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LABORATORY STUDIES OF MIXED-OXIDE POWDER
PREPARATION BY CONTINUOUS AMMONIA PRECIPITATION

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April 1, 1968

ATLANTIC RICHFIELD HANFORD COMPANY
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission by
Atlantic Richfield Hanford Company under Contract #AT(45-1)2130

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I. INTRODUCTION

The nuclear power industry is growing toward fast reactor concepts using mixed plutonium-uranium fuels. The mixed oxides are currently the most favored of these fuels. However, for fast reactor fuel the oxides must be uniform, mixed crystals instead of a mixture of oxides (which may be used in thermal reactors such as PRTR).

The APED of General Electric specifies fuel elements for the SEFOR reactor be prepared from ammonia-coprecipitated uranium plutonium oxides which have been pressed into pellets and loaded into tubes. Test fuel elements have been prepared by their Vallecitos Laboratory using batch techniques.

The potential of using existing Plutonium Finishing equipment and preparing coprecipitated mixed crystal oxides on a continuous basis offers a way to diversify ARHCO's Plutonium production capabilities. The parallel processing requirements of a plutonium button line and a continuous-mixed oxide precipitation facility are shown in Figure 1. A simplified flow diagram (Figure 2) shows the relation of these oxide powder preparation operations to the fuel element production process.

Recently a problem has arisen on the shipping of plutonium nitrate for use in mixed oxide fuels. Radiolysis of the solution (plus valence state changes) has led to gas pressure problems in making the shipments. The customers obviously do not want to receive the simpler-to-ship plutonium oxide because the dissolving of plutonium oxide introduces unwanted fluoride or other impurities. However, if true mixed crystal uranium-plutonium oxides as a "master mix" were shipped, these

PLUTONIUM
BUTTON LINE FLOW SHEET

CO-PRECIPITATED OXIDE FLOW SHEET

FIGURE 1

PARALLEL PROCESSING REQUIREMENTS

FIGURE 2
SIMPLIFIED FLOW DIAGRAM
MIXED OXIDE FUEL
ELEMENT PRODUCTION

could be readily dissolved and blended in as feed for the customer's oxide production facility.

The work covered by this report is devoted to studies on the continuous coprecipitation of uranium diuranate-plutonium hydroxide by ammonia of a product which would meet the powder quality specifications. The goal was twofold: (1) to achieve a high filtration rate for the slurry (relative to plutonium oxalate, and in the same type of continuous precipitator) on a vacuum drum filter; and (2) to achieve satisfactory hydrogen reduction in a continuous vibrating tube reactor so as to give acceptable powder properties.

This experimental study was limited to the data of immediate interest for continuous processing by the ammonium precipitation route. It is further limited to those processes that might be performed in available equipment. It does not extend beyond the powder preparation step. The work was done with a nominal composition of 15% plutonium-85% uranium.

II. SUMMARY AND CONCLUSIONS

Experimental work in laboratory and prototype equipment has established that the existing Plutonium Finishing equipment has the potential of producing mixed oxides by the ammonia coprecipitation process.

Continuous precipitation of a slurry suitable as feed for a continuous drum filter is possible by using close pH control and elevated temperature. A throughput up to the plutonium oxalate filtration rate may be obtained (actinide weight basis).

Continuous hydrogen reduction may be achieved in a vibrating tube reactor if the equipment is capable of providing suitable temperatures, gas flow rates, and residence times. The actinide throughput capability has not been determined for the plutonium vibrating tube fluorinator.

By following the techniques developed in this work, the product oxide physical and chemical properties are suitable for fuel fabrication; the pelletizing characteristics were not measured, however.

Additional work needs to be done on the pelletizing characteristics of the mixed oxide powders and the demonstration of a suitable dryer-solids conveyor, such as the plutonium oxalate screw calciner.

III. BACKGROUND

A. Flow Sheet And Chemistry

The overall flow sheet for producing fast reactor fuel elements using mixed-crystal uranium-plutonium oxide pellets is shown in Figure 2, page 3. The major portion of this report is devoted to those chemical processes for producing the oxide powders required for pellet fabrication.

The basic process for preparing mixed crystal oxides by ammonia precipitation was demonstrated over a decade ago.^(1, 2) More recently it has been studied further,⁽³⁻⁵⁾ and test fuel elements have been fabricated by this technique for reactors such as SEFOR⁽⁶⁾ (Southwest Experimental Fast Oxide Reactor).

The following are the simplified chemical reactions involved.⁽¹⁾

The chemistry, however, for the ADU (ammonium diuranate) precipitation from UNH (uranyl nitrate hexahydrate) is not that simple. A study of the chemistry was required to convert batch

precipitation technology for a mixed crystal product to a continuous precipitation-continuous filtration technology needed for production of the sinterable mixed oxides. Figure 3 shows the uranium system chemistry involved:⁽⁷⁾ this chemistry formed the basis of a continuous ammonia-uranium precipitation technique developed in the laboratory⁽⁸⁾ based on pH control.

