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RECOVERY OF PLUTONIUM FROM OFF-STANDARD FLUORIDES

TO File

FROM K. M. Harmon by R. L. Beede

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RECOVERY OF PLUTONIUM FROM OFF-STANDARD FLUORIDES

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INTRODUCTION

The recycle material from the dry chemistry and metal-reduction operations in the 234-5 Building includes: 1) off-standard runs which have failed to fluorinate properly and which may consist of PuO_2 and/or plutonium-fluorine compounds; 2) materials which may contain calcium, iodine, and calcium iodide in addition to the PuF_4; i.e. hood and equipment sweepings, and off-standard reduction charges which have failed to reduce; 3) the fluoride residues which have been discovered in some of the filter boats, between the shell and liner; and 4) standard reduction residues.

The Recuplex process is sufficiently versatile that it will handle any of the materials listed in items 1, 2, and 4. Items 1 and 2, however, are rich enough in plutonium that it is desirable to process them prior to the start-up of Recuplex, and the accumulation of solids in some of the filter boats has been great enough that the boats should be cleaned out. Consequently, enough laboratory work has been done to define processes by means of which 1) the filter boats could be cleaned out without being dismantled, and 2) the recycle material, other than slag and crucible, could be dissolved and thus be prepared for recovery in 224-T.

As the laboratory work has progressed, the Separations Section has taken steps toward utilization of the procedures developed.

SUMMARY AND CONCLUSIONS

Solutions containing as much as 120 g/l Pu have been obtained by dissolving PuF_4 in boiling 8 M HNO_3 - 0.5 M $Al(NO_3)_3$. A time of two to three hours was required. The same solvent can be used for cleaning out filter boats and for dissolving fluorides which are mixed with Ca and I_2, provided the equipment can safely handle the H_2 and I_2 evolved.

RECOMMENDATIONS

The laboratory work described herein led to the following recommendations, upon which action has already commenced:

1. The filter-boats should be cleaned out periodically, by soaking in a hot solution containing 8 M HNO_3 and 0.5 M $Al(NO_3)_3$.

2. Solid residues which contain Task III reduction chemicals should either be saved for processing in Recuplex or should be dissolved in a stainless steel dissolver (equipped with a caustic scrubber for the off-gas, to trap the iodine evolved) for recycle to 224-T. Those residues which contain no iodine may be dissolved either in this equipment or in the skull dissolver.

RESULTS AND DISCUSSION

For the purposes of this discussion, the off-standard fluorides will be considered in two groups: 1) those which contain PuF_4, PuF_3, PuO_2 and/or metal impurities; and 2) those containing PuF_4, Ca, I_2, and CaI_2. The principal constituent of both groups is PuF_4, which may be readily dissolved in nitric acid solutions containing aluminum ion. The aluminum is effective because it forms a stable complex with fluoride ion.

Group 1: If the skull dissolver is used for these materials, the capacity of the dissolver limits each batch to 150 grams of plutonium. To dissolve batches of 400 grams a vessel with a working volume of at least four liters will be needed. After the addition of one liter of 8 M HNO_3 - 0.5 M $Al(NO_3)_3$ per one hundred grams of plutonium, two to three hours' boiling should be sufficient to completely dissolve any fluoride present, giving a solution which may be processed as recycle in the 224-T Building.

When the HNO_3-$Al(NO_3)_3$ solvent is used for the dissolution of PuF_3, oxidation of the plutonium is accompanied by the evolution of nitrogen oxide fumes. If the material contains PuO_2, the HNO_3 - $Al(NO_3)_3$ treatment may leave a solid residue, which can be dissolved in an 8 M HNO_3 - 0.05 M HF solution. In some cases, it may be advisable to use the HNO_3-HF treatment first.

A sample of PuF_4 (RUN RGX-12-5-269), which had partially fused when the furnace, temperature-controller failed, proved more difficult to handle. Only 85 per cent of the plutonium in the sample was dissolved after treatment for nine hours. Following a fusion with potassium fluoride, the residue dissolved readily in HNO_3-$Al(NO_3)_3$ solution.

The solids which have been found between the liner and shell of some of the filter boats may also be dissolved in HNO_3-$Al(NO_3)_3$ solution. Eighty-five grams of plutonium was recovered from the solids removed from filter boat No. 14. Boat No. 10 was submerged in a hot HNO_3-$Al(NO_3)_3$ solution, with a recovery of 0.5 gram of plutonium. Removal of the liner of No. 10 disclosed no additional solids. Treatment of Boat No. 18 by soaking in the hot solution put 29.5 grams of plutonium into solution. The filter boat shells are apparently not affected by the treatment, but the inconel fittings in the bottoms should be removed before treatment.

Group 2: Volatilization of iodine from the mixture when an HNO_3-$Al(NO_3)_3$ solution is used renders the skull dissolver unsuitable for the dissolution of materials containing iodine or iodides. Carbon tetrachloride was used successfully to extract the iodine from one of these mixtures, but of course left the iodide in the solid phase. Another procedure, which it was hoped, would be suitable for use in the skull dissolver, involved the following steps:

1) metathesis with 5 per cent NaOH, to oxidize the calium metal and to put all the iodide and iodine into solution;

2) filtration, to remove the iodine-bearing solution; and

3) dissolution of the solid residue in HNO_3-$Al(NO_3)_3$ solution.

Step 1 worked moderately well, converting part of the PuF_4 to the hydroxide, but leaving some of the calcium unreacted. Filtration was difficult, because the filter plugged, and the use of the skull dissolver was completely ruled out by the extreme foaming which occurred in step 3. Consequently, the only known procedure which looks useful for this class of material requires the use of a slag and crucible-type dissolver.

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