URANIUM DIOXIDE-PLUTONIUM DIOXIDE CERAMICS

by

A. S. Wilson

Chemical Research
Chemical Research and Development
HANFORD LABORATORIES

March 1, 1958

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

DISTRIBUTION LIST

1. F. W. Albaugh
2. R. J. Anicetti
3. J. G. Bradley
4. D. W. Brite
5. R. J. Brouns
6. L. P. Bupp
7. L. L. Burger
8. R. E. Burns
9. S. H. Bush
10. J. J. Cadwell
11. V. R. Cooper
12. E. A. Coppinger
13. E. A. Evans
14. M. D. Freshley
15. R. G. Geier
16. K. M. Harmon
17. M. K. Harmon
18. O. F. Hill
19. H. H. Hopkins - H. W. Crocker
20. E. R. Irish
21. M. Lewis
22. W. L. Lyon
23. P. R. McMurray
24. J. E. Minor
25. R. H. Moore
26. R. L. Moore
27. J. R. Morrey
28. J. M. Nielsen
29. R. E. Nightingale
30. P. G. Pallmer, Jr.
31. H. J. Pessel
32. A. M. Platt
33. W. H. Reas
34. W. E. Roake
35. C. A. Rohrmann
36. R. J. Sloat
37. R. E. Smith
38. R. E. Tomlinson
39. E. E. Voiland
40. M. T. Walling, Jr.
41. O. J. Wick
42. F. W. Woodfield
43. A. S. Wilson
44. 300 Files
45. Record Center
46. TIS

47 - 57. Extra Copies

DO NOT PHOTOSTAT

URANIUM DIOXIDE-PLUTONIUM DIOXIDE CERAMICS

by

A. S. Wilson

I. INTRODUCTION

This report summarizes the results of experiments performed at the Hanford Laboratories Operation with the ceramic fuel material, uranium dioxide-plutonium dioxide. Ceramic fuels for reactors offer excellent corrosion compatibility with high temperature coolants including high temperature water. Ceramic fuels can also withstand high neutron exposures while maintaining dimensional stability. Plutonium oxide as a fuel offers the additional advantage that processing is readily accomplished by solvent extraction after dissolution of the oxide and that reconstitution of the oxide requires only a drying and calcination of the product solution, i.e., it is not necessary to go through a metallurgical cycle. The uranium dioxide-plutonium dioxide ceramic is of particular interest because of its potential use as a plutonium containing ceramic fuel for the Plutonium Recycle Test Reactor. By means of this oxide material an uniform or spike enriched reactor loading can be achieved. This oxide, moreover, can be made in two forms. One form, called the "oxide mixture", is made by physically mixing uranium dioxide with plutonium dioxide. This oxide contains, therefore, two phases; one is uranium dioxide and the other plutonium dioxide. The other form of the ceramic oxide fuel is called the "mixed oxide". The mixed oxide is a single phase which is a solid solution of uranium dioxide and plutonium dioxide. The mixed oxide can be prepared by the coprecipitation of uranyl ion and plutonium(IV) ion in ammoniacal solutions followed by the hydrogen reduction of the dried precipitate. This mixed oxide, either irradiated or unirradiated, can be readily dissolved in nitric acid, a standard dissolution agent for fuels, in order to be processed by solvent extraction. For this reason many of the experiments reported here were concerned with the preparation and dissolution of the mixed oxide. Some experiments were conducted with the oxide mixture, because it offers the advantage that it can be made easily by a physical blending of the oxides, thus eliminating the need to hydrogen reduce a plutonium containing material. The unirradiated oxide mixture requires a catalyst, ceric ion or fluoride ion, to accomplish complete dissolution in boiling nitric acid. The effect of irradiation upon the dissolution properties of the oxide mixture, however, is not known, and may conceivably result in dissolution behavior identical to that of the mixed oxide.

Magnesium oxide has also been suggested as a promising ceramic diluent for plutonium oxide fuels, and some mixing experiments with magnesium oxide were accordingly conducted.

II. SUMMARY AND CONCLUSIONS

The detailed conclusions and recommendations which follow corroborate to a large extent those reported from the Knolls Atomic Power Laboratory[1] and elsewhere.[2]

A. The starting material, ammonium diuranate-plutonium hydroxide, for the mixed oxide can be prepared by the addition of concentrated ammonium hydroxide to an aqueous solution of uranyl nitrate and plutonium nitrate, as well as by the addition of ammonia gas. In order that an easily handled slurry and precipitate be formed, it is recommended that the initial concentration of uranyl ion be no greater than 0.7 M and that the molar ratio, uranium to plutonium, be no less than five.