A curve of the uranium-plutonium nitrate titration with ammonium hydroxide is shown in Figure 4.⁽⁹⁾ This curve is similar to the curve obtained when ammonium hydroxide was titrated into a U(VI)-U(IV) chloride solution.⁽⁸⁾ Companion curves are shown in Figures 5 and 6. The uranyl nitrate precipitation curve (Figure 5) shows the uranium precipitation occurs between pH 3.0 and pH 4.0. Precipitation is shown in Figure 6 to occur in the region of pH 1.0 in a plutonium nitrate system.

B. Previous Work

The General Electric Vallecitos Laboratory (APED) has prepared mixed oxides on a batch basis limited to a few hundred grams per batch. The Nuclear Materials and Equipment Corporation (NUMEC) has done considerable work with a continuous precipitation-batch filtration process which has been limited to slightly over 1 kg of actinides per batch. DuPont has proposed a plant for mixed oxide fuel preparations,⁽⁵⁾ but the technical basis for their assumptions are not clear. The Appendices give typical mixed oxide preparation conditions for GE-APED, NUMEC, and duPont.

The English have described a full-scale plant based on continuous processing.⁽¹⁰⁾ Their process is described as being a "multi-stage feedback precipitation".⁽¹¹⁾

Most workers appear to have gone from uranium oxide fuel concepts⁽¹²⁾ to the mixed oxide concept in their engineering of fuel preparation. Since there is ample experience with

production of enriched uranium oxide fuel fabrication⁽¹³⁾ with its processing concepts similarly limited by critical mass limitations, the transition to plutonium-bearing oxides is not great.

C. Product Properties

Achieving a continuous process will be successful only if it turns out a product that meets specific requirements. Most important of these requirements is that the oxide is a true mixed crystal with PuO_2 in a lattice of UO_2 . The best method currently known to determine this structure is by x-ray diffraction of the crystals. While this method is subject to interpretation, a "standard" may be easily obtained by using the Vallecitos method of coprecipitation, which assures a mixed crystal precipitation by rapidly going to pH 9.5. A crude test involves dissolution in nitric acid--the true mixed crystal dissolves rapidly and completely; but free PuO_2 present does not dissolve.

The x-ray diffraction results are expressed as percent "free" PuO_2 in the mixed oxide. A value of <1% is the lower limit of detection of both the method and the SEFOR specification.

Another property that is important is the oxygen-to-metal (O/M) ratio. For powders this may be 2.0 to 2.3;⁽¹⁴⁾ but for sintered pellets, it is controlled much closer (e.g., 198 ± 0.01 , or 2.01 ± 0.001 , etc.).

Ensuring the proper fuel properties has been based less on powder properties than on the process used. The SEFOR fuel process specification (ammonia coprecipitation) is based on tests with fuel elements produced by that process. Properly sintering to pellets is a criterion for powders for SEFOR-type elements. A pellet press and a sintering furnace were not available for evaluating the powders produced in this work.

The measure of the capability of a powder to form a sinterable pellet is more difficult. However, conventional powder analyses are used as controls; these include particle size, surface area, etc. Relationships of most of the measurable parameters have been developed through experience with uranium oxide fuels.

Other types of specifications may be considered. Two specifications have been used at Hanford^(15, 16) based on processing rather than powder properties, as well as a specification for the powder.⁽¹⁷⁾ NUMEC characterizes their powders by measurement of their properties.

To support these studies, it was necessary to set up analytical methods. Those now available include x-ray diffraction, O/M ratio,^(18, 19) surface area, particle size, moisture, and x-ray fluorescence.

IV. EXPERIMENTAL WORK

A. Small-Scale Studies

1. Technique

The preliminary precipitation work was done with small-scale (5 to 10 g of actinides to a batch) runs, by the technique that has been detailed previously.⁽⁸⁾

Hydrogen firing was performed after drying the filter cakes at 100 to 150 °C in air. A quartz tube furnace capable of holding three 10 g boats was used. Heating-up was regulated to provide a 12 °C/min temperature increase. The operating temperature (750 °C) was maintained for 6 hr. The hydrogen was introduced as 6% H₂-94% N₂ at a rate of 3 ft³/hr from the beginning of heating up until the system cooled down after firing.

About 50 runs were made, primarily to demonstrate filterability relationships, most of the resulting filter

cakes were dried and hydrogen-reduced to determine if the precipitation technology yielded a true mixed crystal product.

Selected runs are tabulated and their significance pointed out in the Appendices.

