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DP-1146

AEC RESEARCH AND DEVELOPMENT REPORT

CURIUM PROCESS DEVELOPMENT

IV. EQUIPMENT DEVELOPMENT AND TESTING

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Chemical Separations Processes
for Plutonium and Uranium
(TID-4500, UC-10)

CURIUM PROCESS DEVELOPMENT

IV. EQUIPMENT DEVELOPMENT AND TESTING

by

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September 1969

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ABSTRACT

The major equipment required for separating curium, americium, and californium and for preparing purified curium and americium oxides in the Curium Processing Facility of the Savannah River Laboratory was tested under simulated process conditions prior to installation into three shielded cells. Modifications to the equipment were made where necessary for proper performance; operating procedures were developed to ensure satisfactory process control.

FOREWORD

This report is one in a series that describes the development of separations processes for purifying ^{244}Cm produced in Savannah River reactors. The series is being issued under the general title Curium Process Development. Following the general title, a roman numeral designates the subject area of the report, and an arabic numeral designates the series report number in that subject area. A subtitle describes the content of each report. Subject areas foreseen for this series are:

I. General Process Description
II. Chemical Processing Steps
III. Analytical Chemistry Support
IV. Equipment Development and Testing

Reports issued in this series include:

I. General Process Description by I. D. Eubanks and G. A. Burney (USAEC Report DP-1009).

II-1. Separation of Americium from Curium by Precipitation of $K_3AmO_2(CO_3)_2$ by G. A. Burney (USAEC Report DP-1109).

III-1. Analytical Techniques for Characterizing Solvent by R. Narvaez (USAEC Report DP-1010).

III-2. Identification of Solvent Degradation Products by D. L. West and R. Narvaez (USAEC Report DP-1016).

III-3. Analytical Control by E. K. Dukes (USAEC Report DP-1039).

III-4. Evaluation of Potential Hazards from Chlorination of Amines and Ammonia by D. L. West, M. L. Hyder, G. A. Burney, and W. E. Prout (USAEC Report DP-1142).

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INTRODUCTION

Approximately 5.5 kg of ^{244}Cm, 2.5 kg of ^{243}Am, 20 mg of ^{252}Cf, and 8.6 kg of residual ^{242}Pu were produced by the irradiation of plutonium target elements in two consecutive reactor campaigns.(1) The irradiated target elements were processed in existing plant facilities to remove the plutonium and some of the nonlanthanide fission products. The resulting solution containing the curium, americium, californium, and fission products is being processed in the Curium Processing Facility of the Savannah River Laboratory (SRL) to prepare purified curium oxide suitable for the development of heat sources and to recover the byproducts, americium and californium.(1) A blend of purified oxides of the americium and part of the curium will be fabricated into targets for irradiation to produce additional ^{252}Cf. The recovered californium will eventually be purified for assessment of its utility in potential applications as a neutron source.

The curium process, summarized in Figures 1, 2, 9, 10, and 15, includes an initial cycle of solvent extraction with tertiary amine nitrate in diethylbenzene followed by two cycles of Tramex solvent extraction with tertiary amine hydrochlorides in diethylbenzene to separate the curium and americium from californium, lanthanides, and other fission products. Curium is separated from americium by precipitation of $K_3AmO_2(CO_3)\cdot H_2O$, the separated curium and americium are converted to oxalates, and the oxalates are calcined to oxides. The high chloride, high level waste generated in the process is made suitable for storage by evaporation.

The equipment required for the curium process was developed and tested at the SRL semiworks before installation in the Curium Processing Facility. This report summarizes the information obtained from these tests.

SUMMARY

The major equipment items required for the Curium Processing Facility in the Savannah River Laboratory were developed, tested with nonradioactive stand-ins, and modified where necessary at the semiworks to obtain proper operation and to develop operating procedures as summarized below:

- The 16-stage mixer-settlers, which are used in the three solvent extraction cycles of the curium separations process, operated satisfactorily. Observed cocurrent efficiencies were higher than the necessary 80%, and entrainment in endstreams was acceptably low.
- Operability of the solvent washers for the curium separations process was confirmed by full-scale tests. Hydraulic and mass transfer characteristics were satisfactory under all conditions tested. An air lift was demonstrated for recirculating a large fraction of the NaOH wash in the second washers of the Tramex cycles, to reduce the volume of high activity waste.
- Tests of the precipitation-filtration equipment for separating americium and curium (using lanthanum as a stand-in for both americium and curium) showed that a satisfactory precipitation yield ($>99.9\%$) of curium and americium should be obtained. Test precipitations of $K_3AmO_2(CO_3)_2$ (using uranium as a stand-in for americium) demonstrated that satisfactory yields of americium should be obtained.
- The temperature of the precipitate on the curium and americium hydroxide filter can be kept below 45°C, which is necessary to prevent the precipitate from drying, if the filter cooling system is supplemented by procedural controls.
- The oxalate precipitator, the filter housing, two platinum filter boats, and the calciner used in preparing pure curium and americium oxides should perform satisfactorily with a 144-gram batch of curium (based on tests using lanthanum as a stand-in for americium and curium).
- Vertical tantalum condensers for the seven evaporators in the curium process have adequate downflow condensing capacity.
- Operability of the seven evaporators for concentration and adjustment by evaporation of the aqueous feed, waste, and product solutions was demonstrated. Procedural controls were determined for the satisfactory operation of each evaporator.

EQUIPMENT AND PROCESS DESCRIPTION

MIXER-SETTLERS

Process

Six 16-stage mixer-settlers are required in the three solvent extraction cycles described in Figures 1 and 2. In the conversion solvent extraction step, the nitric acid solution of curium, americium, and fission products is converted to a chloride solution by extracting the actinides and rare earths with a mixture of n-octyl and n-decyl tertiary amine nitrates in diethylbenzene (1A bank), and back-extracting them with 8M HCl (1B bank). The resulting chloride solution of americium and curium is then separated from californium, rare earths, and some of the fission products by two cycles of Tramex solvent extraction with tertiary amine hydrochlorides in diethylbenzene (2A, 2B, 3A, and 3B banks).

Development Steps

Initially, a plastic six-stage prototype mixer-settler (Figure 3) was evaluated with simulated Tramex process solutions (tertiary amine hydrochlorides in diethylbenzene, and LiCl in water); nickel was used as a stand-in for curium to determine the mass transfer efficiency. Eventually, two of the six full-scale tantalum mixer-settlers were installed and tested at the semiworks with three prototype solvent washers (Figure 4); nickel was used as the stand-in for curium, to verify the mass transfer efficiency of the full-scale equipment under simulated conditions of all three solvent extraction cycles.

Equipment

The mixer-settlers are a scale-down design of the "Jumbo" mixer-settlers, which are used in one of the Savannah River Plant's (SRP) Separations Areas. However, the smaller unit uses a four-bladed paddle instead of a volute-vaned impeller for pumping and mixing.

A cutaway view of the 16-stage curium mixer-settler is shown in Figure 5. Each stage is 6 inches high, 1-1/4 inches wide, and 7-1/4 inches long, and is divided into an interface weir section, an aqueous inlet section, a solvent inlet section, a mixing section containing a four-bladed paddle (3/4-inch diameter x 1 inch), and a settling section. Aqueous solution from the succeeding stage flows under the dispersion baffle in the end of a settling section, over the interface weir, and into the aqueous

	LINE NO.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
	PROCESS STREAM	Canyon Solution	1AF (2)	1AS	1AX	1AW	1AP	1BX	1BS	1BP	1BW	K_2CO_3 Wash	Water Wash		Spent Water Wash	Spent K_2CO_3 Wash	Solvent Make-Up	LiOH	LiCl	2AF Evap. Overhead	HCl Gas	2AF Acidifier Acid	2AF	2AS	2AX	2AW
	LITERS/DAY	36	36	36	144	72	144	36	82.8	36	226.8	90	75.6		75.6	90		37.7	14.45	56.85		2.9	34.2	36	108	72
g/l	Cm	>1.0	1.0				0.25			1.0													1.05			
	Am	0.46	0.46				0.115			0.46													0.48			
	R.E.	~2.0	~2.0				~0.5			~2.0													~2.1			~1.0
	Cf	5×10^{-4}	5.10^{-4}																							
MOLARITY	Fe (III)	0.08					0.02				0.013					0.032										
	$Al(NO_3)_3$	2.0	2.0			1.0																				
	HNO_3	<1.0	0.45			~0.01				<0.01																
	$LiNO_3$			7.0		4.0																				
	HCl				IN DEB			8.0		5.3	0.6 M "ADOGEN" 364 0.5M HNO_3 IN DEB 0.5 M FREE CHl 0.1 M HCl				1.5					0.07		4.1	0.348			0.02
	NaOH																									
	LiOH						0.61M "ADOGEN" 364 HNO_3 IN DEB 0.16 M HNO_3 EXCESS NOMINAL											4.5							0.61M "ADOGEN" 364-HCl IN DEB 0.01 - 0.05M HCl EXCESS (.025M NOMINAL EXCESS)	
	LiCl			1.0															13.0				11.0	10.9		10.98
	NaCl																									
	KNO_3				0.61M "ADOGEN" 364-HNO_3 0.01 - 0.08M HNO_3 EXCESS (.05M NOMINAL) Ru^{106} 1.64 Ci/l											1.26										
	K_2CO_3											2.6				0.98					ADD AS REQUIRED					
	EDTA (TETRASODIUM SALT)											0.2														
	$KHCO_3$															1.52										
	KCl															0.26										
	HYDRAZINE NITRATE			0.2		~0.1																				
	$SnCl_2$								IN DEB								0.6M "ADOGEN" 364 IN DEB									
	$Na_2Sn(OH)_4$																									
	EDTA SALTS															0.2										
	Hg(II)	0.30					0.08				0.048					0.12										
	Cm α, d/min-ml	1.8×10^{11}	1.8×10^{11}			9×10^{7} (0.1%)	4.5×10^{10}		0.61M "ADOGEN" 364 Ru^{144} 1.64 Ci/l	1.8×10^{11}	3×10^{7} (0.1%)				9×10^{7}					2.1×10^{2}			1.9×10^{11}			9×10^{7} (0.1%)
	$Ce\text{-}Pr^{144}$, Ci/l	170	170			0.09 (0.1%)	42.5			170	0.027 1%				0.08					0.02			179			85
	$Zr\text{-}Nb^{95}$, Ci/l	0.15	0.15			0.07 (90%)	3.8×10^{-2}			9.7×10^{-4}	2.4×10^{-2}				6.0×10^{-3}	1.8×10^{-1}				1.1×10^{-4}			1.6×10^{-4}			7.5×10^{-5}
	$Ru\text{-}Rh^{106}$, Ci/l	82.5	82.5			4.1 (10%)	18.5			0.15	11.6					30				1.8×10^{-5}			0.084			0.04
	HEAT CONTENT, WATT/LITER	~7	~7				~1.7			~6	~0.12					~0.3							6.37			~1.6

If DF >1000, Zr-Nb in 1BP $<1.5\times10^{-4}$
If DF >1000, Ru-Rh <0.08

	LINE NO.	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
	PROCESS STREAM	2BX	2BS	2BW	2BP	Caustic Wash	Solvent Acidifier Acid	Spent Caustic Wash	Spent Acid	2BP Acidifier Acid	2ND Cycle Product	Solvent Make-up	2AP		1AF Evap. Overhead	$Al(NO_3)_3$ or HNO_3 or H_2O	1st cycle Spills Etc.	2nd cycle Spills Etc.		Solvent Acidifier Acid	Spent Acid	$SnCl_2$	2AF ADJ'D	$NaNO_3$ & NaOH	Spent HCl Wash	HCl Wash
	LITERS/DAY	36	36	144	36	216	48	216	48		36		108							72	72	1.0	36		48	48
g/l	Cm			6.25×10^{-3}	0.98						0.975		0.33										1.0		1.9×10^{-3}	
	Am				0.46						0.46		0.15										0.46			
	R.E.										TRACE												~2.0			
	Cf			1.25×10^{-4}																			5×10^{-4}		3.76×10^{-6}	
MOLARITY	Fe (III)																									
	$Al(NO_3)_3$																									
	HNO_3			IN DEB	<0.01M										TRACE	15.8				1.8	0.5					
	$LiNO_3$																									
	HCl				<0.01		4.4		2.5		0.25		IN DEB									0.35	0.35		1.1	0.8
	NaOH		IN DEB			1.27		0.803				IN DEB														
	LiOH																							ADD AS REQUIRED TO INSURE pH >13 AND $(NO_3^-)/(Cl^-)$ >10		
	LiCl	8.98			8.98						8.98											10.0	10.95		0.27	
	NaCl			0.06M "ADOGEN" 364-HCl 0.1M HCl EXCESS				0.433					0.61M "ADOGEN" 364-HCl 0.10M HCl EXCESS		VOLUME VARIES DEPENDING ON FEED COMPOSITION											
	KNO_3															ADD AS REQUIRED DEPENDING ON FEED COMPOSITION	NITRATE SOLUTIONS FROM SUMPS, SPILLS ETC. (1ST CYCLE SOLUTIONS ONLY) (DO NOT EVAPORATE)	CHLORIDE SOLUTIONS FROM SUMPS, SPILLS ETC. (2ND CYCLE SOLUTIONS ONLY)								
	K_2CO_3																									
	EDTA (TETRASODIUM SALT)									ANHYDROUS HCl GAS																
	$KHCO_3$																									
	KCl																									
	HYDRAZINE NITRATE		0.61M "ADOGEN" 364-HCl 0.01 - 0.05M HCl EXCESS 0.025M NOMINAL EXCESS HCl									0.6M "ADOGEN" 364-HCl 0.01 - 0.05M HCl EXCESS .025 M HCl NOMINAL EXCESS														
	$SnCl_2$			0.025									0.03									20	0.1			
	$Na_2Sn(OH)_4$							0.017																		
	EDTA SALTS																									
	Hg(II)																									
	Cm α, d/min-ml			1.1×10^{9} (2.5%)	1.8×10^{11}						1.764×10^{11}		6×10^{10}		2×10^{7}								1.8×10^{11}		3.4×10^{9} (2.5%)	
	$Ce\text{-}Pr^{144}$, Ci/l				0.17						0.16		0.05										170			
	$Zr\text{-}Nb^{95}$, Ci/l			7×10^{-6}									9×10^{-6}										1.5×10^{-4}		2×10^{-7}	
	$Ru\text{-}Rh^{106}$, Ci/l			0.03	1.8×10^{-3}			0.02			7.8×10^{-2}		0.05										0.08			
	HEAT CONTENT, WATT/LITER			Nil	~2.7			Nil			~27		~0.9										~6		Nil	

(1) RESULTING Cm SOLUTION FROM 221-H PROCESSING OF 48 Pu TARGET ASSEMBLIES
5800 Liters
5.8 kg Cm-244
2.67 kg Am-243
11.6 kg R.E.
41.0 kw

MAJOR F. P.	CANYON DF	CURIES TO CAVE	KW
$Ce\text{-}Pr^{144}$	1	1.6×10^{6}	5.6
$Zr\text{-}Nb^{95}$	20	3.0×10	Nil
$Ru\text{-}Rh^{106}$	3	7.2×10^{5}	3.7

(2) FLOWSHEET BASED ON PROCESSING 36 GR Cm/DAY, 24 HR/DAY (215 PROCESSING DAYS) 75% EFFICIENCY
--- RECYCLE OR NON-ROUTINE OPERATION
○ STREAM NUMBER
☐ FLOW RATIO BASED ON 1AF & 2AF FOR 1ST & 2ND CYCLE RESPECTIVELY

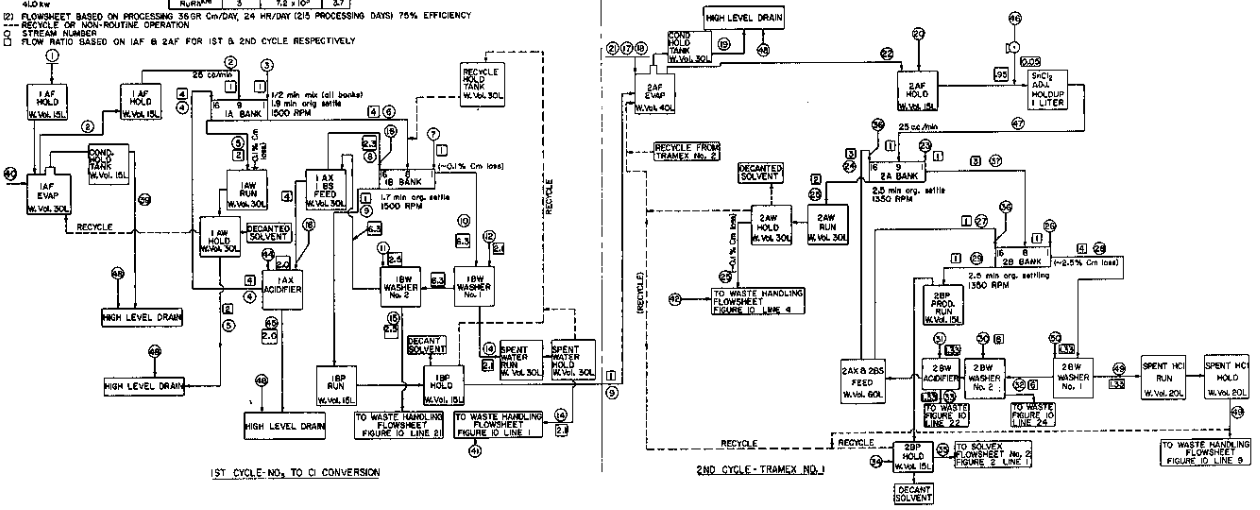

FIG. 1 CURIUM MATERIAL BALANCE FLOWSHEET - 1ST AND 2ND CYCLES OF SOLVENT EXTRACTION

LINE NO.	1[1]	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
	2BP	$NaNO_3$ & NaOH	LiCl	LiOH	EVAP. OVER-HEAD	HCl GAS	3AF ACIDIFIER ACID	3AF	$SnCl_2$ REDUCTANT	3AF ADJ FEED	3AS	3AX	3AP	3AW	3BX	3BS	3BP	3BW		WATER WASH	SPENT WATER WASH	CAUSTIC WASH	SPENT CAUSTIC WASH	SOLVENT ACIDIFIER ACID	SPENT ACID	SOLVENT MAKE-UP	3RD CYCLE SPILLS, ETC.
LITERS/DAY	36		3.19	1.67	10.36		2.34	33.34	1.76	35.1	35.1	105.3	105.3	70.2	35.1	35.1	35.1	140.4		46.8	46.8	210.6	210.6	46.8	46.8		
SP. GR.																											
Cm	0.98							1.05		1.0			0.33				1.0										
Am	0.46							0.49		0.47			0.16				0.47										
RE	TRACE													TRACE													
Cf																											
LiCl	~9.0		13.0					11.2	10.0	11.14	10.9			11.02			≤0.15										
LiOH				4.5																							
HCl	0.25	ADD AS REQUIRED TO INSURE $pH \geq 9$ AND $(NO_3^-/Cl^-) \geq 10$			0.12	AS REQUIRED	4.0	0.35	0.55	0.65		0.61 M "ADOGEN" 344-HCl IN DEB 0.01 - 0.05 M HCl EXCESS 0.026 NOMINAL	0.03 0.6 M "ADOGEN" 344-HCl IN DEB 0.15 M HCl EXCESS	0.02	8.0	0.61 M "ADOGEN" 344 IN DEB .025 M HCl EXCESS	6.5	0.025 0.6 M "ADOGEN" 364-HCl IN DEB ~ 0.4 M HCl EXCESS			1.2			4.4	2.5	0.61 M "ADOGEN" 364 - HCl IN DEB .025 M HCl EXCESS	AS REQUIRED
$SnCl_2$									2.0	0.1																	
NaCl																							0.45				
NaOH																						1.27	0.80				
$Na_2Sn(OH)_4$																							0.017				
Cm α, d/min-ml	1.8×10^8				2×10^7			1.9×10^8		1.8×10^8			6×10^{10}	9×10^7			1.8×10^{11}	4.5×10^7			1.4×10^8						
$Ru\text{-}Rh^{106}$, c/l	1.8×10^{-3}				2.0×10^{-7}			2.0×10^{-3}		1.9×10^{-3}			6.1×10^{-4}				4.1×10^{-8}	4.6×10^{-4}					3×10^{-4}				
$Ce\text{-}Pr^{144}$, c/l	0.16				1.8×10^{-5}			0.17		0.16			8.6×10^{-7}	0.08			2.5×10^{-8}										
HEAT CONTENT, WATTS/LITER	~2.7							~2.9		~2.8			~0.98	Nil			~2.8	nil									