B. The reduction of ammonium diurante-plutonium hydroxide to uranium dioxide-plutonium dioxide proceeds smoothly with the use of two volume percent hydrogen in nitrogen. Such a mixture is recommended for use where an explosion and fire hazard may exist in order not to exceed the explosive limits of hydrogen in air (should a leak develop or the gas collect in a glove box).

C. Dissolution of the mixed oxide in boiling concentrated nitric acid is less rapid than uranium dioxide alone, but can be accomplished in five to ten hours.

D. Cerium nitrate may be used to speed the dissolution of refactory plutonium oxide in boiling concentrated nitric acid.

E. Boiling concentrated nitric acid containing catalytic amounts of hydrofluoric acid will dissolve oxide mixtures in two to three hours.

F. It was shown that uranium dioxide is one of the products when ammonium diuranate is pyrolyzed in an inert atmosphere. It is recommended that further investigation of this phenomenon be conducted because it may offer a method for the production of the mixed oxide without the use of a separate hydrogen reduction.

G. A free flowing powder mixture of magnesium oxide and plutonium dioxide was prepared by precipitation of the oxalates in a neutral to ammoniacal solution and by subsequent decomposition to the oxides at 700 C.

H. A free flowing uniform powder mixture of magnesium oxide and uranium dioxide, substituting for plutonium dioxide, was prepared with a twin shell dry blender. A ball mill does not accomplish this result. It is recommended that a twin shell dry blender be used when it is desired to prepare uniform mixtures of plutonium oxide with uranium oxide or magnesium oxide, etc.

III. EXPERIMENTAL PART AND RESULTS

A. Preparation of the Mixed Oxide. The coprecipitation of ammonium diuranate and plutonium hydroxide and their subsequent reduction to the oxides is the only way which has been successful in preparing a solid solution of uranium dioxide and plutonium dioxide, i.e., the mixed oxide. The mixed oxide is thought desirable because it can be more readily dissolved in concentrated nitric acid than the oxide mixture, i.e., a mixture of plutonium dioxide and uranium dioxide. Precipitation was carried out at different mole ratios of uranium to plutonium. Precipitation was by ammonia gas, by ammonia-air mixtures, or by the addition of ammonium hydroxide to a nitric acid solution of uranyl nitrate and plutonium(IV) nitrate. Precipitates were filtered onto a medium grade sintered glass filter, air dried, at room temperature, and then further dried at ca. 120 C overnight.

Precipitation from a concentrated uranium solution as was done in preparation No. 3, Table I, was not safisfactory. It appears that best results are obtained when precipitation is from an approximately one-half molar uranium solution. Similar conclusions had previously been reached at the Knolls Atomic Power Laboratory.[1]

Reduction of the ammonium diuranate-plutonium hydroxide preparation to the mixed oxide has previously been conducted in pure hydrogen at 800 C.[1] Our reductions were conducted with a two volume percent hydrogen in nitrogen as the reducing gas. The diluted hydrogen was used in order to remain well below the explosive limit of hydrogen in air, which is four volume percent. The samples were introduced at room temperature into a tube furnace located in a glove box, and the hydrogen-nitrogen mixture was allowed to flow for a few minutes to remove any air from the system before turning on the furnace. Oxygen was removed from the nitrogen by passing the nitrogen over copper turnings heated to 400 C. The reduction was conducted at 900 C for an arbitrary time of ten minutes. Samples were cooled in the reducing gas and then examined by X-ray diffraction in order to identify the phases present. The results of the reduction experiments and the resulting X-ray diffraction conclusions are listed in Table I. Samples are also identified as to their preparation method. As previously mentioned, the method of preparation had an influence on the type of solid obtained in the reduction. Notice also in Table I that one sample, No. 2, batch 1, was inadvertantly calcined before reduction occurred. In this case the reduced product was composed of two phases, i.e., the oxide mixture, rather than the single phase, i.e., mixed oxide.