The findings, in general, follow those found in the work on ADU precipitations and filterability.⁽⁸⁾

For obtaining mixed crystals in the hydrogen-reduced oxide, the region pH 4.5 to 5.5 was best; while a wider range (pH 5.0 to 7.) was acceptable for filterability. An elevated temperature (55 °C) is best for precipitation, digestion, and filtration. From the standpoint of waste losses, pH 5.0 was the lower limit to maintain low losses and thus to maintain the desired ratio of plutonium-uranium in the filtered solids.

On the basis of these small exploratory runs, a flow sheet was drawn up to be used in the prototype runs. This flow sheet is shown in Figure 7.

B. Prototype Precipitation And Drum Filter Runs

1. Equipment (Figure 8)

The prototype precipitator was fabricated from a 10 3/4 in. long section of 4 in. schedule 40-type 304L SS pipe. It had a rounded bottom and contained 1.5 liters at overflow. A 1 1/3 in. steel tube was centrally positioned in the vessel, and shrouded the agitator shaft and solution entry lines. The agitator had a curved bottom blade shaped to permit close sweeping of the vessel bottom, plus small paddles to provide agitation inside the shroud tube. An air motor turned the agitator.

The precipitator vessel was externally heated by two turns of a close-fitting "Calrod"*-type resistance

* Trade name, General Electric Company

FIGURE 8
PROTOTYPE CONTINUOUS
PRECIPITATOR AND FILTER

heater. A bracket at the vessel top supported a pH electrode and a thermocouple well outside the shroud tube. Precipitator temperature regulation was by means of an ON - OFF-type indicator-regulator using the thermocouple to control the resistance heater.

The prototype filter was a 3 in. wide x 12 in. diam filter drum. It was partially immersed in a pan shaped to be coaxial with the drum, with a top that was 8 1/2 in. wide and 17 3/4 in. long. The pan had a free volume of 1.3 liters. The drum was provided with a sliding valve to program the vacuum from the waste receiver to the drum segments for filtering, drying, and washing. Synthetic fiber cloth was used as the filter media. An adjustable scraper removed the slurry, and a chute directed it to a receiver. The cake was sprayed with a wash solution after leaving the filter pan and before reaching the scraper. The drum and a reciprocating sweep agitator in the bottom of the pan were driven by variable speed gear electric motors.

Tankage for feed and waste receivers were in an adjacent hood; the tank for ammonium hydroxide was outside the hood. Both feed and ammonium hydroxide were pumped at variable speed and stroke by cam-driven piston pumps. A portion of the feed line was equipped with an electrical heating jacket to aid the temperature control in the precipitator.

2. Procedure

Runs were limited by the available feed tank capacity--about 10 liters. The precipitator was provided with sufficient feed and ammonium hydroxide to provide an agitated slurry for temperature and pH sensing. When the slurry reached the proper temperature (55 °C), the feed and ammonium hydroxide pumping was started.

Feed rate was controlled to the limit of the filtration capability. In some runs the feed was turned on and off to match the filter capability; in other runs the feed pumping rate was changed to match the filter capability.

The ammonium hydroxide was pumped by a pump head on the same shaft as the feed pump. Early runs were made at a fixed ratio of ammonium hydroxide-to-feed. In later runs, the ammonium hydroxide flow was regulated by throttling and by-passing the pump, to maintain pH control.

The filter drum variables of rate of rotation and thickness of cake were adjusted, as required, to obtain a maximum filtration rate. Usually one revolution per minute provided the maximum filtration rate.

C. Prototype Vibrating Tube Hydrogen Reducer Runs

1. Equipment (Figure 9)

The prototype vibrating tube was formed out of 1 7/8 in. ID Hastelloy C tube by flattening it to a 1 1/32 in. x 2 1/4 in. (inside) oval shape. The tube was oriented with its major oval dimension horizontal. The tube was 41 3/4 in. long, with 32 in. of it heated by external resistance furnaces. The entire furnace and tube assembly was mounted on a variable incline bed that may be electromagnetically vibrated. The tube ends were provided with flanges for feed addition and product removal. The unheated portion of the tube was provided with a top flange for off-gas removal, while the gas inlet entry was made in the product receiver attachment.

The incoming gases were preheated by routing them through a resistance-heated section of piping and along the length of the resistance filters of the vibrating tube. A thermocouple well extended down the center of the vibrating tube and three thermocouples, located at different

FIGURE 9
VIBRATING TUBE APPARATUS ASSEMBLY

positions, gave data on the internal temperature of the tube.

The feed mechanism was a variable speed, electric motor-driven screw device fed by a funnel coupling to glass feed jars; it vibrated with the tube to facilitate powder flow. The off-gas was cleaned of powder by a filter separate from the vibrating system before being exhausted to the hood exhaust system. The product receivers were glass jars.

Provision was made to time the frequency of the intermittent vibrations. Both the vibration frequency and its amplitude could be varied.

