**Cover Sheet for a Hanford
Historical Document
Released for Public Availability**

Released 1995

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

HW-18738

Classification Cancelled and Changed To

DECLASSIFIED

By Authority of DOC
May 1973
By J. E. Smyly 11-16-94
Verified By Gerry Maly 11-17-94

RECORD CENTER FILE

- #1 B Weidenbaum
- #2 AB Graninger - OH Greager
- #3 RH Beaton
- #4 JB Work
- #5 RS Bell - VR Chapman
- #6 T Prudich - WN Mobley
- #7 PG Rhoades
- #8 IF Hardy
- #9 PE Collins
- #10 MJ Szulinski
- #11 WL Lyon - JF Facer
- #12 700 File
- #13 300 File
- #14 Pink
- #15 Yellow

**SPECIAL RE-VIEW
FINAL DETERMINATION
DECLASSIFICATION CONFIRMED**
BY JP Derouin DATE 5/5/81
BY JW To Lan DATE 5/6/81

September 1, 1950

This document consists of 4 pages, 1

To: B. Weidenbaum
From: W. L. Lyon - JF Facer

234-5 DEVELOPMENT GROUP--SUMMARY REPORT
USE OF "AT" SOLUTION WITHOUT EVAPORATION

The transfer to the Purification Building process of AT solution without final evaporation will be considered as a supplement to Production Test 231-10. The process has been explored by the Development Group in order to provide some background information prior to testing on a plant scale. A summary of this work is presented.

Conclusions

AT solution without final evaporation in the sample can may be used as starting material for the plus three oxalate purification process providing that the nitric acid concentration is adjusted prior to adding hydriodic acid. If the

RECEIVED

SEP 4 1950
300 AREA
CLASSIFIED FILES

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DECLASSIFIED MASTER

REPRODUCED FROM BEST
AVAILABLE COPY

nitric acid concentration is reduced to 3 molar or lower, the pre-reduction step may be carried on at room temperature. If nitric acid is present at a concentration greater than three molar, cooling of the solution prior to hydriodic acid addition appears to be necessary. Higher losses than experienced by the present process may be expected as the nitric acid concentration of the starting solution is increased. Use of AT solution concentrated to 350 grams of plutonium per liter would be desirable to reduce the volume resulting in the purification vessel after adjustment to the proper nitric acid concentration. Close control of AT concentrations will be necessary.

Experimental Work

AT solution from Run B-10-8-D2 was provided as starting material for the small scale runs. Its composition was as follows:

Pu	227.5 grams per liter
Fe	0.681 grams per liter
H	11.56 grams per liter
Sp. Gr.	1.647
Purity	98.9%

Twenty-two milliliter portions of this solution (5 grams of Pu) were diluted to each of several concentrations prior to the addition of reagents. One to three runs were made at each condition. The amount of 5.5 molar hydriodic acid added in each case was 32 milliliters. The amount of 0.6% molar oxalic acid was adjusted to give an excess equivalent to a concentration of 0.15 to 0.20 molar after precipitation. The results are described below.

1. AT Solution Diluted to 106 Grams Pu per Liter

This condition gives a plutonium concentration equivalent to that in the existing process (cut SC plus rinses) in the 234 building, although the nitric acid concentration in this case was 5.4 molar instead of 1.5 molar. When hydriodic acid was added to this solution at 30° C, a vigorous reaction took place. A mass of iodine was precipitated and oxides of nitrogen were given off. Addition of oxalic acid after a twenty minute period gave a tan precipitate indicating that little or no reduction of plutonium to the plus three valence state had taken place.

2. AT Solution Diluted to 4 Molar HNO₃

Three runs were made using this initial concentration. It was found necessary to cool the solution to 20° C prior to the addition of hydriodic acid to prevent gross precipitation of iodine. Plutonium concentrations in the supernatant solution were higher than normal (0.100 to 0.200 grams per liter, as compared to 0.010 to 0.050 grams per liter) otherwise satisfactory plus three oxalates were prepared.

