SOME METHODS OF PREPARING TETRAVALENT URANIUM SOLUTIONS

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Abstract

A number of processes for the preparation of tetravalent uranium solutions, suitable for use as a reductant for plutonium in the partition cycle of solvent extraction processing of irradiated reactor fuels, have been investigated.

The most attractive process consists of the precipitation of uranyl sulfide by addition of 1.4 M uranyl nitrate to about a 50% excess of 2.5% ammonium sulfide, digestion of the precipitate in the supernate at 40°C for about 90 minutes to decompose uranyl sulfide to UO_2 and sulfur, separation of the solids, and dissolution of the UO_2 in 4 M HNO_3 at 60°C, and finally, separation of the sulfur. A one-hour dissolution under these conditions yields a solution containing 83 grams total U per liter, with 71% in the tetravalent state.

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SOME METHODS OF PREPARING TETRAVALENT URANIUM SOLUTIONS

H. Katz

Introduction

In the solvent extraction processing of spent reactor fuels for separation of U and Pu from fission products, separation of U from Pu is achieved by taking advantage of the preferential solubility of Pu^{+3} in the aqueous phase. Since Pu is in the tetravalent state after the first solvent extraction cycle, a reducing agent must be used in the partition cycle which will reduce Pu to the trivalent state without affecting the U. In the past, ferrous sulfamate has been used for this purpose⁽⁸⁾. While this is a satisfactory reducing agent, its use results in a significant increase in the volume of wastes generated, and it interferes with several processes which could otherwise be used for the concentration and fixation of these wastes.

A logical alternate reducing agent for this process is tetravalent U, since this would end up in the U product stream, and thus not introduce any foreign ions into the waste stream. While the effectiveness of tetravalent U as a reducing agent for Pu has been demonstrated⁽³⁾, the methods which have been used for the production of tetravalent U solutions are complicated and expensive. The method which has been most extensively investigated is electrolytic reduction of uranyl nitrate solutions containing sulfamic acid

as a stabilizer⁽³⁾.

This report describes the results of a series of studies on the development of alternate methods for the production of tetravalent U solutions, and includes a brief evaluation of the feasibility of scaling up each of the methods. The methods which have been considered are:

- 1) Photolytic reduction of uranyl nitrate solution by aldehydes, alcohols, and ethers.

- 2) Precipitation from uranyl nitrate solution of a series of compounds analagous to ammonium diuranate, using hydrazine, hydroxylamine, or methylamine. These compounds are then decomposed, with self-reduction, either by calcining in an inert atmosphere, or dissolving in sulfuric or phosphoric acid, and heating to the appropriate temperature. The resulting compounds are then dissolved, or precipitated as U^{+4} hydroxide, and then dissolved, in nitric-sulfamic acid solution.

- 3) Dissolution of UO_2 (prepared by conventional hydrogen reduction methods) in sulfuric-hydrofluoric acid solutions, followed by precipitation of U^{+4} hydroxide, solids separation, washing, and dissolution of the hydroxide in nitric-sulfamic acid solution.

- 4) Precipitation of uranyl sulfide from uranyl nitrate solution by addition of ammonium sulfide, digestion at about 40°C in the

presence of a slight excess of ammonium sulfide to decompose the uranyl sulfide to UO_2 and sulfur, followed by dissolution of the UO_2 in nitric-sulfamic acid solution under conditions such that only slight re-oxidation of the U occurs, and finally separation of the sulfur.

Only exploratory experiments were done on methods 1) and 2), while methods 3) and 4) were investigated in greater detail; however, in all cases investigation was limited to laboratory-scale process chemistry studies.

I. Photolytic Reduction of Uranyl Nitrate Solutions

It has long been known⁽²⁾ that some uranyl salt solutions, when irradiated by light in the presence of certain organic compounds, such as alcohols, ethers, or aldehydes, are reduced to the tetravalent state. The general reaction can be represented by the equation

where $\underline{\text{A}}$ represents the organic, and $\underline{\text{R}}$ represents a univalent anion. If there is sufficient free acid present, this is a simple method, in principle, for preparing uranous nitrate solutions. If there is not sufficient free acid present, one generally obtains a hydrated U_3O_8 precipitate rather than a tetravalent U solution.

