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SECTIONS FROM CHAPTER 4.4 (PLUTONIUM) OF VOLUME 4
OF THE REACTOR HANDBOOK

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SECTIONS FROM CHAPTER 4.4 (PLUTONIUM) FOR VOLUME 4
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Chapter 4.4 Plutonium Chemistry

Plutonium metal is currently produced by the bomb reduction of plutonium(IV) fluoride with calcium metal. Preliminary steps include: (1) preparation of a plutonium solution having a composition suitable for subsequent processing; (2) precipitation of plutonium peroxide or plutonium(III) or (IV) oxalate; and (3) conversion of the plutonium compound to plutonium(IV) fluoride by high temperature treatment with anhydrous hydrogen fluoride and oxygen.* Several alternate procedures have been successfully tested in the laboratory, but have not been adopted for plant use. It is the purpose of this chapter to present data pertinent to these processes and to the recovery of plutonium from their by-product and waste streams.

A. Properties of Plutonium

The chemical processing of plutonium is complicated by its complex chemistry. For example, plutonium has four stable oxidation states, (III), (IV), (V), and (VI), of which all but the pentavalent state are important in nitric acid systems. As a result, complete conversion of the plutonium in a solution to the desired oxidation state is one of the principal problems in wet chemical operations. Oxidation reduction potentials and methods of producing the various oxidation states are shown in Table A-I.

Some of the other properties of importance (solubilities and properties of solid compounds) are shown in Tables A-II and A-III.

B. Concentration

The precipitation processes now in use require, for efficiency, feed solutions containig 10 to 100 g/l plutonium and appropriate acidities.

*See Figure I for simplified flow diagram.

Figure I
Simplified Flow Diagram

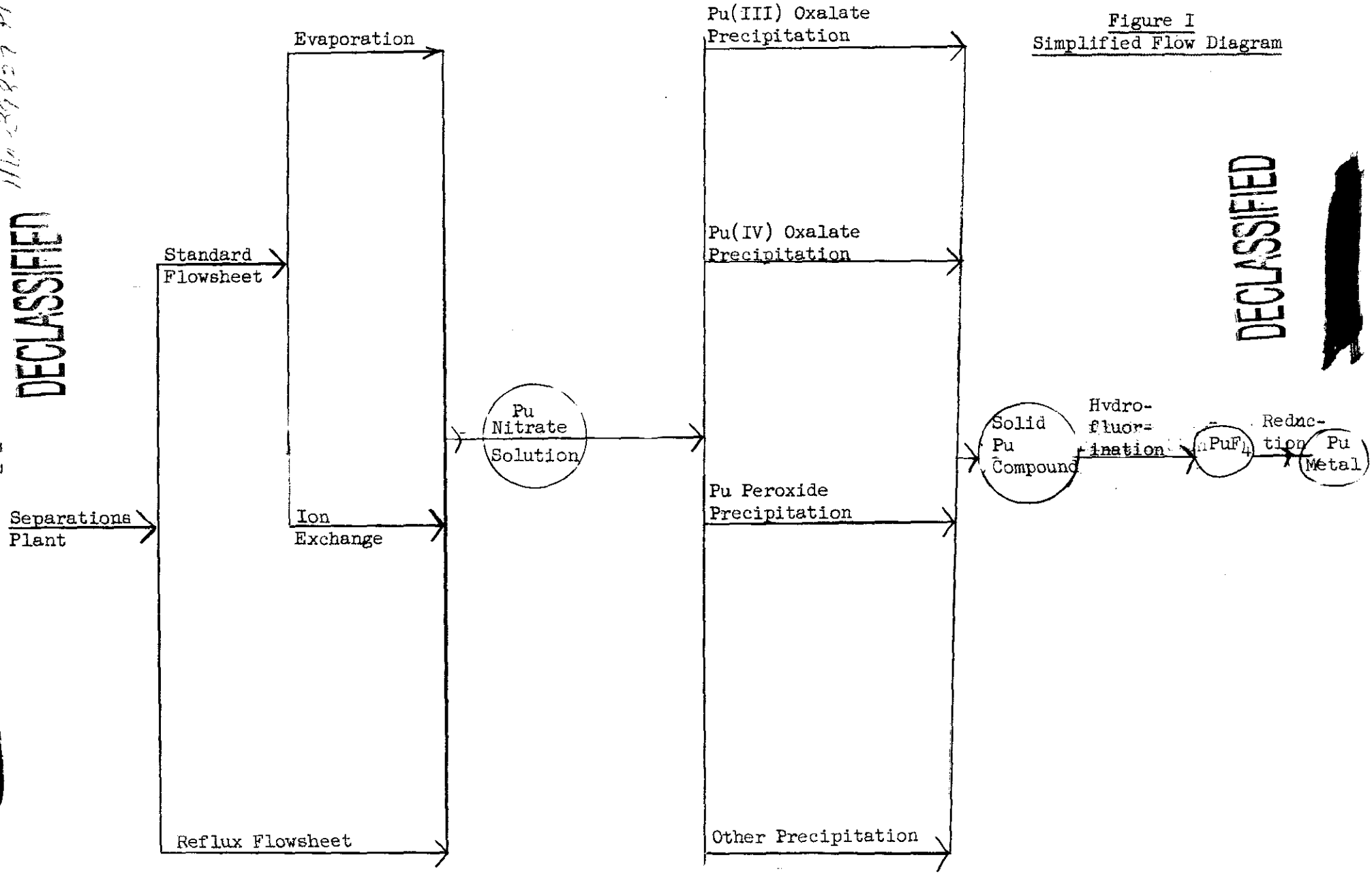

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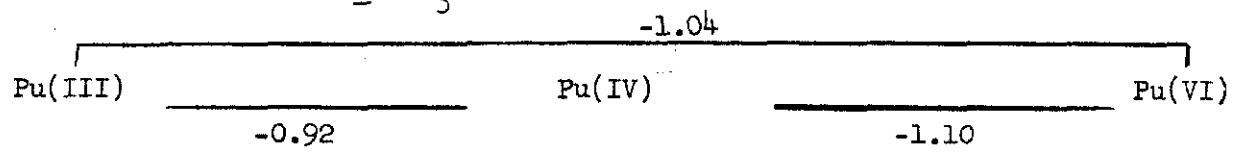
TABLE A-1
OXIDATION AND REDUCTION OF PLUTONIUM

Potential Scheme in 1 M HNO_3:



Valence adjustment in HNO_3 solutions:

Oxidation State Desired	Possible Agents	Remarks
Pu(III)[a]	HI NH_2OH SO_2 Fe(II) H_2O_2-$SO_2(NH_2)_2$	Pu(III) difficult to attain in solutions containing more than 3-4 M HNO_3. Presence of Pu(IV) complexing agents may prevent preparation of 100% Pu(III) solutions.
Pu(IV)[b]	Same as above.	Pu(IV) formed once excess reductant has been oxidized.
	H_2O_2	Pu(III) is frequently an intermediate, and may be long-lived; rate of formation of Pu(IV) increases with temperature, Pu concentration, and presence of impurities which catalyze H_2O_2 decomposition.
Pu(VI)[c]	$Cr_2O_7^=$ MnO_4^- O_3	

NOTES: (a) Excess reductant or addition of a stabilizer needed to prevent NO_2^- - Pu(III) reaction, which results in oxidation to Pu(IV).

(b) In solutions of low acidity, disproportionation may occur, to yield a solution containing Pu(III), (IV), (VI).

(c) Alpha particle action causes slow reduction of Pu(VI) in absence of a holding oxidant.

TABLE A-II

SOLUBILITIES OF SELECTED PLUTONIUM COMPOUNDS

Solubilities are given in grams plutonium per liter, at 25 C, and are not necessarily equilibrium solubilities. xH_2O indicated specific number of water molecules either unknown or variable. Names and formulas are those in common usage and follow no specific rules. Formulas for the peroxides and polymer are somewhat idealized; in practice, wide variations may be expected.