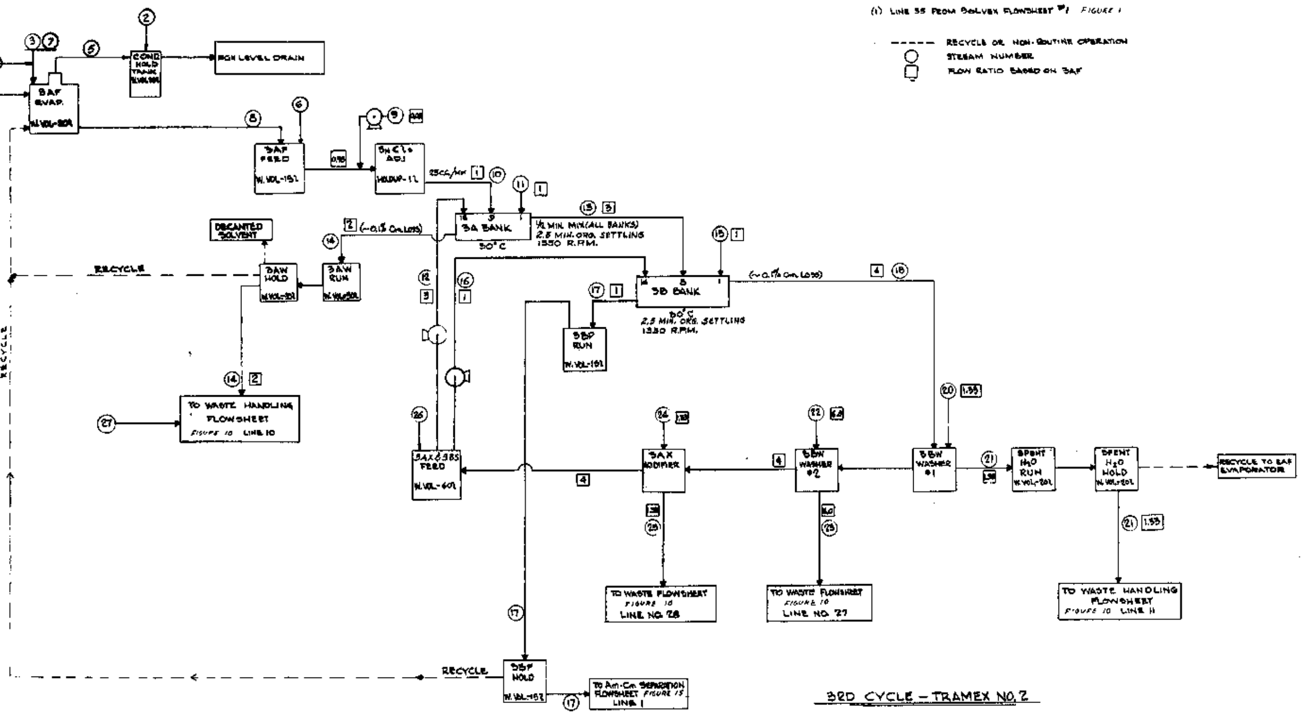

FIG. 2 CURIUM MATERIAL BALANCE FLOWSHEET - 3RD CYCLE OF SOLVENT EXTRACTION

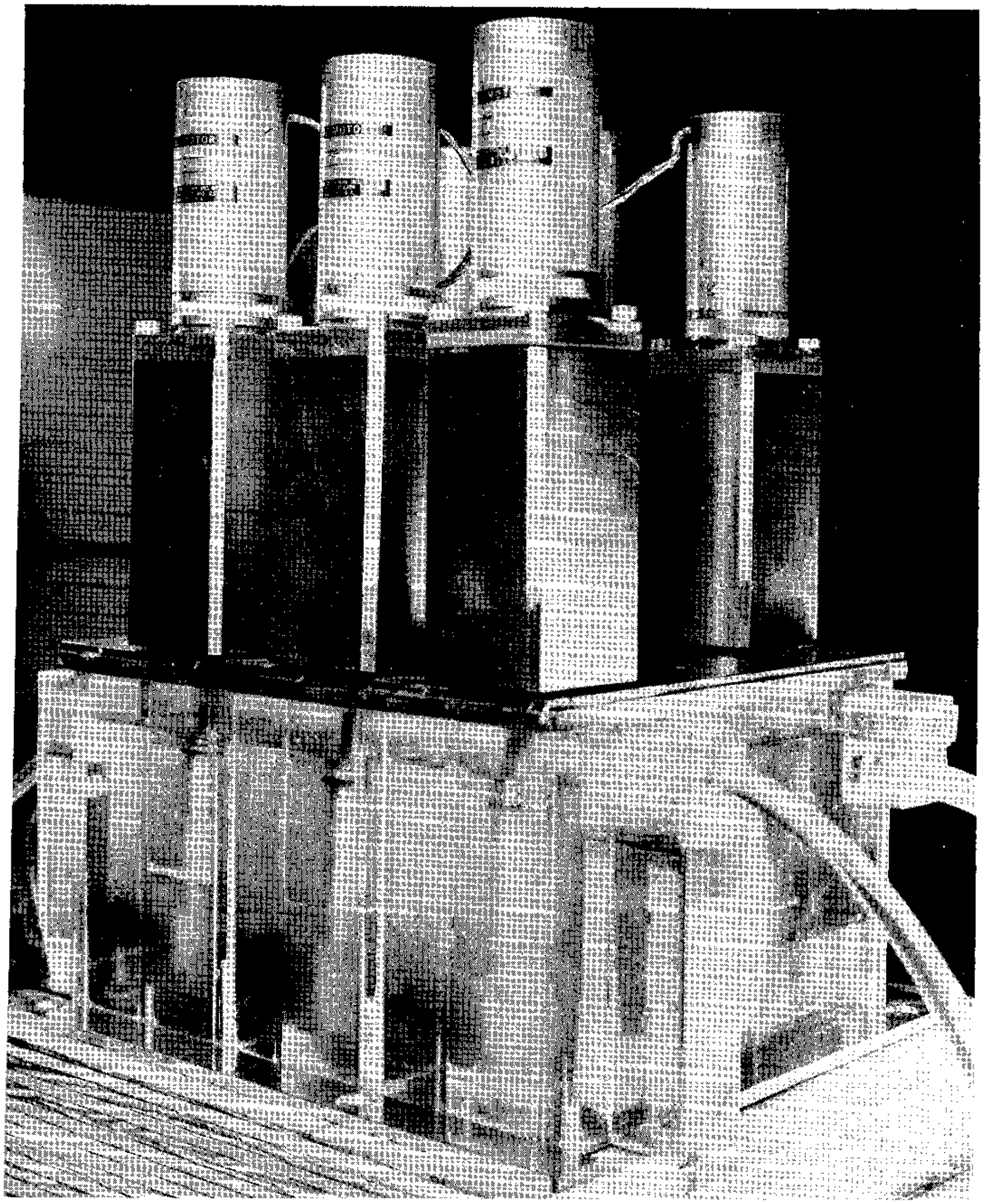

FIG. 3 PROTOTYPE MIXER-SETTLER FOR CURIUM PROCESS

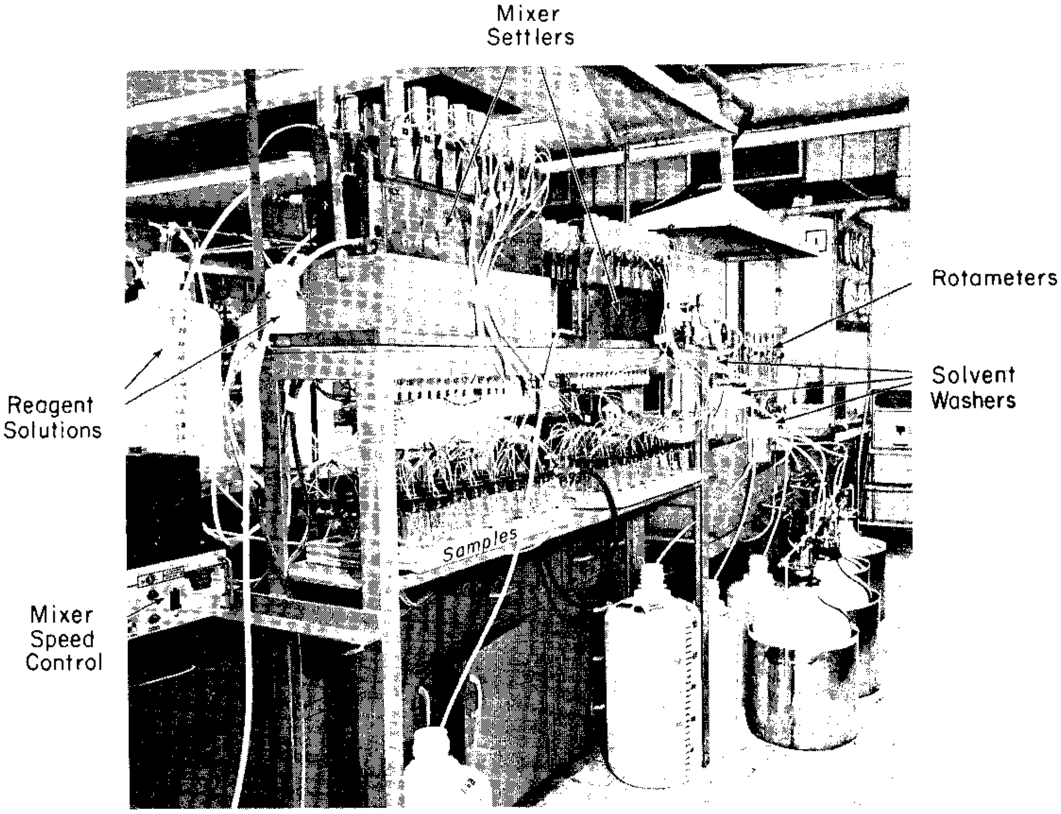

FIG. 4 EQUIPMENT FOR CURIUM SOLVENT EXTRACTION

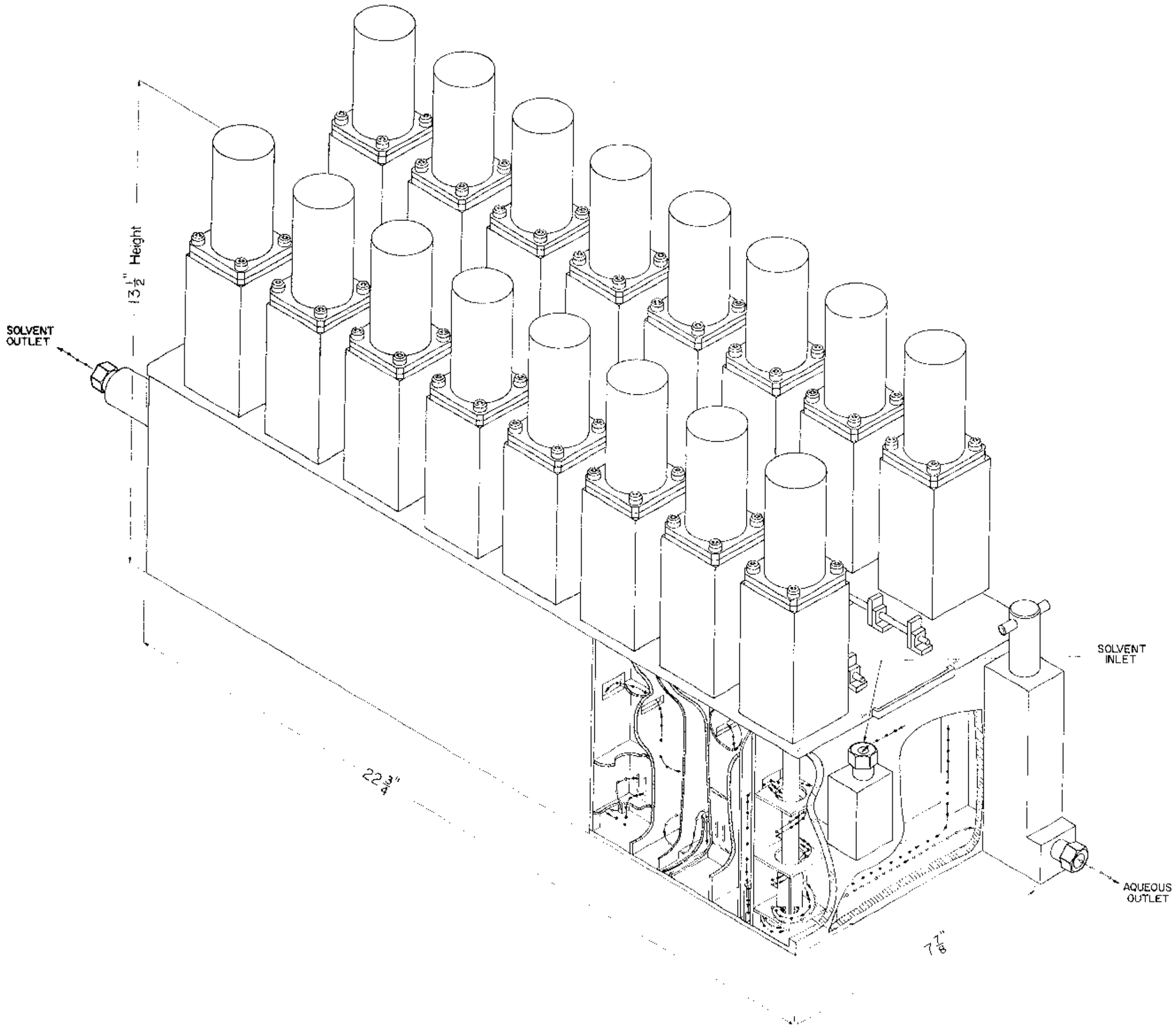

FIG. 5 DETAILS OF MIXER-SETTLER FOR CURIUM PROCESS

inlet section from which it is pumped into the mixing section by the four-bladed paddle. The solvent flows from the preceding settling section through a duct into the solvent inlet section, partly through a circular hole directly into the mixing section at the top of the paddle, and partly through a duct into the interface weir section where the solvent meets the incoming aqueous stream as it enters the mixing section. The two phases are mixed by the paddle and flow out through louvers into the settling section.

The mixer-settlers have remotely adjustable blocks in the solvent settling sections to control the residence time (holdup volume) of the solvent by stepwise raising or lowering of the blocks. The blocks in the plastic prototype mixer-settler, however, were installed permanently to give the minimum residence time for each bank.

The stages are numbered 1 through 16, starting at the aqueous inlet. The solvent leaves the bank over a weir in Stage 1. The aqueous solution leaves over a mechanical weir attached to Stage 16 which controls the aqueous level in Stage 16.

The paddles are driven by individual DC motors; the speed of the motors, as a bank, is controlled by a variable voltage power supply.

SOLVENT WASHERS

Process

Each of the three solvent extraction steps in the curium process requires a solvent washing system consisting of three solvent washers to permit reuse of the solvent as shown in Figures 1 and 2. After the nitrate-to-chloride conversion cycle, the spent solvent is washed with (1) water to recover any residual curium, (2) 2.5M K_2CO_3 to remove fission products such as zirconium and ruthenium, and (3) 1.8M HNO_3 to reconvert the mixture of n-octyl and n-decyl tertiary amines in diethylbenzene to nitrates for reuse.

After the first Tramex cycle to separate the americium and curium from californium and some of the rare earths and fission products, the spent solvent solution of tertiary amine hydrochlorides in diethylbenzene is washed with (1) 0.8M HCl to separate ^{252}Cf and recover any residual curium, (2) 1.27M NaOH to remove both residual tin [Sn(II) is added to the solvent extraction feed to reduce Ce(IV), Cl_2, and HOCl] and fission products (Ru, Nb, Zr), and (3) 4.4M HCl to reconvert the amines to hydrochlorides for reuse.

After the second Tramex cycle to separate the americium and curium from additional rare earths and fission products, the spent solvent solution of tertiary amine hydrochloride in diethylbenzene is washed with (1) water to recover any residual curium, (2) 1.27M NaOH to remove both residual tin and fission products, and (3) 4.4M HCl to reconvert the amines to hydrochlorides for reuse.

Development Steps

Initial tests were made with the prototype solvent washers installed at the semiworks in-line with the two full-scale tantalum mixer-settlers as shown in Figure 4. The equipment was tested simulating the three solvent extraction and washing cycles. Eventually the operability of the Tramex solvent washers was confirmed by full-scale tests using the actual process solvent washers.

Equipment

The prototype solvent washers (Figure 6) are made principally of "Teflon"* and glass. The washers for the curium process (Figure 7) were made of tantalum or Zircaloy-2 (1st and 2nd washers Zircaloy-2, 3rd washer tantalum), since "Teflon" gradually decomposes on exposure to radiation and releases corrosive fluoride.

The solvent washers are similar in design (except smaller) to the newest continuous solvent washers in one of the SRP Separations Areas. The spent solvent and the wash solution are fed to the bottom of the axial mixing compartment, which provides a residence time of about 2 to 3 minutes at the normal flows. The mixed dispersion flows over the circular weir at the top of the mixing chamber, down through an annular duct, and into the annular settling section at approximately midheight. Originally each washer had a 3.3-liter settling section; however, the settling volume of the second process washer of each of the Tramex cycles was increased by ~4.3 liters by extending the length of the settling chamber by 9 inches to provide additional residence time for the aqueous and solvent phases. The volume ratio of the separated organic and aqueous phases is controlled by adjusting the height of the aqueous overflow weir. The residence time of the organic phase is adjusted to about 20 minutes.

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* Du Pont's trademark for its fluorocarbon plastic.

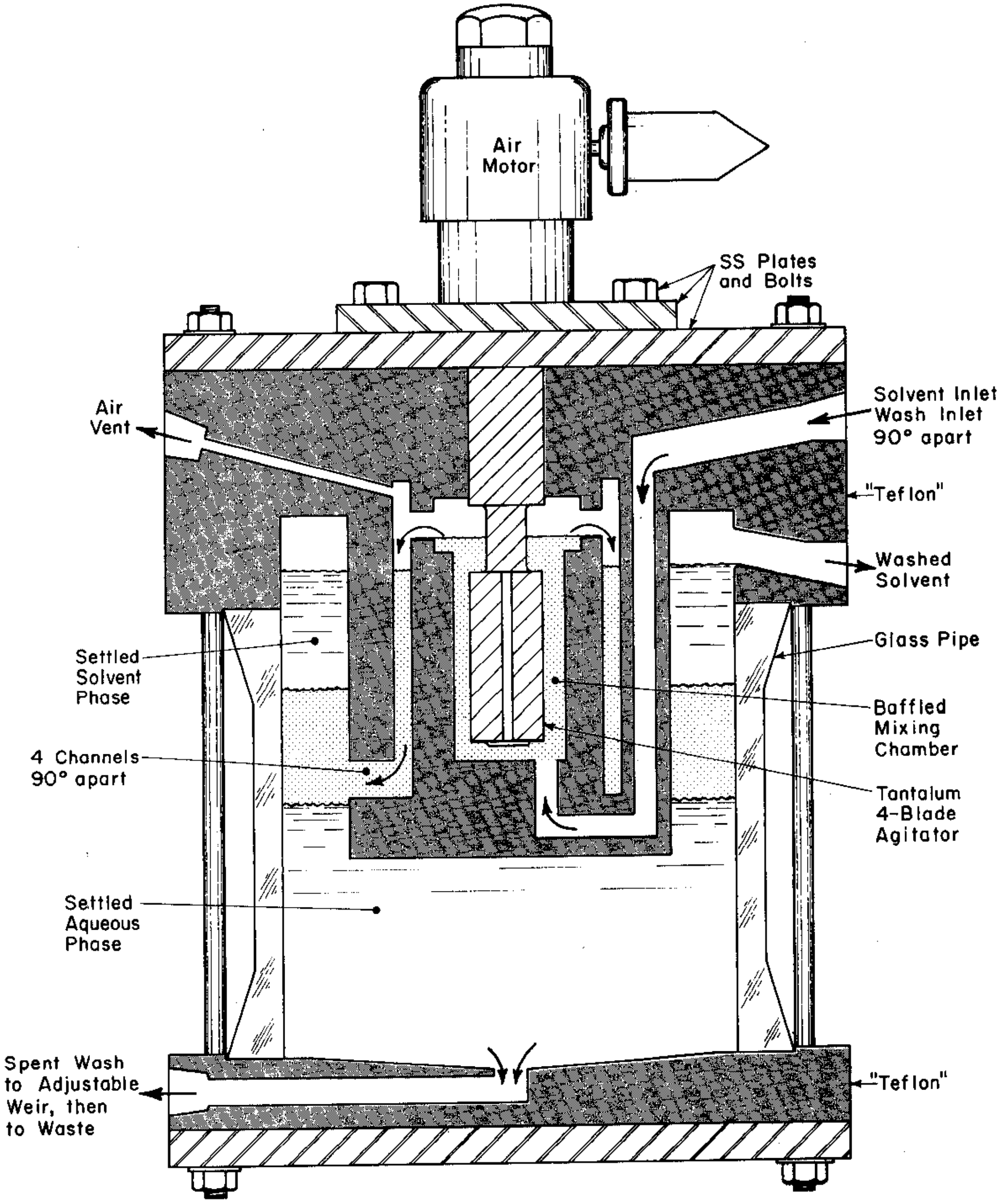


FIG. 6 PROTOTYPE SOLVENT WASHER FOR CURIUM PROCESS

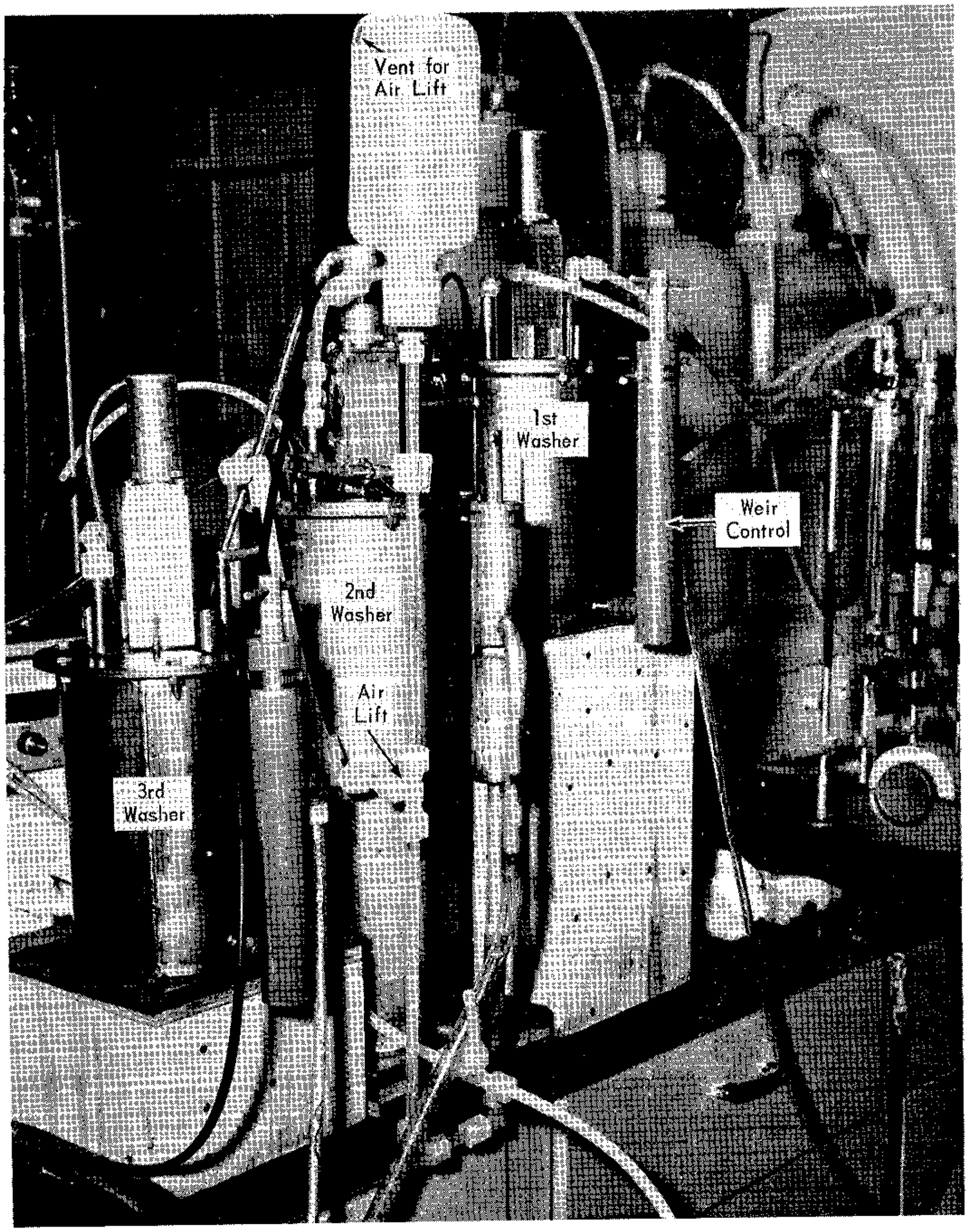


FIG. 7 SOLVENT WASHERS FOR TRAMEX CYCLES

An air lift was installed on each of the 2nd washers of the Tramex cycles (Figures 7 and 8) to recirculate the wash solution and so reduce the volume of wash required for an aqueous/organic ratio of at least 1.5 in the mixing section of the washer (this produces an aqueous-continuous emulsion for best hydraulic operation).