Since the data available in the literature on this process are very old and incomplete, some scouting work was done in order to

determine the feasibility of such a process for the production of uranous nitrate solutions. Since it soon became apparent that this is not a very attractive method, it was not pursued in detail, and the following discussion is based largely on qualitative or semi-quantitative observations.

The first set of experiments was designed to determine roughly the optimum wavelength of light for this reaction. In these experiments, solutions 0.4 M in uranyl nitrate, containing formaldehyde as the reductant, were irradiated in quartz tubes using ordinary incandescent lamps, "daylight" fluorescent lamps, and a photochemical lamp. Although spectrophotometric absorption measurements indicated an absorption peak beginning at the visible violet and rising through the entire ultraviolet region, the experiments indicated an optimum wavelength for this reaction in the visible violet and near ultraviolet region of the spectrum, since the most rapid reaction rates were consistently obtained using the fluorescent lamps, which radiate most strongly in this region. It is also interesting to note that no reaction occurred when this solution was exposed to 4.1×10^5 r/hr of gamma radiation for 24 hr.

In addition to formaldehyde, methanol, di-ethyl and isopropyl ether, methyl cellosolve, and di-butyl carbitol were used as reducing agents. Although they are all effective reducing agents, all of them except formaldehyde resulted, in the absence of free acid, in the formation of a black precipitate which appeared to be

UO_2 , but on exposure to air oxidized to UO_3 . These solutions initially were reduced to uranous nitrate, but after continued irradiation for a period which varied with the reducing agent and U concentration, precipitation always occurred. In the case of formaldehyde, solutions less than 0.4 M in U exhibited the same behavior, but solutions 0.8 M or higher in U resulted in the formation of stable tetravalent U solutions. For solutions less than 0.4 M in U, the addition of acetic acid to 3.5 M stabilized the solution. Lower acetic acid concentrations were not tried. Ammonium acetate was also effective in preventing precipitation but addition of sulfuric acid resulted in vigorous gassing, and no reduction took place. Nitric acid was effective in stabilizing dilute U solutions, but when added to a solution 1.5 M in U, gassing was again observed and no reduction occurred, apparently due to reaction between the nitric acid and formaldehyde.

In the case of methanol, using a solution 1.5 M in U, without excess acid, precipitation occurred in less than 20 minutes of irradiation. The same solution made 3.5 M in acetic acid remained stable, but when made 0.9 M in acetic acid, precipitation resulted after an irradiation of two days. Nitric acid is also known to be effective in stabilizing these solutions.

Using di-ethyl ether as a reducing agent, precipitation began almost immediately. Addition of sufficient acetic acid to

make the solution 3.5 M prevented precipitation, but addition of ammonium acetate did not. In the case of isopropyl ether, solutions greater than 0.3 M in acetic acid or 0.15 M in sulfuric acid remained stable. Solutions 0.25 M in nitric acid or sulfamic acid showed precipitation. It should be noted that ethers are effective reducing agents only in contact with aqueous uranyl nitrate solutions. Ether solutions of uranyl nitrate did not react under any conditions used in these experiments.

Several experiments were performed using uranyl acetate in place of uranyl nitrate, but violet-colored hydrated U_3O_8 always precipitated from these solutions as soon as they were irradiated.

The results of rate experiments indicate that reaction rates with formaldehyde are significantly higher than those with methanol. In fact, the rates obtained with formaldehyde are higher than those obtained with any of the other reducing agents under conditions resulting in a stable solution. It also appears that the rate increases very significantly with increasing formaldehyde concentration. Qualitatively, this effect of concentration was observed with methanol as well. It also appears that the reaction rate decreases with increasing acetic acid concentration in formaldehyde solutions. Because of the more rapid reaction rate, and the solution stability in the absence of free acid, formaldehyde is the most satisfactory reducing agent of those tested. However, even using

formaldehyde under the best conditions found in these experiments, the reaction is still a very slow one. Even under the best conditions the reaction was only 30 to 35% complete in 6 hr, and the rate decreased sharply with increasing U^{+4} concentration.

Because of the low reaction rates, the difficulty of scaling up a photochemical process, and because other processes were found which appeared much more attractive, work on photochemical reduction was terminated at this point.