Name	Formula	Other Hydrates	Measured Solubility	
			Medium	g/l Pu
Arsenate(IV)	$Pu_3(AsO_4)_4$		2.2M H_3AsO_4, 2.1M HNO_3	0.0452
Fluoride(III)	$PuF_3.xH_2O$		1 M HF - 1 M HCl	0.037
Fluoride(IV)	$PuF_4.2.5\ H_2O$	0 H_2O	2 M HF - 2 M HNO_3	0.700
Fluoride(IV)Ammonium	NH_4PuF_5		3 M HF	0.07
Fluoride(IV)Calcium	$CaF_2.PuF_4.xH_2O$	0 H_2O	2 M HF - 4 M HF	0.06
Fluoride(IV)Lanthanum	$2\ LaF_3.PuF_4.xH_2O$		0.5 M HF - 0.5M HNO_3	0.020
Fluoride(IV)Potassium	$KPuF_5.xH_2O$	0 H_2O	3 M HF	0.005
Fluoride(IV)Sodium	$NaPuF_5$		3 M HF	0.007
Hydroxide(III)	$Pu(OH)_3.xH_2O$		5 M NH_4OH	0.090
Hydroxide(IV)	$Pu(OH)_4.xH_2O$		0.01 M $SO_4^=$ - pH 5.4	1.8×10^{-5}
Iodate(IV)	$Pu(IO_3)_4$		0.1 M KIO_3 - 1 M HNO_3	0.004
Nitrate(IV),Ammonium	$(NH_4)_2Pu(NO_3)_6$		0.5 M NH_4^+ - 12 M HNO_3	62
Nitrate(IV),Potassium	$K\ Pu(NO_3)_6$		2 M K^+ - 12 M HNO_3	50
Oxalate(III)	$Pu_2(C_2O_4)_3.9H_2O$	0 H_2O	0.5 M $C_2O_4^=$ - 3 M HNO_3	0.01
Oxalate(IV)	$Pu(C_2O_4)_2.6H_2O$	0,1,3 H_2O	0.1 M $C_2O_4^=$ - 4 M HNO_3	0.003
Oxalate(VI)	$PuO_2(C_2O_4).3H_2O$		0.1 M $C_2O_4^=$ - 2 M HNO_3	3
Peroxide(IV)	$PuO_3NO_3.3H_2O$		3 M H_2O_2 - 1 M HNO_3	0.10
Peroxide(IV),Sulfate	$Pu_2O_6SO_4.2H_2O$		3 M H_2O_2 - 0.1 M $SO_4^=$ .2M H^+	0.02
Phosphate(III)	$PuPO_4.xH_2O$		0.8 M H_3PO_4 - 0.1 M HCl	0.02
Phosphate(IV),Acid	$Pu(HPO_4).xH_2O$		0.33 M H_3PO_4 - 2 M HNO_3	0.03
Phosphate(IV),Acid	$Pu_2H(PO_4)_3.xH_2O$		0.6 M H_3PO_4 - 2 M HNO_3	6.0×10^{-5}
Phosphate(IV)	$Pu_3(PO_4)_4.xH_2O$		0.1 M H_3PO_4 - 0.1 M HNO_3	13×10^{-5}
Polymer	$Pu(H_2O)_x(OH^-)_y$		0.05 M HNO_3	<0.5
Sodium Acetate(VI)	$Na_2PuO_2(C_2H_3O_2)_3$		5 M Na^+ - 0.5 M HNO_3	0.07
Sulfate(III)	$Pu_2(SO_4)_3.xH_2O$		1.4 M K^+ - 0.8 M $SO_4^=$	0.12
Sulfate(IV)	$Pu(SO_4)_2.4H_2O$	0,1/3 H_2O	0.2 M H_2SO_4	2

TABLE A-III

A. COMPOUNDS PREPARED IN QUANTITY

Compounds	Formula	Stable Hydrates	Color and Crystalline Form	Heat of Formation KCal/Mole	Melting Point	Method of Preparation
Bromide, Tri	$PuBr_3$	1,3,6	Lt. Green Orthorhombic	-187.8	685	$Pu(C_2O_4)_2 + HBr + H_2 \xrightarrow{650\ C}$ $PuBr_3(aq) \xrightarrow{HBr}$; $-6H_2O$, 225 C
Chloride, Tri	$PuCl_3$	1,3,6	Green Hexagonal	-228.8	760	$Pu(C_2O_4)_2 + HCl + H_2 \xrightarrow{700\ C}$ $PuCl_3(aq) \xrightarrow{HCl}$; $-6H_2O$, 250 C $PuO_2 \xrightarrow[350 - 500]{CCl_4 \text{ or } COCl_2}$
Fluoride, Tri	PuF_3		Lavender Hexagonal	-374.6	1400	$PuO_2 + H_2 + HF \xrightarrow{300\ C}$ $PuF_4 - F_2 \xrightarrow{800\ C}$ $Pu^{+++} + HF - PuF_3.XH_2O \xrightarrow{HF\ 300\ C}$
Fluoride, Tetra	PuF_4		Salmon Pink Monoclinic	-423	1040	$PuO_2 + O_2 + HF \xrightarrow{400\ C}$ $Pu(C_2O_4)_2 + O_2 + HF \xrightarrow{450\ C}$ $PuF_3 + O_2 + HF \xrightarrow{600\ C}$
Hydride,	PuH_2		Grey F. C. Cubic	-37.4	--	$Pu + H_2 \xrightarrow{25\text{-}400\ C}$. Partial Pressure H_2 0.008 mm Hg at 400 C
Hydride,	$Pu\ H_3$		Black Hexagonal	-4.4	--	$PuH_2 + H_2 \xrightarrow{25\text{-}300\ C}$; Partial pressure H_2 200 mm Hg at 25 C
Iodide, Tri	PuI_3		Bright Green Orthorhombic	-133	780	$Pu + I_2 \xrightarrow{450\ C}$
Nitride	PuN		Brown F.C. Cubic	-95	>2000	$Pu + NH_3 \xrightarrow{1000\ C}$ $Pu + N_2 \xrightarrow{1200\ C}$
Oxide, Di	PuO_2		Yellow Green to Black, Cubic	-251	>2000	Ignition most Pu compounds in air above 300 C

TABLE A-III (Cont'd)

B. COMPOUNDS DETECTED AFTER FORMATION IN SMALL AMOUNT

Compounds	Formula	Color and Crystalline Form	Heat of Formation KCal/Mole	Methods of Preparation
Oxide, Mono	PuO	Black, Metallic Cubic	-135	$PuOCl + Ba \xrightarrow{1250\ C}$
Oxide, Sesqui	Pu_2O_3	Grey, Metallic	---	$Pu + MgO \xrightarrow{1000\ C}$
Oxybromide	PuOBr	Deep Green Tetragonal	-215	$PuBr_3 \xrightarrow{\Delta, H_2O,\ HCl,\ O_2}$ $PuBr_3.6H_2O \xrightarrow{\Delta}$
Oxychloride	PuOCl	Blue Green Tetragonal	-223	$PuCl_3 \xrightarrow{\Delta,\ H_2O,\ HCl,\ O_2}$ $PuCl_3.6H_2O \xrightarrow{\Delta}$
Oxyfluoride	PuOF	Black (?) F.C. Cubic	-270	$PuF_4 \xrightarrow{H_2O,\ O_2,\ \Delta}$
Oxyiodide	PuOI	Bright Green Tetragonal	-197	$Pu + I_2 + O_2 \xrightarrow{300\ C}$ Mixtures of PuO_2, PuOI, PuI_3
Oxysulfide	Pu_2O_2S	Slate Black Hexagonal	---	$PuO_2 + H_2S \xrightarrow{1300\ C}$
Sulfide, Mono	PuS	Bronze Cubic	---	$PuF_3 + BaS + Ca \xrightarrow{\Delta}$
Sulfide, Sesqui	Pu_2S_3	Black Cubic	-286	$PuO_2 + H_2S \xrightarrow{\Delta}$ Mixtures of Pu_2O_2S, Pu_2S_3 $PuCl_3 + H_2S \xrightarrow{800\ C}$
Carbide	PuC	Black Metallic Cubic	-30	$PuO_2 + C + H_2 \xrightarrow{1400\ C}$ $PuF_3 + C + Ca \xrightarrow{1200\ C}$

TABLE A-IV

PROPERTIES OF SELECTED PRECIPITATES AND DRY COMPOUNDS

Compound	Bulk Density (Grams/cc Pu) Filter Cake	Bulk Density (Grams/cc Pu) Dry Compound	Sintered Media Porosity Required To Retain Precipitate	Soluble In
Fluoride(III)		1 - 2.5	15-20 μ	Acid and fluoride-complexing agent
Fluoride(IV)	0.6-1.0	0.5 - 2*	15-20 μ	Acid and fluoride-complexing agent
Fluoride(IV), Calcium	0.9	1	15-20 μ	Acid and fluoride-complexing agent
Hydroxide(IV)	0.1-0.2		60-80 μ	Acids
Oxalate(III)	0.6-0.8		15-20 μ	Acid and oxidant
Oxalate(IV)	0.5-0.6	0.6	15-20 μ	Acid and oxidant
Oxide(IV)	[illegible]	1.8-2.2	15-20 μ	HNO_3-HF; HI
Peroxide(IV)	0.1-0.6		30-80 μ	HNO_3

* The bulk density of PuF_4 depends on its source: hydrofluorination of the oxide gives up to 2 grams/cc Pu; of the peroxide, 0.5 to 1 gram/cc Pu; of of Pu(IV) oxalate, 1 to 1.5 gram/cc Pu.

B. Concentration (continued)

To meet these requirements, the product from the solvent extraction systems of Redox or Purex type plants must be concentrated five-fold or more. Three methods now in use are evaporation, ion exchange, and the reflux - type, solvent extraction flowsheet. Further concentration, by evaporation, is also carried out to prepare concentrated plutonium nitrate solutions for storage or for shipping.