The mixing of the prototype washer is driven by an air motor; the curium process washer, by a DC motor. The speed of the motor is controlled by varying the air pressure or the voltage.

PRECIPITATORS AND FILTERS

Process

After separation from californium and most of the fission products by solvent extraction, the americium and curium are separated from each other and purified by precipitations and filtrations as shown in Figures 9 and 10 and described below:

- Americium and curium from the (chloride) solvent extraction cycles are precipitated with NH_4OH and filtered to remove the chloride and additional fission products.

- The mixed precipitate is dissolved with HNO_3; and the americium is separated from curium by oxidation from Am(III) to Am(V) in 3.5M K_2CO_3 (with an ozone sparge) and precipitation of $K_3AmO_2(CO_3)_2$, which is filtered from the soluble Cm(III) complex.

- $K_3AmO_2(CO_3)_2$ is dissolved with HNO_3; if necessary, it is reprecipitated with K_2CO_3 and refiltered to obtain additional separation from curium.

- The curium is precipitated from the acidified filtrate with NaOH and filtered to remove residual fission products. $Cm(OH)_3$ is then dissolved with HNO_3.

For all hydroxide precipitations, equimolar lanthanum was used as a stand-in for americium and curium. For the carbonate precipitation tests, equimolar uranium was used as a stand-in for the americium. Ozone sparging was simulated by using a mixture of ammonia and nitrogen that precipitated the uranium as ammonium uranyl carbonate in the 3.5M K_2CO_3 solution; lanthanum (curium stand-in) remained in solution. After the uranium was filtered, the lanthanum was reprecipitated as hydroxide to simulate the final precipitation of the curium.

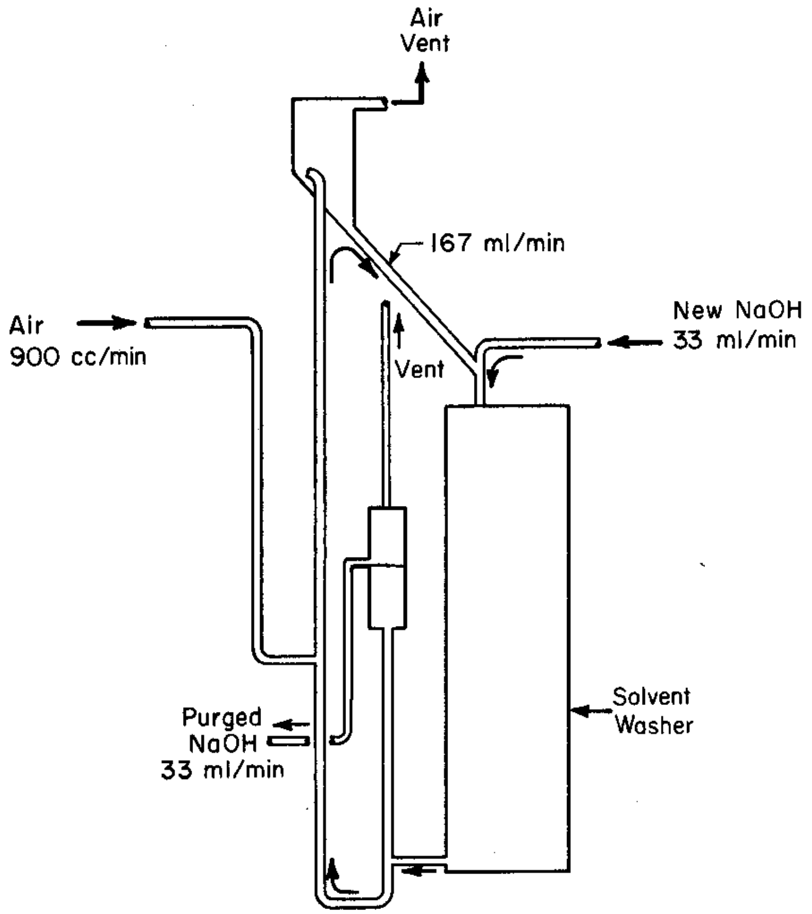


FIG. 8 AIR LIFT CIRCULATION OF NaOH

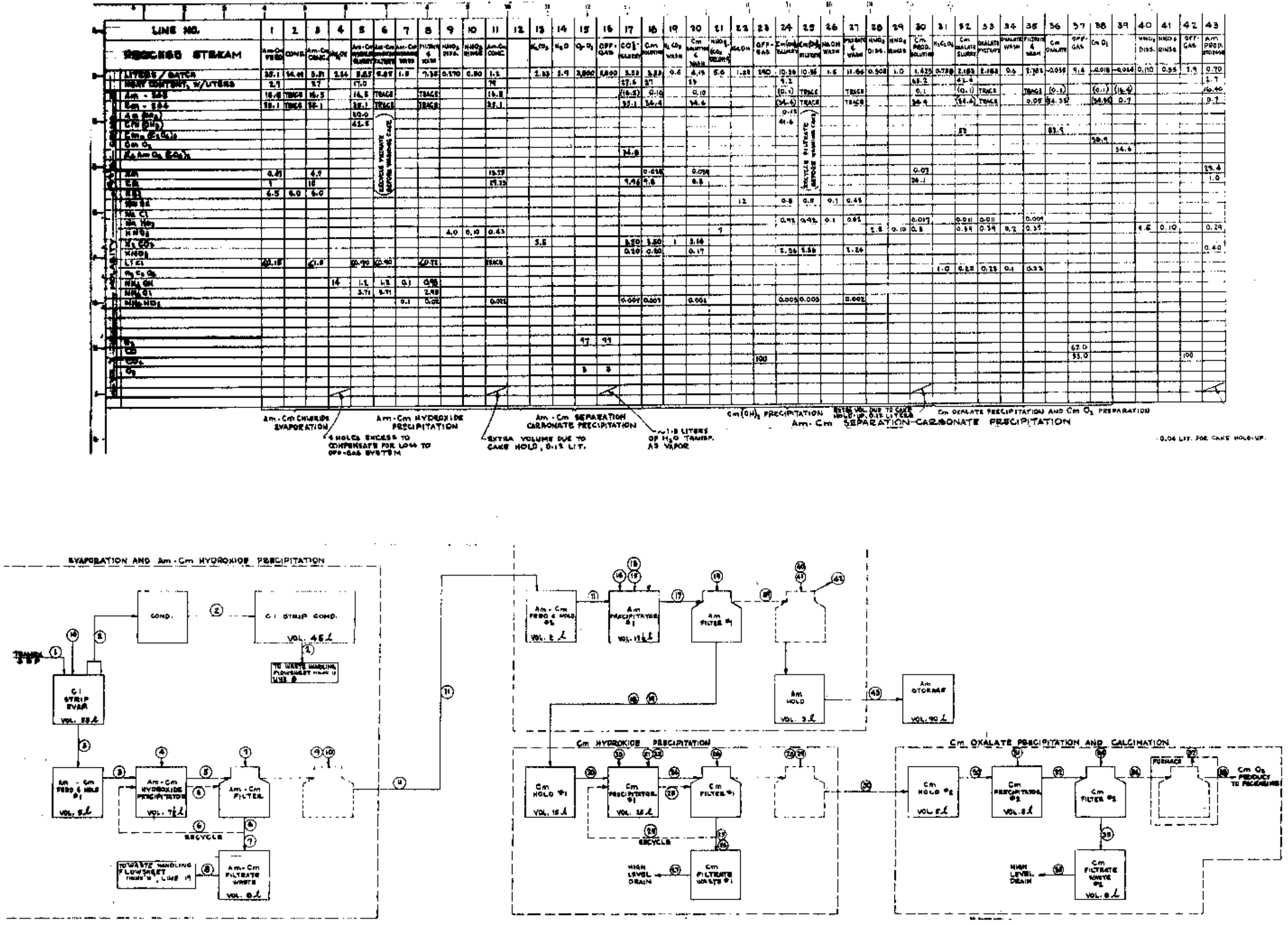
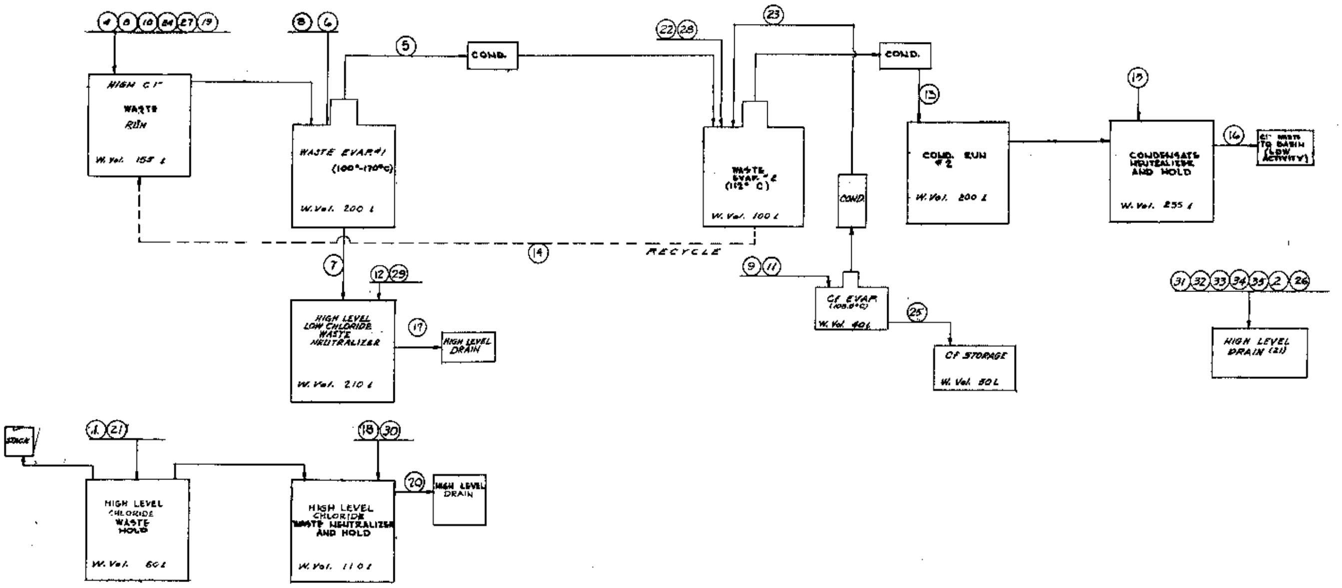


FIG. 9 CURIUM MATERIAL BALANCE FLOWSHEET - AMERICIUM AND CURIUM SEPARATION AND OXIDE PREPARATION WITHOUT CO_3 RECYCLE

LINE NO.	1$^{(1)}$	2$^{(2)}$	3	4$^{(4)}$	5	6	7	8$^{(3)}$	9$^{(9)}$	10$^{(13)}$	11$^{(14)}$	12
PROCESS STREAM	1BW Spent Water Wash	2AF Evap. Cond.	H_2SO_4	2AW	Evap. Over-Heads	Dil. H_2O	Evap. Bottoms	Cl. Strip Evap. Cond.	2 BW Spent HCl Wash	3 AW	3 BW Spent H_2O Wash	NaOH
Liters/Day	74.6	66.8	117.9	72	572.0	261.2	424.4	34.5	48	72	48	122.6
Cm α, d/min-ml	9x10^{7}	2.1x10^{7}		9x10^{7}	0.7x10^{4}		4.6x10^{7}	1.8x10^{7}	1.8x10^{8}	9x10^{7}	1.4x10^{8}	
A.E., g/l				1.2			0.20			TRACE		
Cm, g/l												
Cf, g/l							4.6x10^{-7}		3.25x10^{-6}		None Expected	
Heat Content, Watt/Liter				1.25			0.21			Nil		
NaOH												19
LiCl				11.0					0.27	11.0		
NaCl												
H_2SO_4			18.0				2.42					
Na_2SO_4							0.71					
HCl	1.5	0.07		0.02	3.63		<0.01	6.0	0.83	0.02	1.4	
Li_2SO_4							1.87					
$NaNO_3$												
$Al(NO_3)_3$												
HNO_3												
$LiNO_3$												
$NaAlO_2$												
$KHCO_3$												
$H_2C_2O_4$												
KNO_3												
KCl												
Chloride	1.5			11.02	3.63		<.01	6.0	0.83	11.02	1.4	
K_2CO_3												
NH_4OH												
$NaHSn(OH)_6$							0.017					
Na_2CO_3												
NH_4Cl												
NH_4NO_3												
Ce-Pr 144, c/l	0.08	0.02		85			31			0.14		
Zr-Nb 95, c/l	5x10^{-3}	1.1x10^{-9}		7.6x10^{-6}			8.6x10^{-5}		2x10^{-7}			
Ru-Rh 106, c/l		1.8x10^{-5}		0.04			0.05					

LINE NO.	13	14	15	16	17	18	19$^{(5)}$	20	21$^{(15)}$	22$^{(6)}$	23	24$^{(8)}$
PROCESS STREAM	2nd Stage Evap. Over-Heads	2nd Stage Evap. Bottoms	NaOH 50 Wt %	Cl- Waste (Low Activity)	High Level Waste (Low Cl)	NaOH 50 Wt %	Am-Cm PPTR Filtrate	High Level Chloride Waste	1 BW Spent K_2CO_3 Wash	2AX&2BS Spent Acid	Cf Evap. Cond.	2 BW Spent Caustic Wash
Liters/Day	763.2		138	901.2	551.2	15.3	7.35	359.0	90	48	95	216
Cm α, d/min-ml	2.1			1.28	3.6x10^{7}		TRACE	3.7x10^{7}			~1.4x10^{5}	
A.E., g/l					0.16							
Cm, g/l								19.3				
Cf, g/l					3.6x10^{-7}						~1.8x10^{-8}	
Heat Content, Watt/Liter					0.16			0.30	0.72			
NaOH			19	0.25	0.50	19		0.25				0.76
LiCl							≤0.72					
NaCl				2.66	9x10^{-3}		3.12					0.48
H_2SO_4												
Na_2SO_4					2.41							
HCl	3.14									2.6	1.06	
Li_2SO_4					1.44							
$NaNO_3$							0.02	1.45				
$Al(NO_3)_3$												
HNO_3												
$LiNO_3$												
$NaAlO_2$												
$KHCO_3$									1.60			
$H_2C_2O_4$												
KNO_3								0.32	1.25			
KCl								0.38	0.25			
Chloride	3.14			2.66			3.84		0.25	2.6		0.49
K_2CO_3								0.28	1.0			
NH_4OH							0.98					
$NaHSn(OH)_6$					0.013							0.017
Na_2CO_3								0.28				
NH_4Cl							2.95					
NH_4NO_3							0.02					
Ce-Pr 144, c/l					24							
Zr-Nb 95, c/l					5.6x10^{-5}			0.29	1.8x10^{-3}			1.8x10^{-5}
Ru-Rh 106, c/l					0.04			89	30			0.02

LINE NO.	25	26$^{(10)}$	27$^{(11)}$	28$^{(12)}$	29	30	31$^{(17)}$	32$^{(18)}$	33$^{(16)}$	34$^{(19)}$	35$^{(20)}$
PROCESS STREAM	Cf Evap. Bottoms	3 AF Evap. Cond.	3 BW Spent Caustic Wash	3 AX Spent Acid	$NaNO_3$	$NaNO_3$	2HPF	OPF	1AF Evap. Cond.	1AW	1SW3-AW
Liters/Day	0.96	10.36	216	48	6.0	178.1	16.4	2.79		72	72
Cm α, d/min-ml	1.4x10^{10}	2x10^{7}					TRACE	≤2x10^{9}	2x10^{7}	9x10^{7}	
A.E., g/l							.006	TRACE			
Cm, g/l											
Cf, g/l	1.9x10^{-4}										
Heat Content, Watt/Liter											
NaOH			0.80				0.46				
LiCl											
NaCl			0.45				TRACE				
H_2SO_4											
Na_2SO_4											
HCl	6.08	0.17		2.5							
Li_2SO_4											
$NaNO_3$					2.0	2.0	0.82				
$Al(NO_3)_3$										1.0	
HNO_3								0.35	TRACE	~0.01	0.5
$LiNO_3$										4.0	
$NaAlO_2$											
$KHCO_3$											
$H_2C_2O_4$								0.22			
KNO_3							2.34				
KCl											
Chloride			0.45	2.5							
K_2CO_3											
NH_4OH											
$NaHSn(OH)_6$			0.017								
Na_2CO_3											
NH_4Cl											
NH_4NO_3											
Ce-Pr 144, c/l		1.8x10^{-5}								0.09	
Zr-Nb 95, c/l										0.07	
Ru-Rh 106, c/l		2.6x10^{-7}	3x10^{-4}							4.1	



GENERAL NOTES:

1. Line 14, Solvex Flowsheet #1, Fig. 1
2. Line 19, Solvex Flowsheet #1, Fig. 1
3. Line 2, Am & Cm Separation Flowsheet, Fig. 15
4. Line 25, Solvex Flowsheet #1, Fig. 1
5. Line 8, Am & Cm Separation Flowsheet, Fig. 15
6. Line 33, Solvex Flowsheet #1, Fig. 1
7.
8. Line 32, Solvex Flowsheet #1, Fig. 1
9. Line 49, Solvex Flowsheet #1, Fig. 1
10. Line 5, Solvex Flowsheet #2, Fig. 2
11. Line 23, Solvex Flowsheet #2, Fig. 2
12. Line 25, Solvex Flowsheet #2, Fig. 2
13. Line 14, Solvex Flowsheet #2, Fig. 2
14. Line 21, Solvex Flowsheet #2, Fig. 2
15. Line 15, Solvex Flowsheet #1, Fig. 1
16. Line 39, Solvex Flowsheet #1, Fig. 1
17. Line 27, Am & Cm Separation Flowsheet, Fig. 15
18. Line 35, Am & Cm Separation Flowsheet, Fig. 15
19. Line 5, Solvex Flowsheet #1, Fig. 1
20. Line 45, Solvex Flowsheet #1, Fig. 1
21. Each of these streams must be adjusted with NaOH and $NaNO_3$ to insure pH >13 and $(NO_3^-)/(Cl^-) > 10$ before being sent to the high level drain. Compositions are shown prior to adjustment.

FIG. 10 CURIUM MATERIAL BALANCE FLOWSHEET - WASTE HANDLING AND CALIFORNIUM EVAPORATION

Equipment

Full-scale tests were made of the precipitations and filtrations at the semiworks using the Zircaloy precipitator and filter units to be used in the Curium Processing Facility (Figures 11 through 14). Precipitators and filters were designed from the following information, which was developed using polyethylene bottles as precipitators and standard Corning filters with glass frits:

- Sloped bottoms of precipitators were necessary to avoid holdup of precipitate.
- Coolant to remove at least 2400 Btu/hr was needed in the first hydroxide precipitator.
- A spray system was required for washing the sides and bottom of the precipitators.
- During the Am-Cm hydroxide precipitation, the precipitate must be formed by adding the Am-Cm solution to the hydroxide in a region of high turbulence while the temperature of the solution is maintained below 35°C. (Adding the hydroxide to the Am-Cm stream forms a precipitate that is very difficult to filter.)
- Freeboard $\geqslant 20\%$ was needed in precipitators for foam resulting from the chemical reactions.
- A vent to remove 33 ft^3 of CO_2 and CO in 20 minutes from the second hydroxide precipitator was required.
- Provisions for decanting 50 to 90% of the supernatant solution in the second hydroxide precipitator were desirable to decrease filtration time.
- Filters must be of special design with a paddle rotating at several hundred rpm directly over the filter frit (increases the filtration rate 2- to 3-fold) and a housing around the paddle-frit area to prevent the stirred cake from being pushed up the walls and thereby to facilitate washing and dissolving of the cake.
- Cooling coils to the filters were needed to remove 335 Btu/hr of decay heat from the 36 g of curium while the precipitate is being washed and dissolved.