II. Dissolution of UO_2 in H_2SO_4 -HF Solutions

Another process for preparing tetravalent U solutions, which was investigated in some detail, is dissolution of UO_2 in refluxing H_2SO_4 -HF solutions, precipitation of U(IV) hydroxide from this solution, and dissolution of the hydroxide in a nitric-sulfamic acid solution. Although UO_2 prepared by hydrogen reduction at about $600^\circ C$ is insoluble in most non-oxidizing acids, except phosphoric, it was found that it could be dissolved at reasonable rates in sulfuric-hydrofluoric acid solutions at reflux temperatures, without serious oxidation. Apparently, the HF acts as a catalyst in this process, attacking the UO_2 to form a surface layer of UF_4 , which dissolves in the sulfuric acid, liberating the HF and exposing fresh UO_2 so the process may be repeated.

In these experiments 1 g of Mallinkrodt UO_2 was added to 10 cc of the appropriate acid solution and refluxed for varying

lengths of time; it was then filtered and the remaining UO_2 washed with 0.1 M H_2SO_4 . Experiments were conducted in both glass and Teflon equipment with no significant difference in results. Apparently the surface area of UO_2 available for attack by HF was so large compared with the glass surface that no appreciable attack of the glass occurred. Some typical results of these experiments are shown in Fig. 1 and 2. The shape of these curves is difficult to explain, unless it is related to the unusual solubility relationships in the uranous sulfate-sulfuric acid-water system. There are at least two hydrates in this system which are distinct molecular species and have different solubilities. One of these, the tetrahydrate, also has a polymeric modification which is insoluble in sulfuric acid. It is possible that the unusual shape of these curves may be related to the formation of different hydrates on cooling solutions of different concentration, or to the formation of supersaturated solutions which eventually crystallize out as the insoluble tetrahydrate form.

From Fig. 1 it can be seen that increasing the sulfuric acid concentration from 0.5 to 2 M results in a large increase in both rate and solubility, but above this value further increases in sulfuric acid concentration have no significant effect. Several runs made with 8 M sulfuric acid showed that the solubility of uranous sulfate drops very sharply at this high acid concentration to a value below the solubility in 0.5 M acid. Also, the rate of

oxidation in 8 M acid becomes very rapid, about 50% of the dissolved U appearing in the hexavalent state after refluxing for 2 hr. With solutions up to 4 M sulfuric acid, between 85 and 95% of the U was in the tetravalent state after 4 hr, dropping to about 70% after 6 hr.

From Fig. 2 it can be seen that the dissolution rate increases rapidly as the HF concentration increases from 0.01 to 0.05 M, and appears to level off at this concentration. However, the concentration at which the rate levels off may be a function of the surface area of the UO_2 present and the volume of the solution, with leveling-off occurring at a concentration which is sufficient to form a surface layer of UF_4 on the solid surface. The UO_2 used in these experiments had a surface area of $4 \text{ m}^2/\text{g}$, as determined by nitrogen adsorption. In any event, the HF concentration would probably be limited by other considerations, such as corrosion and the danger of exceeding the solubility product of UF_4 .

The two high points obtained with 0.1 M HF probably represent supersaturated solutions. Similar results were obtained fairly frequently with 0.1 M HF solutions, particularly at higher sulfuric acid concentrations. In some cases, on continued refluxing of these solutions, green, water-soluble crystals began to appear, indicating that these solutions had been supersaturated.

For the conditions used in these experiments, a 2 M H_2SO_4 -0.05 M HF solution appears to be optimum with respect to both rate and solubility, and will yield a solution containing about 50 g/l of tetravalent U after 1-1/2 hr of refluxing. It may be desirable from consideration of corrosion and waste treatment to convert this to a nitrate solution for use in the partition step of the Purex process. This can be done by addition of a slight excess of 50% sodium hydroxide to precipitate U^{+4} hydroxide, filtering and washing the precipitate, and redissolving in 4 M HNO_3 -0.1 M $\text{NH}_2\text{SO}_3\text{H}$ at room temperature. Although this step was not studied in detail, it was established that solutions containing 100 g/l of tetravalent U could be prepared in several minutes with essentially no oxidation of the U. It might also be possible to accomplish this step of the process by ion exchange, but this was not investigated.

Although this is a relatively simple and rapid process for preparing tetravalent U solutions, it uses a highly corrosive solution, which may dictate the use of expensive construction materials. It also requires the use of UO_2 , which may not be as readily available as uranyl nitrate. If a denitration and reduction step have to be added, the process becomes considerably longer and more complex.

