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DEVELOPMENT OF A BATCH PROCESS FOR THE PRODUCTION
OF A $\text{ZrO}_2\text{-UO}_2$ SOLID SOLUTION

Work done by:

S. W. Hayter
R. E. Smith
A. C. Dumrose
R. J. Bard
H. R. Baxman
J. P. Bertino
J. A. Kircher

Report written by:

S. W. Hayter
R. J. Bard

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ABSTRACT

A batch process on the 2-kg scale was developed for the production of $\text{ZrO}_2\text{--UO}_2$ solid solution in the weight proportion of about 4 to 1. The product is tetragonal $\text{ZrO}_2\text{--UO}_2$ solid solution, with no UO_2 lines showing on the X-ray powder diffraction patterns. The solid solution is prepared from a precipitate of $\text{Zr(OH)}_4\text{--(NH}_4)_2\text{U}_2\text{O}_7$ which is filtered, dried, milled, screened to minus 325 mesh, and heated at 900°C in H_2 for 4 hours. The success of the preparation depends strongly on the conditions of the precipitation, with precipitation from dilute salt solution being necessary to avoid undissolved UO_2 in the final product.

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1. INTRODUCTION

A process for the production of $\text{ZrO}_2\text{--UO}_2$ solid solution was developed in anticipation of the need for commercial grade ZrO_2 —depleted UO_2 solid solution and low-hafnium ZrO_2 —enriched UO_2 solid solution, to be used for the preparation of ZrC--UC_2 in the weight proportion of 4 to 1. Because of the possibility that relatively large quantities of these solid solutions would be required, it was desired to keep the temperature of preparation down to that which could be attained in existing UO_2 hydrofluorination equipment. A maximum temperature of 900°C was chosen in this connection.

Pure ZrO_2 transforms from the low-temperature monoclinic structure to the high-temperature tetragonal structure at about 1000°C .¹⁻³ Room-temperature X-ray powder patterns on samples of various specimens of ZrO_2 quenched from temperatures⁴ between 900°C and 2315°C and on samples of ZrO_2 quenched from temperatures up to and above the melting temperature⁵ have been reported to show only the monoclinic phase. It has been reported that ZrO_2 will take up to 20 mole % of UO_2 into solid solution below the monoclinic—tetragonal transformation temperature and that the solid solution lowers the monoclinic—tetragonal transformation temperature.^{5,6} It has also been reported that reactions of ZrO_2 with oxides of larger tetravalent ions, such as CeO_2 and UO_2 , may yield tetragonal solid solutions which exist at room temperature.⁷

2. MATERIALS

In the present development work, normal or depleted uranium compounds and zirconium compounds containing about 2% hafnium were used. The weight percentages reported for ZrO_2 are really those for ZrO_2 plus accompanying HfO_2 . The solid solution composition sought was 82.3 wt. % $\text{ZrO}_2(\text{HfO}_2)$ —17.7 wt. % UO_2 (9.1 mole % UO_2).

Preliminary experiments were carried out with CP grade ZrO_2 and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Spectrographic analysis showed the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ to be of good purity. Experiments on the attempted determination of optimum

precipitation conditions (Section 3.2) and the full-scale precipitation experiments (Section 3.3) were carried out with samples from a 50-lb lot of CP grade $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Spectrographic analysis of this material showed greater than 1% Na, 0.2 to 0.5% Si, 0.1% K, 0.1 to 0.3% Ca, 0.1 to 1% Ti, and 0.1% Fe as major impurities after calcination. The material assayed 1.8 wt. % hafnium in zirconium plus hafnium. Aqueous solutions of this material were slightly cloudy even after attempted clarification through filter paper. However, as described in Section 3.2, the success of the process does not appear to depend on the purity of reagents within the impurity limits encountered.