1. Evaporation of Plutonium Nitrate Solutions

Plutonium nitrate - nitric acid solutions containing up to 800 g/l plutonium have been prepared by evaporation. Typical data, including batch evaporation curves (without reflux) for a variety of feed solution compositions, and an equilibrium diagram for the plutonium nitrate - nitric acid - water system, are shown in Figure B-1-1 and B-1-2.

a. Valence Distribution

The tetra - and hexa - valent states of plutonium are the only ones stable under the usual conditions of evaporation. Plutonium(V) cannot exist at the high acidities involved, and plutonium(III) is oxidized immediately by hot or concentrated nitric acid. Plutonium(IV) is oxidized to plutonium(VI) by nitric acid at acidities below 4 M, the maximum rate occurring around 1 M. No appreciable oxidation of plutonium(IV) occurs at nitric acid concentrations greater than 6 M, because of the formation of nitrate complexes. Slow reduction of plutonium(VI) occurs, with evolution of oxygen and hydrogen, as a result of alpha particle radiation effects. Because of these effects, plutonium in nitric acid solutions generally occurs as a mixture of the (IV) and (VI) valence states, a factor which is usually disregarded in studies of the physical properties of nitrate solutions.

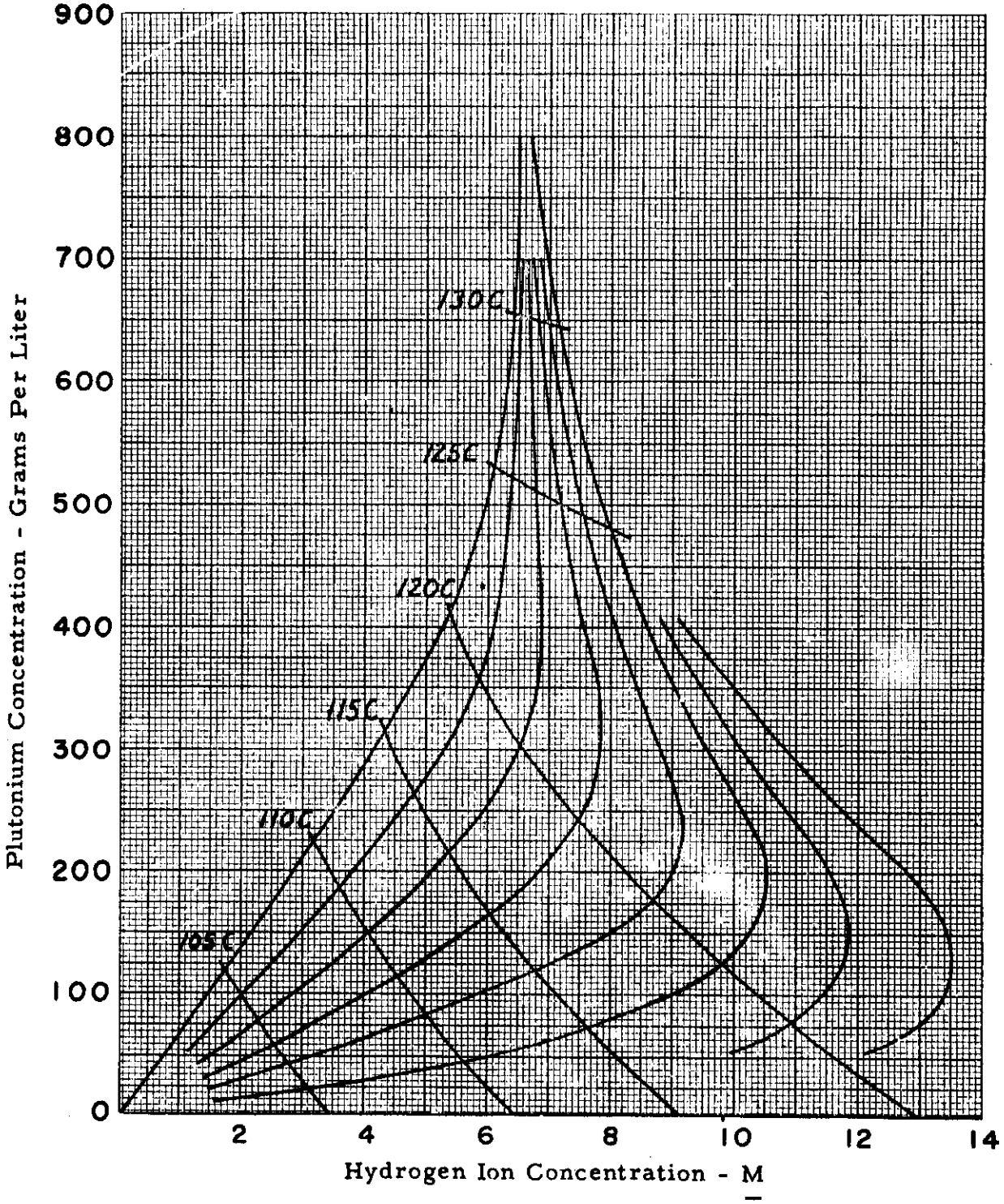


FIGURE 1 B-1

BOILING TEMPERATURES

Plutonium Nitrate - Nitric Acid

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Figure B-1-2

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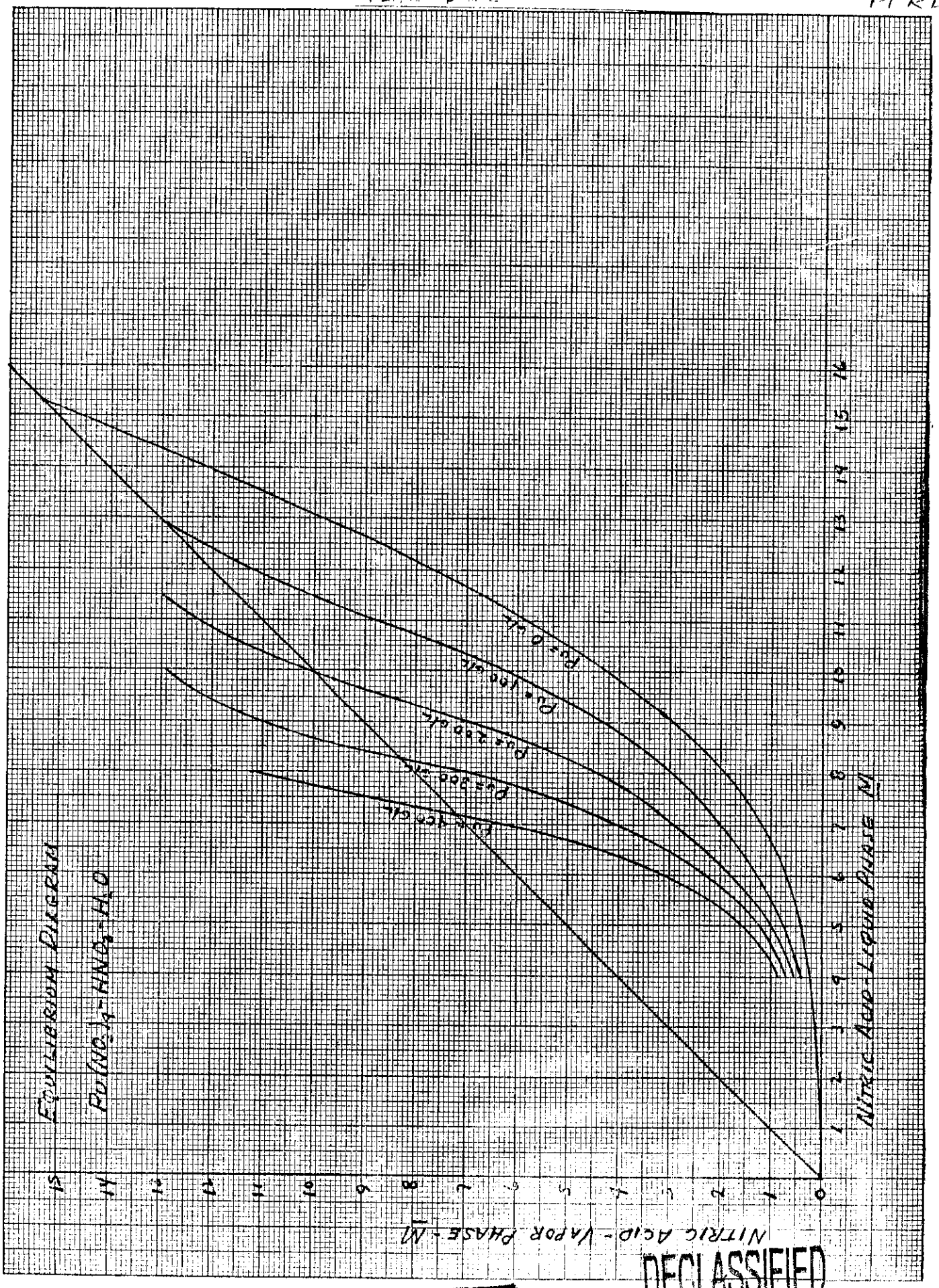

b. Physical Properties

The specific gravity of plutonium nitrate solutions can be represented by the following equation, with a precision of ± 5 per cent:

$$\text{Specific gravity} = 1 + 0.031\ (\text{moles/l } HNO_3) + 0.00146\ (\text{g/l Pu})$$

At plutonium concentrations greater than 500 g/l, the solutions are quite viscous; above 900 g/l, a plastic mass with a density of 2.2 to 2.3 is formed.