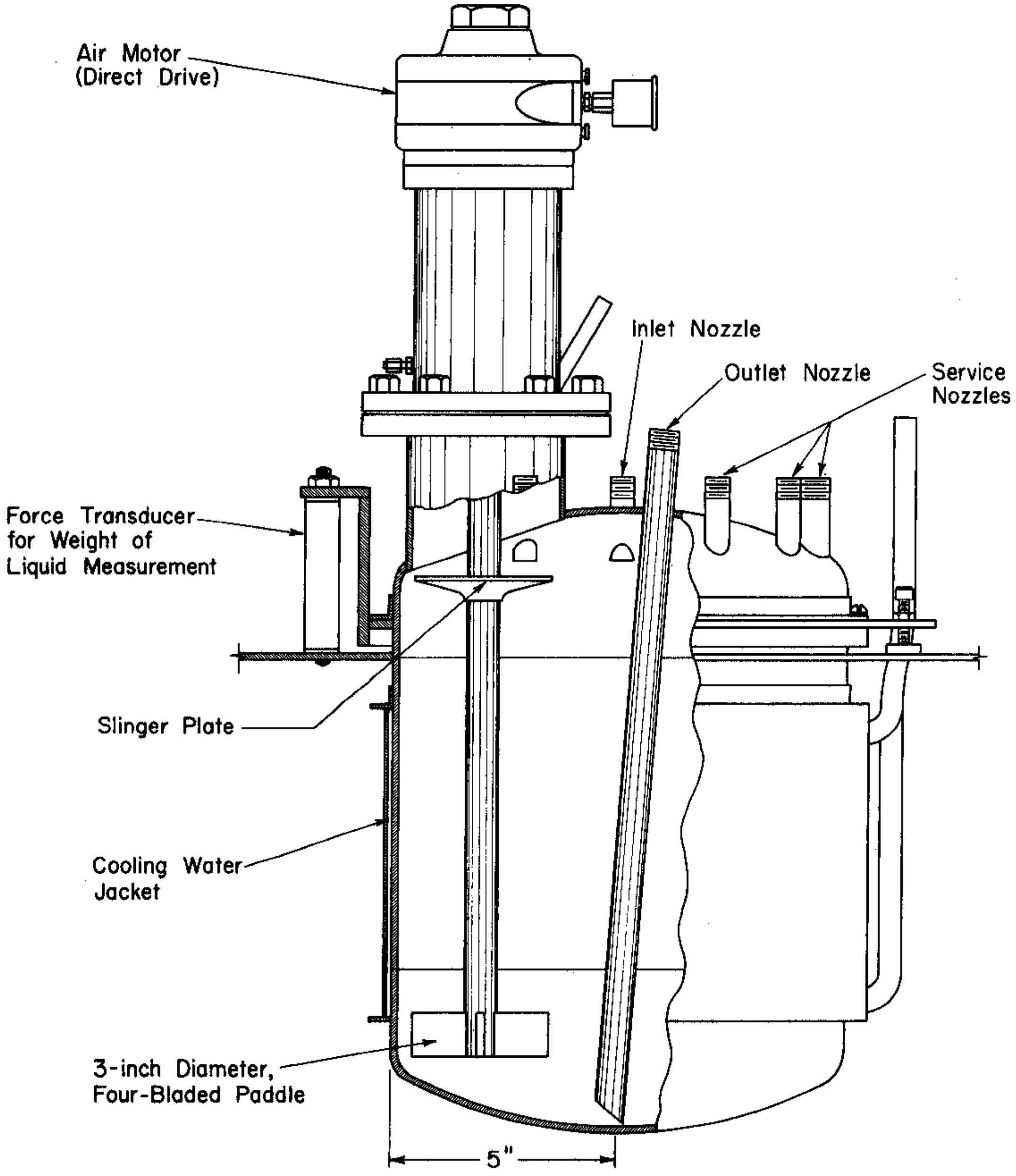


FIG. 11 AMERICIUM-CURIUM HYDROXIDE AND CURIUM 1 PRECIPITATORS

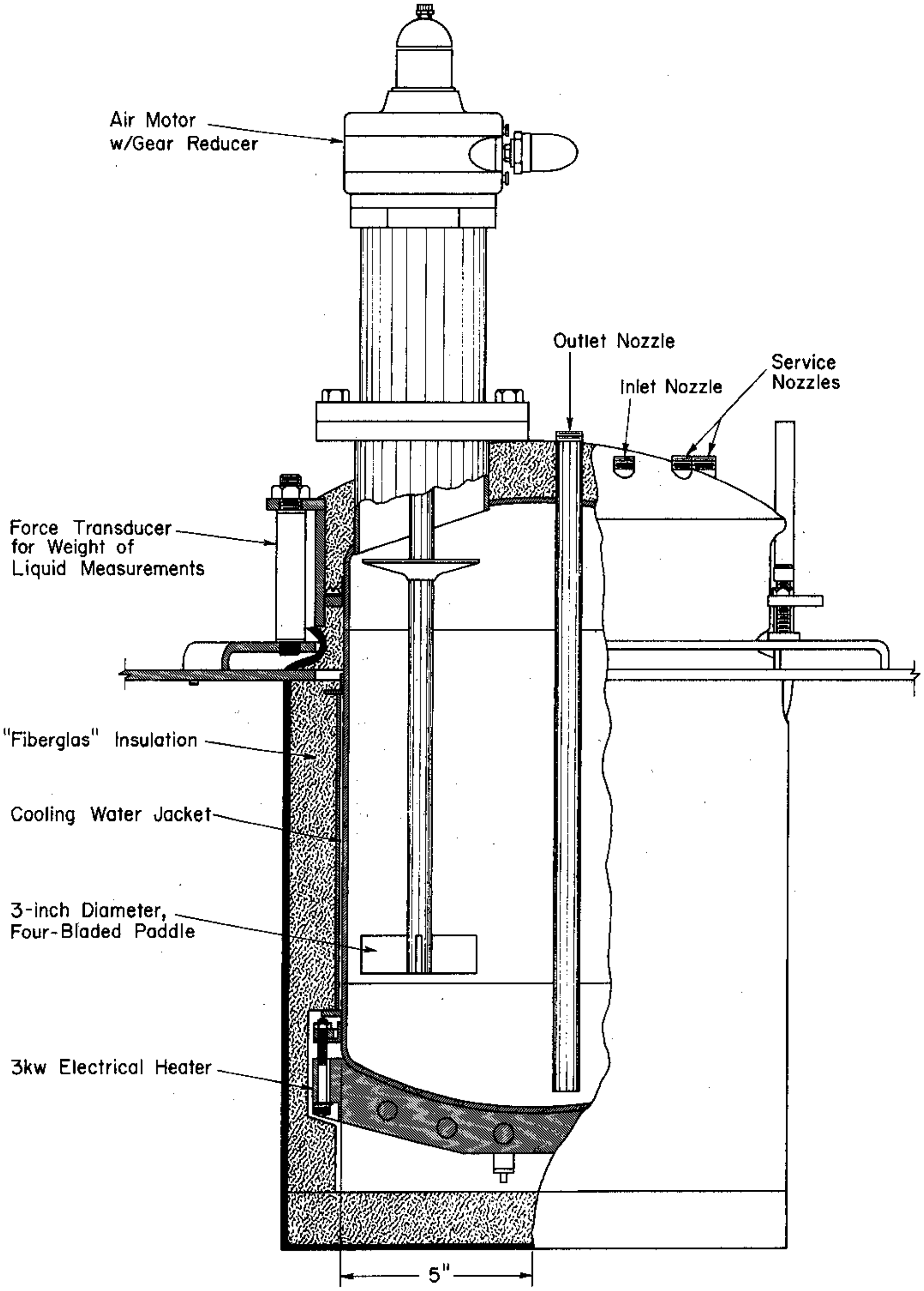


FIG. 12 AMERICIUM 1 PRECIPITATOR

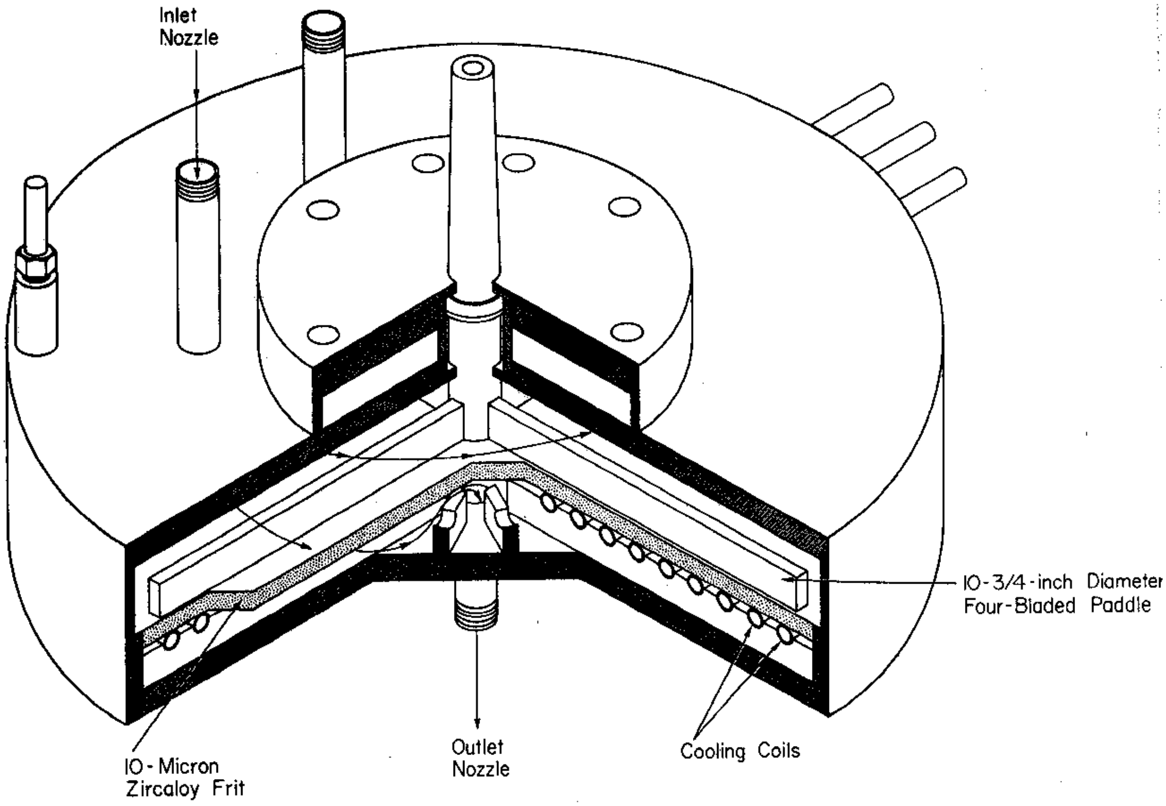


FIG. 13 AMERICIUM-CURIUM HYDROXIDE AND CURIUM 1 FILTERS

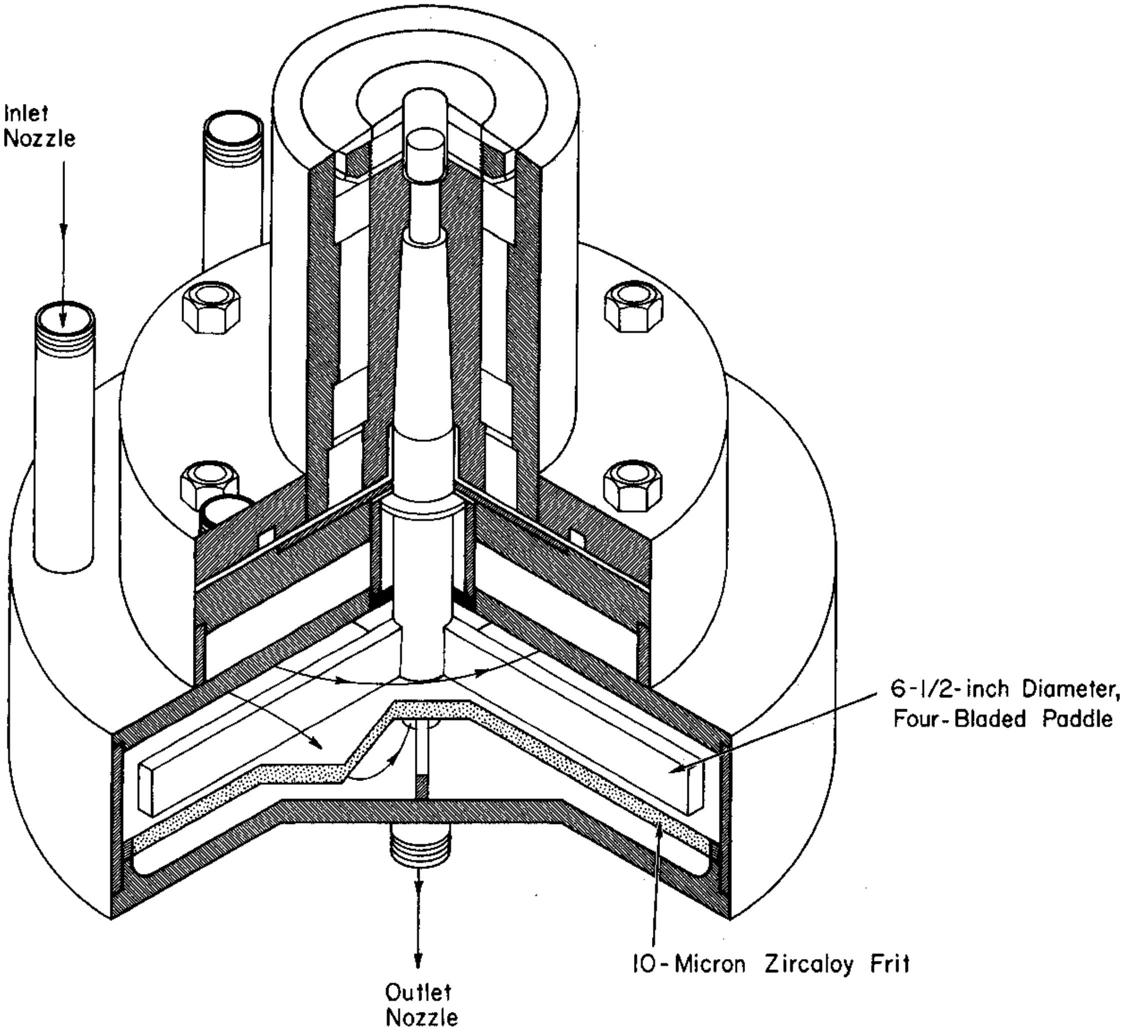


FIG. 14 AMERICIUM 1 FILTER

Full-scale Zircaloy paddles rotate at 500, 333, and 700 rpm for the americium-curium hydroxide, americium 1, and curium 1 precipitators, respectively (driven by air motors). A slinger plate on the agitator shafts distributes wash water around the wall near the top of the precipitators. A paddle rotating at 300 rpm above the Zircaloy filter frits aids filtration and dissolution of the precipitates.

PREPARATION OF OXALATES AND CALCINATION

Process

The preparation of curium oxide and americium oxide in the curium process requires precipitation of each oxalate followed by filtration, washing, and calcination in a furnace with air flow, as shown in Figure 15.

Equipment

The oxalate precipitator, which is similar to the americium-curium hydroxide and curium 1 precipitators (Figure 11), is an 8-liter stainless steel vessel with a 333-rpm agitator (driven by an air motor), cooling jacket, gas purge, liquid level bubbler, off-gas exhaust, thermocouple, and sparge. A slinger plate on the agitator shaft distributes wash water around the wall near the top of the vessel.

The filter, shown in Figure 16, has an outer stainless steel housing and lid, a removable platinum-lined filter, and a platinum frit. The housing is sealed to the filter with "Viton"* O-rings.

The calciner, shown in Figure 17, has twenty 130-watt heaters around the central cavity that holds the platinum filter boat and is insulated with two layers of 1/2-inch-thick "Fiberfrax"** and one layer of 1-inch-thick "Fiberglas"*** pipe insulation. An air-cooled jacket between the heaters and the insulation shortens the cooling period. A thermocouple in a platinum-sheathed thermowell monitors and controls the temperature of the process material during the calcination.

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* Du Pont's trademark for fluoroelastomer.

** Trademark of the Carborundum Company.

*** Trademark of Owens-Corning Fiberglas Corporation.

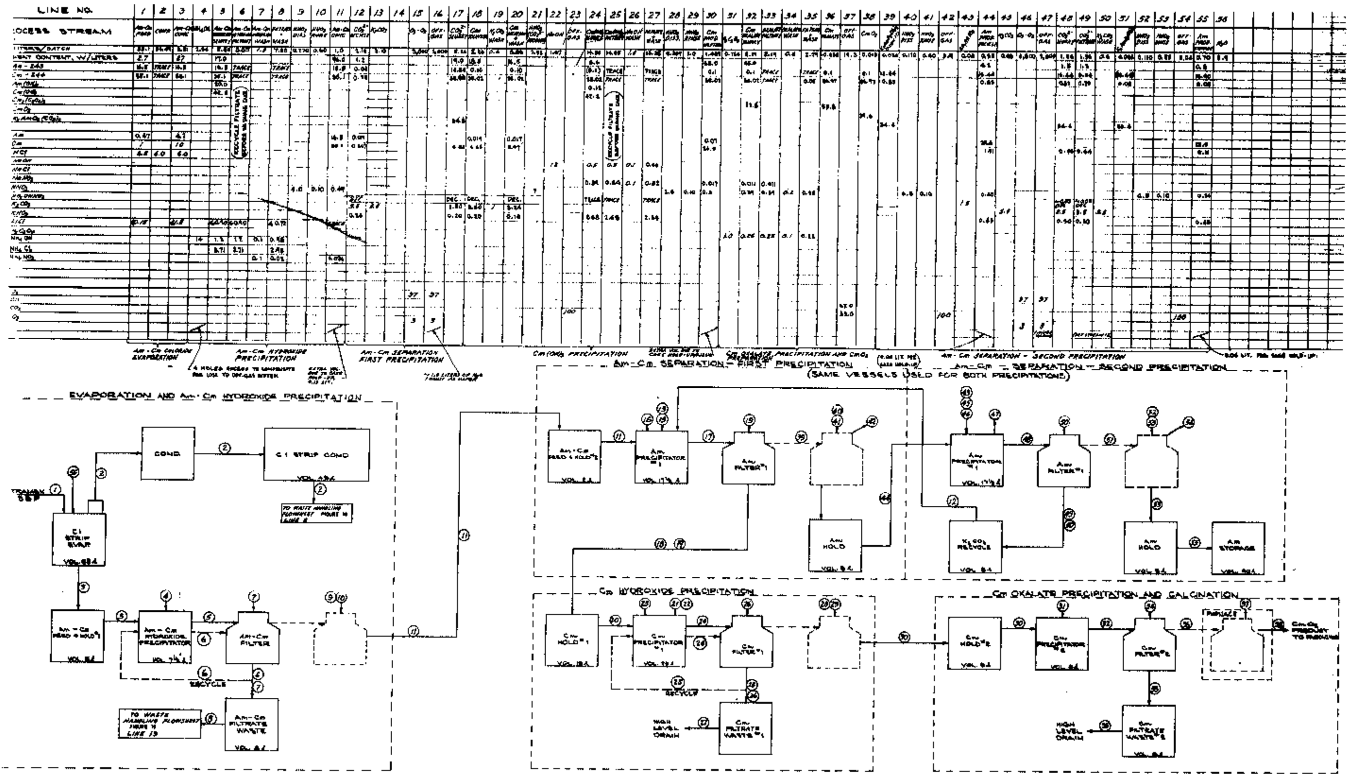


FIG. 15 CURIUM MATERIAL BALANCE FLOWSHEET - AMERICIUM AND CURIUM SEPARATION AND OXIDE PREPARATION

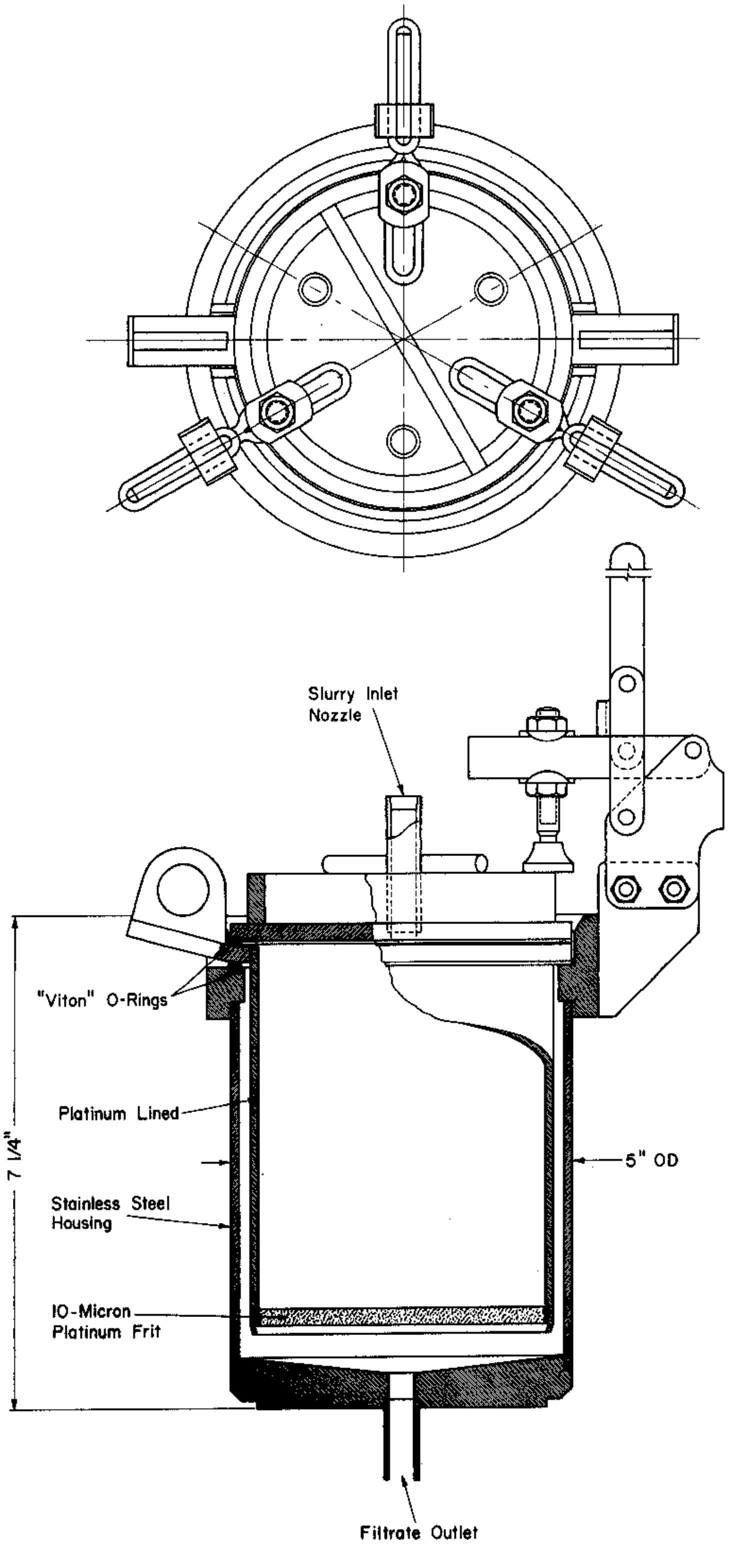


FIG. 16 CURIUM 2 FILTER

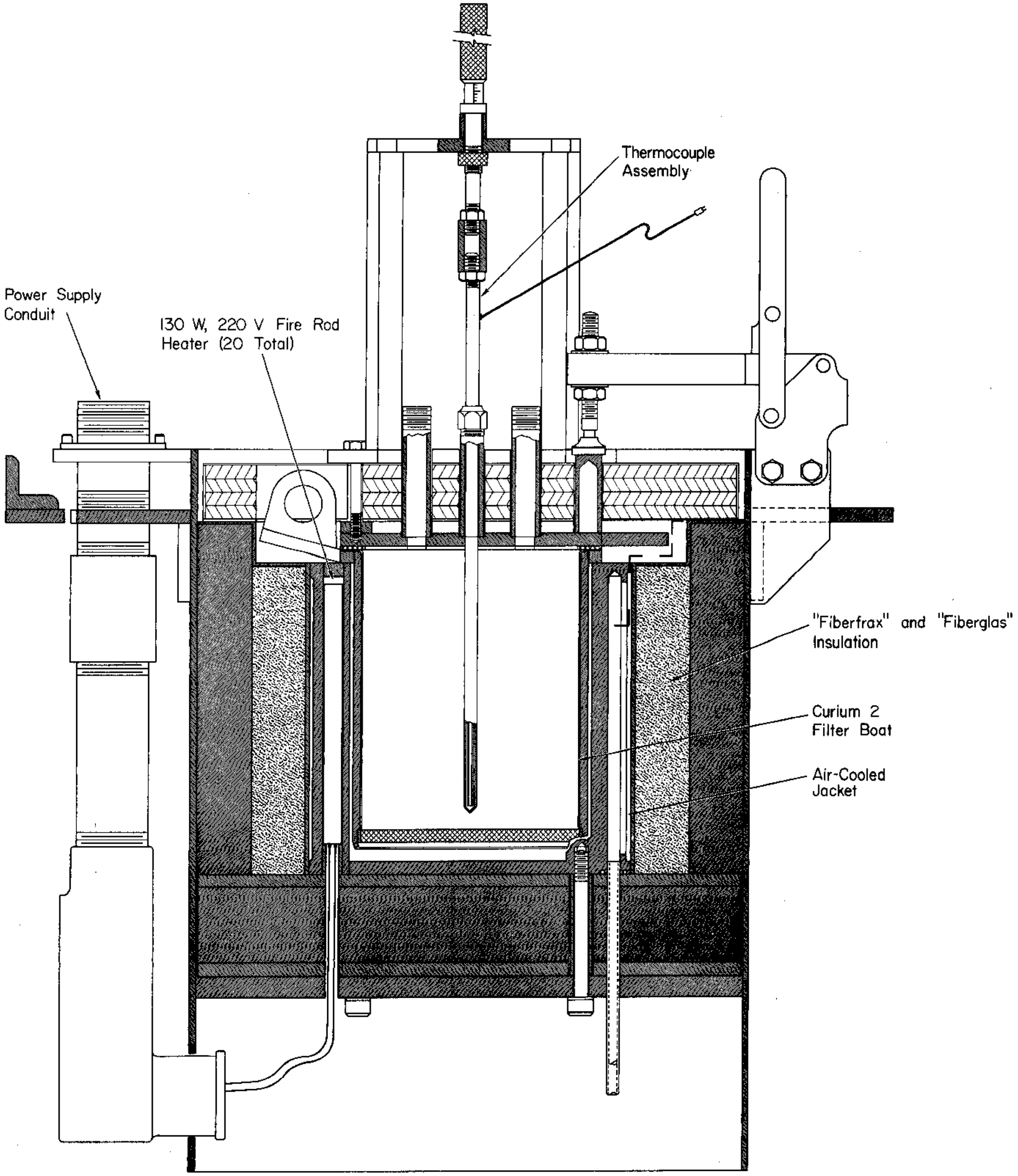


FIG. 17 CALCINING FURNACE

EVAPORATORS AND CONDENSERS

Process

In the curium process most of the aqueous feed, waste, and product solutions will be concentrated by evaporation as shown in Figures 1, 2, 9, 10, and 15. An exception will be the aqueous waste and the solvent washes from the nitrate-to-chloride conversion cycle which will not be evaporated because of the presence of potentially hazardous compounds. The individual evaporator vessels are identified, and the solutions evaporated in each are described in Table I.