DECLASSIFIED

3. AT Solution Diluted to 3 Molar HNO_3

Hydriodic acid could be added to this solution without the necessity of cooling below room temperature. Losses to the supernatant solution were similar to those experienced with 4 molar nitric acid in the starting solutions.

4. AT Solution Diluted to 2 Molar HNO_3

Pre-reduction was carried on immediately after dilution without difficulty. Concentrations of plutonium in the supernate were in the range of 0.040 to 0.055 grams per liter.

Scale-up Considerations

From a process standpoint, adjustment of the nitric acid concentration of the AT solution to approximately 2 molar before addition of reagents appears to be desirable. A serious limitation to this as a process, however, is the capacity of the precipitation vessel of Hood 5, 6, or 7. A freeboard of about 35 per cent as a minimum should be allowed for a vessel of this type. This minimal 10 liter vessel should therefore not be filled to greater than about 6.5 liters.

This will limit the dilution of the present AT solution (250 grams per liter, 11.5 molar HNO_3) to approximately 1 molar HNO_3 . Further boil-down of AT solution--for instance, to 350 grams per liter, 11.5 molar HNO_3 --is therefore indicated. Tables I and II have been prepared to give the total volumes resulting on a plant scale flowsheet for both the present AT and for a 350 gram per liter AT diluted to various concentrations with addition of reagents to the purification vessel.

AT solution at the higher plutonium concentration may be diluted to approximately 3 molar nitric acid without an excessive volume resulting in the precipitation vessel. It is felt that the latter condition should be recommended for initial testing on the plant scale. The following process steps are suggested:

- (a) Receive AT solution (350 grams Pu per liter) in a sample can.
- (b) Transfer to the Purification Reactor of Hood 5, 6, or 7.
- (c) Rinse SC twice with 0.650 liter portions of distilled water, transferring the rinses successively to the reactor.
- (d) Agitate the solution for 5 minutes.
- (e) Check to see that temperature is below 30° C. If not, cool to below 30° C.
- (f) Add 1.100 liters of 3.5 molar HI.

DECLASSIFIED

- (g) Agitate the solution for 20 minutes.
- (h) Add 3.350 liters of 0.67 molar oxalic acid over a 10 minute period with agitation. Proceed as per normal procedure.

It is important that only those batches containing plutonium at 350 grams per liter as a minimum concentration be chosen for production testing according to the above flowheet. This will prevent attaining nitric acid concentrations in excess of 3 molar after dilution.

Close control of the AT concentration will be imperative if this solution is to be used successfully as the final product of the Isolation Building.

TABLE I--Purification Process Volumes

Basis: AT solution at 250 grams Pu/liter and 11.5 molar nitric acid.

Volume of AT (liters)	Dilute to	Volume after Dilution (liters)	Volume 5.5M HI (liters)	Volume 0.67M $H_2C_2O_4$ (liters)	Total Volume (liters)
0.640	2M HNO_3	3.68	1.10	4.63	8.96
0.640	2.5M HNO_3	2.94	1.10	3.86	7.90
0.640	3.0M HNO_3	2.45	1.10	3.65	7.20
0.640	3.5M HNO_3	2.10	1.10	3.50	6.70
0.640	4.0M HNO_3	1.84	1.10	3.39	6.33

TABLE II--Purification Process Volumes

Basis: AT solution at 350 grams Pu/liter and 11.5 molar nitric acid.

0.457	2M HNO_3	2.63	1.10	3.72	7.45
0.457	2.5M HNO_3	2.10	1.10	3.50	6.70
0.457	3M HNO_3	1.75	1.10	3.35	6.20
0.457	3.5M HNO_3	1.50	1.10	3.25	5.85
0.457	4M HNO_3	1.31	1.10	3.16	5.57

DECLASSIFIED