It is seen from Table I that the largest lattice constant observed was 5.480 ± 0.004 Å and the smallest was 5.415 ± 0.003 Å. These cell dimensions indicate that no pure plutonium dioxide was present in these preparations for the plutonium dioxide constant is reported[3] as 5.397 ± 0.001 Å, which is 0.02 Å less than that observed for the phase with the smallest lattice constant. The lattice constant for uranium dioxide is reported[4] as 5.460 Å for $UO_{2.00}$, but can be as high as 5.477 Å for $UO_{1.75}$ or as low as 5.40 Å for $UO_{2.34}$. It, therefore, seems reasonable to conclude that all the phases observed here are of the mixed oxide variety with more or less plutonium occurring with the uranium, i.e., a plutonium "poor" phase. However, it is not possible to attempt to define quantitative compositions of the phases based upon lattice constant measurements because of the uncertainty as to the uptake of oxygen by the samples after preparation and before diffraction analysis. As shown above, the uptake of oxygen by uranium dioxide changes the observed lattice constant, and although these samples were cooled to room temperature in the hydrogen-nitrogen gas mixture, there were noticeable surface color changes when they were removed for the X-ray diffraction investigations.

B. Dissolution of the Oxides. The dissolution studies conducted with the mixed oxides prepared in this investigation confirmed the earlier results reported by KAPL.[1] These results showed that boiling concentrated nitric acid dissolved the mixed oxide completely in five hours. One of our oxide preparations required seven and one-half hours to dissolve completely, but this fact does not alter substantially the previous conclusions. In those cases where the preparations are oxide mixtures, the rapid dissolution of these substances requires hydrofluoric acid or some similar catalyst in

TABLE I

PREPARATION OF URANIUM-PLUTONIUM MIXED DIOXIDES

Preparation	Initial Solution Concentrations	Precipitation Method	Precipitate Quality	X-Ray Results	Remarks
1	0.14 M U, 0.11 M Pu, ca. 7 M HNO_3, M U/M Pu = 1.27.	NH_3 (gas)-air	Gelatinous and washed with difficulty.	UO_2 phase, a_o = 5.470 ± 0.004 Å; PuO_2 phase, a_o = 5.435 ± 0.007 Å.	Sample Calcined before reduction.
2	0.41 M U, 0.084 M Pu, ca. 5 M HNO_3, M U/M Pu = 4.9.	NH_3 (gas)-air	Filtered and washed easily.	Reduction batch # 1: UO_2 phase. a_o = 5.465 ± 0.002 Å; PuO_2 phase, a_o = 5.415 ± 0.003 Å.	This batch was calcined before reduction.
				Reduction batch # 2: single phase, a_o = 5.418 ± 0.008 Å.	Batches 2 and 3 not calcined before reduction.
				Reduction batch # 3: single phase, a_o = 5.475 ± 0.003 Å.	
3	1.75 M U, 0.35 M Pu, 3.5 M HNO_3, M U/M Pu = 5.	NH_3 (gas)	Very thick and viscous; filtered easily, but precipitation slow because of viscous slurry.	Reduction batch # 1: UO_2 phase, a_o = 5.463 ± 0.002 Å; PuO_2 phase, a_o = 5.435 ± 0.006 Å.	It is believed that the precipitation method used resulted in these two phases.
				Reduction batch # 2: UO_2 phase, a_o = 5.461 ± 0.002 Å; PuO_2 phase, a_o = 5.446 ± 0.012 Å.	
4	0.67 M U, 0.14 M Pu, 2 M HNO_3, M U/M Pu = 4.8.	Equal volume of concentrated NH_4OH.	Filtered and washed easily.	Reduction batch # 1: single phase, a_o = 5.467 ± 0.010 Å.	
				Reduction batch # 2: single phase, a_o = 5.480 ± 0.004 Å.	

in boiling concentrated nitric acid. In an experiment with an oxide mixture the mixture was completely dissolved in about three hours in boiling concentrate nitric acid containing 0.1 M sodium fluoride. The final concentration of the solution was 0.9 M uranium and 0.15 M plutonium. This mixture was not a mixture of pure uranium dioxide and pure plutonium dioxide, but most likely contained a mixture of two mixed oxides, one rich in plutonium and the other poor in plutonium. Plutonium oxide which contains no dissolved uranium dioxide can be dissolved with nitric acid-hydrofluoric acid mixtures as is well known.