Solubility data are given in Table A-II.

c. Precipitation of Plutonium "Polymer"

Plutonium(IV) may polymerize in nitric acid solutions and precipitate, at acidities below 1.5 M. The region of acid and plutonium concentrations in which precipitation has been observed is shown in Figure B-1-4. At acidities above 0.1 M, the precipitation is slow at room temperature; while at acidities below 0.01 M or at elevated temperatures, precipitation may occur in a few minutes.

d. Tributyl Phosphate - Plutonium Nitrate Reaction

The formation of a red-brown liquid, similar to uranium "red-oil", has been observed during the evaporation of solutions containing plutonium nitrate, nitric acid, carbon tetrachloride, and tributyl phosphate (TBP). The liquid is soluble in carbon tetrachloride. Evaporation of solutions containing a TBP to plutonyl nitrate weight ratio of 0.15 or greater, until a pot temperature of 150C was reached, caused reactions which produced enough heat to bring the pot contents to red heat with copious evolution of gases. No reactivity was observed at lower weight ratios or lower temperatures.

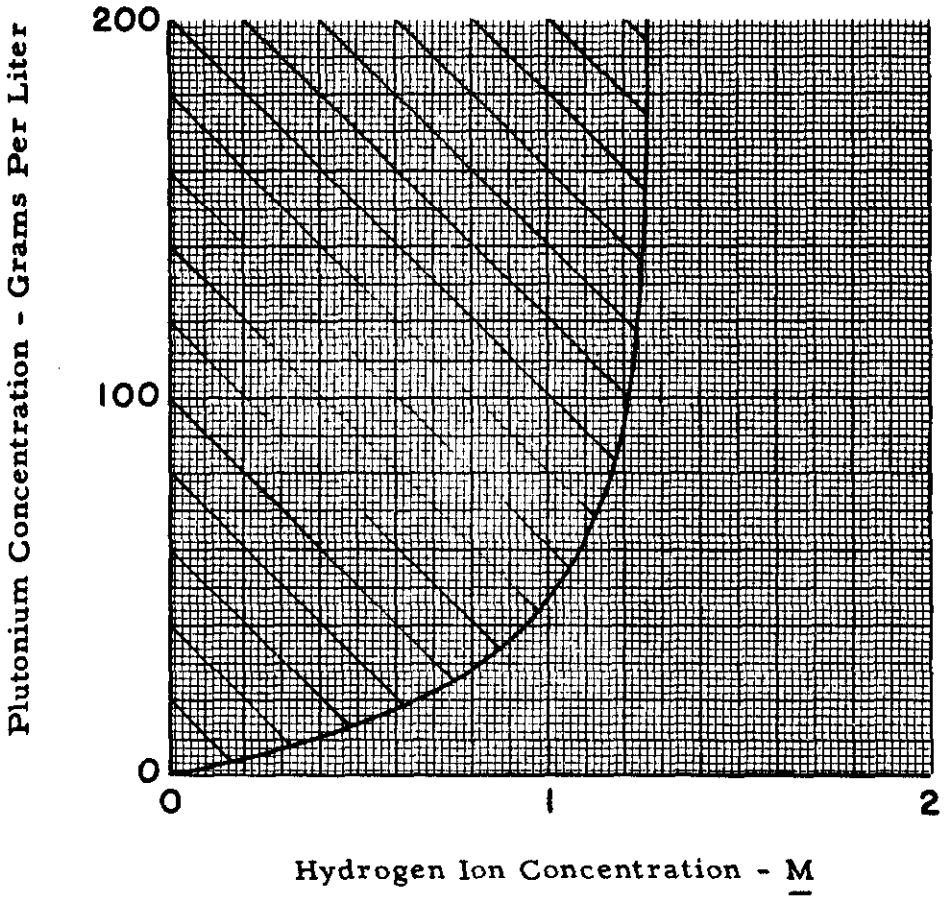

FIGURE ~~X~~ B-1-4

REGION OF POLYMER FORMATION

B. Concentration

2. Ion Exchange

Plutonium concentration by ion exchange has been found satisfactory in several processes. It is now used at the Savannah River Plant in concentrating Purex 2BP to yield a satisfactory feed for the peroxide precipitation (see flowsheet in Figure B-2-1).

Using a Dowex 50 cation exchange resin, Purex process feeds ranging from 0.2 g/l to 4.0 g/l Pu have been concentrated to 40 g/l and further purified. The process consists of three main steps: (1) adsorption of the plutonium (along with other positive ions), reduced to the +3 state from Purex 2BP; (2) elution of uranium, if necessary; and (3) elution of the major portion of the plutonium.

a. Adsorption

In the adsorption step, Purex 2BP feed material is passed through the resin column in a downflow direction at flow rates ranging from 0.4 to 15 ml/min-cm^2, depending upon feed concentration and waste losses acceptable. Purex 2BP feed material may range in plutonium concentration from 0.2 g/l to 4.2 g/l and is adjusted in acidity between 0.2 M and 0.4 M. Waste losses commonly run from 10^{-3} to 10^{-1} per cent; under ideal conditions, 10^{-4} per cent may be obtained.

b. Valence Adjustment and Adsorption Coefficients

The adsorption coefficient ($= \frac{\text{grams of plutonium per gram of resin}}{\text{grams of plutonium per gram of solution}}$) for Pu(III) and Pu(IV) are 4.3×10^3 and 2.6×10^4, respectively. Despite the higher adsorption coefficient of Pu(IV), it is desirable to keep the plutonium in the Pu(III) oxidation state

throughout the resin cycle, for these reasons: (1) one-fourth less resin is required; (2) Pu(III) is more easily eluted; and (3) Pu(III) complexes less with the sulfate ion, resulting in lower plutonium losses during the uranium elution.

c. Uranium Elution

The uranium elution is made with 0.25 M sulfuric acid, which also contains 0.05 M hydroxylamine sulfate as a holding reductant for the Pu(III). The elution is made in a downflow direction.

The higher adsorption coefficient for Pu(III) (4.3×10^3 compared to 1×10^2 for U(VI)), combined with the sulfate-complexing characteristics of uranium, allows an excellent separation of uranium from plutonium. Separation factors, depending upon the flow rate and decontamination required, range from 150 to 900, with plutonium losses from 10^{-4} per cent to 10^{-3} per cent.

d. Plutonium Elution

The plutonium elution is routinely made with a solution containing 6 M nitric acid and 0.05 M sulfamic acid, in an upflow direction. Several other elutriating agents have been used. Table B-2-I lists these and their characteristics.

To obtain a plutonium concentration of 40 g/l, the nitric acid concentration must be approximately 6 M and the flow rate from 0.22 to 0.30 ml/min-cm^2, depending upon the length of the plutonium band. Elution in the upflow direction also contributes to a higher plutonium concentration. The sulfamic acid prevents oxidation of the Pu(III) by nitric acid, which would result in evolution of heat and violent gassing. The eluate is split into

three fractions: the first contains one resin bed displacement volume and very little plutonium; the second is the desired product; and the third contains one resin bed displacement volume of reconditioning wash with a little plutonium. The first and third fractions are recycled, and a heel of approximately ten per cent of the original plutonium is left on the resin.

e. Resin Column Cleanup

After a number of cycles, fission product accumulation on the resin must be removed if column shielding is to be avoided. This is accomplished by first eluting the plutonium heel with nitric acid-sulfamic acid and then washing the resin with 2 1/2 volume changes of 0.5 M oxalic acid. This decreases the contamination by a factor of ca ten. If further decontamination is desired, 2 M ammonium citrate may be used. In either case, the column should be reconditioned with 0.1 M nitric acid before another adsorption step.

f. Decontamination by Ion Exchange

Decontamination is accomplished in all three steps of the plutonium concentration cycle. During the adsorption, approximately 40 per cent of the ruthenium originally in the feed remains with the effluent. In the second step, small amounts of ruthenium and rare earths are eluted with the uranium. In the third step, some radiochemical contaminates are left on the column when the plutonium is removed. Table B-2-II records the radiochemical decontamination expected.

Although appreciable separation from ionic constituents are obtained, the separation factors are varied and are not, as yet, known reliably. Table B-2-III shows the range of factors for several ions.

g. Pressure Drop

Pressure is usually necessary to maintain proper column flow rates. The following pressure drop equations were found valid for 50-100 mesh Dowex 50 with fines removed by hydraulic grading.