Several attempts were also made to prepare tetravalent U solutions by dissolving Mallinkrodt UO_2 in nitric-sulfamic-hydrofluoric acid solutions, but the rate of oxidation was so rapid compared

with the rate of dissolution, that essentially all of the U appeared in the hexavalent state.

III. Dissolution of UO_2 Prepared at Low Temperatures

Although the dissolution of UO_2 is a simple and direct way of preparing tetravalent U solutions, the use of sulfuric-hydrofluoric acid solutions presents some difficulties. Since it is known that, in general, the chemical reactivity of UO_2 increases as the temperature at which the UO_2 was prepared decreases, it was thought that UO_2 prepared at lower temperatures might be dissolved directly in nitric-sulfamic acid solutions under conditions of temperature and concentration mild enough so that the dissolution could be accomplished without serious oxidation. Therefore two general methods of preparing UO_2 at low temperatures were investigated. The first, utilizing various amines as reducing agents, did not look attractive, and therefore it was investigated only very briefly. The second method, decomposition of uranyl sulfide, worked successfully, and is the basis for what is probably the best process developed during the course of this work.

A. Amines as Reducing Agents

The reducing agents investigated were hydrazine, hydroxylamine, mono- and dimethylamine, and hexamethylene tetramine. Each of these reagents was added to a uranyl nitrate solution to precipitate compounds analagous to ammonium diuranate, and the

precipitates washed and dried at 110°C. The dried precipitates were calcined in a nitrogen atmosphere at varying temperatures in order to decompose them, with self-reduction, as has been done with ammonium diuranate. Using dimethylamine, 60% of the U was reduced to the tetravalent state on calcining for 2 hr at 400°C. Under the same conditions, monomethylamine reduced 54.5% of the U, while hexamethylene tetramine reduced only 27% of the U. The kinetics of these reactions was not investigated, and it may be that further reduction would occur with longer periods of calcination. For comparison, it is interesting to note that self-reduction of ammonium diuranate does not begin until 450°C. However, this investigation was not pursued, since several attempts to dissolve this incompletely reduced material indicated that its behavior was not significantly different from that of the Mallinkrodt UO_2 previously tested. In the case of hydrazine and hydroxylamine, the results were very erratic, although one would expect hydrazine to be an effective reducing agent at about 150°C⁽⁷⁾. There is some evidence to indicate that UO_2 prepared in this manner is so active that it oxidizes fairly rapidly on exposure to air, which could account for the poor results obtained from these experiments. With the latter two reducing agents, several experiments were performed in which the washed precipitates were dissolved in 50% H_2SO_4 and refluxed. Significant reduction was obtained in this manner, as judged by the green color of the solution. However, this method

seemed to offer no great advantage over the dissolution of Mallinkrodt UO_2 , and so was not investigated in any detail.

B. Uranyl Sulfide Process

The second method for preparing UO_2 at low temperatures is by the decomposition of uranyl sulfide. In this process uranyl sulfide is precipitated by addition of uranyl nitrate to an ammonium sulfide solution. The precipitate is then digested in the supernate at a temperature of 40° to 100°C to decompose the uranyl sulfide to UO_2 and sulfur. The solids are then separated and the UO_2 is dissolved in nitric or nitric-sulfamic acid at temperatures from 60° to 100°C , and the sulfur is then separated from the solution.

1. Precipitation of Uranyl Sulfide

The precipitation of a brown, flocculent uranyl sulfide precipitate by addition of ammonium sulfide to dilute aqueous uranyl nitrate solutions which have been neutralized with ammonium hydroxide, or to alcoholic uranyl nitrate solutions, has been reported⁽⁴⁾. The decomposition of uranyl sulfide to UO_2 and S has also been reported⁽⁵⁾, but these reactions have not been studied in any detail.

The results of this work indicate that the precipitate may contain several different compounds, not all of which can be decomposed to UO_2 and S, and that the composition of the precipitate depends on reaction conditions. The precipitate under certain

conditions may contain, in addition to uranyl sulfide, ammonium diuranate or "uranium red."⁽¹⁾ The composition of this latter compound is not well defined, but the U is present in the hexavalent state, and it decomposes partially in dilute acids to ammonium diuranate with the release of both H_2S and free sulfur. This may be due to the presence of a hydrogen polysulfide group in the compound. In any event, it is clear that the reaction conditions must be carefully controlled in order to insure the precipitation of uranyl sulfide. The variables investigated were concentration of reagents, excess of ammonium sulfide, and method and order of addition of reagents. The effect of these variables was determined by measuring the extent to which the precipitate could be decomposed to UO_2 and S, as determined by tetravalent and total uranium analyses of the product in phosphoric and nitric acid solutions. No attempt was made to determine the composition of the undigested precipitate. In most cases the precipitation was done at room temperature, since earlier experiments in which the temperature was varied showed that this is not a significant variable. Several runs in which sodium sulfide was substituted for ammonium sulfide were not successful, apparently due to a much greater tendency toward uranium red formation in this system.