Plutonium dioxide itself dissolves slowly in boiling concentrated nitric acid. It was found, however, that its dissolution can be speeded by the use of cerium nitrate.[5] Either ceric or cerous nitrate can be used. In the experiments represented in Figure 1, cerous nitrate was used. These experiments were conducted in a fifty milliliter Erlenmeyer flask fitted with a reflux condenser and a side-arm for sample removal. Total plutonium concentration was determined after the remaining oxide sample had been completely dissolved in a few minutes by the use of 0.1 M sodium fluoride catalyst. The results indicate that 0.015 M cerium has decreased the total dissolution time of the oxide used from an estimated thirty-five to forty-five hours to thirteen hours.

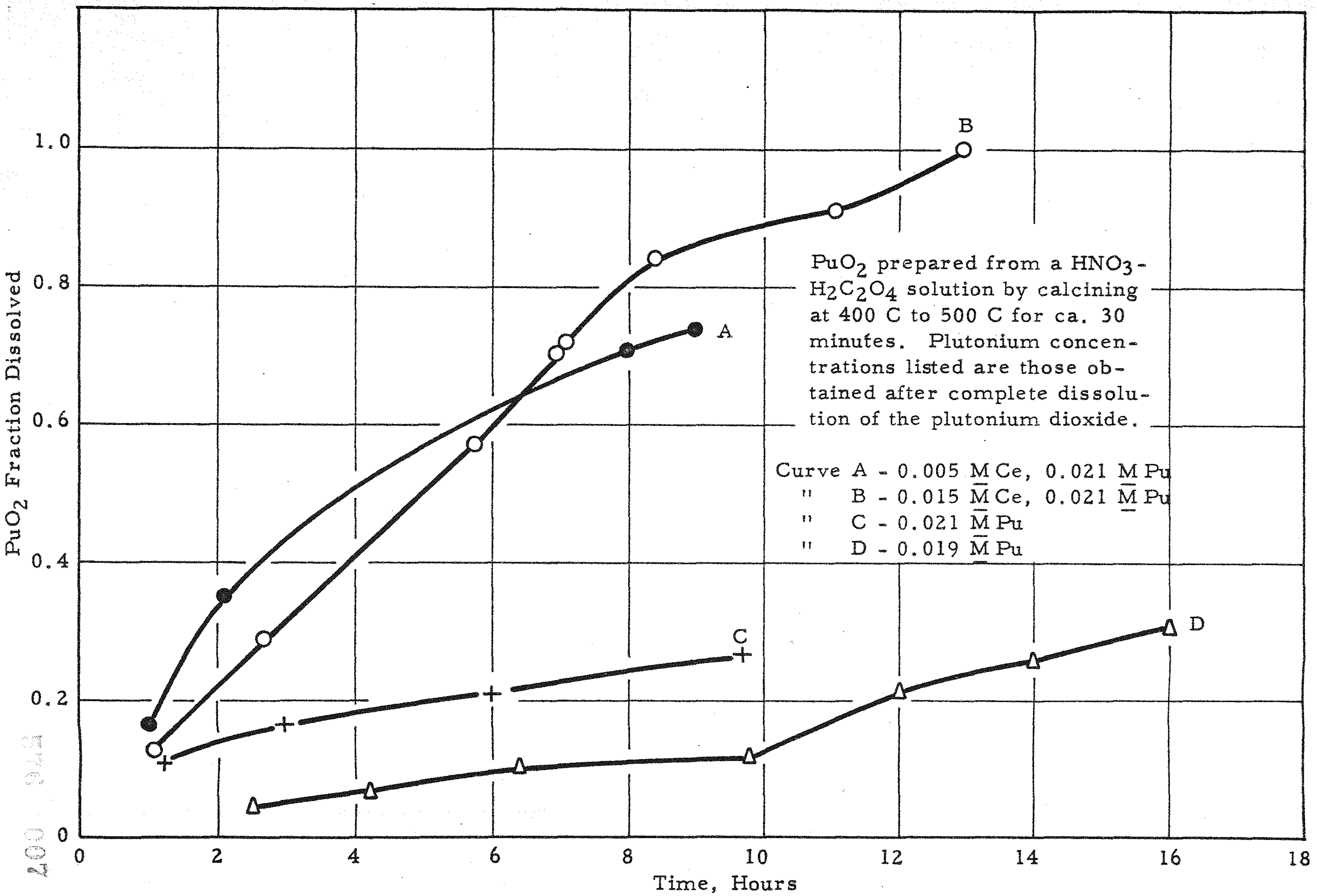
C. Thermal Decomposition of Ammonium Diuranate. The thermal decomposition of ammonium diuranate in air has been shown by other investigators[6] to give UO_3, U_3O_8, and $UO_{3.5}$. The product obtained depended upon the temperature of decomposition. When ammonium diuranate is decomposed in an inert atmosphere, however, one of the products is uranium dioxide. This fact presents the possibility of decomposing ammonium diuranate completely to uranium dioxide according to this equation.