$\Delta p = 0.33\ F_a L$ $\qquad$ F_a = ml/min-cm^2

$\Delta p = 0.023\ F_b L$ $\qquad$ where $\qquad$ F_b = gal/hr - ft^2

$\Delta p = 0.064\ \frac{F_c L}{d^2}$ $\qquad$ F_c = ml/min
d = ID of column, inches
L = length of bed, feet

For 20-50 mesh Dowex, the pressure drop is significantly lower.

$$\Delta p = 0.021\ F_a L$$

$$\Delta p = 0.0014\ F_b L$$

$$\Delta p = 0.0040\ \frac{F_c L}{d^2}$$

h. Resin Excess

. A 2.3 fold excess of resin was found necessary to hold plutonium losses to 10^{-3} per cent or better with conditions and flow rates described in the Savannah River flowsheet (Figure B-2-1). Flow rate, hydrogen ion concentration, and impurities greatly affect the practical resin capacity; therefore, exact resin quantity must be determined for each process considered.

Figure B-2-1

FLOWSHEET FOR CONCENTRATION OF PLUTONIUM NITRATE SOLUTION BY ION EXCHANGE

(ORNL-1357, D. C. Overholt, F. W. Tober, D. A. Orth, "An Ion Exchange Process for Plutonium Isolation and Purification", p. 8A)

Table B-2-I

ALTERNATE ELUTING AGENTS FOR DOWEX 50

Agent	Molality	Flowrate	Plutonium Conc. 90% Removal	Charateristics
HNO_3 + NH_2SO_3H	5.7 0.3	0.26 ml/-min-cm^2	40-50 g/l	Standard Agent usually some gas evolution occurs
NH_4AC + H AC	2.0 0.4	0.35 ml/-min-cm^2	40-50 g/l	Eliminates gassing problems encountered with HNO_3
NH_4NO_3 + HNO_3	4.0 1.0	0.22 ml/-min-cm^2	40 g/l	Oxidation of Pu occurred
H_2SO_4	3.0	0.26 ml/0 min-cm^2	60 g/l	No gassing - unstable to ppt of Pu(III) sulfate causing plugging of lines
$(NH_4)_2SO_4$	1 and 2	0.30	40 g/l	NH_4 Pu $(SO_4)_2$ forms in the product solution

[redacted]

Table B-2-II

B, γ DECONTAMINATION

Reference	Total β	Total γ	Ru	Zr	Nb	$UX_1 + UX_2$
	7	3.9	11	6.7	1.5	4.5
ORNL-1357	3	2.3	6.9	2.3	7.5	3.1
	16	4.0	4.2	36.6	35	15.5
Average	8.6	3.4	7.4	15.2	14.7	7.7
	4.9	3.7	3.0	5	9.4	
HW-30063	2.9	3.4	2.8	10.6	129 ?	
			8.0	10.3	14.8	
Average	3.9	3.5	4.6	8.6	?	
ORNL-1449						
Average of 6 examples	2.9	6.8	2.0	26.5	8.4	5.1

[redacted]

Table B-2-III

IONIC SEPARATION FACTORS

Ion	Range	Reference
Fe	0 to 195	ORNL-1357 and ORNL-1520
Cr	0 to 18	ORNL-1357 and ORNL-1520
Ni	1 to 6.7	ORNL-1357 and ORNL-1520
Mn	0 to 32	ORNL-1357 and ORNL-1520
Al	1 to 22	ORNL-1357 and ORNL-1520
Pb	0 to 5.5	ORNL-1357 and ORNL-1520
Cu	7 to 65	ORNL-1357 and ORNL-1520
U	2 to 1000	ORNL-1357 and ORNL-1520
PO_4	Very High	ORNL-1357 and ORNL-1520
Ca	1 to 44	ORNL-1357 and ORNL-1520

B. Concentration

3. Reflux Flowsheet

C. Conversion - Wet to Dry Chemistry

Three precipitation processes have been used in the manufacture of starting materials for the preparation of plutonium(IV) fluoride: The plutonium peroxide and plutonium(IV) oxalate processes, which are currently in use; and the plutonium(III) oxalate process, which was discarded in favor of one or the other of the first two. These processes, along with others which have been tested in the laboratory, are described below.

1. Plutonium Peroxide Precipitation

a. Precipitation Conditions

Plutonium peroxide has been precipitated satisfactorily from feed solutions containing 10 to 100 g/l Pu (any valence; hexavalent and trivalent plutonium are converted to the tetravalent state by hydrogen peroxide, making a separate valence adjustment step unnecessary), 1.5 to 6 M HNO_3, and large concentrations of other metallic ions (e.g., 60 g/l lanthanum, in product solution from the bismuth phosphate separations process). A flowsheet for precipitation from a typical feed solution is shown in Figure C-1-1.

The composition of the compound varies widely with precipitation conditions. It usually contains about three peroxide-oxygen atoms per plutonium atom and indefinite amounts of nitrate, sulfate, hydroxide, oxide, and water.

The solid may precipitate as either a hexagonal crystal, in large, easily filtered particles, or as a cubic crystal, in fine particles. The hexagonal form is produced by the addition

of sulfate, the use of a strike temperature above 30 C, or precipitation with enough acid present to give a slurry acidity of 2.5 M or more. Generally, since H_2O_2 is unstable and the use of a low temperature is desirable to reduce its decomposition rate, sulfate is added to give the desired crystal form.

The precipitation is made by the addition of enough 30 to 50 per cent hydrogen peroxide to yield a final slurry concentration of eight to twelve per cent, or about 3 M. A strike temperature below room temperature is desirable for feeds containing more than one g/l iron (which catalyzes H_2O_2 decomposition). Laboratory precipitations have been made with good results at temperatures up to 50 C, from feeds containing little iron.

Addition of the hydrogen peroxide should be done slowly (one-half hour or longer) to prevent the formation of a finely divided precipitate. The digestion period required varies from a few minutes for pure feed and elevated strike temperatures to two hours for feed containing gross quantities of metallic impurities.

Final slurry acidities between one and three M are optimum. At lower acidities, precipitate particle size tends to be small, and separation of certain elements such as uranium, vanadium, thorium, and zirconium is less efficient. At higher acidities, solubility increases rapidly and is more or less complete above 6 M.

Most cationic impurities have little effect on plutonium peroxide precipitations up to mole ratios of impurities to

plutonium of about five, except that the separation of some impurities may not be adequate at these high levels (Table C-1-I). Elements which form peroxides, such as uranium and thorium, or strong peroxy complexes, such as zirconium, titanium, cerium, vanadium, and manganese, are exceptions. The permissible concentrations of such elements vary from one to five grams per liter. High acid strikes will prevent co-precipitation of uranium and thorium and diminish the effect of complexing cations. Iron is detrimental only in that it catalyzes decomposition of the hydrogen peroxide.

Anionic impurities which form strong plutonium complexes, such as fluoride, phosphate, and oxalate (except sulfate) increase solubilities and give poorly formed precipitates. The effect of fluoride may be alleviated to some extent by the addition of aluminum.

The relative effect, upon solubility of plutonium peroxide, of variations in precipitation conditions is shown in Table C-1-II.

b. Cake Properties

The bulk density of plutonium peroxide filter cakes, as freshly precipitated, varies from 0.1 to 0.6 g/cc Pu. The coarser precipitates can be retained by sintered filter media of 60 micron average pore size, while 30 micron pore size media are necessary for the finely divided precipitates.

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c. Dissolution

Plutonium peroxide dissolves readily in nitric acid above six molar. Small batches may require some heating, but in larger batches, the heat of reaction is sufficient in some cases to heat the solution to boiling with much foaming. Plutonium solutions as low as 1.0 M in nitric acid or as high as 500 grams per liter plutonium may be obtained by adjustment of the dissolving acid concentration and volume. The minimum acid required for complete dissolution is about four moles per mole, using 72 per cent nitric acid.