3. EXPERIMENTAL WORK, RESULTS, AND DISCUSSION

3.1 Preliminary Experiments

Lambertson and Mueller⁵ obtained a mixture of tetragonal and monoclinic phases when a mixture prepared from ZrO_2 and 18.6 mole % of UO_2 was heated in H_2 at 1400°C and cooled. When samples of a mixture of ZrO_2 and UO_2 in the weight ratio of about 4 to 1, which had been repeatedly mixed, ground with a mortar and pestle, and screened, were heated in H_2 for 24 hours at 1200°C and at 1450°C , the X-ray powder patterns showed UO_2 lines in addition to those of monoclinic ZrO_2 for the 1200°C product and lines of only monoclinic ZrO_2 and tetragonal $\text{ZrO}_2\text{--UO}_2$ solid solution for the 1450°C product.⁸

It was thought that solid solution formation might take place at 900°C if an intimate enough mixture of the oxides could be prepared. Two possibilities considered were the mixing of active (low-fired) compounds of zirconium and uranium and the preparation of intimately mixed zirconium and uranium compounds by simultaneous precipitation from a mixed salt solution. Of the systems considered for precipitation, only the hydroxides looked promising. ZrO^{++} and UO_2^{++} are precipitated from cold solution by ammonium hydroxide as $\text{Zr}(\text{OH})_4$ and $(\text{NH}_4)_2\text{U}_2\text{O}_7$, respectively. The values of pH at which these precipitates form from dilute salt solutions are reported to be 2 and 4.2, respectively.⁹ On the other hand, both zirconium and uranyl oxalates are appreciably soluble; and zirconium peroxide is soluble in acid solution.¹⁰

To check the above possibilities, mixtures were made as follows and were heated at 900°C in H_2 for 4 hours:

1. A mixture of CP grade ZrO_2 powder and microcrystalline UO_2 , which had been prepared from U_3O_8 by reduction with H_2 at 700°C , was ball-milled for $\frac{1}{2}$ hour.

2. A mixture of precipitated Zr(OH)_4 , which had been heated for 16 hours at 300°C , and " UO_3 ", which had been prepared by heating uranium peroxide for 16 hours at 300°C , was ball-milled for $2\frac{1}{2}$ days. [The Zr(OH)_4 was prepared by adding 120 ml of concentrated ammonium hydroxide, a 20% excess, containing 16 g of salicylic acid, dropwise to a stirred solution containing 121 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 1 liter of solution. This is a procedure reported for the preparation of Zr(OH)_4 in readily filterable form.^{11]}
3. A mixture of precipitated Zr(OH)_4 , which had been heated for 16 hours at 300°C , and UO_2 , which had been prepared by reduction of the " UO_3 " described above with H_2 for 2 hours at 700°C , was ball-milled for $2\frac{1}{2}$ days.
4. A precipitate of $\text{Zr(OH)}_4-(\text{NH}_4)_2\text{U}_2\text{O}_7$ was made by adding ammonium hydroxide to a solution of zirconyl chloride-uranyl nitrate. The filtered precipitate was dried at about 120°C for several days. The resulting material was ground with a mortar and pestle and the fraction passing a 325-mesh screen was taken.
5. A precipitate of $\text{Zr(OH)}_4-\text{U(OH)}_4$ was made by adding ammonium hydroxide to a solution of zirconyl nitrate-uranous chloride. The filtered precipitate was treated as in item 4.

X-ray powder patterns were taken on as-milled Mixture 1 and on the products from heating the five mixtures at 900°C in H_2 for 4 hours. Results for each mixture were as follows:

1. Both unfired and fired samples gave identical patterns, which showed a mixture of monoclinic ZrO_2 and UO_2 .
2. The fired sample was composed of tetragonal ZrO_2-UO_2 solid solution, monoclinic ZrO_2 , and UO_2 . The proportion of tetragonal ZrO_2-UO_2 solid solution was somewhat greater than that of monoclinic ZrO_2 .
3. The fired sample was composed of tetragonal ZrO_2-UO_2 solid solution, monoclinic ZrO_2 , and UO_2 . The proportions of tetragonal ZrO_2-UO_2 solid solution and monoclinic ZrO_2 were about equal.
4. The fired sample was composed of about a 2:1 mixture of tetragonal ZrO_2-UO_2 solid solution and monoclinic ZrO_2 . No UO_2 could be detected.
5. The fired sample was composed almost entirely of tetragonal ZrO_2-UO_2 solid solution, with only a very small proportion of monoclinic ZrO_2 . No UO_2 could be detected.