2. Procedure

The prototype vibrating-tube apparatus was used to hydrogen-reduce the powders resulting from the vacuum-drum filter runs. The apparatus was adjusted (tube slope and vibrating conditions) to give a 2-hr powder residence time. The gas was an 8% H₂-92% nitrogen mixture which was metered into the apparatus under standard temperature and pressure conditions.

V. DISCUSSION

A. Continuous Precipitation-Filtration

1. Rates

A total of 9 significant runs were made in the prototype precipitation-filtration apparatus. The essential data from those runs are recorded in Table I.

This apparatus has a maximum demonstrated plutonium oxalate processing rate of 7.5 g of Pu/min; the Table shows the total actinide filtration rate relative to this value. Runs which significantly exceeded pH 7 suffered in respect to the filtration rate achieved.

TABLE I
PROTOTYPE DRUM FILTER RUNS

Run	Feed Temperature	Feed Rate Regulation	Ammonium M	Hydroxide Control	pH Range	Run Duration Hr	Average Filtration Rate, g/min	Relative Filtration Rate, %
1	Hot	Flow rate	N.A.	Flow ratio	N.a.	-	N.A.	N.A.
2	Ambient	on - off	3	Flow ratio	4.0-10.0	7	*2.7 (5.0)	36 (67)
3	Ambient	On - off	3	Flow ratio	2.1-9.5	5	4.8	64
4	Hot	Flow rate	3	Flow ratio	3.7-7.4	2.25	5.3	70
5	Hot	Flow rate	3	pH-bypass	4.6-5.2	3	4.5	60
6	Hot	On - off	1	pH-bypass	4.8-8.8	1.25	4.1	55
7	Ambient	On - off	1	pH-bypass	3.7-5.9	1.25	4.1	55
8	Hot	Flow rate	3	pH-bypass	3.7-7.8	3.75	4.3	58
9	Hot	On - off	2	pH-bypass	2.4-9.3	6	3.2**	42
10	Hot	On - off	3	pH-bypass	5.2-8.2	5.25	4.2	56

* Error in makeup, high in uranium.

** Low vacuum during this run.

On the basis of the experience with these runs, it was found that smoother operation was obtained when the feed was preheated to 60 °C and the filter pan was maintained at 45 °C. Adjustment of flow rates to maintain a constant filter pan level, rather than the ON - OFF regulation, was also preferred. Some sort of responsive ammonium hydroxide flow control is required, since the pH drifts when set flow ratios are used. It was noted that there is some color change in the filter cake, as a function of pH. Use of different filter cloths, or fresh ones, during a run had little effect on prolonged operation.

Samples of feed from Runs 3 and 4 were checked by the batch filtration test method and gave relative filtration rates (M") of 3.5 and 5.1, or 70 and 100% of the M" value for plutonium oxalate filtration. Since the prototype Runs 3 and 4 gave respectively 64 and 70% of plutonium oxalate precipitate filtration rate, we have some basis for comparison of results. It was concluded that on a total actinide weight basis, a drum filter can readily handle half of its plutonium oxalate rate, and that two-thirds of its rate is easily possible. The batch runs indicate that with optimum conditions, a drum filter can equal the plutonium oxalate filtration rate with ammonia coprecipitated plutonium-uranium slurries; this is somewhat less optimistic than for ADU slurries.⁽⁸⁾

Four samples of prototype drum filter cakes were hydrogen-fired by the small batch method. The following results were obtained:

HYDROGEN-FIRED FILTER DRUM PRODUCT

Run No.	X-Ray Diffraction % "Free" PuO ₂	Density, g/cc	
		Bulk	Tap
3	>1	1.61	2.36
4	<1	1.28	1.91
5	1-5	1.06	1.57
9	<1	1.49	2.01

These results have little meaning, it seems, since these filter cakes were used in the prototype vibrating tube runs (see next Section) in which only acceptable (<1% "free" PuO₂) x-ray diffraction results were found. (On the basis of these tests alone, Runs 3 and 5 did not produce acceptable powders.)

B. Operation Of Prototype Vibrating-Tube Hydrogen Reducer

Eight runs were made in the vibrating-tube reducer; these are tabulated in Table II. Table III shows the results of analyses for the products from these runs.