Figure C-1-1

TYPICAL FLOWSHEET FOR PRECIPITATION OF PLUTONIUM PEROXIDE

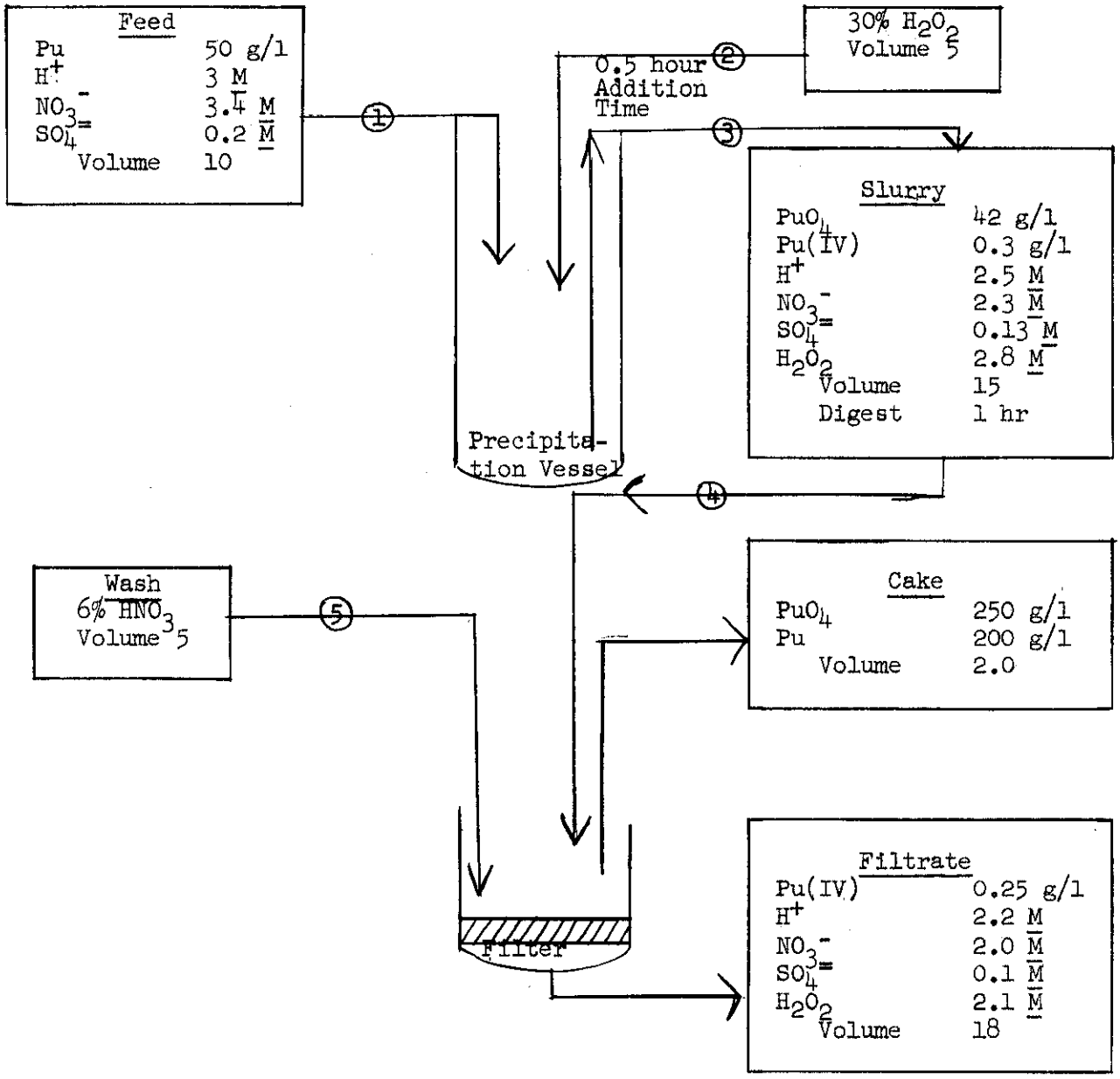

Table C-1-I

TYPICAL SEPARATION FACTORS FOR PRECIPITATION OF PLUTONIUM PEROXIDE
(100,000 parts contaminant per 10^6 parts plutonium)

Element	Separation Factor
Al	1,000
Be	10,000
Ca	1,000
Co	500
Cr	200
Fe	100
K	1,000
La	1,000
Mg	1,000
Mn	50
Ni	200
U	100
U (Slurry 1 M H^+)	10
Zr	50
Ru (2×10^4 c/m/ml)	4
Zr-Nb (1×10^5 c/m/ml)	4

Table C-1-II

TYPICAL SOLUBILITIES OF PLUTONIUM PEROXIDE

Conditions, except as noted in table: 10 per cent H_2O_2; 0.25 M $SO_4^{=}$; 2 M HNO_3; 25 C; Pu(IV) in feed; digestion time, two hours.

Conditions	Solubility, g/l
Digestion - 4 hours	0.01
Peroxide concentration 5 per cent, digestion 4 hours	0.06
Peroxide concentration 1 per cent, digestion 4 hours	0.7
Acidity 1 M	0.05
Acidity 4 M	1.0
Digestion 18 hours	0.003
Sulfate absent	0.2
Sulfate absent, strike temperature 50 C, digestion 1/2 hour	0.6
Iron 1 g/l	1.0
Iron 1 g/l, strike temperature 15 C	0.1
Fluoride 1 g/l	2.0
Lanthanum 50 g/l, potassium 10 g/l	0.5

C. Conversion - Wet to Dry Chemistry

2. Plutonium(IV) Oxalate

a. Precipitation Conditions

A typical flowsheet for the precipitation of plutonium(IV) oxalate is shown in Figure C-2-1.

The compound has been precipitated satisfactorily from solutions containing from one to 300 g/l plutonium and enough acid to make the final slurry 1.5 to 4.5 molar in nitric acid. At acidities below 1.5 molar, the co-precipitation of impurities is favored, and the precipitate is too finely divided for rapid settling or filtration. At slurry acidities above 4.5 molar, plutonium(IV) oxalate solubility (Figure C-2-2) is high and the precipitate is thixotropic.

The hydrogen peroxide is added for valence adjustment, either before or during the oxalic acid addition, at a rate governed by the extent to which foaming occurs. The valence adjustment, which may produce plutonium(III) as an intermediate, is rapid at 50C; but at lower temperatures it may be prohibitively slow for solutions which contain less than 30 g/l plutonium and are devoid of impurities which catalyze the decomposition of hydrogen peroxide.

Equilibrium solubilities of plutonium(IV) oxalate are much lower than those obtained in the usual quick precipitation process. They vary both with acidity and with free oxalic acid concentration (Figure C-2-2), the best range for the latter being 0.05 to 0.15 molar, depending on the purity of the solution (the presence of oxalate - complexing

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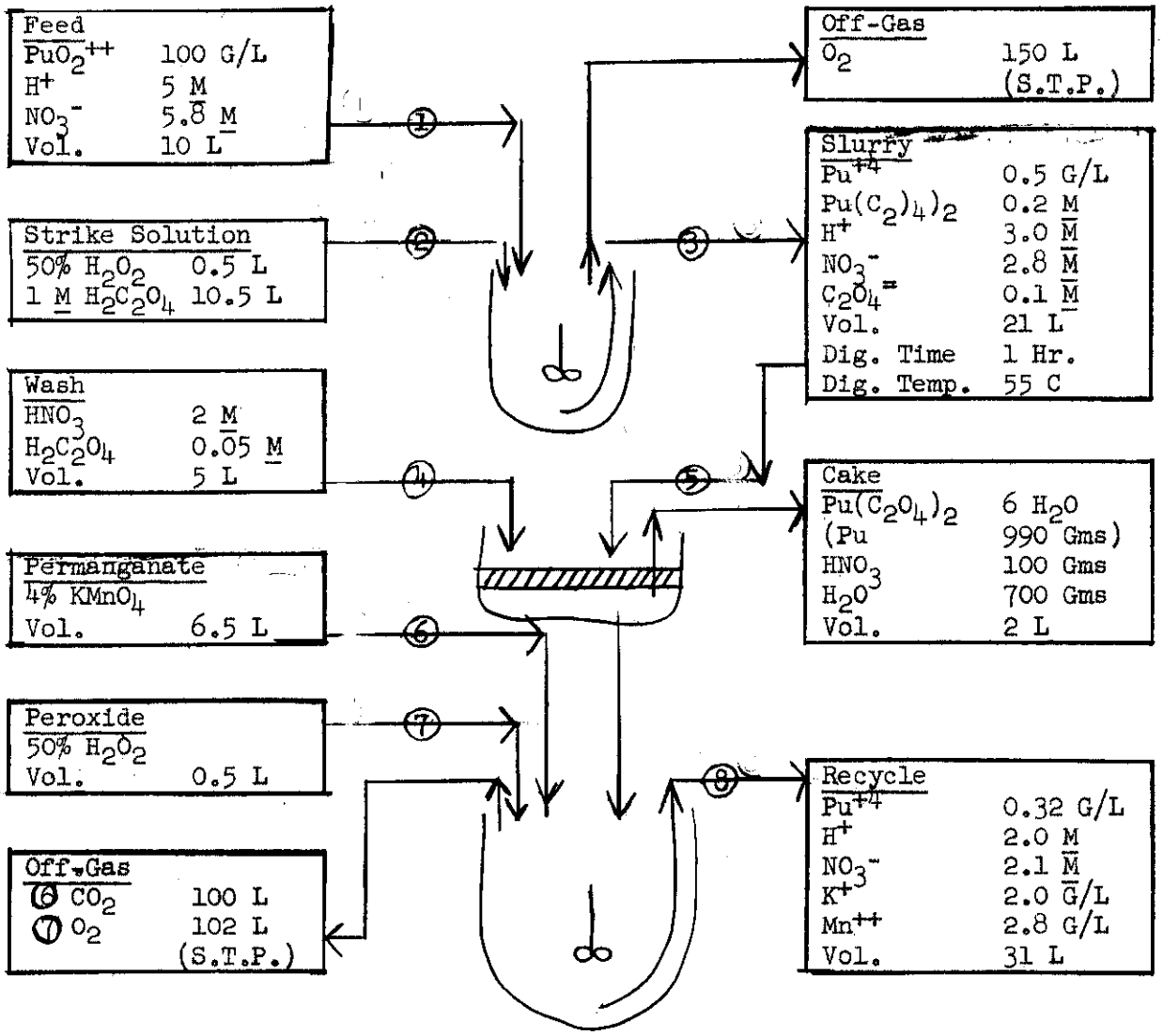
Figure C-2-1