$$(NH_4)_2U_2O_7 \longrightarrow 2\ UO_2 + 3\ H_2O + N_2 + H_2.$$

This could make possible the production of uranium dioxide-plutonium dioxide fuel material without the necessity of using a hydrogen reduction, thus eliminating the associated explosion hazards. Some experiments in which ammonium diuranate was decomposed in a nitrogen atmosphere were accordingly conducted. Ammonium diuranate dried at 110 C was placed in a nickel boat to a depth of about one-half inch. The boat was placed in a cool portion of a tube furnace while nitrogen, which had been freed of oxygen by being passed over 400 C copper turnings, was used to flush the system. After flushing of the system, the boat was quickly placed in the 900 C portion of the furnace. The nitrogen flow was continued. Steam ceased issuing from the furnace in about ten minutes. The furnace was turned off, and the sample cooled in nitrogen. The upper one-eighth inch layer of the oxide was colored black while the underneath layer was olive-brown in color. Samples were taken from the boat as shown in Figure II. The interpretation of the X-ray diffraction results follows:

Only two phases detected: UO_2 and U_3O_8

Sample	% UO_2	% U_3O_8
A	46	54
B	53	47
C	55	45
D	67	33



PuO$_2$ prepared from a HNO$_3$-H$_2$C$_2$O$_4$ solution by calcining at 400 C to 500 C for ca. 30 minutes. Plutonium concentrations listed are those obtained after complete dissolution of the plutonium dioxide.

Curve A - 0.005 M Ce, 0.021 M Pu
" B - 0.015 $\overline{M}$ Ce, 0.021 $\overline{M}$ Pu
" C - 0.021 $\overline{M}$ Pu
" D - 0.019 $\overline{M}$ Pu

FIGURE 1
DISSOLUTION RATE OF PLUTONIUM DIOXIDE IN
BOILING CONCENTRATED NITRIC ACID CATALYZED BY CERIUM ION

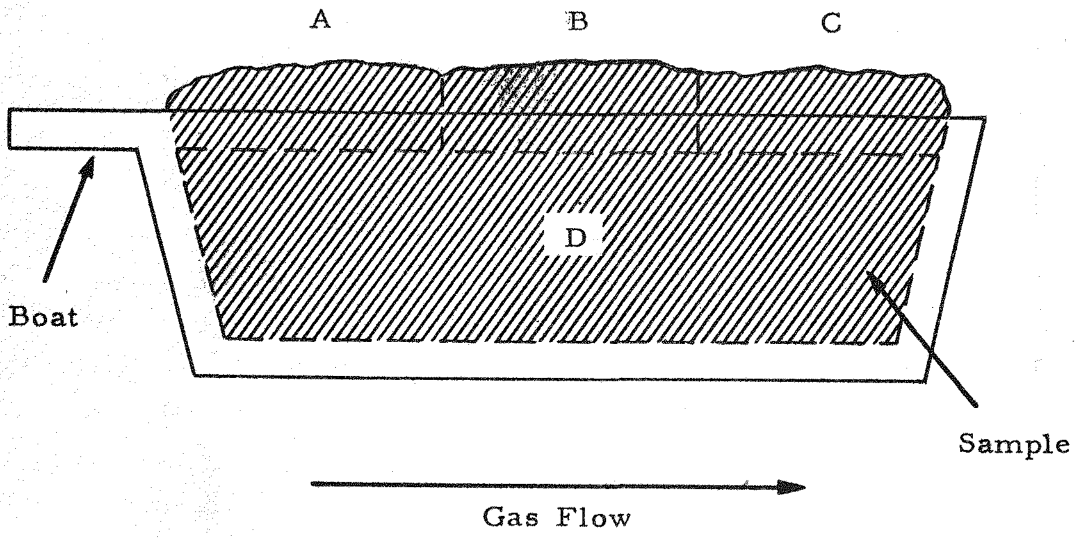


FIGURE 2
SELF REDUCTION OF AMMONIUM DIURANATE
SAMPLE LOCATION

It is seen that the top layer contains a higher percentage of uranium dioxide than the bottom layer. This fact would indicate that complete reduction may possibly be obtained if the evolved gases are recirculated over the material or if the evolved hydrogen and/or ammonia can be prevented from leaving the sample site before reduction occurs.