TABLE II
PROTOTYPE VIBRATING TUBE
HYDROREDUCTION RUNS:
RUN CONDITIONS

Run No.	U + Pu g	U + Pu g/hr	Exit Temp. °C	N ₂ -H ₂ Flow ft ³ /hr STP	Powder Residence Time, Hr	Remarks
6-1	735	200	600	166	2	Rerun of 6-1 product.
6-2	500	200	680	200	2	
6-3	745	135	620	189	2	
6-4	625	140	600	255	2	
6-5	600	200	700	200	2	
6-6	600	100	750	100	2	
6-7	550	100	740	100	2	
6-8	1671	240	740	100	4	

TABLE III
 PROTOTYPE VIBRATING TUBE
 HYDROREFUCTION RUNS:
 ANALYTICAL RESULTS

Run No.	X-Ray Diffraction % "Free" PuO ₂	O/M Ratio	Density, g/cc Bulk	Tap	H ₂ O %	Surface Area M ² /g
6-1	<1	2.169	2.27	2.75	-	-
6-2	N.D.	2.073	2.15	2.32	0.196	4.28
6-3	N.D.	2.090	1.55	2.1	0.274	5.52
6-4	N.D.	2.010	1.47	2.37	0.424	4.25
6-5	N.D.	2.251	1.09	1.48	0.335	7.05
6-6	N.D.	2.202	1.07	1.47	0.443	8.14
6-7	N.D.	2.162	1.18	1.55	0.389	11.0
6-8*	<1	2.266	1.82	2.51	0.223	4.36
6-9**	N.D.	2.204	1.58	2.55	0.124	4.21

* Sample early in run.

** Sample late in run.

All runs exhibited good mixed-crystal patterns by the x-ray diffraction technique. The O/M ratio may be seen to vary as a function of solids flow rate, gas flow rate, and residence time, as seen in Table IV.

TABLE IV
 PROTOTYPE VIBRATING TUBE
 HYDROREDUCTION RUNS:
 PARAMETERS FOR O/M RATIO

O/M Ratio	Run No.	Residence Time	Grams Actinide Per Hour	Gas Flow
2.01	6-4	2	140	255
2.07	6-2	4*	200	186*
2.09	6-3	2	135	189
2.16	6-7	2	100	100
2.17	6-1	2	200	166
2.20	6-6	2	100	100
2.20	6-8b	4	240	100
2.25	6-5	2	200	200
2.27	6-8a	4	240	100

* Run 6-2 was a rerun of 6-1, so the powder had a residence time of 4 hr (2 in each run), an average gas flow of 186.

As may be expected, low O/M ratios are found on those runs having high gas flows and longer residence times, but low actinide flow rates. The O/M ratios of 2.1 to 2.3 are acceptable (see III C).

Temperature effects are harder to relate to the powder properties; this may be because of the nature of the equipment heating problems. The relatively-high gas flows gave significant temperature variations along the tube. Since the gas entered at the exit end of the tube, the exit temperature was usually the lowest. The temperature profile along the tube for Run 5 at one time during a run was 703, 868, and 835 °C (from powder exit to powder entry) at a gas flow of 200 ft³/hr. For Run 6, a typical set of temperature readings along the tube was 704, 740, and 865 °C. Changes of gas flows during a run had significant effects on the tube temperatures.

These results show a vibrating-tube hydrogen reducer will turn out acceptable powders. The throughput relative to a vibrating tube plutonium fluorinator has not been derived. Additional work is needed to design such an apparatus to give optimum throughputs with a powder of a selected oxygen-to-metal ratio. An alternate for the vibrating tube might be the rotary kiln demonstrated in UO₂ fuels work.⁽¹³⁾ See Section V-C-4 for another consideration of the hydrogen reduction unit operation.

C. Other Processing Considerations

1. Precipitation Waste Losses⁽⁸⁾

To prevent excessive waste losses in drawing up the initial flow sheet, a pH of >9.0 of the combined filtrates was assumed. A dilute ammonia wash of the filter cake was included for the usual wash reasons, as well as for providing the extra ammonia to raise the pH to 9 in the composited strike filtrate and wash. Using a polish filter on this high pH composite would permit disposal of

the stream with very low actinide losses. From the titration curves, a wash composition corresponding to 0.25 moles of ammonia per mole of feed uranium is recommended.

It should be noted that "carbonate-free" ammonium hydroxide was used in this work to ensure that actinide losses would not be raised due to actinide carbonate solubility. CP grade (30% NH_4OH with 0.002% carbonate content) was used to prepare the strike solutions used.

2. Ammonium Nitrate

A wash of the filtered solids is specified to reduce the ammonium nitrate content of the solids. In laboratory runs and prototype work, no problems have occurred due to the presence of ammonium nitrate in these solids.

Ammonium nitrate does cause a problem, however, in hood exhaust filters. During the prototype drum filter runs, the hood exhaust filter plugged completely, probably due to buildup of NH_4NO_3 because of alternate exposure to NH_3 and HNO_3 fumes. No unusual fog formation or hood window coating, such as might be expected, were noted.