TYPICAL PLUTONIUM(IV) OXALATE FLOWSHEET



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-9-b-

FIGURE C-2-2

SOLUBILITY OF Pu(IV) OXALATE

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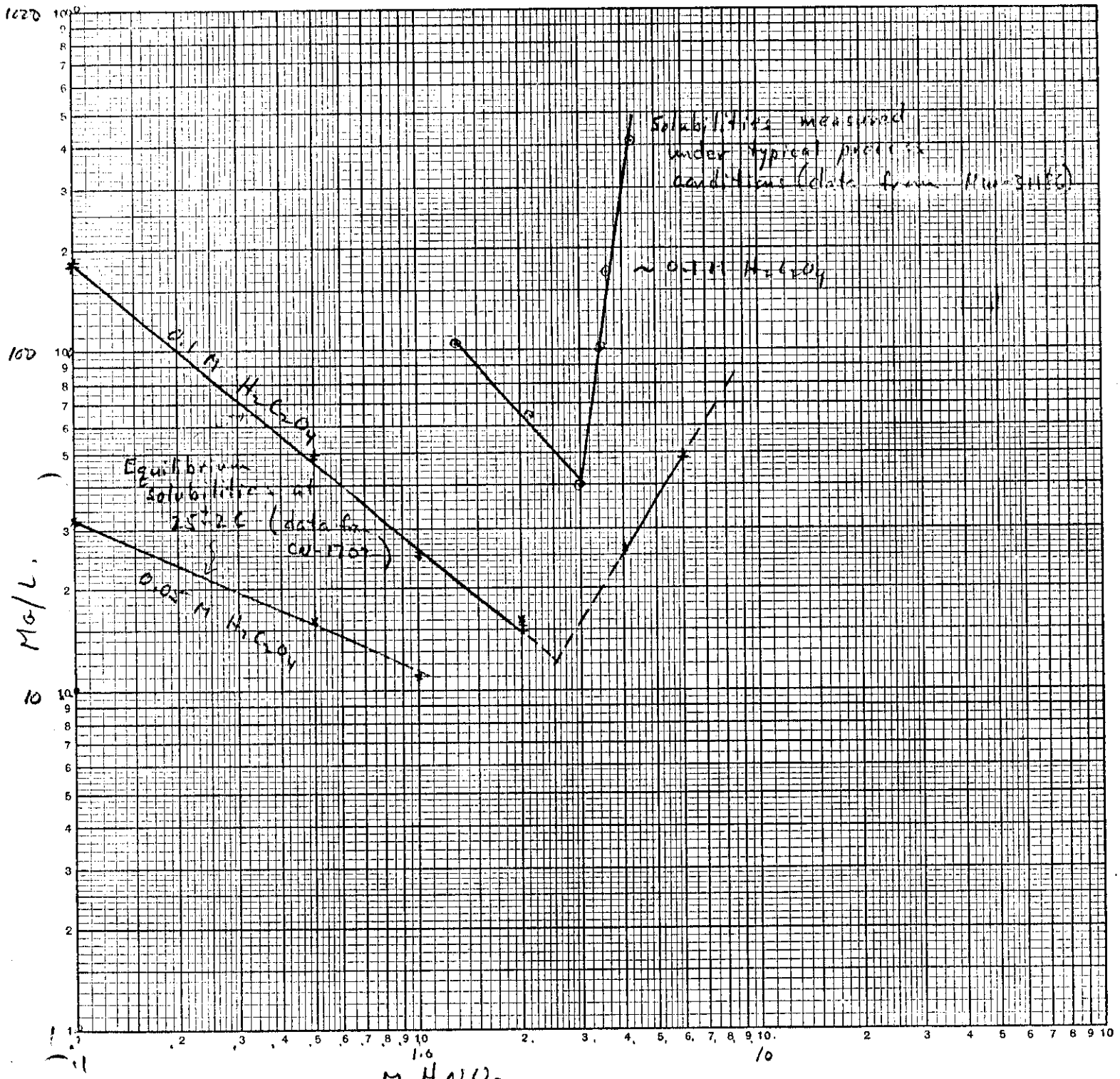

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a. Precipitation Conditions (continued)

cations in appreciable concentration requires a larger excess of oxalic acid). Solubilities are also dependent upon slurry temperature, measured values in one case increasing from about 0.05 g/l Pu at 25 C to ca 0.06 g/l Pu at 50 C and 0.4-1.16 g/l Pu at 75 C.

The best precipitations appear to occur at a temperature of 50 to 60 C, with the oxalic acid addition spread over a time of 10 to 60 minutes, depending upon the agitation and slurry volume. Too rapid an addition or too low a temperature may produce a finely divided, hard-to-filter precipitate. Temperatures above 60 C have been found to produce a gummy precipitate.

b. Continuous Precipitation

A process for the continuous precipitation and filtration of plutonium(IV) oxalate has been demonstrated at HAPO, with a plant-scale, laboratory unit. The precipitation is carried out, at room temperature, by continuously and simultaneously metering plutonium(IV) nitrate solution (the plutonium is pre-reduced with H_2O_2) and oxalic acid solution into a vessel containing an agitated plutonium(IV) oxalate slurry. The slurry for start-up is prepared by making a batch strike, of the required volume, at room temperature. Once the process is running, the slurry is allowed to overflow to a continuous filter. (A drum filter, with a Dynel, D-2000 filter cloth, was used in these studies.) The cake is washed on the filter and then dropped directly into a drier-calciner for the start of the dry chemistry operation. Chemically, the process is much the same as the batch process described above,

using the same feed and reagent compositions and achieving the same product purity and yield.

c. Separation Factors

Decontamination factors have been measured for plutonium(IV) oxalate precipitations as follows: 3 to 6 for Zr, Nb; 12 for Ru; 1 for Am; 1 for UX_1 (thorium). Separation factors for bulk contaminants (100,000 parts impurity per million parts plutonium) averaged about 100 for aluminum, chromium, and nickel, and about 60 for uranium.

3. Plutonium(III) Oxalate, $Pu_2(C_2O_4)_3 \cdot 9\ H_2O$

Plutonium(III) oxalate is a blue green solid with a low solubility (mg/l Pu = $3.24\ (H^+)^3\ (H_2C_2O_4)^{-3/2}$) and the desirable property that it settles rapidly and is easy to filter. The compound may be precipitated at room temperature from any acid plutonium(III) solution containing one or more grams of plutonium per liter and not more than 4 molar acid. Oxalic acid is added as either a solution or a solid, as rapidly as desired, with a digestion period of about one-half hour.

Hydriodic acid has been used extensively as a reducing agent in the plutonium(III) oxalate process, with resulting handling and corrosion problems. The lack of a suitable alternate to HI was a major factor in the process being dropped in favor of the precipitation of plutonium peroxide or plutonium(IV) oxalate.

The Los Alamos Scientific Laboratory has developed a plutonium(III) oxalate process in which the compound is precipitated from the product

3. Plutonium(III) Oxalate (continued)

stream from a tributyl phosphate solvent extraction process for plutonium recovery. The plutonium stream contains 5 to 15 g/l plutonium(III) (0.1N hydroxylamine nitrate is used as the solvent stripping solution) and about 0.1N HNO_3. The average plutonium concentration in the combined filtrates and washes is 20 mg/liter.

4. Development Conversion

Laboratory attempts have been made to simplify the conversion and dry chemistry processes. Direct calcination of plutonium nitrate has been tried only on a small scale, with unfavorable results: the nitrate spattered, and the resultant oxide was difficult to hydrofluorinate.

a. Precipitation of $CaPuF_6$

The most successful process thus far has been the precipitation of calcium plutonium(IV) fluoride, several batches of which have been dried in argon or nitrogen, to give a compound which was successfully reduced to plutonium metal. A possible flowsheet for this process is shown in Figure C-4-1.

