**Cover Sheet for a Hanford
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234-5 DEVELOPMENT - SUMMARY REPORT - RECOVERY OF PLUTONIUM FROM SKULLS

COPY 1 OF 1

Introduction

A process for recovery of skull material by dissolution in hydriodic acid has been outlined in a previous memorandum, HW-17117. This process as used at Los Alamos gives a solution which is recycled to the oxalate purification process.

Installation of the hydriodic acid process at Hanford has been considered undesirable for several reasons which might be summarized as follows:

- a) This process has not been completely satisfactory at Los Alamos due to higher impurity concentrations in the buttons produced from recovery batches.
- b) The process requires the use of construction materials other than stainless steel.
- c) Future change to a peroxide purification process (or other purification process eliminating hydriodic acid) would make recycle of the hydriodic acid skull solution impractical without further development work and equipment modification.

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Development work has been done on an alternate process for the dissolution of skulls. This process uses a solution of 70% nitric acid which is made about 0.04 molar in hydrofluoric acid. The plutonium solution resulting from dissolution with this acid is suitable for recycle to the Hanford process stream in existing equipment. Production testing on this alternate process is contemplated, but the present report has not been delayed till test completion because of the urgency for preparing a Project Proposal.

Process Using HNO₃-HF

The essential steps for this process are given below:

1. Receive the packaged skulls from storage.
2. Remove the material from the containers and weigh to within 1 gram the required amount for the batch to be charged. The batch size is to be approximately 300 grams element weight.
3. Transfer the batch to a dissolver.
4. Add 500 ml. of 70% nitric acid per 100 grams of skull material.
5. Add sufficient 47% HF to make the solution 0.04 molar in HF. (Since this is only 0.75 ml. 47% HF per 500 ml. 70% nitric acid, it may be preferable to prepare the mixed acid externally to the hood in somewhat larger batches.)
6. Heat the mixture to boiling and boil gently for 4 hours, refluxing the vapors.
7. Cool the solution to room temperature.
8. Withdraw the solution from the dissolver, filtering to remove solids which may be present.
9. Measure either the weight or the volume of the product solution to within 1%.
10. Obtain a representative sample of the solution and submit for Pu assay, specific gravity, and acidity.
11. Load the batch into a PR can.
12. Dilute to 10 grams of Pu per liter and 2 grams H / per liter. (About 28.5 liters of 1.5 M HNO₃ will be required.)
13. Transfer the PR can containing the solution to the Isolation Building for processing through two peroxide cycles and shipment to 234 Building in routine fashion.

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Discussion

The facilities should be designed to handle 1500 grams of skulls per month. Skulls have been found to contain an average Pu content of 90% by weight.

Use of the four hour boiling period may result in the retention of a small heel of undissolved material. This will depend upon the physical nature of the skulls charged and will vary considerably. It is probably not practical to retain each batch until solution is complete since the rate of dissolution becomes quite slow as the surface decreases. It is necessary to be able to inspect the dissolver visually for the presence of a heel at the end of a cycle although a material balance is to be maintained for each operation.

The flowsheet given has indicated that the recovered solution would be processed through the two peroxide cycles in the Isolation Building. One peroxide cycle, however, together with the oxalate purification, has been demonstrated to purify this solution to the desired extent. The latter procedure would require more complicated handling in the existing cells.

The alternate possibilities of transferring a concentrated skull solution to the Isolation Building; and then making the dilution or of diluting before loading the PR can should be considered.

The corrosive nature of the boiling nitric acid - HF mixture should be pointed out. This is due to the oxidizing action of hot concentrated nitric acid as well as to the small amount of fluoride ion present. It is believed, however, that a suitable material for construction of the dissolver may be found among the types of stainless steel.

Due to the necessity for testing with plutonium present, corrosion tests under approximate process conditions have been run in the development laboratory on a limited number of specimens. These data are summarized in Table I. All tests were made with four hour specimen exposure to acid which was initially 16 M HNO₃ - 0.04 M HF and finally 11 M HNO₃ and 80 g/l Pu. It is admitted that these tests were short and may need confirmation before a firm choice of equipment can be made. The confirmatory tests would not need to be made in the presence of plutonium since samples run with plutonium present consistently showed lower corrosion rates than without Pu.

Of the materials tested, the type 309 SCb stainless appears to be the least corroded. Other materials may be superior; preliminary promising results were obtained in corrosion tests with tantalum. It should be noted that the penetration values are given in inches per year on a continuous operation basis. If taken on the basis of actual service hours (say 8 hours per week) the corrosion rate for this material is well within an acceptable limit.

Table I -- Corrosion of Stainless Steels During Skull Dissolution
With 16 M HNO_3 - 0.04 M HF

Material		Penetration In Inches Per Year	
		In Boiling Acid	In Vapors
Stainless Type 309SCb	Sensitized	0.292	0.150
Stainless Type 309SCb	Commercially annealed	0.191	0.100
Stainless Type 304ELC	Sensitized	0.617	
Stainless Type 304ELC	Commercially annealed	0.440	
Stainless Type 347	Sensitized	0.590	
Stainless Type 347	Commercially annealed	0.515	0.116
Stainless Type 347 TaCb	Sensitized	0.510	0.706
Stainless Type 347 TaCb	Commercially annealed	0.501	0.696

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