TABLE I

Evaporators in Curium Process

Evaporator	Solution Evaporated
1AF	First cycle feed from plant (nitrate)
2AF	Product from conversion cycle (chloride)
3AF	Product from first Tramex cycle (chloride)
3BP (chloride strip)	Product from second Tramex cycle (chloride)
Cf	Aqueous streams from 1st solvent washer of each Tramex cycle (chloride)
Waste 1	Chloride waste streams plus concentrated H_2SO_4
Waste 2	Evaporator overheads from waste evaporator 2

Equipment

The feed and product evaporator vessels are 75-liter cylindrical tantalum tanks (Figures 18 and 19) fitted with condensers (Figure 20) for removal of the distillate. Waste evaporators 1 and 2 (Figures 21 and 22) are similar but larger -- 300 and 150 liters, respectively. The evaporators are all heated by electric immersion heaters.

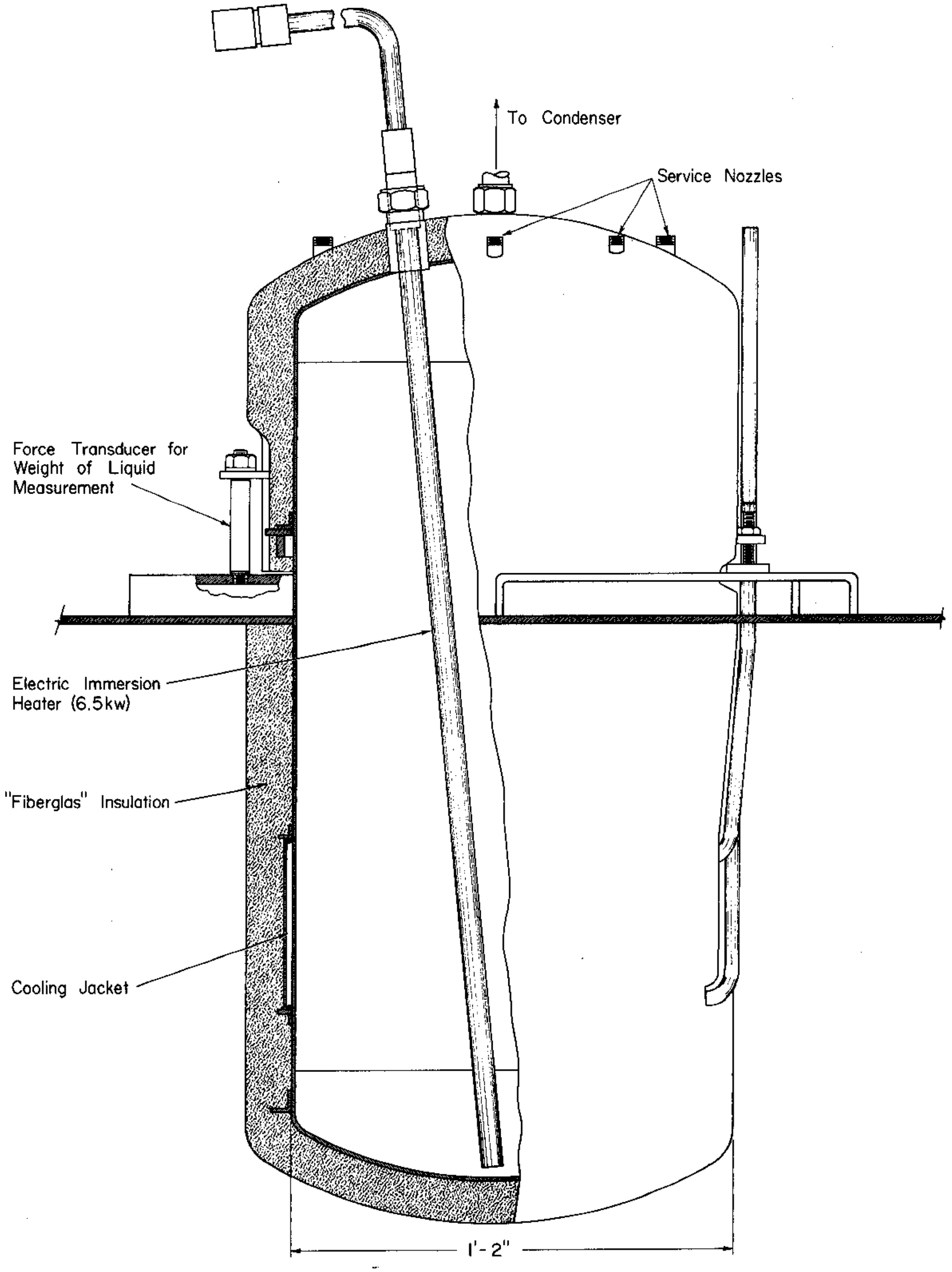


FIG. 18 1AF, 2AF, 3AF, AND CALIFORNIUM EVAPORATORS

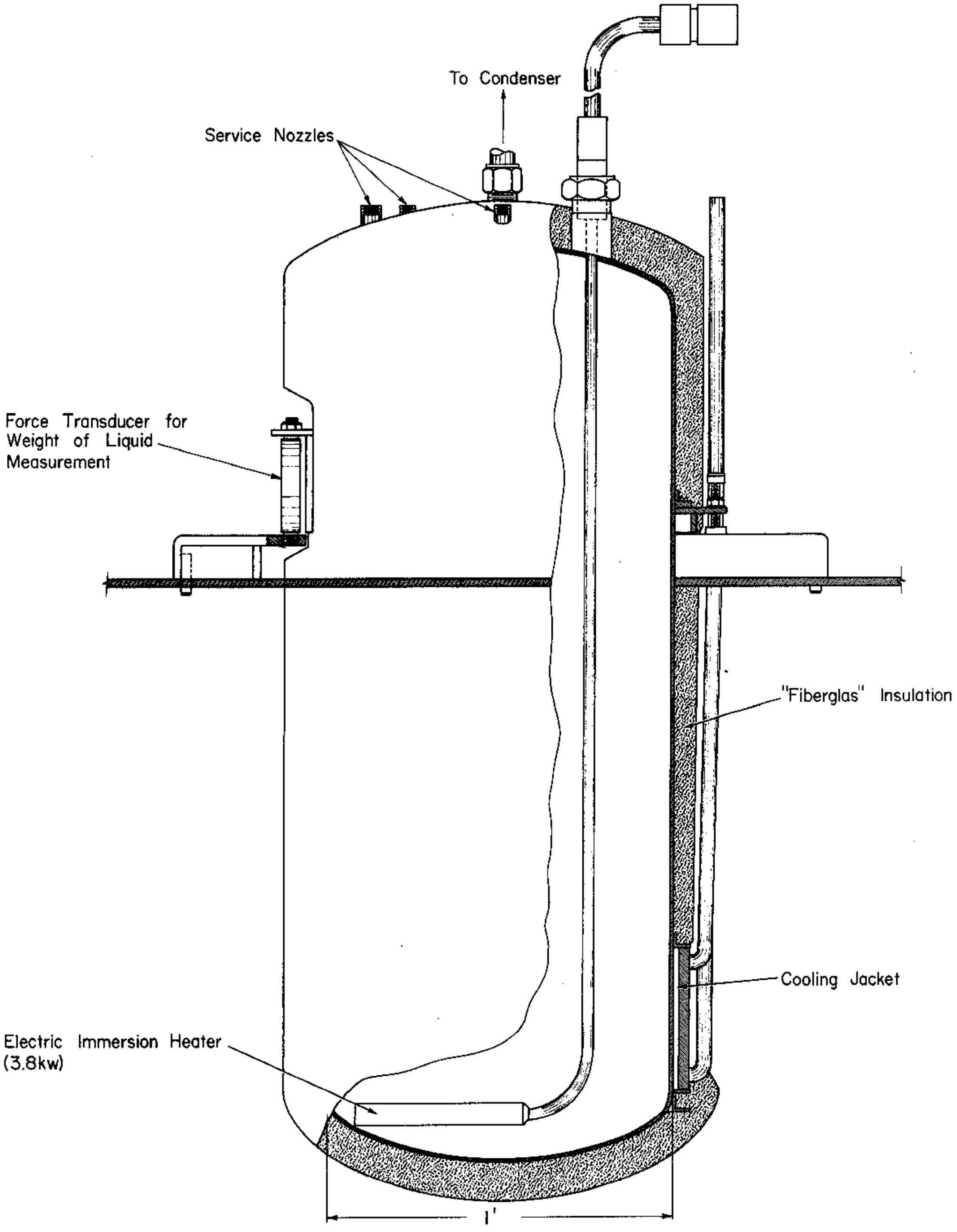


FIG. 19 CHLORIDE STRIP EVAPORATOR

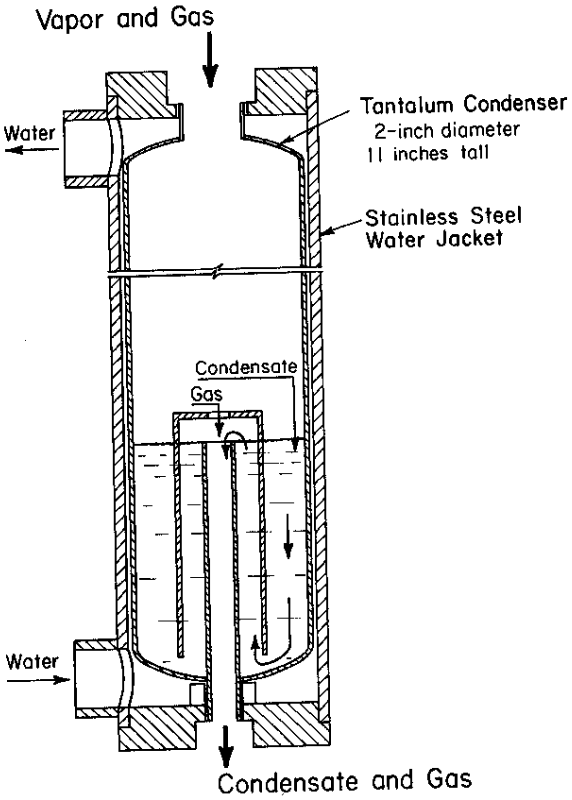


FIG. 20 CONDENSER FOR CURIUM EVAPORATORS

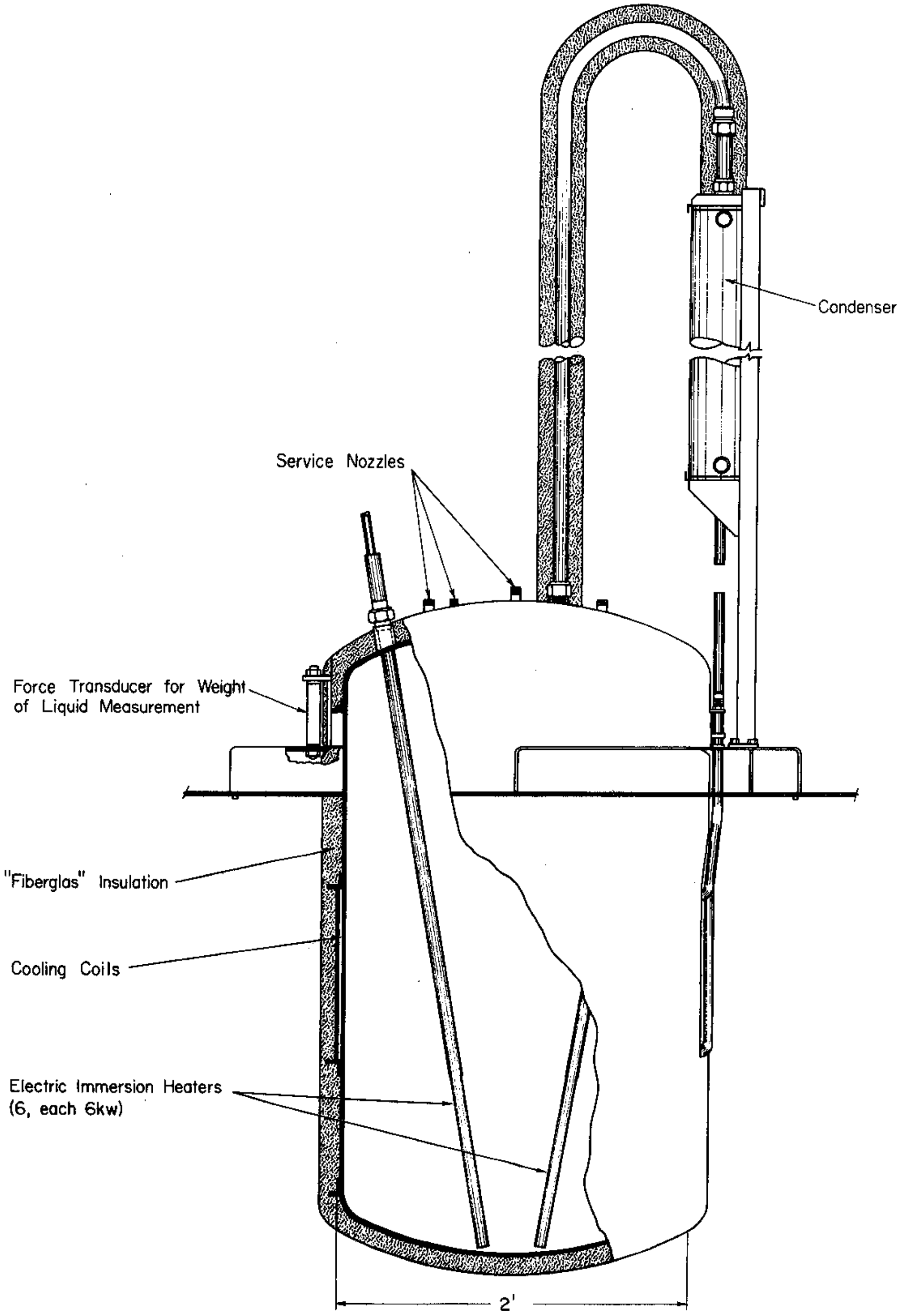


FIG. 21 WASTE EVAPORATOR 1

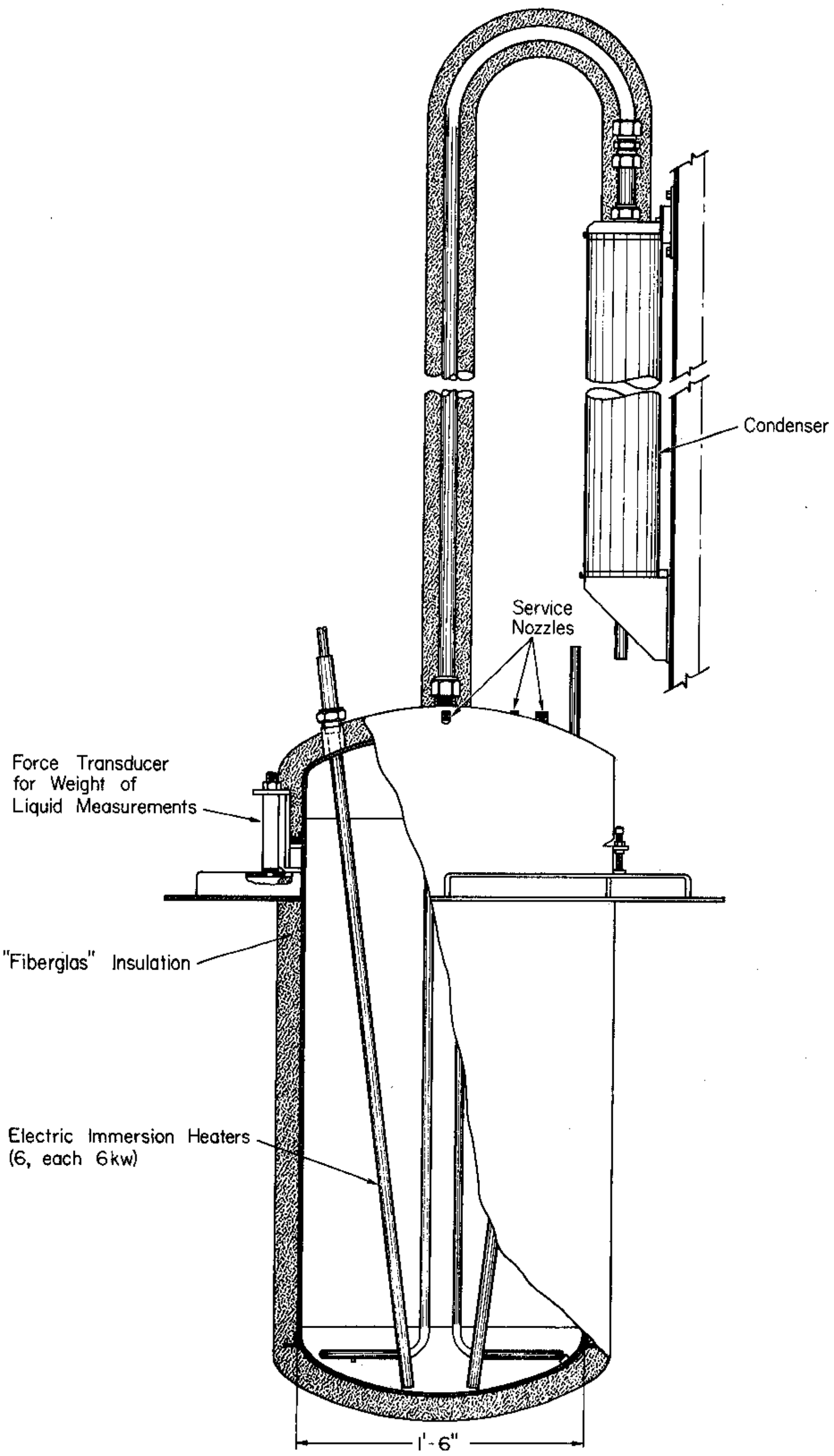


FIG. 22 WASTE EVAPORATOR 2

TEST PROCEDURES AND RESULTS

MIXER-SETTLERS

The suitability of mixer-settlers for the curium process was determined during tests with a plastic, six-stage prototype using simulated Tramex process solutions as shown in Table II.