The most important variable in this reaction is the method and order of addition of reagents. The recommended procedure is slow addition of uranyl nitrate to ammonium sulfide, with good

agitation. If ammonium sulfide is added slowly to uranyl nitrate, precipitation occurs locally when the two liquids meet, but the precipitate redissolves rapidly with agitation, until the pH of the solution is raised sufficiently to allow precipitation of uranyl sulfide. When the initial precipitate redissolves, ammonium sulfide is liberated and is rapidly decomposed in the acid solution, and when the pH is finally raised sufficiently, ammonium diuranate is precipitated along with uranyl sulfide. The presence of ammonium diuranate in the precipitate has also been noted by Schwarz⁽⁶⁾. Thus, when ammonium sulfide was added slowly to uranyl nitrate, and the precipitate was decomposed and dissolved in phosphoric acid, only about 50 to 70% of the U appeared in the tetravalent state. When the order of addition was reversed, so that the precipitation was conducted in a basic solution, at least 85% of the U appeared in the tetravalent state. This latter result might also be obtained by very rapid addition of ammonium sulfide to uranyl nitrate, thus raising the pH of the solution before appreciable decomposition of ammonium sulfide could occur, but this procedure did not always yield reproducible results. Further evidence for the decomposition of ammonium sulfide when it is added slowly to uranyl nitrate is the fact that when this addition was made to the point where the pH was just below that required for the precipitation of uranyl sulfide, and the solution was filtered, free sulphur was separated from the solution. Contrary to statements in the literature, the addition of

ammonium hydroxide to the uranyl nitrate prior to sulfide precipitation had no effect on the results. It was not possible by this means to raise the pH of the solution sufficiently without precipitating ammonium diuranate, to prevent decomposition of ammonium sulfide.

Another important variable which was investigated is the final pH of the supernate. According to the stoichiometry of the reaction, one mole of ammonium sulfide is required per mole of uranyl nitrate. Using the stoichiometric amount of ammonium sulfide results in a supernate having a pH of ~ 4.5 . At this pH there is some tendency to form "uranium red", and when decomposition of this precipitate is attempted, there is considerable evolution of H_2S and very little reduction of U to the tetravalent state. In order to avoid "uranium red" formation, the final pH of the supernate should be at least 7.5, which corresponds to a 47.7% excess of ammonium sulfide.

The extent of "uranium red" formation is also somewhat dependent on the concentration of reagents used. In most of these experiments, the uranyl nitrate concentration was constant at 1.39 M, and the ammonium sulfide concentration was varied from 1.1 to 5.7% (based on dilution of Baker and Adamson reagent grade 22.6% solution). The upper limit of ammonium sulfide concentration was set by the fact that, at this concentration, the slurry became so thick that good agitation became difficult toward the end of the precipitation. Under these conditions, even with a sufficient excess of ammonium sulfide, there may be local areas of low pH where

"uranium red" will be formed. In order to end up with a mobile slurry, and a final pH of 7.5, the maximum ammonium sulfide concentration that can be used with this uranyl nitrate concentration is about 2.5%.

It should be noted that the presence of 1 M HNO_3 in the uranyl nitrate solution has no effect on the reaction, except, of course, to increase the ammonium sulfide consumption if the excess acid is not neutralized prior to precipitation.

2. Decomposition of Uranyl Sulfide

Because of the complex composition of the precipitate, a detailed study of kinetics of uranyl sulfide decomposition was not undertaken. However, from a process point of view, the important variables affecting the extent and rate of decomposition are the decomposition temperature and the concentration of reagents used to prepare the uranyl sulfide.

Although uranyl sulfide is unstable even at 20°C, the rate of decomposition at temperatures below 40°C is too low to be of practical interest. Therefore, decomposition temperatures of 40°, 60°, and 100°C were selected for study. Although the rate increases rapidly with increasing temperature, the lower decomposition temperatures are of interest because of the effect of this variable on the ease of dissolution of the UO_2 product without re-oxidation, which will be discussed in detail in a later section.

