})$$

where C_x = instantaneous concentration of U(V).

Combining equations (A8) and (A16) gives :

where K_T is the apparent constant of this pseudo-reaction of the second order with respect to NO_2^- (not taking acidity into account) :

$$-\frac{dC_A}{dt} = K_T C_A C_B^2 \quad (\text{A19})$$

the apparent stoichiometric excess is $\Delta = C_{B_0} - 2C_{A_0}$. Now these tests were such that $\Delta = 0$, in which case integration of

$$-\frac{dC_A}{dt} = K_T C_A^3 \quad (\text{A20})$$

immediately leads to the solution :

$$\frac{1}{2} \frac{1}{C_A^2} = 4K_T \cdot t + \frac{1}{2} \frac{1}{C_{A_0}^2} \quad (\text{A21})$$

The experimental results are found to follow this law (Fig. 4.2-1) and, for an acidity of $1M$, it is found that:

$$K_T = 75M^{-1} \text{ min}^{-1}$$

This constant could be considered the true rate constant for the second order reaction with respect to NO_2^- (A9), but in the process, the acidity should not play any role. Now the experimental results reveal a slight effect of acidity (Fig. 3.2.1-6) in the opposite sense to its effect on the disproportionation; this observation thus confirms a process of the type (A8)-(A16).

In fact as $K_2 \gg K_T$, it can be said that $K_1 \neq K_T$ ($= 75M^{-1} \text{ min}^{-1}$ for $H^+ = 1M$) since :

$$\frac{1}{K_T} = \frac{1}{K_1} + \frac{1}{K_2}$$

Anyway, it thus appears that the rate of reoxidation of U^{4+} by nitrites is approximately 1000 times greater than that of auto-oxidation, which is found to be $6 \times 10^{-2} M^{-1} \text{ min}^{-1}$ (2).

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NOTE. This flowsheet is not suggested as the one to be adopted for using uranium(IV) nitrate as reducing agent for plutonium in the U-Pu partition cycle. Flows and compositions are merely illustrative in order to define the stability problems raised by using U(IV).

FIG. 3.1.2-1- ABSORPTION SPECTRA OF VARIOUS
U(IV) SOLUTIONS

UCl₄ in aqueous solution
U(IV) = 4 g/l
HCl = 1.5 M

U(NO₃)₄ in organic solut.
(30% TBP in SST, equili-
brated with HNO₃ 2 M)
U(IV) = 6 g/l

FIG. 3.1.3.1 APPARATUS FOR STUDY OF $\text{NO}_2^- + \text{U(IV)}$
REACTION UNDER VACUUM

FIG. 3.2.1-1

REOXIDATION OF $U(NO_3)_4$ IN
NITRIC ACID WITHOUT STABILIZER

$U(NO_3)_4 = 2 \text{ g/l}$

$HNO_3 = 1 \text{ M}$

Spectrophotometric analysis
at ambient temperature

□ — □ } without addition of NO_2^-
○ — ○ }
Δ — Δ } with addition of
 NO_2^- ($U(IV)/NO_2^- = 1$)

FIG. 3.2.1-4: REOXIDATION OF UCl_4
BY NO_2^-

FIG. 3.2.1-5-

REOXIDATION OF UCl_4 BY NO_2^- IN
 PRESENCE OF AIR AT CONSTANT
 $[\text{Cl}^-]$ (1M)

FIG. 3.2.1-6-

REOXIDATION OF UCl_4 BY NO_2^-
UNDER VACUUM AT
CONSTANT $[Cl^-]$ (1 M)

FIG. 3.2.1-7- REOXIDATION OF UCl_4 IN PRESENCE OF NO_2^- - WITH AIR ATMOSPHERE AND UNDER VACUUM

$\text{NO}_2^- = 0.02\text{M}$	$\frac{\text{U(IV)}}{\text{NO}_2} = \frac{1}{2}$
$\text{U(IV)} = 2\text{g/l}$	Ambient temp.

U (IV) 10 g/l
HNO₃ 3 M
Temper: 23-25 °C
in light

FIG. 3.2.1-9-

REOXIDATION OF U(IV) IN SOLUTION
EFFECT OF $N_2H_5^+$ CONCENTRATION

16-

ETR-181

FIG.3.2.1-11- REOXIDATION OF U(IV) NITRATE SOLUTIONS STABILISED BY HYDRAZINE NITRATE (in thermostat in absence of light)

48-
CTR-181

FIG.3.2.1-15-REOXIDATION OF U(IV) NITRATE IN SOLUTION
EFFECT OF ATMOSPHERE AND SOURCE
OF NO_3^- IONS

FIG.3.2.3-2 VARIATION OF $U(NO_3)_4$ CONCENTRATION IN AQUEOUS
 PHASE IN CONTACT WITH 30 % TBP-SST
 effect of acidity

FIG. 3.2.3-8- EFFECT OF AQUEOUS PHASE ACIDITY
ON THE REOXIDATION OF U(IV) IN EMULSION O/A = 1

Fig. 4.2_1

DETERMINATION OF APPARENT RATE CONSTANT
FOR OXIDATION OF U(IV) BY NITRITE IONS
IN HCl SOLUTION AT AMBIENT TEMPERATURE
(UNDER VACUUM)

-66-

Fig. 5.1-1

Internal Distribution

1. R. E. Blanco
2. D. E. Ferguson
3. H. E. Goeller
4. W. M. Sproule
- 5-6. CR Library
7. Y-12 Library
- 8-17. Laboratory Records
18. Laboratory Records-RC

External Distribution

- 19-20. O. F. Hill, ISOCEM
21. J. T. Christy, HOO
- 22-23. J. R. Bower, ICPP
24. J. W. Pollock, IDO
- 25-26. V. R. Thayer, duPont, Wilmington
27. D. Sandburg, SROO
28. J. Novak, ANL
29. B. Manowitz, BNL
30. E. L. Van Horn, Brookhaven Area Office
31. F. L. Cuthbert, FMPC
32. C. L. Karl, Fernald Area Office
33. Division of Production, USAEC, Washington
34. Research and Development Division, ORO
35. Technical Exchange Branch, DIA
- 36-51. DTIE