The data on Mixtures 2 and 3 show an effect of the state of consolidation of the uranium oxide before mixing on the kinetics of ZrO_2-UO_2 solid solution formation. " UO_3 " obtained from uranium peroxide by heating in air below 400°C is amorphous and of large surface area, whereas UO_2

prepared by reduction of "UO₃" with H₂ at 700°C has crystallites in the size range of a few tenths of a micron.¹² In the heating up of the mixture of Zr(OH)₄ and "UO₃" in H₂, reduction of the "UO₃" to UO₂ takes place quite rapidly above about 550°C, and prior to any extensive ZrO₂-UO₂ solid solution formation a very intimate mixture of ZrO₂ and UO₂ exists. That this mixture is more intimate than the one obtained by heating a mixture of Zr(OH)₄ and previously prepared UO₂ is evidenced by the larger proportion of tetragonal ZrO₂-UO₂ solid solution in the product from the former.

Analyses on unfired samples of Mixtures 4 and 5 showed proportions of zirconium and uranium equivalent to only 11.9 wt. % of UO₂ and 10.9 wt. % UO₂, respectively. After these analyses had been reported, a check on the relative amounts of salts used in the precipitations revealed an error. However, the possible utility of the precipitation method for the preparation of suitable mixtures of the desired composition was strongly indicated.

Following these initial experiments, three lots of ZrO₂-UO₂ solid solution were prepared for use in preliminary development work on the preparation of ZrC-UC₂.

Six precipitations were made using the conditions of the preparation of Mixture 4 above, with corrected amounts of zirconium and uranium salts. For each precipitation 108 g of ZrOCl₂ · 8H₂O was dissolved in 2 liters of distilled water. A solution of 9.4 g of U₃O₈ in 28 ml of concentrated nitric acid was mixed with the zirconyl chloride solution. (These quantities correspond to 50 g of ZrO₂-UO₂.) Five hundred milliliters of 1:1 NH₄OH was added slowly to the zirconyl chloride-uranyl nitrate solution with stirring by a Mag-Mix. (The choice of these precipitation conditions was purely arbitrary and, as will be seen later, very fortunate.) The voluminous, gelatinous precipitate was filtered on a medium frit. The combined precipitates were dried in an oven at about 120°C for several days. The resulting material, which was extremely hard and brittle, was ball-milled in a steel ball mill. The ground material was screened to give a minus 325-mesh powder, which was then heated at 900°C in H₂ for 4 hours. The X-ray powder pattern of a sample of this product showed only tetragonal ZrO₂-UO₂ solid solution. Analysis of the product for zirconium and uranium showed 81.0 wt. % ZrO₂ and 19.0 wt. % UO₂. A sample of the combined filtrates from the precipitations showed no detectable zirconium (less than 0.2%) or uranium (less than 1 mg/liter).

Six precipitations of Zr(OH)₄-(NH₄)₂U₂O₇ were made on the scale of 100 g of ZrO₂-UO₂ by slow addition of 1 liter of 1:1 NH₄OH to 4 liters of salt solution containing zirconyl chloride and uranyl nitrate. The combined precipitates were processed to final product as before. The X-ray powder pattern of a sample of the final product showed only tetragonal ZrO₂-UO₂ solid solution. Analysis of the final product for zirconium and uranium

showed 80.9 wt. % ZrO_2 and 19.2 wt. % UO_2 .

Six precipitations of $\text{Zr}(\text{OH})_4-(\text{NH}_4)_2\text{U}_2\text{O}_7$ were then made on the scale of 200 g of ZrO_2-UO_2 by simultaneous slow addition of 600 ml of 1:1 NH_4OH and 600 ml of salt solution containing zirconyl chloride and uranyl nitrate to 4 liters of distilled water. The combined precipitates were processed to final product as before. The X-ray powder pattern of a sample of the final product showed only tetragonal ZrO_2-UO_2 solid solution, except for several percent of an impurity which was identified as iron by spectrographic analysis. Analysis of the final product for zirconium and uranium showed 80.8 wt. % ZrO_2 and 17.2 wt. % UO_2 .

Spectrographic analyses of samples of each of the above three lots showed the products to be of reasonably good purity, except for the third lot which had picked up iron from grinding with stainless steel balls in a steel mill.