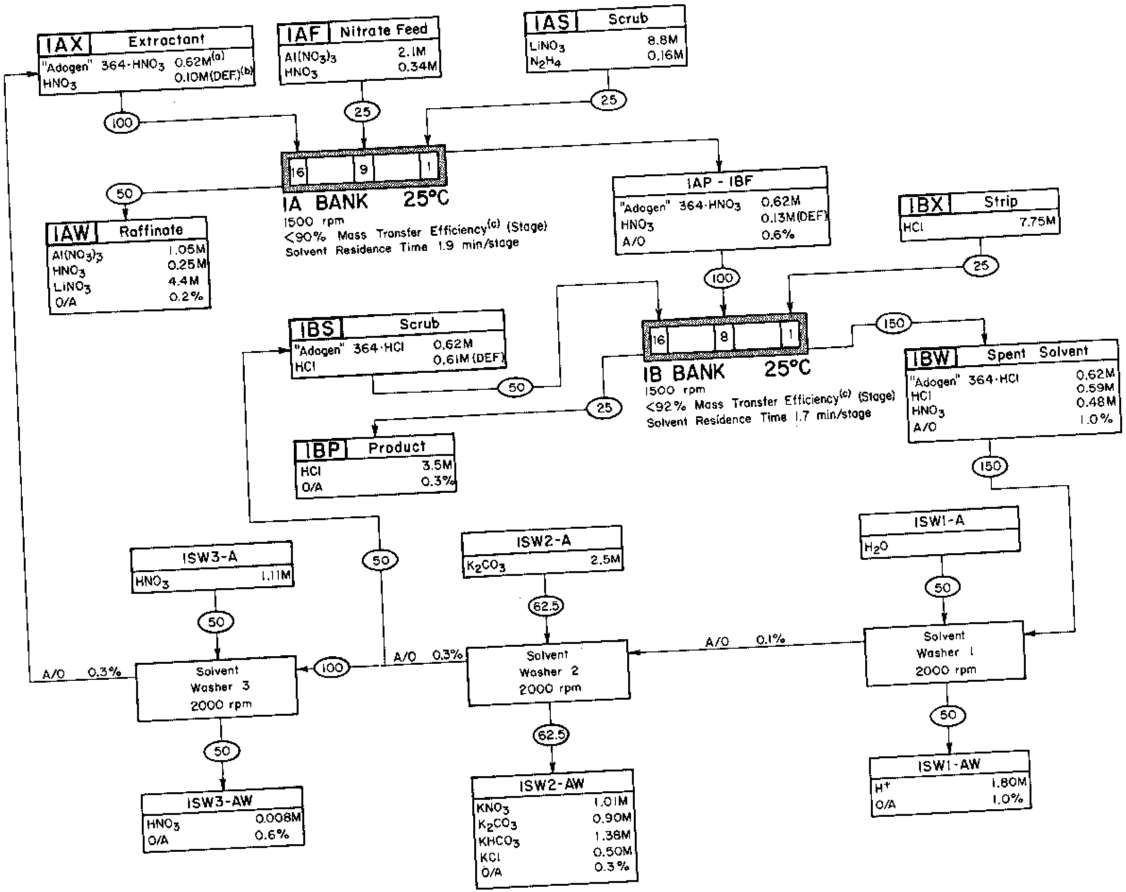
TABLE II

Tests of Prototype Mixer-Settlers

Simulated Bank	Paddle Speed, rpm	Settling Time, min		Endstream Entrainment, vol %		Average Cocurrent Stage Efficiency, %
		Aqueous	Organic	A/O	O/A	
1A	1500	2.2	1.5	0.4	1.0	88
1B	1500	4.0	1.0	(not operable)		-
2A, 3A	1350	3.0	2.0	0	0.5	90
2B, 3B	1350	6.0	1.5	0	0.1	86

The observed cocurrent efficiencies were higher than the necessary 80% (using nickel as a stand-in for curium). The endstream entrainment was satisfactory in all banks as long as the solvent residence time in the settling section was $\geqslant$1.5 minutes. Blocks in the plastic prototype mixer-settler, however, were installed permanently to give the minimum residence times for each bank; more residence time should have been allowed in the 1B bank. The 1B bank was predicted to operate satisfactorily with 1.5 to 2 minutes of solvent settling time; under these conditions the cocurrent stage efficiency was expected to be similar to that in the 2B and 3B banks. In the event that the actual curium process solutions develop greater dispersion, the paddle speeds can be reduced somewhat, since the transfer efficiencies are relatively high. The optimum speed can be determined most satisfactorily during the processing of the curium in the Curium Processing Facility.

To verify the mass transfer efficiency of the prototype mixer-settler, two of the six full-scale tantalum mixer-settlers were tested with three prototype solvent washers simulating the three solvent extraction and washing cycles without radioactivity, and with nickel as the stand-in for curium. Satisfactory hydraulic and mass transfer characteristics of the mixer-settlers were confirmed as shown in Figures 23 through 25 (solvent washing data shown in figures are discussed on page 44). The cocurrent transfer efficiencies in all cases were between 87 and 93%, and entrainment in the endstream was small. The remotely adjustable blocks in the solvent settling sections to control the residence time (holdup volume) were positioned to give solvent residence times of ~1.8 and ~2.5 minutes in the conversion and Tramex cycles, respectively. In initial trials, up to 1% aqueous was entrained in the solvent endstreams; this was reduced below 0.2% by stopping the mixer paddle in the solvent-exit stage of each bank (Stage 1). This change is practical because Stage 1 is not required for adequate mass transfer. Operating with solution temperatures below ~25°C significantly increased the entrainment in the endstreams. Some of the feed compositions for these tests differ slightly from the final flowsheets presented in Figures 1 and 2 because of minor modification to the curium process after the tests were completed.



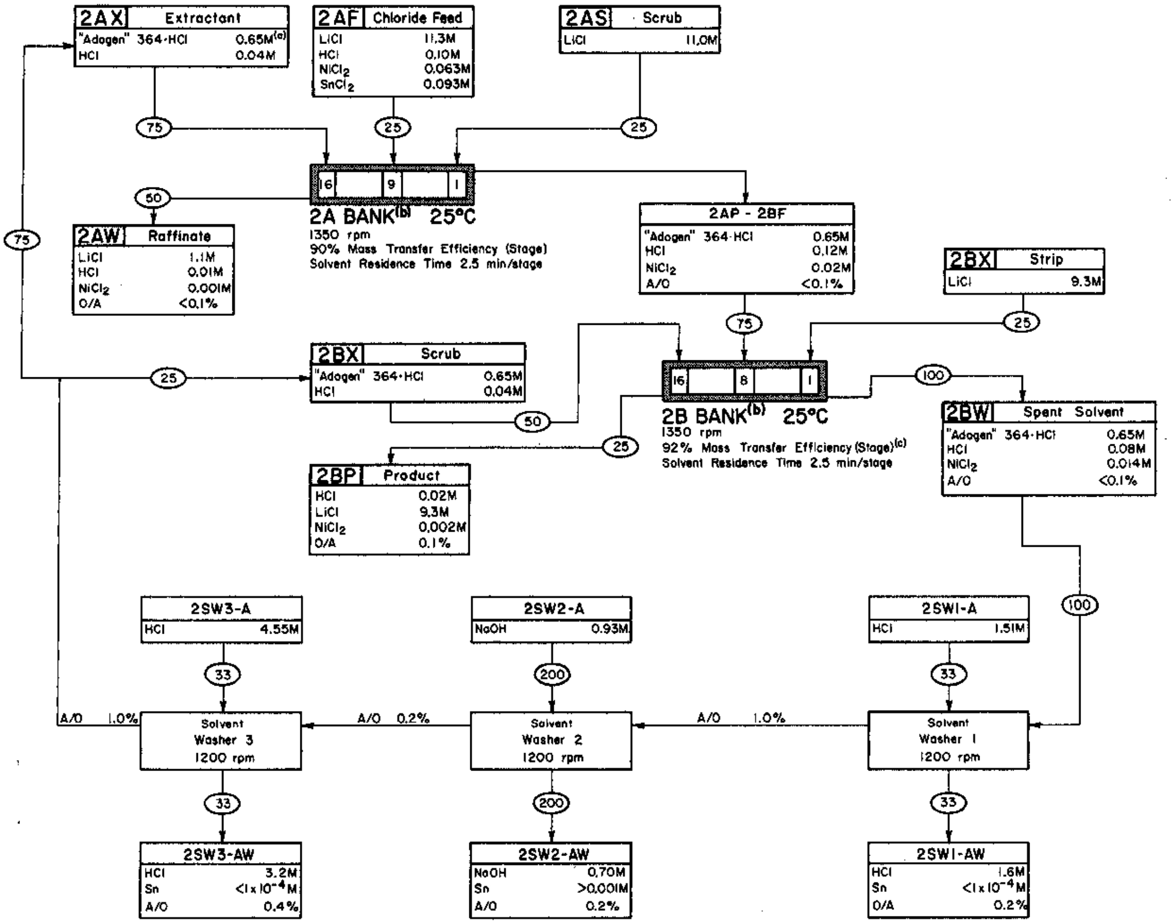
(a) "Adogen" 364 is a mixture of n-octyl and n-decyl tertiary amines; "Adogen" is a trademark of Archer Daniels Midland Company.

(b) HNO_3 in ISW3 should have been 1.8M to provide 0.01-0.05M excess HNO_3 in IAX.

(c) Assumed to be at least as high as 2A and 2B banks; no mass transfer data obtained since Ni does not extract in IA bank.

(cc/min)

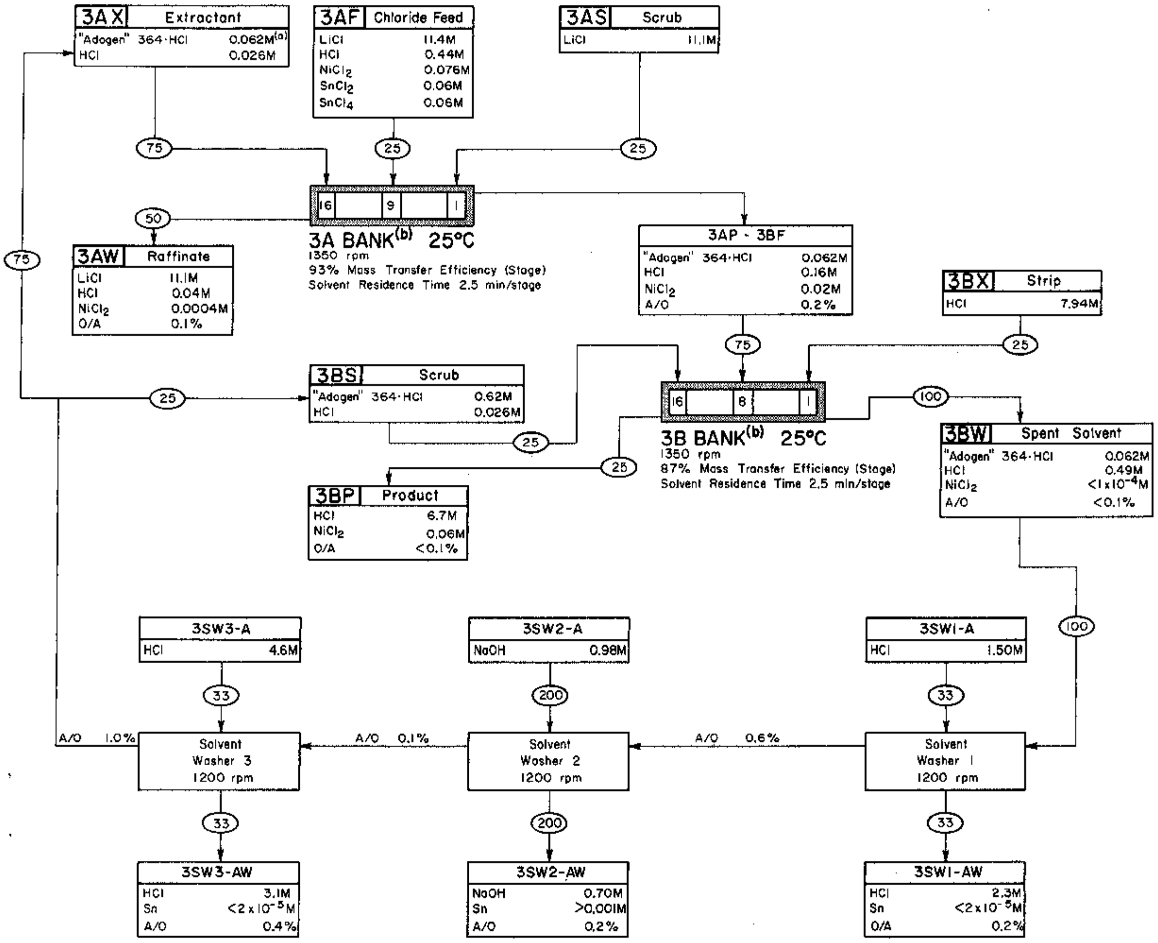
FIG. 23 TEST OF CONVERSION CYCLE



(a) "Adogen" 364 is a mixture of n-octyl and n-decyl tertiary amines; "Adogen" is a trademark of Archer Daniels Midland Company.
(b) Stage 1 paddle off.
(c) Efficiency obtained by feeding 2BF into Stage 16 along with 2BS; during normal flowsheet operation, most of the Ni remains in the solvent.

(cc/min)

FIG. 24 TEST OF FIRST TRAMEX CYCLE



(a) "Adogen" 364 is a mixture of n-octyl and n-decyl tertiary amines; "Adogen" is a trademark of Archer Daniels Midland Company.
(b) Stage 1 paddle off.

(cc/min)

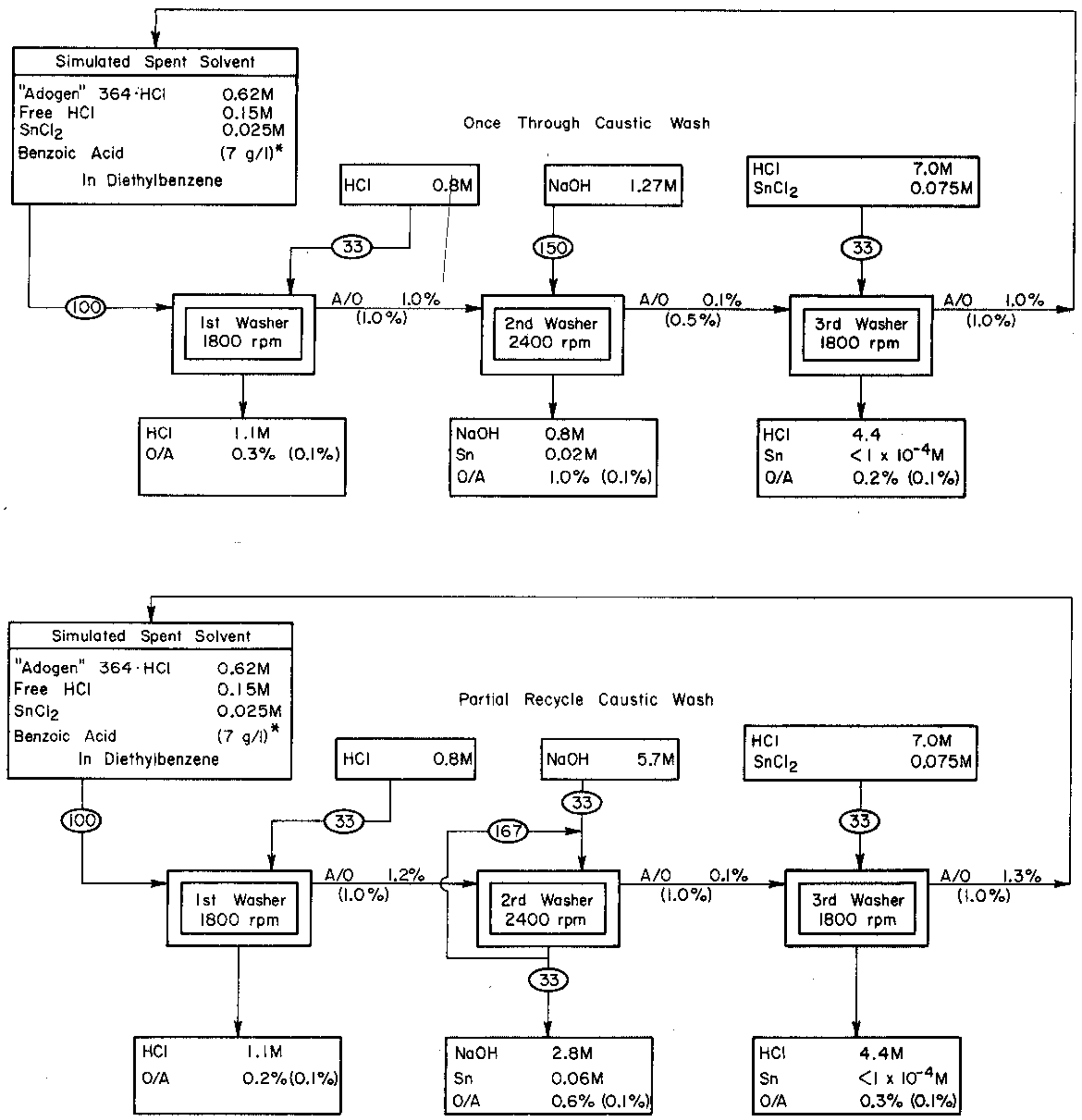
FIG. 25 TEST OF SECOND TRAMEX CYCLE

SOLVENT WASHERS

The operability of the solvent washers for the three extraction cycles of the curium process was satisfactorily demonstrated. The performance of the conversion cycle solvent washers was demonstrated when the prototype solvent washers were operated with the two full-scale tantalum mixer-settlers (described on page 40), as shown in Figure 23. Entrainment in the endstreams was low, and adequate mixing was obtained when the agitator speed of each washer was maintained at 2000 rpm.

The hydraulic and mass transfer characteristics under Tramex conditions were satisfactory using the full-scale process solvent washers as shown in Figure 26. Tin was precipitated in the alkaline solvent washers, as expected, but the precipitate did not plug the exit lines and most of it was removed with the spent wash solution. The agitator of the second washer was operated at 2400 rpm, which provided the optimum mixing intensity to prevent trapping of solvent in the tin precipitate. The agitator speed in the other washers was maintained at 1800 rpm although adequate performance can be obtained at speeds as low as 1200 rpm. The A/O mixing ratio ($\leqslant 1.5$) in the basic washer, with proper agitation intensity, produces Sn(II) solids which trap the least solvent and are sufficiently dense to disperse uniformly in the wash rather than collecting at the wash-solvent interface. The data in Figure 26 reveal an unexplained peculiarity; at the optimum intensity of agitation, the presence of benzoic acid decreases the trapping of solvent in precipitate. Previous laboratory tests(3) showed that entrainment in the alkaline wash is generally increased by ethylbenzoate, a radiolysis product that is removed in the alkaline wash; benzoic acid should have a similar effect.

Tests of earlier Tramex flowsheets using the prototype solvent washers with the full-scale tantalum mixer-settlers (Figures 24 and 25) showed that satisfactory washing and hydraulic stability of the alkaline washer could be maintained at low paddle speeds (1200 rpm) by using relatively high volumes of alkaline wash. However, in contrast to these data, laboratory tests in miniature solvent washers (Mini) using radioactivity showed that ~10% of the solvent would normally be carried with the Sn(II) hydroxide.(2) Subsequent Mini solvent washer tests showed that solvent entrainment with the tin precipitate would be satisfactorily reduced if (1) the wash flow rate was sufficient (>150 cc/min) to give an A/O ratio of 1.5 in the mixing section of the washer to produce an aqueous continuous emulsion, (2) at least 17 and 28 minutes of residence times are provided for the aqueous and solvent phases, respectively, and (3) adequate mixing intensity was maintained. The second washer was operated with and without the air lift for recirculating wash. Each test was equivalent to five recycles of the solvent in the Tramex cycles.



* Values in parentheses are for test with benzoic acid to simulate effects of radioactivity on emulsion

(cc/min)

"Adogen" 364 is a mixture of n-octyl and n-decyl tertiary amines. "Adogen" is a trademark of Archer Daniels Midland Company

FIG. 26 TRAMEX SOLVENT WASHING TESTS

The air lift designed for the second washers allowed the desired high A/O ratio to be maintained in the mixing section of the washer, while lowering the overall rate of wash used; such operation will reduce the volume of high activity waste to the first evaporator. This method of operation has not been demonstrated with full activity feed in the Mini equipment because the small volumes are difficult to control. Therefore, the next demonstration of this technique will be in the Curium Processing Facility. A calibration of the air lift recirculation rate is shown in Figure 27.

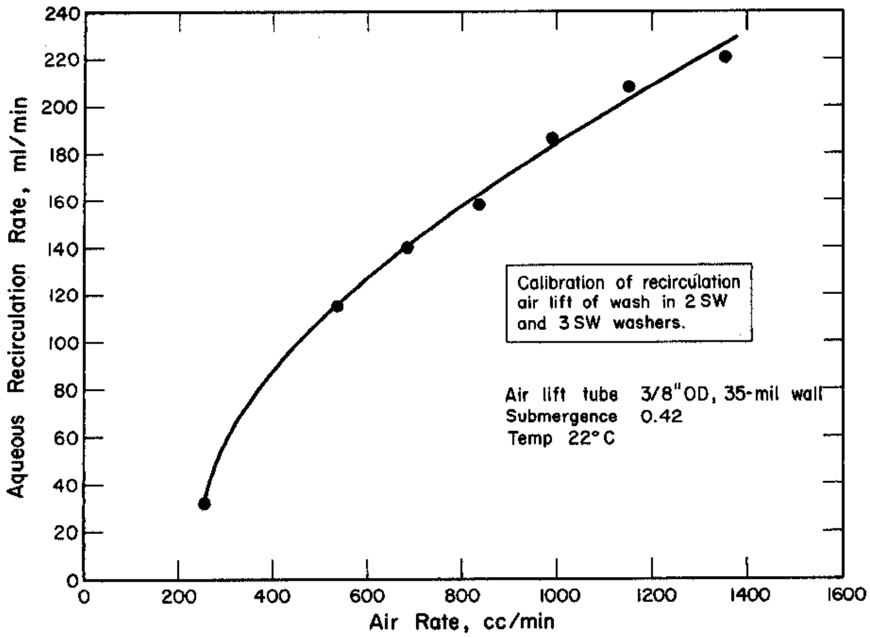


FIG. 27 CALIBRATION OF AIR LIFT CIRCULATOR

The weirs for controlling the aqueous-solvent interface in the washers required the following modifications for satisfactory operation:

- Replace the PVC material of construction with Zircaloy-2 to prevent solids from sticking to the surfaces and eventually causing pluggage.

- Enlarge the ID of the weir components to at least 0.5 inch to reduce the variation of pressure drop as solids exit. This change in pressure significantly changes the interface level in the washers, causing upsets. Also, there is less chance of pluggage occurring in the larger equipment.

- Add a brace to the top of the weirs to prevent vibration.

- Modify the number and size of threads in the variable-height weir "stem" to prevent rotation of the "stem" by vibration.

Performance of the thermistor-type interface level probe in the settling chamber of the second washer was satisfactory even with the Sn(II) present. The following modifications to the probe were required to obtain maximum performance:

- Increase the distance between the thermistors from 0.5 to 1.5 inches to allow a greater movement in the interface level before the weir setting has to be changed.

- Install the probes to detect the interface level between 5.75 and 7.25 inches below the solvent outlet of the 1st and 3rd Tramex washers and between 4.75 and 6.25 inches below the solvent outlet of the 2nd Tramex washers.

- Open the bottom of the probe to allow easier access of liquid to the thermistors.

PRECIPITATORS AND FILTERS

The full-scale process precipitators and filters will satisfactorily separate and purify americium and curium providing the following procedural requirements are followed:

- The filtrate from hydroxide precipitations must be recycled after filtrations to reduce the losses of curium and americium to waste to <0.1%.