3. Continuous Filter Cake Drying And Powder Conveying

The filter cake from the prototype drum filter was batch-dried and batch-fed to the prototype vibrating tube hydrogen reducer. A continuous dryer-solids conveyor-type of apparatus should be used to make the entire conversion continuous. As was pointed out in the Introduction, it is possible that a screw dryer might be used for this operation. This concept should be tested, since it is possible that intermediate mastic stage of the diuranate might ball-up or gum-up such a dryer. A rotating tube dryer-calciner was used at Oak Ridge for converting UNH to U_3O_8 on a similar scale. (13)

4. Reactivity Of Hydrogen-Reduced Oxide

Freshly-reduced UO_2 is quite reactive in air--especially when warm. (13, 20) The small-scale batch hydrogen reduction cycle was established to provide some sintering to reduce the pyrophoric tendency of the product oxides; no re-oxidation of the oxide from the small-scale runs was observed.

The prototype vibrating hydrogen reducer did not have special features to ensure production of a non-reactive oxide. However, care was taken to keep the powder contained or cool. Since the O/M values of the powders from the runs correlate with gas flows and residence times of the runs, no re-oxidation of the powders is indicated. Any production of $\text{UO}_2\text{-PuO}_2$ should have provisions to ensure that re-oxidation does not take place.

VI. RECOMMENDATIONS

As a result of the preceding findings, several recommendations may be made:

1. A flow diagram for continuous production of mixed oxide fuel elements is shown in Figure 10.
2. A flow sheet for providing acceptable powders under conditions giving optimum continuous equipment operation is shown in Figure 7, page 12.
3. Pelletizing and sintering work should be done on this material to confirm its acceptability for ceramic fuel fabrication.
4. Additional work should be done on the design of an optimum continuous hydrogen reducer.
5. A suitable dryer-solids conveyor (screw dryer?) should be demonstrated.

FIGURE 10
FLOW DIAGRAM
MIXED OXIDE FUEL ELEMENT PRODUCTION

6. Investigations should be made on the optimum possible "master mix" powder that might be shipped and still be readily-solubilized. (21, 22)

VII. ACKNOWLEDGMENTS

The major portion of the experimental work was done by J. P. Martelli, who also set up or modified apparatuses, wrote operating procedures, and compiled the results of the work. Assistance was provided in the prototype drum filter runs by D. M. Creighton and H. D. Merritt, who also did larger batch-scale work not covered in this report. The comments by E. L. Moore on the context of this report are appreciated.

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M. H. Curtis

APPENDIX A

VALLECITOS PREPARATION OF MIXED OXIDE FUEL SAMPLES

Compositions of 20% plutonia are made on a 300 g batch-scale. The mixed oxides are prepared by the following process steps:

1. The starting solutions are made up to contain 100 g/liter concentrations of heavy element (U + Pu) and 1.0 to 2.3 molar nitric acid.
2. Coprecipitation of ammonium diuranate and plutonium hydroxide is carried out by a quite rapid addition to 14.7 M ammonium hydroxide. The precipitations are all done at 25 to 35 °C with stirring and with final pH values of ~9.5.
3. The coprecipitates are filtered immediately, washed with water, and air-dried at 120 °C. (An 0.1 N NH_4OH wash may be used.)
4. The dried precipitates are reduced in 6% H_4 -94% He for 8 hr at 750 °C, and cooled under the reducing gas (5 cfh).
5. Batches are ball milled 1 hr in an alumina jar with alumina balls, and screened through a Tyler 300 mesh sieve.
6. The powders are pressed without binder to about 50% of theoretical density in an 0.267 in. diam die.
7. The pellets are fired at ~1575 °C for 4 hr in 6% H_2 -94% He gas containing about 1 vol % water vapor.

APPENDIX B

NUMEC MIXED OXIDE PREPARATION*

<u>Run Composition</u>	<u>Run 297 Pu 53</u> <u>UO₂-50 wt % PuO₂</u>
Precipitation conditions	
Method	Continuous
Temperature, °C	55
Feed composition	
Pu, g/liter	50
U, g/liter	50
U ⁺ , <u>M</u>	1.0
Feed rate, liter/hr	1.2
Precipitant composition	NH ₃ gas
Precipitant flow, cc/min	380 @ 24.7 psi
Precipitant holdup, min	30
Total no. of throughputs	4.6
Drying temperature, °C	100
Drying time, hr	16
Gas atmosphere	N ₂ -6% H ₂
Gas flow, scf/hr	6
Conversion temp., °C	840
Time at temperature, min	160
Furnace charge, g	742

* NUMEC-2389-4. Similar conditions used for other compositions in other reports.

APPENDIX C

DuPONT FLOW SHEET FOR MIXED OXIDE POWDERS

- A. Mixed ammonium diuranate (ADU)-Pu(OH)₄ is precipitated from nitric acid solution by ammonium hydroxide. The precipitate is reduced to PuO₂-UO₂ by calcining.
1. Heat mixed feed solution to 80 °C.
 2. Slowly add approximately 50 liters of 29% ammonium hydroxide to reach pH 9. Elapsed time: 75 min.
 3. Transfer slurry to continuous filter.
 4. Wash cake with 50% ammonia-50% acetone.
 5. Remove precipitate from filter, and dry.
 6. Place powder in calcining furnace.
 7. Heat powder to 700 °C for 2 hr and cool under atmosphere of 50% hydrogen and 50% nitrogen.
 8. Remove powder from furnace, and weigh.
 9. Transfer calcined powder to crushing station.
 10. Cycle time: 3 hr per 2 kg Pu; one operator.
- B. Equipment
1. Precipitator.
 2. Continuous filtration unit.
 3. Transfer system.
 4. Calcining furnace.
- C. Processing Rate: 83.0 kg mixed oxide/day.

