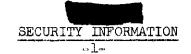
					\mathbf{D}_{i}	(
			HW-28789				
	AINS INFORMATION AFFE		DATE	COPY NO.	20109		
WITHIN HE MEANING	SE OF THE UNITED ST	AWS,	6-29-53				
MISSION OF TEVELATI	CCS. 793 AND 794, THE TI ON OF WHICH IN AN MA	RANS-	FILE DESIGN	^TIONT	HM	CIEN	
TO AN UNAUTHORIZED	PERSON IS PROHIBIT D B	YLAW."		Utl	JEAUD	it ilu	
		· · · · · · · · · · · · · · · · · · ·	SUBJECT OR	TITLE ,			
<u> </u>	RICTED DATA			· · · · · · ·			
THIS DOCUMENT CONTAINS RESTRICTED DATA ALL DEFINED IN THE TOMIC ENERGY ACT OF			RECOVERY OF PLUTONIUM FROM OFF-STANDARD				
1946 ITS TRANSMITTAL OR THE DISCLOSURE OF IL CONTENTS IN ANY MANNER TO			FLUORIDES				
UNAUT ORIZED PERSO	The second secon	TAXY	то			Α.	
	RECEIVE		FROM	File		100	
	50104		K	. M. Harm			
THIS DOCUME T MUST		MED (C) W	HERE AN UNA	JORIZED	PERSON M	HAVE ACCI	ESS
TO IT, WHEN NOT IN L	E IT IS IN TOSOM	S W SEP	DVED LOCKE	ED TEPOSIT	ORY WITHII	N ALAPPROV	ED Om _
	T IS YOUR WEEK	()	11 7 115	CONTENTS	WITHIN IF	IE LIMME C)F =
	HANY TED. IT IS NOT TO E		TS TRANSMET CATED, IF AD			AT YOUR E REQUIRE	
OBTAIN THEM FROM T	HE RELITED ISSUING FIL						
TO SIGN IN THE SPAC	E PROVIDED BELOW.	DATE	50:17	то.	55.45		
A. E. Smith	199	1/0/10	ROUTE	701	READ	₽ (;	DATE
UB Kasar		(/	71	ELLE-N		<u></u>	<u> </u>
6 11 12 al	Machine "	4-53		WIN	AP	PROVEDFO)
1.1.	V 4 - 1 - 2	7-4-04-			PU	BLIC RELEA	NOT.
4-13a	and a second	1	· = 1 ***	R AG ,	1 4	Harvan	
	PACL. Han	7/25/54	間條	ERENCE	//	\\9\10\ \9 \	7
No Vouspron 200	-w Timet	829/57	A CONTRACTOR OF THE PARTY OF TH	OPYCE	//	· · · · · · · · · · · · · · · · · · ·	
lile	NA OV	11 6	TY W	FO DE	AVAI	LABLE (COV
7 - 0005	Remod	#					,
	Mister Soull	4/2/58	UN	VCLASCI-	CONTRILE	D .	
	7.9.6	11-1-0	NOT	EAR IN	31.	W	
À	pmn	12/1/65		301		90 IV 90 148	
ANI	in warmen	1 CAL flas	of the		of of a		
101710		-	(r &)			ACA - 120 A	——
			1				
			Classification (Cancelled (Ch	ange to	.	
INTENTAL	IFN Law.	1		ASSIFIED)		
MAEMIN		+	By Authority of dinator, , Batter	of Classification	on Coor- t. ;		
AUG 17 1	953		13 1 11 1/hel	G Date 3	/24/73		
			PN CCK	7-19-9	7	ווחמנונ	irn
DOCUMENT AUD	NIT				111-1		
C-205-US (2-52)						HUUN	I Louis
G -40-04 (8-04)		442111	V-1.			∫	



HW-28789

BEST AVAILABLE COPY

- O. F. Beaulieu E. G. Pierick
- R. L. Beede
- R. S. Bell V. R. Chapman
- A. G. Blasewitz R. W. McKee
- V. R. Cooper
- O. H. Greager
- K. M Harmon
 - O. F. Hill
- H. H. Hopkins, Jr.

Th<u>is document consi</u>sts of

- L. M. Meeker
- 11. W. N. Mobley
- 12. T. Prudich
- W. H. Reas 13. A. E. Smith
- 15. 17. Extra
- 18. 700 Files
- 19. 300 Files
- 20. Yellow Files

June 29, 1953

APPROVED FOR

TO: File

K. M. Harmon, Leader FROM:

234-5 Development, Plant Processes Unit

Separations Technology Sub-Section

Technical Section

by: R. L. Beede, Junior Engineer

RECOVERY OF PLUTONIUM FROM OFF-STANDARD FLUORIDES

is docume ted data fined in et or ia transi osure of its authorized

FORMATION

Classification Cancelled (Change to **UNCLASSIFIED**

pages

By Authority of Classification Coordinator, /Battelle Northwest.





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 PuO₂ and/or plutonium-fluorine compounds; 2) materials which may contain calcium, iodine, and calcium iodide in addition to the PuF4; 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

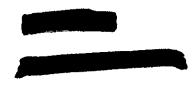
Solutions containing as much as 120 g/l Pu have been obtained by dissolving PuF₄ in boiling 8 M HNO₃ = 0.5 M Al(NO₃)₃. A time of two to three hours was required. The same solvent can be used for cleaning out filter boats and for dissolving fluorides which are mixed with Ca and I₂, provided the equipment can safely bandle the H₂ and I₂ evolved.

RECOMMENDATIONS

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

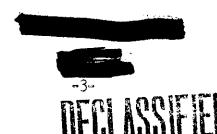
- 1. The filter-boats should be cleaned out periodically, by soaking in a hot solution containing 8 M HNO3 and 0.5 M Al(NO3)3.
 - 2. Solid residues which contain Task III reduction chemicals should either be saved for processing in Recuplex or should be dissolved in a stainless steel dissolver (equipped 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.







HW-28789



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.

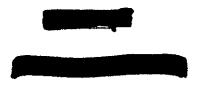
Group 1: If the skull dissolver is used for these materials, the capacity of the dissolver limits each batch to 150 grams of plutonium. To dissolve batches of 400 grams a vessel with a working volume of at least four liters will be needed. After the addition of one liter of 8 M HNO3 - 0.5 M Al(NO3)3 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 PuF4 (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 HNO3-Al(NO3)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 HNO3-Al(NO3)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 incomel fittings in the bottoms should be removed before treatment.









Group 2: Volatilization of iodine from the mixture when an HNO3 Al(NO3)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 PuFh 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.