- The acid to be added to the filter to dissolve the $K_3AmO_2(CO_3)_2$ must first be diverted to the precipitator to dissolve precipitate not transferable from the precipitator to the filter.

- The pressure drop across the filter is used to monitor filtration; at completion of filtration the pressure drop decreases from ~20 to ~13 inches of mercury.

Am-Cm Hydroxide Precipitation Tests

Test Procedure

Single batch runs, using equimolar lanthanum as a stand-in for both americium and curium, were based upon 3.51 liters of chloride strip evaporator concentrate (6M HCl) containing 10 g/l of curium and 4.7 g/l of americium (constitutes a normal "single batch" in the curium process). The concentrate will probably also contain ~1M LiCl from entrainment carryover from the 3A to the 3B bank during solvent extraction. The procedure used in these tests follows:

<u>Step 1</u>. Meter the product solution into the precipitant with the precipitator agitator at 500 rpm, vessel vent at 10 inches of H_2O, N_2 purge at 3 liters/min, and the reaction temperature maintained at <30°C.

<u>Step 2</u>. Digest precipitator slurry for 15 minutes prior to vacuum transfer through filter unit.

<u>Step 3</u>. Wash the precipitate on the filter with three 200-ml washes (0.1M NH_4OH - 0.1M NH_4NO_3) added to the precipitator via the slinger ring; leave each wash on the filter (with mixing) for 5 minutes prior to filtering.

<u>Step 4</u>. Dissolve filter cake with three HNO_3 fractions.

1st - 270 ml of 4.0M HNO_3
2nd - 400 ml of 0.1M HNO_3
3rd - 200 ml of 0.1M HNO_3

<u>Step 5</u>. Flush precipitator and frit with nitric acid followed by water flushes for inventory purposes.

NH_4OH Versus NaOH as Precipitant

NH_4OH is a better precipitant than NaOH because of less filtration time, as demonstrated using 3.51 liters of feed containing equimolar lanthanum concentrations equivalent to a double curium batch (Table III).

TABLE III

Comparison of Precipitate Filtration Time and Liquid Holdup Using NH_4OH and NaOH as Precipitants

	NaOH	NH_4OH
Filtration period, min	55	13
Cake holdup, cc	289	120

NH_4OH Requirements

Quantities of NH_4OH over and above that calculated to give the desired excess hydroxide (1.0M) in the supernatant must be added to the precipitator because of the volatility loss of NH_3. In addition, the excess hydroxide in the supernatant is a function of whether N_2, required to dilute H_2 formed by radiolytic decomposition, is added as a sparge or introduced into the vapor space as shown in Table IV.

TABLE IV

Effect of NH_3 Losses to Vent on Excess Hydroxide in the Supernatant During Lanthanum Precipitation

N_2 Flow 3 liters/min	Excess NH_4OH, moles[a]	OH^- in Supernatant, M
Sparge	1.0	0
Sparge	6.16	0.56
Sparge	11.00	1.18
Purge	4.5	1.04
Purge	4.75	1.30
Purge	5.00	1.41

(a) Quantity of NH_4OH in addition to stoichiometric quantities

The NH_4OH stock must be analyzed frequently to assure that it is of sufficient strength to give the required excess OH^- in the supernatant without exceeding the volume of the precipitator, Table V. In addition, the nitrogen purge rather than sparge should be used to maintain maximum freeboard. Bottled ammonium hydroxide normally ranged from 13.0M to 14.8M by laboratory analyses.

TABLE V

Effect of NH_4OH Stock Concentration Upon Precipitator Freeboard - Single Curium Charge (3.51 liters)

NH_4OH in Precipitant, M	Resultant Freeboard, liters N_2 Sparge	Resultant Freeboard, liters N_2 Purge
14.8	0.34	0.78
14.3	0.24	0.68
13.8	0.14	0.61
13.3	0.03	0.52
12.8	-	0.42
11.8	-	0.19

Reduction of Product Losses

Reduction of lanthanum losses to the filtrate (waste) from 0.7% to 0.07% by recycling the filtrate through the filter via the precipitator was demonstrated in a 7-run series using NH_4OH as the precipitant (Tables VI and VII). The product loss of 0.7% to the filtrate results from that retained in the Zircaloy filter frit following dissolution (the frit always retains about 150 ml of solution) during the previous cycle.

TABLE VI

Lanthanum Recovery in Single-Batch Hydroxide Precipitation-Filtration Series Without Filtrate Recycle
(Average of 4 runs)

Stream	La, g	% of Feed (Feed 28.6 g La)
Filtrate		
Supernatant	0.02	0.07
Precipitate[a]	0.20	0.70
Cake wash	0.005	0.017
Cake dissolution	28.10	98.4
Frit retention[b]	0.460	1.61
Precipitator and line retention	0.015	0.05
Total	28.800	100.85

(a) These losses occur in the last 3 runs only; during an individual run, losses were as high as 1.34% of a single charge.

(b) Obtained from last run only.

TABLE VII

Lanthanum Recovery in Single-Batch Hydroxide Precipitation-Filtration Series with Filtrate Recycle
(Average of 3 runs)

Stream	La, g	% of Feed (Feed 28.3 g La)
Filtrate		
Supernatant	0.02	0.07
Precipitate[a]	0.02	0.07
Cake wash	0.01	0.04
Cake dissolution	28.00	99.0
Frit retention[b]	0.46	1.62
Precipitator and line retention	0.02	0.07
Total	28.53	100.87

(a) Based on last two runs only.

(b) Obtained from last run only.

Carbonate Precipitation Tests

Test Procedure

Equimolar uranium was used as a stand-in for americium during the carbonate precipitation tests. Ozone sparging was simulated by using a mixture of ammonia and nitrogen that precipitated the uranium as ammonium uranyl carbonate in the 3.5M K_2CO_3 solution. The Zircaloy carbonate precipitator and americium 1 filter to be used in the Curium Processing Facility were used for these tests. During the product stream addition to 5.5M K_2CO_3 in the precipitator, the bottom heater element on the precipitator was used to maintain a pot temperature of ~65°C.

The feed solution used in the carbonate precipitation tests consisted of 1 liter of 0.3 to 0.5M HNO_3 containing 20 g/l of lanthanum and 16.1 g/l of uranium which simulates the stream containing americium and curium from the 1st hydroxide precipitation and subsequent acid dissolution. The procedure for these tests is outlined as follows:

Step 1. Meter in the product stream to 1.825 liters of 5.5M K_2CO_3, precipitator agitator at 333 rpm.

Step 2. Sparge mixture with a 50% N_2 - 50% NH_3 mixture through the precipitator sparge ring.

Step 3. Vacuum transfer slurry through Zircaloy frit.

Step 4. Wash filter cake via precipitator (using slinger ring) with three separate 200-ml volumes of 1M K_2CO_3 saturated with NH_3.

Step 5. Dissolve filter cake with three HNO_3 fractions.

1st - 110 ml of 6M HNO_3
2nd - 226 ml of 0.15M HNO_3
3rd - 134 ml of 0.15M HNO_3

Step 6. Thoroughly rinse precipitator and frit with HNO_3 and water for inventory purposes.

Precipitator Heater Tests

The carbonate precipitator heating element was tested with 1.83 liters of 5.5M K_2CO_3 solution in the precipitator; results summarized in Table VIII show that the desired 65°C temperature can be maintained with power control set at 50 volts.

TABLE VIII

Evaluation of Bottom Heater on Carbonate Precipitator

Max Power - 2.97 kw at 220 volts
Agitator Speed - 333 rpm

Time, min	Pot Temp, °C	Heater Cast Temp, °C	Amperes	Volts
0	22	22	6.75	100
16	65	70	3.5	50
20	63	65	3.5	50
35	63	65	3.5	50

Incomplete Precipitate Transfer to Filter

Although the lanthanum (curium stand-in) remained in solution as expected during the carbonate precipitation-filtration test, 33% of the uranium (americium stand-in) remained in the precipitator after filtration as shown in Table IX. After subsequent runs, inspection of the precipitator following washes revealed the walls to be clean, but precipitate had collected on the bottom around the transfer dip tube. Washes introduced into the open precipitator had no effect upon the residual precipitate. Apparently the loss of agitation, which occurs during the transfer as the liquid surface falls below the agitator, allows the precipitate to settle rapidly as an untransferable agglomerate.

TABLE IX

Uranium-Lanthanum Recovery in Carbonate Precipitation-Filtration Test

Stream	Uranium (16.25 g) g	Uranium (16.25 g) %	Lanthanum (20.14 g) g	Lanthanum (20.14 g) %
Filtrate	2.49[(a)]	15.30	19.50	96.8
Washes	0.15	0.92	0.52	2.6
Dissolution	7.77	47.80	0.05	0.25
Frit rinse	0.11	0.68	0.10	0.50
Precipitator rinse	5.35	32.90	0.30	1.50
Total	15.87	97.6	20.02	99.4

(a) Expected due to solubility

Recovery of Precipitate Heel

Since the lanthanum (curium stand-in) retentions in the precipitator and frit were negligible in all runs, the acid dissolution volumes to be added to the filter cake should be introduced by way of the precipitator to dissolve the untransferred precipitate, rather than installing small dip and sparge tubes. Use of a 1/4-inch-diameter transfer dip tube in place of the original 3/8-inch-diameter tube and a 1/8-inch-diameter sparge tube, which terminated adjacent to the end of the dip tube, to facilitate continuous agitation throughout the transfer significantly reduced precipitate retention in the precipitator as shown in Table X. However, the smaller transfer dip tube necessitated pressurizing the precipitator to effect a rapid solution transfer.

TABLE X

Uranium-Lanthanum Recovery in Carbonate Precipitation-Filtration Test with Continuous Sparge

Stream	Uranium (16.28 g) g	Uranium (16.28 g) %	Lanthanum (19.65 g) g	Lanthanum (19.65 g) %
Filtrate	1.92	11.8	18.78	95.6
Washers	0.21	1.3	0.37	1.9
Dissolution	12.91	79.3	<0.50	
Frit rinse	0.36	2.2	<0.19	
Precipitator rinse	0.53	3.3	<0.11	
Postprecipitate				
Wash(a)	0.02	0.1	0.24	1.2
Filtrate(a)	0.12	0.7	0.21	1.1
Total	16.07		19.60	
Overall recovery		98.7		99.8

(a) A trace of precipitate formed in the wash and filtrate streams upon standing for 2.5 days. The precipitate was isolated, acidified, and analyzed.

Curium I Precipitation

The curium, contained in the filtrate from the carbonate precipitation, is further decontaminated by precipitation as the hydroxide with subsequent filtration and dissolution of the cake in nitric acid.

Test Procedure

The simulated feed solution used for test purposes consisted of 3.425 liters of ~3M K_2CO_3 containing 20 grams of lanthanum to simulate the curium content. NaOH is used in this second hydroxide precipitation of curium (instead of NH_4OH) to remove additional cation impurities (such as Al, Zr) not removed using NH_4OH during the Am-Cm hydroxide precipitation. The procedure for this test is outlined below:

Step 1. With precipitator agitator at 700 rpm, meter in sufficient 7M HNO_3 to destroy the $CO_3^{=}$ and yield a solution 1M in HNO_3.

Step 2. Meter in sufficient 12M NaOH to precipitate the lanthanum and yield a final solution containing 0.5M excess OH^-.

Step 3. Vacuum transfer slurry to the Zircaloy frit.

Step 4. Wash filter cake via precipitator (slinger ring) with three, separate 500-ml fractions of 0.1M NaOH - 0.1M $NaNO_3$ wash solution.

Step 5. Dissolve washed cake with three HNO_3 fractions.

1st - 270 ml of 3.5M HNO_3
2nd - 400 ml of 0.15M HNO_3
3rd - 200 ml of 0.15M HNO_3

Step 6. Rinse precipitator and frit with HNO_3 and water for inventory purposes.

Test Results

The curium 1 precipitation test, summarized in Table XI, shows that the filtrate must be recycled to eliminate product losses to waste (1.5%), as was the case in the simulated Am-Cm hydroxide tests. The product stream volume was 1.042 liters at 0.52M HNO_3 and contained 0.135 mole/liter of lanthanum. Cake holdup using NaOH as the precipitant was 172 cc and the filtration time was 23 minutes.

Evaluation of Cooling System for Filter Units

The cooling system, as designed, for the curium and americium hydroxides will keep the precipitates below the specified 45°C at the heat load equivalent to a single batch providing: (1) a 25-

TABLE XI

Product Recovery During Curium 1 Precipitation and Filtration Step

Stream	La Recovered, g	Feed, % (Feed - 20.1 g La)
Filtrate	0.03	0.15
Wash	0.01	0.05
Acid dissolution	19.51	97.10
Precipitator rinse	0.08	0.40
Frit rinse	0.31	1.54
Total	19.94	99.2

minute limit for the period between each cake wash and between the end of the final wash and the start of acid dissolution is observed; and (2) if the acid dissolution is to be delayed, the final wash is left on the frit, with agitation and without vacuum.

Curium generates sufficient heat (e.g., 2.65 watts/gram of curium) to require cooling of the Am-Cm hydroxide filters to prevent heating of the hydroxides above a specified limit of 45°C (higher temperatures produce a dry insoluble cake). The cooling device is a coil of 1/4-inch Zircaloy tubing designed to be in contact with the bottom of the frit. Because the delivered filters had a 1/8-inch gap between the coil and the frit, a stainless steel (1/4-frit-area) mockup of the assembly was constructed to measure the transfer of heat from simulated curium hydroxide.

Lanthanum hydroxide was precipitated as stand-in for curium, filtered, and aspirated on the frit until no further removal of moisture was visible. The heat generation of a batch of ^{244}Cm hydroxide was simulated in preliminary tests with a coiled 1/8-inch-diameter "Calrod"* at the central plane of the hydroxide. Later tests were made with the hydroxide as its own resistance heater (Figure 28) in place of the "Calrod" heaters to produce a more realistic temperature. All heat transfer measurements were made with 20°C cooling water flowing at 1.3 liters/min, with no vacuum below the frit.

The steady-state temperatures are summarized in Table XII. Although the "Calrod" produced unrealistically high temperature in the hydroxide, the effect of the cooling coil position was determined readily. With the 1/8-inch air gap, the frit temperature was high, and about half of the heat flowed radially through the frit to the outside wall and vertically into the atmosphere above the precipitate. When the cooling coil was in contact with the frit, the frit temperature was lower and twice as much heat was transferred through the frit -- but the hydroxide temperature was decreased only 3°C.

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* Trademark of General Electric Co.

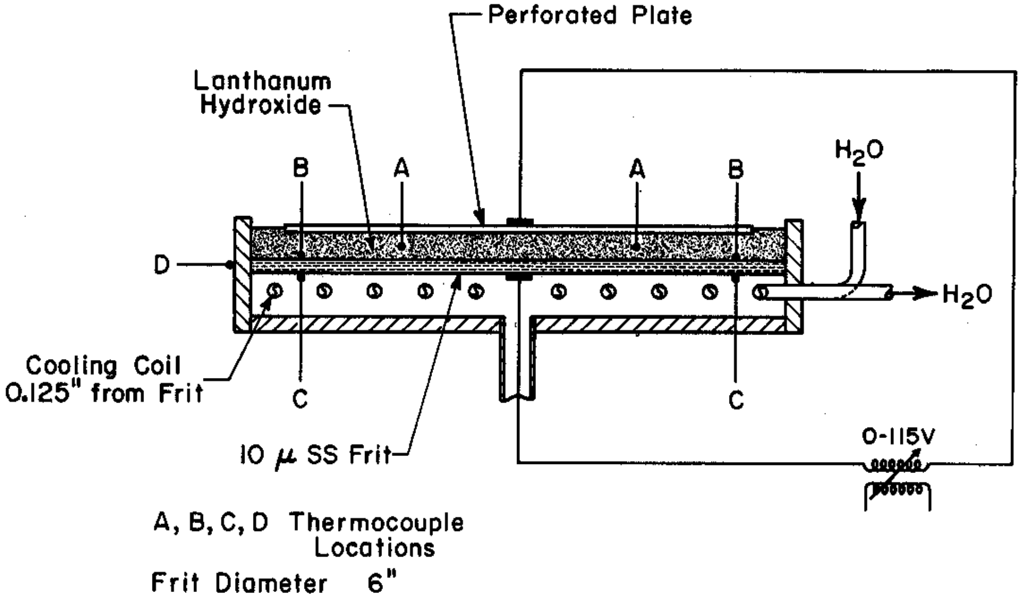

FIG. 28 MOCKUP OF ^{244}Cm HYDROXIDE FILTER

TABLE XII

Cooling of Filter for ^{244}Cm Hydroxide[a]

	Steady-State Temperature, °C Center of Hydroxide	 Top of Frit	 Bottom of Frit
Imbedded "Calrod"; cooling coil in contact with frit			
24 watts	70[b]	42	32
Imbedded "Calrod"; 1/8-inch air gap between cooling coil and frit			
24 watts	73[b]	51	46
48 watts	133[b]	71	63
Current through hydroxide; 1/8-inch air gap between cooling coil and frit			
24 watts	59	55	50
48 watts	90	77	68
Current through hydroxide; 1/8-inch gap but space below frit filled with water to improve heat transfer to coil			
24 watts	55	49	36
48 watts	83	56	41

(a) 24 watts provides same heat flux in test filter as one batch of ^{244}Cm in full-scale filter.

(b) Surface temperature of "Calrod".

During the tests using the hydroxide as its own resistance heater, the heat was generated by the IR drop through the hydroxide which produced a more realistic hydroxide temperature. The 1/8-inch cooling coil gap was not changed in this arrangement, but some of the measurements were made with the space below the frit filled with water. This flooded 1/8-inch gap provided better heat transfer than the unflooded direct coil-frit contact as shown by the larger Δt across the frit. As before, increasing the heat flow from the frit to the cooling coils had very little effect on the hydroxide temperature. Analysis of the heat flow shows that the average thermal conductivity of the precipitate is essentially the same as that of water.

The time required to reach steady-state conditions for power levels of 24 and 48 watts is shown in Figure 29. An unsuccessful attempt to determine the increase in precipitate temperature by monitoring the exterior wall temperature is also shown.

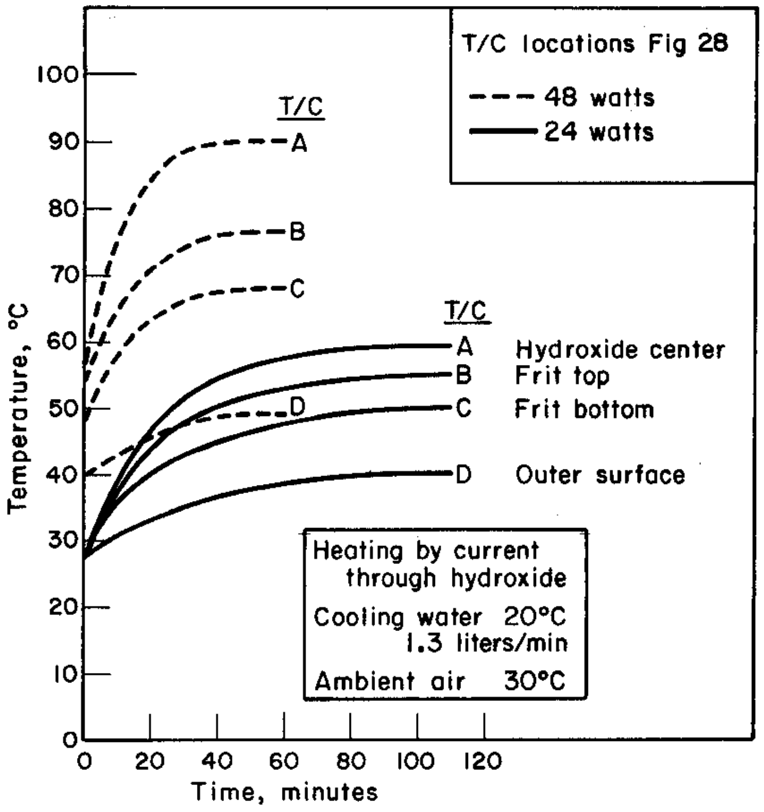

FIG. 29 HYDROXIDE HEATING ON 1/4 AREA FILTER

The effect of drawing air through the precipitate was evaluated in the calrod tests and produced marked effects. "Calrod" surface temperatures and frit temperatures were reduced 15°C. Extrapolating these data to the second series of tests indicates that the precipitate temperature could be kept at ~45°C for a single curium batch. However, the precipitate will be difficult to dissolve if it is dried by the air.

The critical period in the hydroxide precipitation, filtering, and acid dissolution procedure is between each cake wash and between the end of the final wash and the start of the acid dissolution. The following recommendations should be followed to prevent the drying of precipitate on a filter.

- Limit curium feed to one batch per filter unless experience under actual process conditions indicates otherwise.
- Install a Zircaloy-2 sheath thermocouple through the side of the filter wall immediately above the frit and protruding 1 to 2 inches onto the top surface of the frit with sufficient clearance between the paddle and the thermocouple. Reliance upon a thermocouple attached to the side of the filter housing is not recommended.
- If dissolution of the precipitate cannot proceed shortly after the final wash (within 25 minutes), leave the final wash on the frit with agitation and without vacuum.
- Use vacuum to cool precipitate only in case of an emergency such as loss of cooling water.

Relocating the cooling coils against the frit was not recommended for the following reasons: (1) Because the frits were bowed (discovered during inspection), lowering the frit would bring only a fraction of the coils in contact with the frit unless the coil supports are appropriately modified. (2) The effect on the precipitate temperature of relocating the coils against the frit was small.

PREPARATION OF OXALATES AND CALCINATION

The performance and characteristics of the oxalate precipitator, the filter housing, two platinum filter boats, and the calciner (including power supply and controls) were determined to be satisfactory. Tests showed that the equipment will perform properly if the nitrogen flows through the vapor spaces of the precipitator only, and if an orifice is installed in the furnace air purge line to limit the flow to 0.5 cfm in order to avoid entrainment of the oxide.

During the initial tests, 4.1 liters of a simulated curium feed solution containing 20 g/l of lanthanum in 0.5M HNO_3 was transferred from the hold tank to the precipitator. 2.54 liters of 1.0M oxalic acid was added to the precipitator at 56 ml/min, with the agitator operating at 333 rpm. 14 liters/min of nitrogen was sparged into the vessel to hold the concentration of radiolytic hydrogen (when curium is present) below the explosive range and to suspend the oxalate precipitate. The temperature in the precipitator was held at ~30°C, and the solution was then transferred by vacuum to the platinum filter. The filtered oxalate was washed with three 400-ml portions of 0.2M HNO_3 - 0.1M oxalic acid; each portion of wash solution was introduced through the precipitator.