Concurrently with the above preparations several attempts were made to improve the character of the $\text{Zr}(\text{OH})_4-(\text{NH}_4)_2\text{U}_2\text{O}_7$ precipitate, which was very difficult to filter due to its gelatinous nature. In an experiment on the 25-g scale a homogeneous precipitation was carried out by heating a mixed salt solution containing urea. The precipitate formed as clumps of opaque jelly. X-ray examination of the final product obtained by processing this precipitate in the usual way showed the UO_2 pattern plus that of monoclinic ZrO_2 . Undoubtedly the slow and homogeneous rise in pH during the precipitation resulted in the precipitation of the zirconium prior to the uranium. In another experiment, carried out on the 100-g scale, 600 ml of 1:1 NH_4OH and 600 ml of salt solution containing zirconyl chloride and uranyl nitrate were slowly added simultaneously to 2 liters of water containing 20 g of salicylic acid. No improvement in the character of the precipitate resulted from the use of salicylic acid. The precipitate was processed to final product in the usual way. X-ray examination of the final product showed the UO_2 pattern plus that of monoclinic ZrO_2 .

3.2 Attempted Determination of Optimum Precipitation Conditions

A production-batch size of 2 kg of ZrO_2-UO_2 solid solution was selected, in keeping with nuclear safety requirements for aqueous solutions containing enriched uranium. A series of precipitations from zirconyl-uranyl nitrate solutions with NH_4OH were made on the 200-g scale (one tenth of planned production scale) in an attempt to find the best procedure for obtaining the fastest filtering precipitate with the smallest volume. More concentrated solutions than had been used in the preliminary experiments were employed, with the view of cutting down the volume of filtrate which might have to be

processed for recovery of enriched uranium. The effects of dilution, order of reagent addition, rate of reagent addition, temperature of the precipitation, and pH were briefly surveyed. Conditions of the experiments are given in Table 1.

A 50-lb lot of CP grade $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and good purity normal U_3O_8 were used in preparing the mixed salt solutions for Experiments 1 through 12 and for experiments to confirm the results of these. A standard salt solution containing 36.8 g of U_3O_8 dissolved in 24 ml of concentrated nitric acid (20% excess of acid) plus 350 g of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, all brought into solution at a volume of 500 ml, was made up for each experiment. [The 350 g figure for the $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was based on a composition factor of 0.98, which was determined by calcination prior to receipt of the spectrographic analysis on this material.] Vigorous agitation was used in all experiments during the addition of reagents and for a few minutes after completion of the addition. Four-liter beakers were used for all 2000 ml experiments, and eight-liter battery jars were used for all 4000 ml experiments. The base-addition experiments were made by adding 500 ml of 1:1 NH_4OH (20% excess) to the standard salt solution diluted to either 1500 ml or 3500 ml. The simultaneous-addition experiments were made by streaming 500 ml of 1:1 NH_4OH and 500 ml of standard salt solution into either 1000 ml or 3000 ml of water, with the flows being regulated to maintain the desired pH range during precipitation. In the salt-addition experiments 500 ml of salt solution was added to 1500 ml of NH_4OH solution. The latter contained 250 ml of concentrated NH_4OH in Experiment 10 and 500 ml of concentrated NH_4OH in Experiments 11 and 12. All precipitates were filtered on No. 42 Whatman paper using a 2000 ml porcelain Buchner funnel.

During the precipitations of Experiments 1 through 9 a very heavy gel formed at the stoichiometric point. The gel was beaten into a heavy slurry after addition of the excess base.

It was thought that formation of a rigid gel might be a problem in production and that it might not form if the pH of precipitation were always greater than 7.5. Thus the salt-addition method of Experiment 10 was tried, and the rigid gel did not form. During the precipitation in Experiment 10, the agitator was stopped for adjustment, and it was noted that the precipitate settled very fast. At the end of the precipitation at a pH of 8 the suspension behaved similarly to those in Experiments 1 through 9. Therefore the conditions of Experiment 11 were tried, in which all the precipitation occurred in highly basic solution. A fast-settling, fast-filtering precipitate, with a smaller volume of filter cake than previously encountered, was obtained. The precipitate was somewhat granular and contained white globules dispersed among the yellow particles. Experiment 12 was made to reproduce Experiment 11.

