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BISMUTH PHOSPHATE CONCENTRATION PROCESS STUDIES
RECYCLE OF LANTHANUM FLUORIDE BY-PRODUCT
PRECIPITATION REWORK SOLUTION

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BISMUTH PHOSPHATE CONCENTRATION PROCESS STUDIES
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INTRODUCTION

The material entering the bismuth phosphate concentration process from the canyon (19-4-P) is a nitric acid solution of bismuth phosphate containing plutonium and small amounts of fission products. Following an oxidation step, the solution is diluted to about 4.5 times its original volume and a bismuth phosphate by-product precipitation is made. This is followed by a lanthanum fluoride by-product precipitation in which two or three per cent of the plutonium is carried on the solid. To recover this plutonium, the lanthanum fluoride is subjected to a rework treatment resulting in a rework solution (D-3) which is combined with the supernatant from the lanthanum fluoride by-product precipitation. A lanthanum fluoride product precipitation is then made from the combined solutions.

The lanthanum fluoride product precipitation is a very time-consuming step in that three successive strikes are made, the entire solution being centrifuged after each. Because of the nature of the lanthanum fluoride precipitate, the centrifuge throughput rate is low, thus adding to the total time consumed in the operation. Since the volume of the rework solution is appreciable with respect to that of the by-product precipitation supernatant, processing it at this point adds materially to the time required.

Since the solution entering the concentration process must be diluted by a large factor to effect the bismuth phosphate precipitation, it was suggested by W. G. Browne that the rework solution be used as part of this dilution. Time would thus be saved in the lanthanum fluoride product precipitation and some saving in the total volume of waste produced in the concentration process would result. However, the rework solution is acidic and contains some fluoride. The bismuth phosphate by-product precipitation would thus be made

at somewhat higher acidity than is currently the case. Also, the fluoride might cause excessive corrosion of the equipment as well as increased loss of plutonium due to "corrosion reduction". This report deals with a laboratory investigation of the feasibility of so recycling the rework solution.

SUMMARY

These studies indicate that no appreciable increase in plutonium losses need be anticipated if the rework solution is recycled to the bismuth phosphate by-product precipitation step in spite of the increased acidities encountered and the presence of fluoride. Although plutonium losses sustained in these laboratory-scale studies were somewhat higher than those obtained in the plant, the losses sustained when following the proposed modification were not appreciably higher than those obtained when following the current procedure.

EXPERIMENTAL

In order to establish the magnitude of the plutonium losses to be expected in the various concentration process steps when done on a laboratory scale, two runs were made in which the current plant process to the metathesis step was approximated as closely as possible. One of these involved synthetic 19-4-P and D-3 solutions while the other involved actual plant solutions. Other runs were then made in which the rework solution (D-3) was added to the 19-4-P solutions after the oxidation step. Plant procedures followed were obtained from M. J. Szulinski in July 1950.[1] They were in use at the time these studies were made. Although the reactions were carried out in glass equipment, stainless steel wire stirrers were used. Also, additional stainless steel wire was present in the reaction vessel to give a calculated metal surface area to solution volume ratio of about twice that in the plant. Centrifugation was with a Clinical centrifuge capable of developing about 700 G's acceleration.

Plutonium analyses, by direct evaporation, were made at all points of interest in the processes. Results obtained for the runs mentioned are shown in Table I.

The rework solution (D-3) contains some hydrofluoric acid (0.18M).

Since the plant sample was contained in Duraglas, the possibility existed that the fluoride might have been removed by reaction with the glass before the solution was used in these experiments. A run was made in which hydrofluoric acid equivalent to that originally present was added to the rework solution immediately prior to its addition to the oxidized 19-4-P solution. Plutonium loss in the bismuth by-product precipitation was 0.2 per cent. A similar run was made in which the bismuth phosphate by-product precipitation was carried out at 35°C. instead of 75°C. as used in the plant. Plutonium loss to the bismuth phosphate by-product cake was again 0.2 per cent.

DISCUSSION

Precipitates of bismuth phosphate formed at high temperature in contact with stainless steel and in the presence of oxidized plutonium are found to contain appreciable amounts of plutonium if fluoride is present. The plutonium carried is apparently reduced at the surface of the metal container as a result of reaction between the metal and hydrofluoric acid. Corrosion reduction is the term commonly applied to the phenomenon and, since the rework solution contains fluoride, it was thought that recycling it to the bismuth phosphate by-product precipitation step might result in high plutonium losses due to corrosion reduction. However, the results shown in Table I do not indicate any appreciable increase in plutonium losses due to the fluoride, at least under the conditions of the experiments. Plutonium losses were comparably low when the bismuth phosphate precipitation was carried out at 35°C., a temperature known to be adequately low to minimize corrosion reduction.

Recycle of the rework solution to the bismuth phosphate by-product precipitation increases the acidity throughout the concentration process to the metathesis step. This increase appears to have no appreciable effect on plutonium recovery.

ACKNOWLEDGMENT

The writer wishes to express appreciation to H. L. Brandt who performed some of the laboratory work mentioned in this report.

REFERENCES

(1) HW-2658-T, pg. 127. Details of plant procedures used for reference.

(2) HW-3428-T. J. S. Kane. Laboratory notebook containing fundamental data used in this report.

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Table I

PLUTONIUM LOSSES IN CONCENTRATION PROCEDURES

Material Analyzed	Typical Plant Run	Plutonium Losses - Per Cent				
		Synthetic Solutions		Plant Solutions		
		Current Procedure	Rework Solution Recycled to $BiPO_4$ Pptn.	Current Procedure	Rework Solution Recycled to $BiPO_4$ Pptn.	
					Run A	Run B
$BiPO_4$ by-product cake	0.09	0.33	0.34	0.25	0.58	0.27
LaF_3 by-product cake after rework	0.025	0.03	0.16	0.28	0.04	0.008
*Rework solution	2 - 3	0.14	0.65	0.43	0.44	0.058
Supernatant from LaF_3 product precipitation	0.1	0.22	0.14	0.68	0.27	0.04

* Not actually a loss since most of the plutonium will be recovered in subsequent procedures.