The results of decomposition studies are shown in Figs. 3 and 4. These data were obtained by dissolving the product in concentrated phosphoric acid with an inert gas sparge, and analyzing the solution for tetravalent and total U . It should be noted that careful washing of the solids prior to dissolution in phosphoric acid is essential, since any ammonium nitrate present in the liquid still remaining after filtration will be decomposed by concentrated phosphoric acid, causing some oxidation, and yielding results which are not reproducible. However, thorough washing is difficult due to the tendency of UO_2 prepared in this manner to peptize, which not only makes filtration difficult, but results in an increased tendency to oxidation because of the extremely fine particles which are produced. The most satisfactory procedure is to wash twice with 1% ammonium sulfide, which is just as effective as a water wash, and results in less tendency to peptization.

Although the data show considerable scatter, presumably due to the presence of residual nitrate in the samples, it is nevertheless possible to draw certain significant conclusions. It is apparent that the rate of decomposition varies inversely with the nitrate concentration in the supernate during digestion, possibly because of some re-oxidation of the product with increasing nitrate concentration. Although it appears that the rate of reaction begins to slow down after about 80% completion, it is difficult to tell

from these data whether the reaction proceeds slowly to completion, or whether the reaction ceases after this point. It is possible that reduction does not proceed beyond this point due to the presence of compounds other than uranyl sulfide in the precipitate. For purposes of developing this process, the exact shape of the curve for decomposition greater than 80% is not important, since the oxidation which occurs during dissolution in nitric acid results in a final solution containing approximately the same ratio of tetravalent to total U concentration, under the same conditions of dissolution, independent of the tetravalent U content of the digested precipitate provided that this is above 80%. Thus, decomposition at 40°C at a nitrate concentration of 0.218 M, corresponding to use of 1.24% $(\text{NH}_4)_2\text{S}$, is essentially complete in about 45 min, while at a nitrate concentration of 0.464 M, 2.48% $(\text{NH}_4)_2\text{S}$, about 90 min is required. At 60°C, at a nitrate concentration of 0.464 M, decomposition is essentially complete in about 15 min. At 100°C, the reaction rate was too rapid to be measured, reduction being complete in about 2 min. It should be noted that these rates are independent of the pH of the supernate over the range 7.5 to 9.1.

These results are confirmed by the data shown in Fig. 8, which shows the ratio of tetravalent to total U in the final nitric acid solution as a function of dissolution time. The points in Fig. 8 represent decomposition conducted at nitrate concentrations

ranging from 0.139 to 0.464 M. All of the decompositions at 60°C were run for 30 min, while the 40°C decompositions were run for 90 min at 0.464 M nitrate, and one hour at the lower concentrations. The results show that the decomposition times indicated are sufficient to yield satisfactory solutions on dissolution in nitric acid. Extrapolation of the curves shown in Fig. 8 to zero time indicates about 86% decomposition, which is in agreement with the curves shown in Fig. 3.

It should be noted that a useful qualitative indicator of the extent of decomposition is the color of the precipitate. During decomposition the precipitate turns from light brown to black, and a completely black precipitate is indicative of complete decomposition. The appearance of a deep red or purple color indicates that decomposition to UO_2 is not taking place, and is indicative of too low a pH. It should also be noted that washing of the separated solids prior to dissolution in nitric acid is not recommended, for reasons previously cited.

3. Dissolution of UO_2 .

The selection of a satisfactory set of conditions for dissolving this UO_2 in nitric acid is determined by the rate of re-oxidation as well as the dissolution rate. It was therefore necessary to first define those conditions under which dissolution could be accomplished with an acceptably low rate of oxidation.

There appear to be two types of oxidation which can occur during dissolution. The more serious of the two is an autocatalytic oxidation, probably due to reaction with nitrous acid, which results in complete oxidation in about 1 min after it starts. This type of oxidation is dependent on dissolution temperature, nitric acid concentration, disposition of overhead vapors during dissolution, concentration of reagents used to precipitate uranyl sulfide, and digestion temperature. The first three of these variables determine the concentration of nitrous acid in solution, while the latter two are thought to be related to the surface area of the particles.