Table 1
PRECIPITATION DATA

Experiment Number	Volume of Suspension, ml	Method of Precipitation	Temperature		pH			Time, minutes		Volume of Precipitate, cm ³
			Initial	Final	Initial	During Precipitation	Final	Reagent Addition	Fil- tration	
1	2000	Simultaneous addition	28°C	32°C	--	2-3	8.5	7	24	1400
2	2000	Simultaneous addition	27°C	27°C	--	6-7	8.5	43	29	1200
3	2000	Base addition	33°C	30°C	0.6	--	7.6	34	13	1200
4	2000	Base addition	30°C	30°C	0.6	--	8.0	5	18	1400
5	4000	Simultaneous addition	25°C	27°C	--	6-7	7.5	35	72	1800
6	4000	Simultaneous addition	24°C	24°C	--	5-6	8.0	5	45	1600
7	4000	Base addition	30°C	33°C	0.7	--	8.0	4	45	1800
8	4000	Base addition	29°C	28°C	0.7	--	7.5	33	65	1800
9	2000	Base addition*	80°C	70°C	0.7	--	7.5	3	13	1400
10	2000	Salt addition	Approx. room		2.5N (OH ⁻)	--	8.0	5	12	1000
11	2000	Salt addition	Approx. room		5.0N (OH ⁻)	--	1.9N (OH ⁻)	5	5	<1000
12	2000	Salt addition	30°C	35°C	5.0N (OH ⁻)	--	1.9N (OH ⁻)	3	4	850

*Precipitate was digested on the steamplate for 4 hours, at a temperature ranging from 55°C at the top of the beaker to 92°C at the bottom.

Samples of the filter cakes from Experiments 10 and 11 were dried, ground, screened, and heated at 900°C in H₂ for 4 hours. The X-ray powder patterns of these products showed UO₂ lines in addition to those of tetragonal ZrO₂-UO₂ solid solution and monoclinic ZrO₂. Experiment 11 was duplicated, except that the reagents were heated to 80°C prior to precipitation. The precipitate was granular, but dispersed white globules were not discernible. The X-ray powder pattern of final product made from this precipitate showed UO₂ lines.

Final product made from the filter cake from Experiment 9 showed only tetragonal ZrO₂-UO₂ solid solution, with no detectable UO₂, upon X-ray examination. Experiment 9 was duplicated, except that the 4-hour digestion was eliminated. The X-ray powder pattern of final product made from this precipitate showed UO₂ lines.

The conditions of Experiment 4 were thought to be most desirable from a production standpoint. Consequently, a sample of final product made from the filter cake from Experiment 4 was submitted for X-ray analysis. The X-ray pattern showed UO₂ lines. Prior to the receipt of this analysis, six precipitations had been made using the conditions of Experiment 4. A sample of final product from the combined precipitates was also found to have UO₂ lines in the X-ray powder pattern. Likewise, final products made from the filter cakes from Experiments 3 and 8 had UO₂ lines in the X-ray powder patterns.

Because of these results, an attempt was made to reproduce results of the successful original experiments on a 50-g scale. CP grade ZrO(NO₃)₂ · 2H₂O from the 50-lb lot, CP grade ZrO(NO₃)₂ · 2H₂O from another source, and CP grade ZrOCl₂ · 8H₂O were used in three experiments. In each experiment 9.4 g of normal U₃O₈ dissolved in 28 ml of concentrated nitric acid plus the proper amount of zirconyl salt was dissolved in 2 liters of water, and 500 ml of 1:1 NH₄OH was added slowly to the vigorously stirred salt solution. Samples of final product prepared from each of these precipitates were similar. The X-ray powder pattern of each showed tetragonal ZrO₂-UO₂ solid solution and an appreciable proportion of monoclinic ZrO₂, but no detectable UO₂.

These experiments showed quite conclusively that the completeness of solid solution in the final ZrO₂-UO₂ product obtained by treatment at 900°C in H₂ for 4 hours is strongly dependent on the conditions of mixed hydroxide precipitation. A satisfactory precipitate can be prepared by slow addition of a large excess of 1:1 NH₄OH to a salt solution 0.17M and 0.017M in zirconyl salt and uranyl nitrate, respectively, whereas the precipitate prepared by slow addition of a 20% excess of 1:1 NH₄OH to a salt solution as dilute as 0.38M and 0.038M in zirconyl nitrate and uranyl nitrate, respectively (Experiment 8), is not satisfactory. This is the opposite of the effect of concentration that would be expected. Since the simultaneous precipitation of Zr(OH)₂ and

$(\text{NH}_4)_2\text{U}_2\text{O}_7$ results from local high concentrations of base during the neutralization, with the result that the more soluble $(\text{NH}_4)_2\text{U}_2\text{O}_7$ is precipitated and occluded with the $\text{Zr}(\text{OH})_4$, it would be expected that more concentrated salt solutions would yield more intimately mixed hydroxides.

