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TITLE

AMMONIUM BIFLUORIDE FUSION OF IGNITED PLUTONIUM DIOXIDE

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AMMONIUM BIFLUORIDE FUSION OF IGNITED PLUTONIUM DIOXIDE

By

H. W. Crocker

234-5 Development Operation
Research and Engineering Operation
Chemical Processing Department

February 24, 1961

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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AMMONIUM BIFLUORIDE FUSION OF IGNITED PLUTONIUM DIOXIDE

I. INTRODUCTION

Plutonium dioxide powders are currently processed in a nitric acid - hydrofluoric acid solution to recover the plutonium. The dissolution method requires relatively large solution volumes, is very corrosive, and requires an eight-hour time cycle. Furthermore, a low plutonium batch limit is fixed by the large solution volume. A process is desired which utilizes small volumes, short time cycle, and is adaptable to more favorable vessel geometry.

The new incinerator equipment will be used for burning solid plutonium-bearing combustible waste materials. The resulting mixture of ash and ignited plutonium dioxide must be processed for plutonium recovery. The nitric acid - hydrofluoric acid dissolution method may be used for ash processing, but it would present problems similar to the plutonium dioxide processing system. A new process is desirable here also.

Pressurized autoclave aqueous dissolution or salt fusion have been considered for ignited plutonium dioxide recovery. Fusion[1][2] of low temperature plutonium oxide in ammonium bifluoride has been successful on small-scale applications. The fusion method described in this report was chosen in preference to an autoclave system for initial study because it can be operated at essentially atmospheric pressure, thus avoiding some of the problems associated with a pressurized autoclave.

II. SUMMARY AND CONCLUSIONS

An ammonium bifluoride fusion process for plutonium recovery from ignited (1000 C) plutonium dioxide has been developed. The fusion mass can be readily taken up in aluminum nitrate solution. Results of these studies show an average plutonium recovery of 95 percent in the final aqueous solution.

The fusion method has a short time cycle (three hours), utilizes small aqueous solution volumes (one liter ANN per 35 grams of original PuO_2), and the plutonium product solution in aluminum nitrate is suitable for direct blending into the existing Recuplex system. In addition, the only off-gas handling equipment required is a small water scrubber. It is recommended that the method be given further testing in a plant-scale production test.

The method also has application for plutonium recovery from incinerator ash, and for plutonium metal or skulls which have previously been converted to plutonium dioxide by steam oxidation or controlled burning. Direct fusion of metal or skulls may be possible, but the uncertain reactivity of these materials may make this approach un-

desirable.

III. DISCUSSION

The ammonium bifluoride fusion of plutonium dioxide proceeds according to the following equation:

$$2PuO_2 + 5NH_4FHF \longrightarrow 2PuF_4 \cdot NH_4F + 3NH_3\uparrow + 4H_2O\uparrow$$

The double salt product breaks down under heat to form solid plutonium tetrafluoride and volatile ammonium fluoride. All the reaction off-gas products are water-soluble.

Laboratory fusions were carried out in a 1-3/4 inch diameter by four inch deep stainless steel reactor. The experimental runs were on a 17 - 35 gram scale. Table I contains the experimental data. Average plutonium recovery in the experimental runs was 95 percent.

Typical experimental run conditions for recovery of plutonium from ignited plutonium dioxide are:

1. Thirty-five grams PuO_2 are mixed with ammonium bifluoride in a 1:8 mol ratio (one gram PuO_2 per 1.7 grams NH_4FHF).

2. The mixed powders are placed in a stainless steel reaction vessel equipped with a thermocouple, sparge tube, and off-gas line.

3. The reactor is sealed, connected to the argon sparge, and then joined to the off-gas line which terminates at the water scrubber.

4. Vessel and contents are heated to 200 C, and held at that temperature for two hours. The argon sparge is activated during the entire heat cycle. Off-gases are bubbled through the water scrubber during the heating cycle (the system is essentially at atmospheric pressure throughout the experiment).

5. After two hours at 200 C, the heat is turned off, the reactor opened, and the molten salt poured into one liter of heated (100 C) 2 M ANN (or the ANN can be poured into the vessel) to put the plutonium into solution. This dissolution step is accompanied by copious gas evolution and should be done in an open container. The resulting solution is filtered through a medium glass frit.

Residues containing plutonium were not encountered in the laboratory work. The unaccounted five percent was mechanically lost in handling.

Corrosion was not appreciable during the eight runs in the stain-

less steel pot.

The same 500 ml volume of water scrubber solution was used for all the experimental runs. A short off-gas line should be used to prevent solidification of ammonium bifluoride, which could plug the line. An off-gas line heated to 150 C could be used as an alternate.

Plutonium dioxide spiked with ash has been processed by the fusion method. Plutonium recovery from this material in preliminary experiments was 95 percent. At present, the primary problem for ash treatment is the filtration of the plutonium solution from residual ash particles. Additional work will be done on the ash treatment program.

The plutonium tetrafluoride resulting from the ammonium bifluoride fusion could be reduced directly to the metal if purity was satisfactory. Removal of any excess ammonium bifluoride and handling methods would have to be worked out.

IV. REFERENCES

(1) Tolley, W. B., The Preparation Of Plutonium (IV) Ammonium Fluoride And Its Decomposition To Plutonium Tetrafluoride For Subsequent Reduction To Metal. HW-31211, March 16, 1954 (Unclassified).

(2) Tolley, W. B., and R. C. Smith, Report Of Invention - The Preparation Of Plutonium(IV) Ammonium Fluoride And Its Decomposition To Plutonium Tetrafluoride For Reduction To Metal. HW-30753, February 3, 1954 (Secret).

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TABLE I

RECOVERY OF PLUTONIUM FROM IGNITED (1000 C) PLUTONIUM DIOXIDE

Run No.	Reactor Charge	Time Hours	Temperature ° C	Pu Charged Grams	Pu Recovered Grams	Recovery Yield, %
2	31.8 g PuO_2, 54 g NH_4FHF	2	200	28.0	32.8	>100
3	35.0 g PuO_2, 59.9 g NH_4FHF	2	200	30.8	29.1	94.5
4	35.0 g PuO_2, 59.9 g NH_4FHF, 2 g ash	2	200	30.8	27.6	90.0
5	35.0 g PuO_2, 59.9 g NH_4FHF, 2 g ash	2	200	30.8	27.2	88.5
6	35.0 g PuO_2, 59.9 g NH_4FHF, 2 g ash	2	200	30.8	28.6	93.0
8	17.5 g PuO_2, 30 g NH_4FHF, 4 g ash	2	200	15.4	19.6	>100
9	17.5 g PuO_2, 30 g NH_4FHF, 4 g ash	2	200	15.4	16.0	>100