* DP-838. (5)

APPENDIX D

SMALL-SCALE BATCH RUN RESULTS

I. FILTRATION RATES

Small-batch precipitations were initially made to test filtration rates. Direct and reverse strikes were made, testing the variables feed and ammonia concentrations; hot and cold precipitations and filtrations; digestion time and temperature; and final pH. Variations of filtration rate were found, but not until the pH data were expanded to show the pH over the entire precipitation did the data show a correlation. It was noted that the Vallecitos flow sheet did not produce a readily-filterable slurry.

The next phase of the work was more sophisticated. Small-scale continuous precipitations were made with the intent to maintain a narrow range of pH values through the precipitation period. Also, resulting filter cakes were hydrogen-reduced and powder characteristics were determined.

The data now fitted the scheme found for an uranium-only system: since the derivation of the parameters for the uranium-only system has been shown in a previous report,⁽⁸⁾ they will not be given here for the uranium-plutonium system. Table V shows the typical process specifications for an ADU (ammonium diuranate) precipitation.

Table VI shows some of the run conditions used in small-batch runs studies of mixed oxide precipitation. From these results it was concluded that the ammonia precipitation of uranium-plutonium salts could be made under conditions giving relative filtration rates comparable to plutonium oxalate; and thus filterable on a continuous drum filter. A continuous precipitation at a pH 5.0 ± 0.5 should be used. The feed should be about 100 g/liter total actinides, and a dilute (3 M) ammonium hydroxide strike solution should be used

TABLE V
TYPICAL PROCESS SPECIFICATIONS
FOR ADU PRECIPITATION*

<u>Variable</u>	<u>Basis</u>
<u>Feed Solution</u>	
Nitrate or chloride system	Tested, laboratory work.
<1.25 <u>M</u> uranium	Limit tested.
> 0.1 <u>M</u> uranium	Excessive solution volumes.
0.5 <u>N</u> to 3.0 <u>N</u> acid	Limits tested.
Purity better than product	Little purification demonstrated.
<u>Strike Solution</u>	
CP grade	Used in laboratory work.
Low carbonate	To keep waste losses down.
Low impurities	To keep product purity up.
<u>M</u> NH_4OH = <u>N</u> (feed acid) + 2.3 <u>M</u> (feed U)	Keeps feed and strike volumes about equal for ease of control.
<u>Strike Conditions</u>	
Continuous	Demonstrated.
55 $\pm$ 5 °C	Based on results of prior work.
Vigorous agitation	Used in development work.
10-20 min digestion	Used in development work.
Maximum pH 6.0	Filterable below this value.
Minimum pH 4.0	Losses high below this value.
<u>Wash Solution</u>	
Flow, to give dry cake	Required for handling.
Composition - to be pH >7.0 for composited feed and wash	Ensure low waste loss.

* From RL-SEP-924.

TABLE VI
SMALL BATCH RUNS
URANIUM-PLUTONIUM AMMONIA COPRECIPITATION
FILTRATION RATE STUDIES

Run	Strike		Rate g/min	Temperature, °C		pH	
	Form	Control		Strike	Filtration	Final	Range
P-1	Continuous	pH	1	50	50	5.3	
3-13	Continuous	pH	1	50	25	5.3	4.5-6.5
50-4	Continuous	pH	1	50	50	6.3	4.5-6.5
5-4	Continuous	pH	1	50	50	5.9	4.6-6.0
3-11	Continuous	pH	1	50	25	4.6	4.5-6.0
50-3	Continuous	pH	1	50	50	7.7	4.2-7.7
3-10	Continuous	pH	1	50	25	5.6	4.0-6.8
3-14	Continuous	Flow	1	50	25	7.0	6.5-7.5
4-18	Continuous	pH	5	50	25	8.0	5.9-7.0
P-2	Continuous	pH	≈ 1	50	50	6.3	4.5-5.0
2-C	Direct	-	0.6	25	25	-	-
3-5	Direct	-	2.5	50	25	8.0	0.0-8.1
5-3	Continuous	pH	1	50	50	4.4	4.5-5.0
3-1	Direct	-	5	50	25	9.4	0.0-9.4
3-6	Direct	-	2.5	50	25	8.5	0.0-8.5
2-J	Direct (Vallecitos)		1	25	25	9.5	0.0-9.5

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A

to facilitate pH control. Agitation and digestion time comparable to plutonium oxalate technology should be used. The precipitation, digestion, and filtration should be 55 ± 5 °C. A dilute ammonium hydroxide wash will keep actinide losses down if the filtrate is raised to pH 7.0 or above.