The oxalate was then dried by drawing air through the filter for 30 minutes, and the filter boat containing the oxalate was transferred to the calciner and heated 1 hour at 300°F. The temperature was then raised to 1100°F and held ~2 hours to convert the oxalate to oxide. An air flow of 0.5 cfm was maintained over the filter boat during the calcining.

The precipitator agitator maintained a suspension of the precipitate; a purge through the vapor space was substituted for the sparge to reduce the deposition and subsequent retention of the precipitate. Initial tests showed that a 14-liter/min sparge of nitrogen in the precipitator caused considerable splashing and carried entrainment into the off-gas line, particularly near the end of the precipitation when the vessel was nearly full. The three washes did not rinse all of the sparge-splashed precipitate from the walls.

The first wash displaced virtually all of the mother liquor from the filtered oxalate even though the filtered oxalate was distributed nonuniformly -- thick at the wall of the filter and absent from the region below the entrance.

To assure good vacuum sealing between various parts of the oxalate filter, the platinum lip of the filter boat must be cleaned, particularly of all remnants of the asbestos gasket that sealed the lid of the calciner. Also, the lid clamps must be tightened sufficiently to seal the platinum cylinder to the stainless steel frame of the filter boat -- no O-ring is used at this seal. With these precautions to eliminate vacuum leaks, filtering rates of about 1.5 liters/min were obtained at a vacuum of 20 inches of Hg. The filter housing is essentially a stainless steel pipe, closed at the bottom (filtrate exit) and flanged at the top. The lid (slurry entrance) is closed against the flange and tightened with three clamps that are hinged to the housing. The filter boat is a thin platinum cylinder with a lip at the top and closed at the bottom by the platinum frit; strength is provided by a surrounding (cylindrical) stainless steel frame that also has a lip at the top but is open at the bottom. This tightly fitting assembly is lowered into the housing and two O-ring seals are made between the lip of the steel frame of the boat and the flange of the housing, and between the lip of the platinum cylinder and the lid of the housing.

A test of the nuclear heating rate of 144 grams of ^{244}Cm showed that the curium alone will raise the furnace temperature above the preheat temperature of 300°F (to 810°F); therefore, no preheat furnace power will be necessary. The furnace controls held the oxalate satisfactorily at the 1100 ±5°F temperature for calcining.

An air flow of 0.5 cfm through the furnace prevented the undesirable accumulation of carbon from decomposition of the oxalate during the calcination. The oxide product is a very finely divided powder, and is entrained at air flows >1.75 cfm. The filter frit retains all of the fine oxide -- no detectable residual oxide passed through the frit during filtration of the next batch of oxalate.

EVAPORATORS AND CONDENSERS

Vertical Condenser

Adequate downflow condensing capacity was demonstrated for the vertical tantalum condensers for five evaporators in the 5.5-kg ^{244}Cm separations process. These are the feed evaporators for 1AF, 2AF, and 3AF, the chloride strip evaporator, and the californium evaporator. The larger condensers for waste evaporators 1 and 2 should perform similarly and were not tested separately from the evaporators.

The capacity was measured with saturated steam mixed with nitrogen. Nitrogen must be sparged into the evaporators to sweep out radiolytic hydrogen and thereby maintain the concentration of hydrogen below 2% in the evaporator vapor space. At nitrogen flows from 0.45 to 7.0 liters/min, the downflow condensing capacity was determined for two exit condensate temperatures: (1) slightly below the 50°C maximum recommended to prevent excessive hydrogen chloride in the purge gas flowing to the ventilation system, and (2) the temperature at the maximum capacity of the condenser (at the higher rates of operation, steam is carried through the non-condensible gas exit). The test data are summarized in Figure 30.

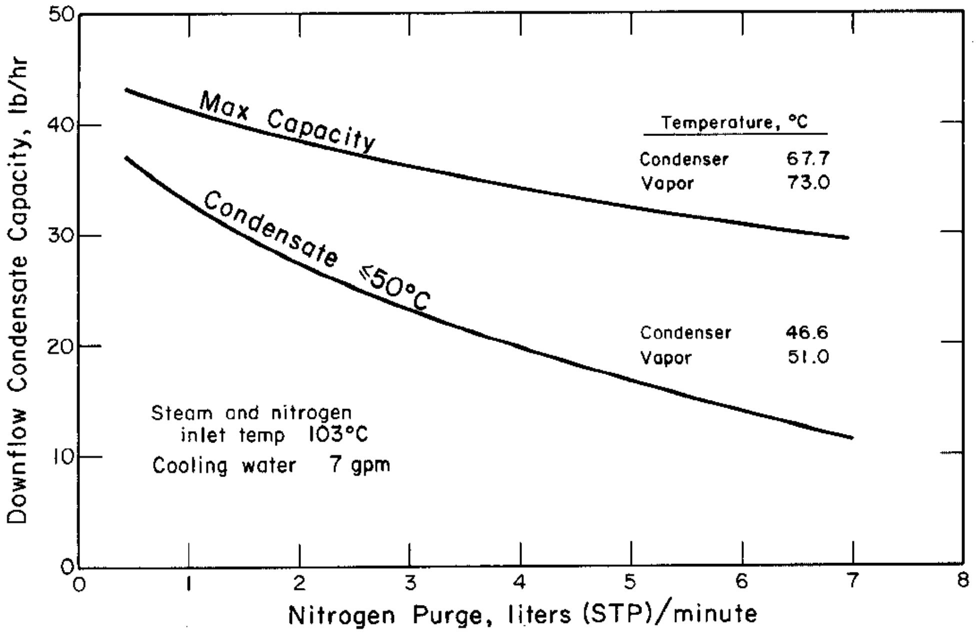

FIG. 30 CAPACITY OF VERTICAL CONDENSERS

Feed and Product Evaporators

The 3AF tantalum evaporator and its power console were tested satisfactorily at the semiworks in operations simulating those of the 1AF, 2AF, and chloride strip evaporators. These tests also covered adequately the conditions for evaporating the 3AF and californium solutions.

1AF Evaporator

The steam stripping operation of the 1AF evaporator adjusted the concentrations of $Al(NO_3)_3$ and HNO_3 within the specified limits, while maintaining the incoming concentration of stand-in lithium. However, the increase in specific gravity of the bottoms during boildown will require a critical-flow orifice for the nitrogen purge line (or a differential pressure regulator) to maintain a constant nitrogen purge to prevent accumulation of hydrogen in the vapor space.

Process Requirements

The concentrated curium-americium solution from the plant must be adjusted within the following limits for solvent extraction in the conversion cycle:

	Nominal	Minimum	Maximum
$Al(NO_3)_3$, M	2.0	1.8	2.4
HNO_3, M	0.25	0.1	0.4
Curium, g/l	1.0	-	-

If the feed is not within these limits, adjustments may require evaporation to remove excess water and/or steam stripping to remove HNO_3.

Test Results

To evaluate the steam stripping operation, 36 liters of simulated feed was processed, containing 1.18M $Al(NO_3)_3$, 1.2M HNO_3, and 0.97 g/l Li (as a stand-in for Cm). The $Al(NO_3)_3$ concentration was increased to ~40 wt % by evaporation, and the excess HNO_3 was then removed by metering water into the evaporator at a rate equal to the boiloff. The boiling temperature was used to monitor the evaporation. $Al(NO_3)_3$ solution was then added to adjust the volume to the initial value of 36 liters and to increase the Al^{3+} concentration to ~2.0M. The test data are summarized in Figure 31.

2AF Evaporator

The 2AF evaporator boilup, thermal efficiency, decontamination factor (freedom from entrainment), and cooldown characteristics were determined with simulated 2AF evaporator feed (0.02M HNO_3, 4.26M Cl^-, 4.11M Li^+) for a 30-g batch of curium (Figure 32). The

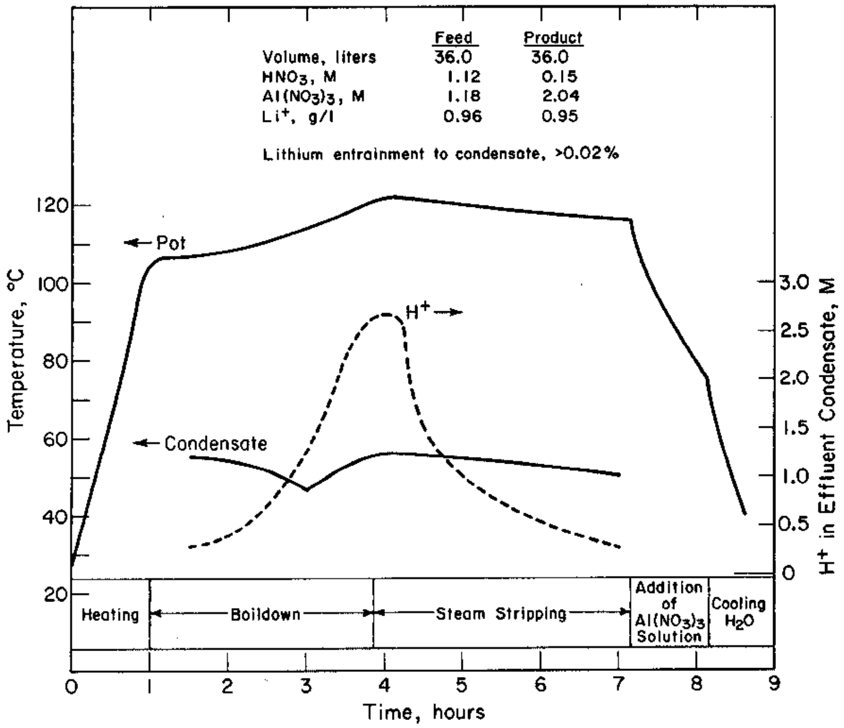

FIG. 31 EVAPORATION OF 1AF

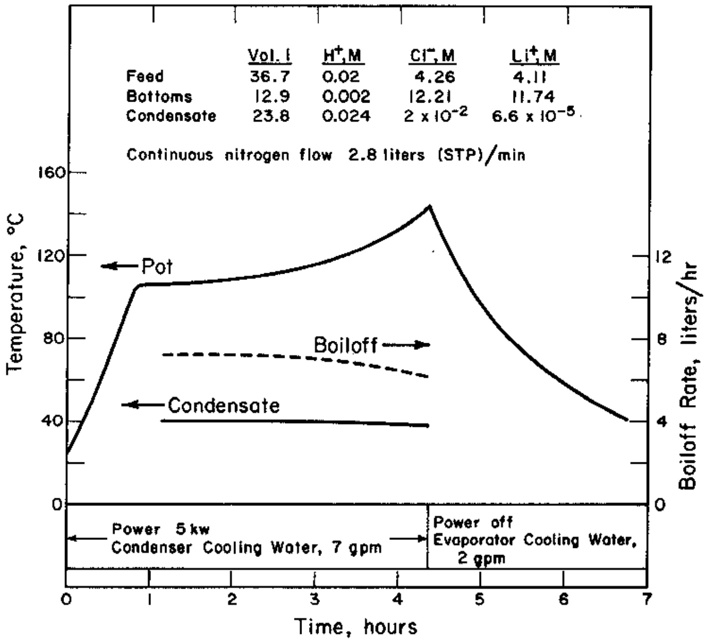

FIG. 32 EVAPORATION OF 2AF

demonstrated boilup rates will permit acceptable cycles, and the entrainment of bottoms to the condensate (based on Li) is satisfactorily low. Thermal efficiencies range from 73 to 90% over the evaporator cycle. The cooling water jacket is relatively ineffective because the liquid level at the end of a cycle is below the bottom of the cooling water jacket.

Chloride Strip Evaporator

Operation of the chloride strip evaporator showed that the 3BP stream to the evaporator must be diluted to a HCl concentration less than the $HCl-H_2O$ azeotrope (6.08M HCl) to prevent exceeding the vertical condenser capacity for HCl vapor.

Process Requirements

The preparation of americium and curium oxides from the solvent extraction product solution (3BP) includes a tenfold concentration of the 3BP by evaporation. Because the expected concentration of HCl in the 3BP is in excess of that in the $HCl-H_2O$ azeotropic mixture (6.08M HCl at 1 atm), large quantities of HCl vapor were expected to be evolved from the condenser.

Test Results

Simulated 3BP stream was diluted to reduce the concentration of HCl below the azeotropic value (5.6M HCl and 0.15M LiCl) and evaporated to 17.0 liters. The condensate temperature was maintained at 47°C (below the maximum of 50°C recommended to prevent excessive escape of HCl). No HCl was evolved initially, and the material balance below indicates no loss of HCl to the off-gas system:

	Feed	Condensate	Bottoms
Volume, liters	36	19	17
HCl, M	5.60	5.38	6.04
HCl, moles	202	101	101

To verify the need for diluting the 3BP stream, 36 liters of simulated 3BP (6.92M HCl, 0.15M LiCl) was placed in the evaporator. As soon as the boiling temperature was reached, ~4.3 moles of HCl vapor escaped immediately from the condenser and required shutdown. On the basis of this test, even the addition of packing to the condenser would not prevent excessive evolution of HCl.

The anticipated feed and product evaporator time cycles are summarized in Table XIII.

TABLE XIII

Anticipated Feed and Product Evaporator Time Cycles

Evaporator	Initial Charge, l	Power Input, kw	Heatup, hr	Boildown, hr	Cooldown, hr
1AF	36	5.0	1.2	6.5[(a)]	1.5[(b)]
2AF	44	5.0	1.0	4.3	2.5
3AF	21	5.0	0.4	0.8[(c)]	1.5
Cl^- Strip	36-39	3.7	1.5	7.5[(c)]	<1.0

(a) Includes time for steam stripping.
(b) Includes time to bring evaporator contents back to 36 liters.
(c) Based upon 80% thermal efficiency.

Waste Evaporators

Tests on the evaporators in the Curium Processing Facility with simulated waste verified the adequacy of boildown rate (38 liters per hour) and DF (~10^4 over each evaporator). Pluggage of the H_2 sparge and waste concentrate transfer tubes in the first waste evaporator was eliminated by sparging through the exit transfer tube (to keep free of solids during evaporation), which is larger (1/2- versus 3/8-inch tubing) and does not plug when sparging with dry heated N_2.

Process Requirements

The chloride concentration of the curium process waste must be reduced significantly to avoid stress corrosion cracking of stainless and carbon steels during the transfer of the waste to the Savannah River Plant and subsequent containment in the waste storage tanks. Laboratory tests showed that this reduction is obtained by conversion of the chloride salts to sulfates by the addition of 100% excess of concentrated H_2SO_4 and stripping off the HCl in a waste evaporator (WE 1). The degree of removal of HCl is indicated by the boiling point. For example, when the boiling point reaches ~140°C, the HCl concentration has been reduced to 0.02M (Figure 33). The waste bottoms will be diluted to less than 5M sulfate before transfer to a hold tank for neutralization. Prior to storage in the SRL waste handling facility, this solution will be neutralized to an excess of 0.15M NaOH and

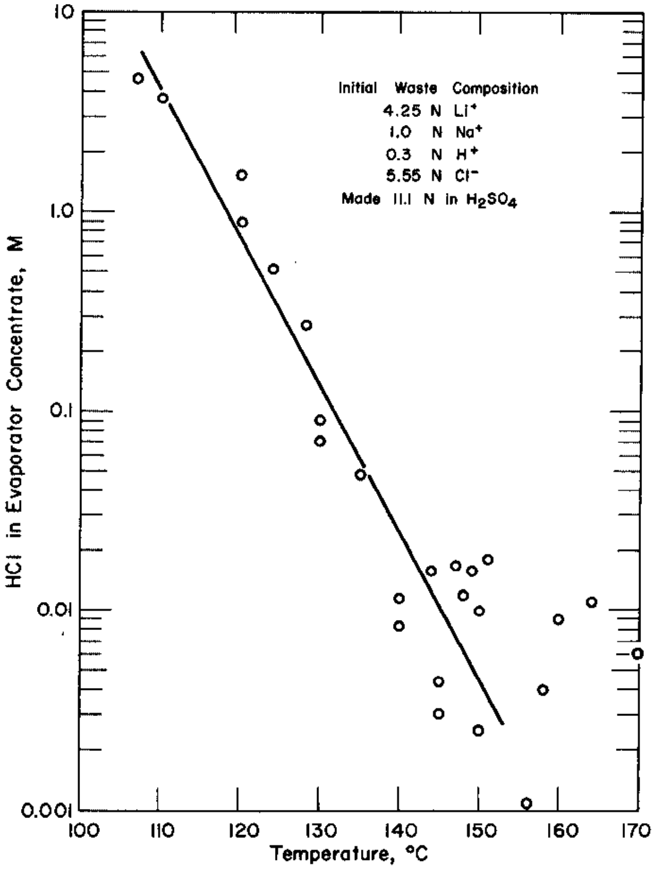

FIG. 33 STRIPPING OF HCl FROM WASTE

adjusted with $NaNO_3$ to maintain a NO_3^- to Cl^- ratio of at least 10. No problem will arise from handling this waste in stainless steel equipment if the free hydroxide is maintained >0.1M and the NO_3^- to Cl^- ratio is high.

The condensate from the HCl stripping evaporator will be evaporated again (WE 2) to obtain additional decontamination and then will be sent to the laboratory seepage basin.

Test Results

Laboratory investigations revealed that the rate of release of excess HCl from feed to the waste evaporator can be excessive under normal operating conditions. Therefore, limits on feed rate must be established for this evaporation. The HCl solubility is a function of sulfate concentration and is summarized in Figure 34 at the boiling point of the mixture.

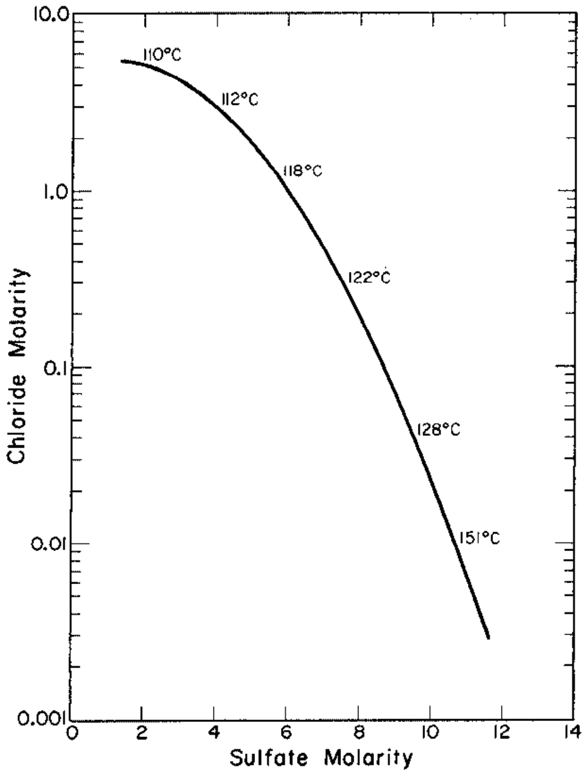

FIG. 34 SOLUBILITY OF HCl IN H_2SO_4 AT BOILING POINT

Only a 2-batch per day semicontinuous operation of WE 1 is possible, based upon the estimated daily volume of waste to be processed (~734 liters including sulfuric acid additions) and the expected evaporator boildown rate of 38 liters/hr. Batches will probably consist of the following stream volumes.

Source	Batch 1, liters	Batch 2, liters
Tramex 2A and 3A Banks Aqueous Waste (2-3AW)	72	72
Chloride Strip Evaporator Condensate (CSEC)	0-33(a)	0-33(a)
Filtrate from 1st Hydroxide Precipitation (1HPF)	7	-
Aqueous Waste from 2nd Washer of Tramex Cycle (2-3SWBW)	216	216

(a) When it becomes necessary to recycle WE 2 bottoms (25 liters, 6M HCl), all the CSEC must be processed in one batch and the recycle volume (high chloride) included in the other batch.

The laboratory tests showed that the chloride content of the waste may be safely reduced to less than 0.03M with negligible losses of HCl to the vent system if the following procedure is used.

Step 1. Initial charge to evaporator (maximum volume of 200 liters).

a. Add 72 liters of 2-3AW

b. Calculate volume of 18M H_2SO_4 required to stoichiometrically convert chloride salts in 2-3AW charge to sulfates (add in Step 1-f and again, for 100% excess, in Step 5).

c. Add 0 to 33 liters of CSEC.

d. Add 7 liters of HPF*.

e. Add volume of 2-3SWBW* which will give total charge of 200 liters after addition of H_2SO_4 in Step 1-f.

f. Meter in H_2SO_4 calculated in Step 1-b at a maximum rate of one liter per minute.

* Previously acidified with 18M H_2SO_4 to neutralize OH^- and convert chloride salts with 100% excess to sulfates.

Step 2. Boil charge down to 75-85 liters.

Step 3. Increase evaporator waste volume back to 200 liters with 2-3SWBW (heaters left on). Once boiling resumes, meter in the remainder of 2-3SWBW at a rate equal to the boiloff rate.

Step 4. After all the 2-3SWBW feed is added, boil off enough condensate to make room for the 100% excess H_2SO_4 calculated in Step 1-b.

Step 5. Shut off heaters, wait until boiling stops, and then meter in the volume of H_2SO_4 calculated in Step 1-b at a maximum rate of one liter per minute.

Step 6. After sulfuric acid addition is completed, evaporate contents to a pot temperature of 140-142°C (~13M H_2SO_4).

Step 7. Reduce power to heaters and add water (with sparging) to reduce the sulfate concentration to 4.5M. Hold pot temperature at 85-90°C for 15 minutes before turning heaters completely off.

Laboratory and full-scale tests showed that the nitrogen sparge tube in WE 1 will plug with precipitate as the boildown proceeds unless nitrogen gas is preheated to 150°C. The nitrogen sparge is required to maintain the radiolytically generated hydrogen gas concentration substantially below the minimum explosive concentration of hydrogen in air.

The excessive heat which is evolved upon sulfuric acid addition requires the evaporator's heaters to be shut off prior to metering in H_2SO_4, to prevent exceeding the condenser capacity. (Condensate effluent temperature must be $\leqslant 50^\circ C$ to prevent excessive release of HCl to vent.) At the recommended maximum acid addition rate of 1 liter/min, the normal boiloff rate of 38 liters/hr would be increased approximately 70% if the heaters are left on.

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1. I. D. Eubanks and G. A. Burney. Curium Process Development - I. General Process Description. USAEC Report DP-1009, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1966).

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