The conditions under which dissolution can be accomplished without autocatalytic oxidation are summarized in Table I. It can be seen that the only condition under which this UO_2 can be dissolved in nitric acid without an oxidation inhibitor are digestion at 40°C and dissolution at 60°C . Under these conditions, even at the maximum ammonium sulfide concentration used for the precipitation, dissolution in 4 M HNO_3 is possible without return of overhead vapors to the solution. At 60°C no solution makeup is required even without any provision for condensation. At higher digestion and dissolution temperatures some oxidation inhibitor is required, even without return of overhead vapors. Sulfamic acid was the only inhibitor studied in detail. A few scouting experiments were made using hydroxylamine, and indicated that this is a satisfactory inhibitor, but requires much higher concentrations than were used with sulfamic acid.

The results of dissolution rate studies are shown in Figs. 5, 6 and 7. In case of UO_2 prepared at 40°C and dissolved at 60°C , the initial nitric acid concentration was varied from 1 to 4 M, and all other dissolution studies were done in 4 M nitric acid. It was assumed that the product is $\text{U}(\text{NO}_3)_4$, thus requiring four moles of acid per mole of U dissolved. The reaction appears to be first order with respect to nitric acid concentration, and independent of variations in surface area of the UO_2 during dissolution. The ratio of solids to solution volume was varied by a factor of six, but all attempts to correlate the data using rate equations which took into account variations in surface area, failed. Also, it would be expected that variations in reagent concentrations and agitation rate during uranyl sulfide precipitation, and possibly digestion temperature, would affect particle size, but none of these variables, with the exception of digestion temperature, had any effect on the dissolution rate. Surface area was not measured because of the difficulty of outgassing this material without changing the area, and because the presence of occluded sulfur would probably prevent a true measurement of the UO_2 surface area. The lack of dependence of dissolution rate on surface area tends to indicate that the rate controlling step is chemical reaction between UO_2 and adsorbed nitric acid.

It should be noted that simple first order kinetics are not obeyed through the entire dissolution. In the case of material

prepared at 40° and 60°C , there is a short period at the beginning of the dissolution when the rate is more rapid than the first order rate followed later. This is probably due to more rapid dissolution of hexavalent U which is present either because of incomplete decomposition to UO_2 (due to the presence of compounds other than uranyl sulfide in the precipitate) or because of surface oxidation during handling between the digestion and dissolution steps.

In the case of material prepared at 60° and 100°C, it does not appear possible to prepare solutions containing more than 70 to 75 g U/l. Thus dissolution at 60°C of UO_2 prepared at 60°C followed first order kinetics for about 50 min after which the dissolution apparently stopped. The data for the dissolution of this same UO_2 at 80°C scattered so widely that it cannot be meaningfully correlated. Until the reasons for this scatter can be resolved, it was tentatively assumed that the reaction is first order as shown for about 20 min, after which the reproducibility is so poor that it is difficult to plot the cause of the reaction. With UO_2 prepared at 100°C, the dissolution is first order at both 60° and 100°C over the entire range studied, but the maximum concentration reached in any of these runs was 75 g/l. Dissolution at 60°C of UO_2 prepared at 40°C appears to be first order over the entire range investigated, although there is somewhat more scatter when the U concentration exceeded 70 g/l.

At least part of the reason for this scatter is the fact that the UO_2 was not dried prior to dissolution, and there may have been varying amounts of liquid associated with it, depending on the efficiency of separation, which diluted the acid. This effect would be greatest for solutions of high U concentration, and this is where the scatter is greatest.

That portion of the data which can be represented as a first order reaction follows the Arrhenius equation very closely, as shown in Fig. 9. With the exception of the point representing the dissolution at 60°C of material prepared at 100°C , the correlation is surprisingly good. From this plot, the activation energy for the dissolution is 10,300 cal/mol, and the rate of dissolution can be expressed by the following set of relationships for U concentrations up to 75 g/l:

$$\ln(1 - C/H_0) = -kt$$

$$\text{where } k = 2.14 \times 10^6 e^{-5180/T}$$

C = concentration of U, mol/l

t = dissolution time, hr,

H_0 = initial acid concentration, mol/l

The oxidation rates during dissolution are shown in Fig. 8. The oxidation rate is essentially independent of nitric acid concentration, provided the recommended concentrations of inhibitor are used, and appears to be a first order reaction. At 60°C , about 71% of the U is in the +4 state after 1 hr, while at 80°C about 74%

of the U is in the +4 state after 1/2 hr.