3.3 Full-Scale Precipitations

The procedure which had been successful on the 50-g scale was scaled up by a factor of 40 for the preparation of a production-size batch (2 kg of $\text{ZrO}_2\text{--UO}_2$). A total of 3570 g of CP grade $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was brought into solution at a volume of around 5 liters along with 368 g of depleted U_3O_8 which had been dissolved in 1130 ml of concentrated nitric acid. The mixed salt solution was diluted to 80 liters in a 30-gallon glass-lined kettle. After the salt solution had been agitated for a few minutes, 20 liters of 1:1 NH_4OH was added over a period of 60 minutes. Agitation was excellent and no rigid gel formed. A sample of slurry was taken. Filtration was carried out on a stainless steel star filter with an effective area of 9 square feet and a mean pore opening of 65 microns. Filtering time was 1 hour. Steam was run through the jacket of the filter can for 2 hours. The resulting filter cake was still moist but was slightly crumbly. Samples were taken from several places at the bottom of the cake and were combined. The material was then stripped from the filter and was dried in the lower part of the filter can with 100 psi steam applied to the filter can steam jacket. Drying was complete in about 8 hours. The sample from the slurry and the combined sample from the filter cake were processed to final product by drying, milling, screening, and heating at 900°C in H_2 for 4 hours and were submitted for X-ray analysis. X-ray powder patterns of these products showed each to contain only tetragonal $\text{ZrO}_2\text{--UO}_2$ solid solution, with no detectable UO_2 . Analysis of the final product for zirconium and uranium showed 80.5 wt. % ZrO_2 —18.7 wt. % UO_2 .

A second full-scale precipitation of $\text{Zr}(\text{OH})_4\text{--}(\text{NH}_4)_2\text{U}_2\text{O}_7$ was made. All conditions were essentially the same as in the first full-scale precipitation, except that the 20 liters of 1:1 NH_4OH was added to the stirred salt solution over a period of only 20 minutes instead of over a period of 60 minutes. Samples of final product prepared from this precipitate were found by X-ray diffraction to contain a small amount of undissolved UO_2 .

A third full-scale precipitation of $\text{Zr}(\text{OH})_4\text{--}(\text{NH}_4)_2\text{U}_2\text{O}_7$ was then made, with all the conditions the same as in the first full-scale precipitation. Final product prepared from this precipitate was exclusively tetragonal $\text{ZrO}_2\text{--UO}_2$ solid solution. Analysis of the dried precipitate for zirconium and uranium showed 79.0 wt. % ZrO_2 —19.3 wt. % UO_2 .

It should be noted that in the successful preparations by direct addition of base to the salt solutions more than a fivefold excess of nitric acid was used to dissolve the U_3O_8 and that more than a fourfold excess of NH_4OH was used in the precipitation. It is not known if satisfactory precipitates can be obtained using a small excess, say 20%, of these reagents in conjunction with dilute salt solution. Also, the limiting conditions for preparation of a satisfactory precipitate by simultaneous addition of salt solution and NH_4OH solution to water were not established. The project was discontinued after the three full-scale precipitations were made.

4. SUMMARY

Tetragonal ZrO_2-UO_2 solid solution in the weight proportion of about 4 to 1, with no UO_2 lines showing on the X-ray diffraction powder patterns, can be prepared by heating a dried, milled, and screened precipitate of $Zr(OH)_4-(NH_4)_2U_2O_7$ at $900^\circ C$ in H_2 for 4 hours. A suitable precipitate can be made on a scale corresponding to 2 kg of ZrO_2-UO_2 by adding a large excess of 1:1 NH_4OH slowly with stirring to a mixed salt solution 0.17M in zirconyl nitrate and 0.017M in uranyl nitrate. The preparation of a satisfactory precipitate, which will yield a final product containing no undissolved UO_2 detectable by X-ray diffraction, is strongly dependent on the precipitation conditions, as evidenced by the fact that a satisfactory precipitate could not be prepared by slow addition of a 20% excess of 1:1 NH_4OH to mixed salt solutions as dilute as 0.38M in zirconyl nitrate and 0.038M in uranyl nitrate.

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