II. OXIDE PROPERTIES

Since considerable effort was devoted to achieving favorable slurry filtration rates, there were a large number of small batches of filtered precipitates available for evaluation. Selected batches were air-dried, hydrogen-reduced; and powder samples submitted for analysis. As powder analysis techniques were being developed throughout the program, only x-ray diffraction analyses were taken on early samples-- Table VII shows these results. About two-thirds of these x-ray diffraction results had the specification value of <1% "free" PuO_2 .

Later runs, especially those with favorable filtration rates, were only partially examined; Table VIII shows these runs, which had run conditions given in Table VI, page 34.

The correlation of the x-ray diffraction data was possible only with pH; all other parameters being studied (concentrations, temperatures, etc.) in relation to filtration rates, did not give any correlation with the % "free" PuO_2 determined in the x-ray powder diffraction patterns. Where pH data are complete, it appears that the system must not see an extended period of pH less than 5.5; direct strikes (runs which go from 0.0 to higher pH's) do not confirm this-- possibly because the transition period is rather rapid.

The data of Table VII were also difficult to correlate. Except for O/M ratio (which probably has very little dependence on precipitation conditions), the results varied greatly. Since the prototype runs were made at the more advanced stages

TABLE VII
 SMALL BATCH RUNS
 URANIUM-PLUTONIUM AMMONIA COPRECIPITATION
 X-RAY DIFFRACTION RESULTS

<u>Run No.</u>	<u>% "Free" PuO₂</u>	<u>Strike</u>	<u>pH Range</u>	<u>Final pH</u>
1-2	<1	Continuous		
1-3	<1	Continuous		8.0
1-4	<1	Continuous		
1-5	<1	Continuous		
1-6	<1	Continuous		
1-7	<1	Reverse		7.7
1-A	<1	Continuous		
1-B	<1	Continuous		
1-C	<1	Continuous		
1-D	<1	Continuous		7.7
1-F	<1	Direct		9.0
1-G	<1	Continuous	7.1-8.2	
1-H	<1	Continuous	6.5-8.0	8.5
1-I	<1	Reverse		8.2
1-J	<1	Direct		
1-L	<1	Reverse		9.5
1-M	<1	Continuous	6.5-8.5	9.0
1-O	<1	Reverse		-
1-P	<1	Reverse		9.3
2-D	4	Continuous	5.2-7.0	-
2-G	3	Continuous	5.4-7.0	-
2-H	<1	Continuous	6.0-7.1	-
2-I	<1	Continuous	6.3-7.5	-
2-Q	≈1	Continuous	4.0-7.0	4.0
2-T	1	Direct		
44-1*	<1	Continuous	2.8-7.0	7.5
44-2*	<1	Continuous	5.5-6.0	-
44-3*	≈1	Continuous	5.4-7.3	7.3

* These runs were larger-scale runs which took longer than the others.

TABLE VIII
 SMALL BATCH RUNS
 URANIUM-PLUTONIUM AMMONIA COPRECIPITATION
 POWDER ANALYTICAL RESULTS

Run No.	X-Ray Diffraction	O/M Ratio	Density, g/cc		Surface Area M ² /g
	% "Free" PuO ₂		Bulk	Tap	
P-1	<1	2.282	0.72	1.10	18.6
3-13	3-5	1.997	0.65	1.02	3.4
5-4	<1	2.135	1.35	2.13	3.9
3-11	1-3	2.150	0.93	1.47	4.2
3-10	<1	2.154	0.73	1.20	12.3
P-2	<1	2.034	0.75	1.12	17.7
3-1	3-5	2.075	1.18	1.72	4.4
3-6	<1	2.083	1.23	1.63	4.0
2-J	<1	2.010	-	1.62	4.1

of the program, the results of these small batch runs is not given as much weight as are the powder properties from the prototype runs.

Extensive work has been done at the Oak Ridge Y-12 plant on UNH precipitation conditions for producing sinterable-grade UO₂ powder.⁽¹³⁾ The application of those data to the mixed oxide precipitation step should be weighed with care, since Y-12 precipitated from a fluoride-bearing media, and the feed did not have plutonium present. However, the Y-12 workers note that temperature, feed concentration, and agitation are important variables in respect to final oxide surface area.

It has further been claimed⁽²⁰⁾ that pH affects the sinterability of uranium dioxide formed from continuously-precipitated ADU--with low densities below a pH of 5.0, and high densities above 6.5 pH.

Complete evaluation of powder properties was not done during this work. Further investigation in this area is needed, especially in respect to sinterability of pellets.