A detailed investigation of the stability of these solutions was not undertaken. However, in several instances analyses were not performed until the day following the run, so these solutions were kept at room temperature for about 20 hr. These results are included in Fig. 8, and do not deviate significantly from the other data. Qualitatively, it was observed that the higher the U concentration, the more stable the solution.

This method of preparing uranous nitrate solutions is the most attractive of those studied and is recommended for further study on a larger scale. The operations and equipment involved are simple and conventional, no difficult corrosion problems are anticipated, and the reactions are reasonably rapid and do not require the use of excessively costly chemicals.

Summary and Conclusions

Several methods of preparing uranous nitrate solutions have been investigated on a laboratory scale. The most promising method is based on precipitation and decomposition of uranyl sulfide, followed by dissolution of the resulting UO_2 in nitric acid, and separation of the sulphur. The major conclusions regarding the various steps of this process are:

- 1) The precipitation is best done by slow addition, with agitation, of 1.4 M uranyl nitrate to ammonium sulfide, of concentrations not greater than 2.5% so that the final pH of the supernate is at least 7.5 or higher. This requires the use of at least a 47.7%

excess of ammonium sulfide.

2) Decomposition is accomplished by digesting the precipitate in the supernate at a temperature of 40°C. If 2.5% ammonium sulfide is used, 90 min is required for decomposition, while if 1.25% ammonium sulfide is used, 50 min is sufficient. The solids should be separated without washing, following the digestion step.

3) The dissolution is best accomplished at 60°C in 4 M HNO₃. The reaction is first order with respect to nitric acid concentration, and has an activation energy of 10,300 cal/mol. A 1-hr dissolution under these conditions will yield a solution containing 83 g U/l. The rate of oxidation during dissolution is approximately linear and results in a solution in which 71% of the U is in the tetravalent state after a 1-hr dissolution. The rate of oxidation during storage at room temperature is negligible after 24 hr for a solution of this U concentration, but increases rapidly with decreasing U concentration.

4) Although many variations in process conditions are possible, the conditions just outlined are recommended because they permit dissolution of the UO₂ in nitric acid without an oxidation inhibitor. Raising either the decomposition or dissolution temperature will make the use of an inhibitor during the dissolution necessary.

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Table I

Inhibition of Oxidation during Dissolution

Digestion Temp. °C	(NH ₄) ₂ S Conc. Used in Precipitation	Dissolution Temp.	Condenser Updraft	HNO ₃ Conc.	NH ₂ SO ₃ H Conc.
40	1.25	60	yes	4	0
40	2.5	60	no	4	0
60	2.5	60	yes	4	0.02
60	2.5	80	yes	4	0.02
100	2.5	60	yes	4	0.10
100	2.5	100	yes	4	0.15

Literature Cited

1. Gmelin, L., "Handbook of Inorganic Chemistry and Isotopes", TID 82 (Supplement 1), March 1952, p. 2.
2. ibid, Supplement 2, November 1954, p. 57.
3. Jenkins, E.N., and Streeter, R.J.W., "The Use of U IV as a Reagent in the Aqueous Processing of Irradiated Uranium", Dec. 1959.
4. Kern, E. F., J. Am. Chem. Soc. 23, 701 (1901).
5. Remele, A., Compt. Rend. 58, 717 (1864).
6. Rodden, C. J., Ed., Analytical Chemistry of the Manhattan Project McGraw-Hill, New York, 1950.
7. Sanlaville, J., P/1259, Geneva Conference, 1958.
8. Stoller & Richards Ed. Reactor Handbook, Vol. II, 2nd Ed., Interscience, N. Y., 1961

Figure 1. Effect of H_2SO_4 concentration on dissolution of UO_2 in H_2SO_4 -HF solutions.

Figure 2. Effect of HF concentration on dissolution of UO_2 in 2 M H_2SO_4 .

Figure 3. Decomposition of uranyl sulfide at 40°C.

Figure 4. Decomposition of uranyl sulfide at 60°C.

Figure 5. Dissolution of UO_2 at 20°C and 40°C.

Figure 6. Dissolution of UO₂ at 60°C.

Figure 7. Dissolution of UO₂ at 80°C and 100°C.

Figure 8. Oxidation of uranium during dissolution.

Figure 9. Arrhenius plot for dissolution of UO_2 .