D. Chemical Preparation of Free Flowing Magnesium Oxide-Plutonium Dioxide Powder. Free flowing magnesium oxide-plutonium dioxide was prepared as follows: To a 1 M magnesium nitrate, 1 M nitric acid solution was added a nitric acid solution of about 1000 mg plutonium. This solution was heated to 50 C and oxalic acid added to make the solution 1.1 M oxalic acid. At this point a small amount of precipitate formed. Concentrated ammonium hydroxide was then added to raise the pH to neutral and precipitate completely the oxalates of magnesium and plutonium. The precipitate was light green in color and filtered slowly. The precipitate was air dried and then transferred to a furnace. The calcination was carried out at 700 C for thirty minutes. The powder was cooled and removed from the heating tube. The light green powder was of a fluffy character and free flowing except for some chunks which easily powdered in a mortar. This powder could be poured easily into a mold for pressing into fuel element shapes.

E. Physical Mixing of Oxides. Plutonium oxide can be physically mixed with another oxide in a simple manner to produce a resulting diluted plutonium dioxide. In the tests, uranium dioxide was used as a substitute for plutonium dioxide. In one experiment, eighty-five grams of Baker's Analyzed magnesium oxide powder and about two grams of finely divided uranium dioxide powder were ball milled for four hours. A rubber lined quart jar with twenty ceramic balls was used. After milling, the powder was not free flowing, whereas it had been before. The powder was divided randomly into sixteen samples and the analyses of these samples showed an average uranium content of 2.15 ± 0.35 weight percent. The expected average deviation for identical samples was 0.02 percent for the analytical method used. Thus, it appears that ball milling does not give a uniform product.

In another mixing test, a twin shell dry blender manufactured by the Pattersons-Kellog Company of East Straudsberg, Pennsylvania gave favorable results. One gram of uranium dioxide was added to about ninety grams of the same kind of magnesium oxide as used above. The uranium dioxide was added to one arm only of the blender. The blender was then rotated and stopped periodically for sampling. The product mixture was free flowing. The analytical results are recorded in Table II. These data indicate that blending was complete in thirty minutes or less. Thus, it appears that the twin shell dry blender can be satisfactorily used for the physical mixing of oxide powders and that it gives superior results to ball milling.

TABLE II

MAGNESIUM OXIDE AND URANIUM DIOXIDE

Blending by the twin Shell Dry Blender

Mixing Time		Weight Percent Uranium	
Minutes		Side 1	Side 2
30		1.27	1.27
60		1.30	1.32
90		1.27	1.27
120		1.22	1.15
150		1.27	1.27
	Average	1.27 ± 0.01	1.26 ± 0.04

IV. ACKNOWLEDGEMENTS

I wish to thank Mr. H. W. Crocker of the 234-5 Development Operation for assisting with the reductions. I am also grateful to Mr. Paul G Pallmer, Jr., of the Plutonium Metallurgy Operation who gave necessary assistance in the obtaining of the X-ray diffraction diagrams.

V. REFERENCES

1. KAPL-1573, Report of the Chemistry and Chemical Engineering Section, May, June, and July, 1956.

2. Mulford, R. N. R., Ellinger, F. H., J. Am. Chem. Soc. 80, 2023 (1958).

3. Seaborg, G. F., Katz, J. J., The Actinide Elements, NNES, IV-1413, McGraw-Hill Book Company, Inc., New York, New York, (1954), p. 394.

4. Katz, J. J. and Rabinowitch, E., The Chemistry of Uranium Part 1, NNES, VIII-5, McGraw-Hill Book Company, New York, New York, (1951), p. 261.

5. Wilson, A. S., HW-52772, A Method for Speeding the Dissolution of Plutonium Oxide, August, 1957.

6. Katz, J. J. and Rabinowitch, E., op. cit., p. 321.