The laboratory results indicated that to assure control of

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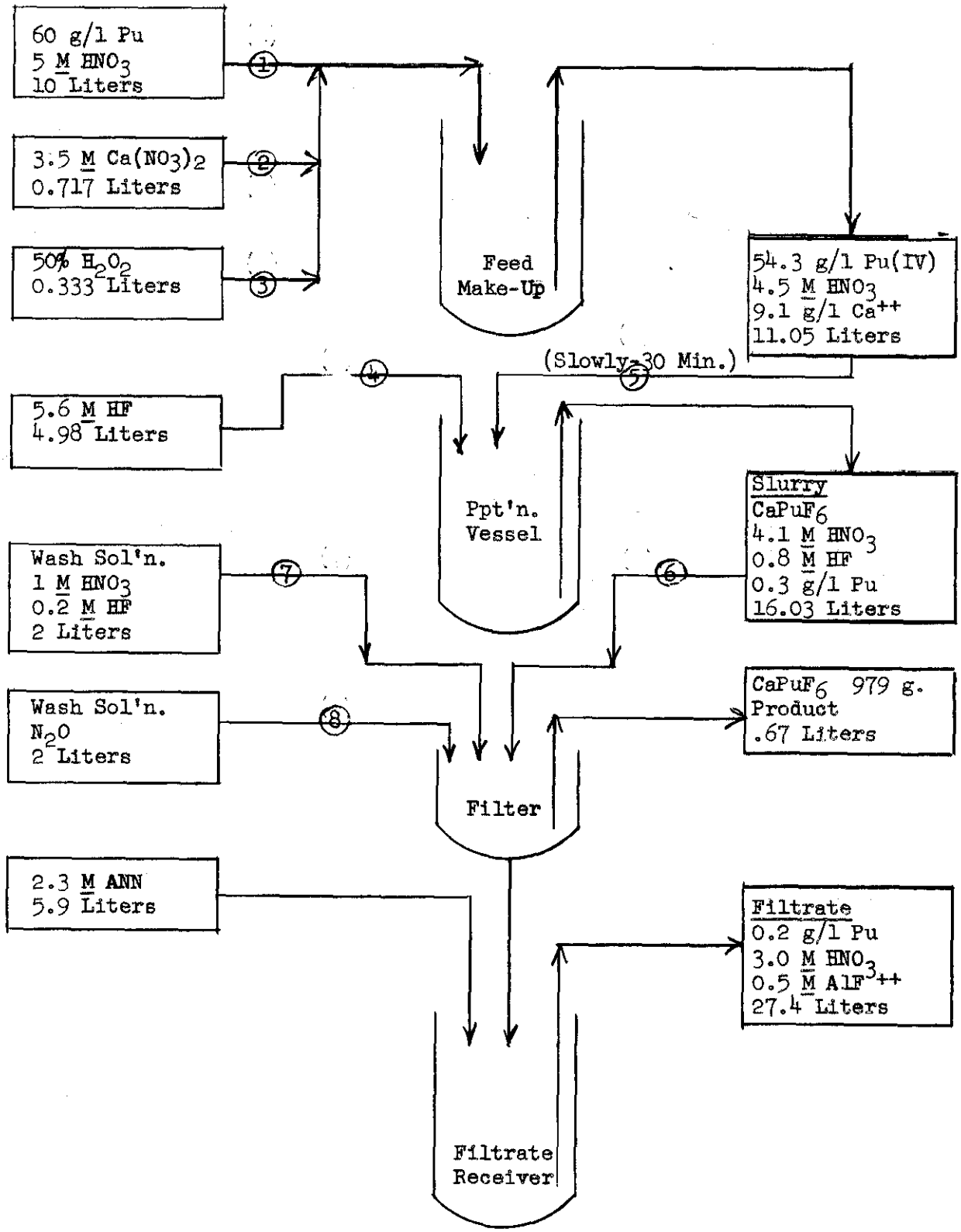
FIGURE C-4-1
TYPICAL FLOWSHEET FOR PRECIPITATION OF $CaPuF_6$



a. Precipitation of $CaPuF_6$ (Continued)

the precipitate composition and easy filterability, (1) the feed should contain equi-molal concentrations of plutonium and calcium; and (2) the feed should be added slowly to 6 M or less HF solution. The precipitation gave little or no separation from aluminum, iron, chromium, nickel, or lanthanum; separation factors of 80 to 200 for uranium; and a decontamination factor of 3.5 for Zr-Nb.

b. Precipitation of PuF_3

Most attempts to precipitate the simple plutonium fluorides (PuF_3 and PuF_4) have given precipitates which were difficult to wash without peptizing and which were difficult to separate from the supernatants. Recent work at Savannah River, however, has shown that plutonium(III) fluorides can be precipitated in an easily-filtered crystalline form from fresh resin column effluent. Precipitation of the trifluoride has two attractive advantages: 1) it can be readily dried and reduced to the metal without a high temperature fluorination step; and 2) conditions can be adjusted such that waste losses to the filtrate will probably be low enough that the filtrate can be discarded. On the other hand, the process does not give very good separation from some impurities, such as aluminum.

Feed to the trifluoride process must be plutonium(III), which can be obtained from several sources. At the Savannah River Plant, the feed solution is the ion exchange column effluent (50 g/l Pu, 5.7 M HNO_3) with plutonium already in the trivalent state. Plutonium produced from Hanford Purex or Redox processes can be reduced to the trivalent state and provides a satisfactory feed if purity is sufficiently high. Several methods can be

used to reduce plutonium(IV) to plutonium(III) in these separation plant product streams. A solution of 35 g/l Pu in 0.2 M sulfamic acid is completely reduced by 0.1 M ascorbic acid. At acid concentrations greater than 5 M HNO_3, the instability of the plutonium(III) increases sharply even in the presence of holding agents, and prevents the reduction. Plutonium may also be reduced by sulfur dioxide gas.

Savannah River has reported two procedures for precipitating plutonium trifluoride from ion exchange column effluent (50 g/l Pu, 5.7 HNO_3). In one case, 2.7 M HF is added over a thirty minute period to an equal volume of feed solution at a temperature of 40 C or higher. In the second method, equal volumes of 2.7 M HF and feed solution at 25 C are added simultaneously over a thirty-minute period to one-half volume of 0.1 M HNO_3. Vigorous agitation is quite important. Both methods are followed by a thirty-minute digestion and both methods result in readily filterable precipitates, although the second method results in larger crystal size. After filtration, the precipitate is washed with 0.8 M HF to prevent oxidation. Two alcohol washes (optional) and aspiration at room temperature are employed to dry the cake. The precipitate can be made anhydrous by passing helium at 200 C over the cake for several hours or drying at 600 C for one-half hour. The latter procedure results in a material with less than 0.2 per cent water.

Development of a continuous trifluoride precipitation process is under way at Hanford. Feed has been prepared both by the ascorbic-sulfamic acid and by the sulfur dioxide-sulfamic acid reductions. A typical feed composition was 35 g/l Pu and 3.5 to 5 M HNO_3, and 3 M HF was used as precipitant. The two streams were fed into a vigorously agitated reactor and the slurry drawn

[redacted]

off through a filter. With a 1 M HF excess in the reactor and a 15 to 20 minute slurry residence time, a good precipitate is obtained and the filtrate losses are expected to be less than 50 mg/l. Early data indicates separation factors across the process of greater than 10 for iron, 20 for nickel, 10 for chromium, and four for magnesium.

Rocky Flats has produced coarse crystalline precipitates of plutonium trifluoride from hydrochloric acid solutions containing 50 g/l Pu, with filtrate losses of around 16 mg/l (0.05 per cent).

D. Dry Chemistry

Plutonium(IV) oxide and the anhydrous halides are the compounds of chief interest in the dry chemistry operations associated with the production of plutonium metal: the oxide, because it is frequently an intermediate; and the halides, because they can readily be reduced to the metal. Methods of preparation and properties of the most important of these compounds are described in the following section (see, also, Tables A-III

[redacted]

and A-IV).

1. Plutonium(IV) Oxide

Plutonium dioxide may be produced by the calcination of many compounds, including the oxalates, the peroxide, and the nitrate. A final temperature of 900 C is necessary to produce a constant-weight oxide (PuO_2), but essentially complete conversion has been reported at the following temperatures: for plutonium(III) and (IV) oxalates, 300 C; for the peroxide, 150 C; and for the nitrate, 230 C. The reactivity of plutonium(IV) oxide is dependent upon its source and upon the conditions of calcination. Denitration of the nitrate usually produces pellets of refractory oxide which are difficult to convert to other compounds. Thermal decomposition of the (III) and (IV) oxalates is accomplished by means of a gradual transition in degree of crystallinity from nearly amorphous material at low temperatures to well crystallized PuO_2 at high temperatures, a transition which is accompanied by a loss of reactivity. As measured by optical properties, X-ray diffraction patterns, and dissolution experiments (measurement of the extent of dissolution of a sample of oxide in an HCl-KI solution), oxides ignited to temperatures below 700 C retain a high reactivity. Comparison of the hydrofluorination rates for oxides prepared at temperatures between 300 and 600 C (see Fig. D-1-1), however, has shown that heating the oxide prepared from an oxalate to a temperature greater than 480 C for as short a time as five minutes greatly reduces its reactivity. If not controlled, the oxalates may burn upon heating in air. A sudden rise in temperature of a powder batch, to a point 200-300 C higher than the furnace temperature has been observed.

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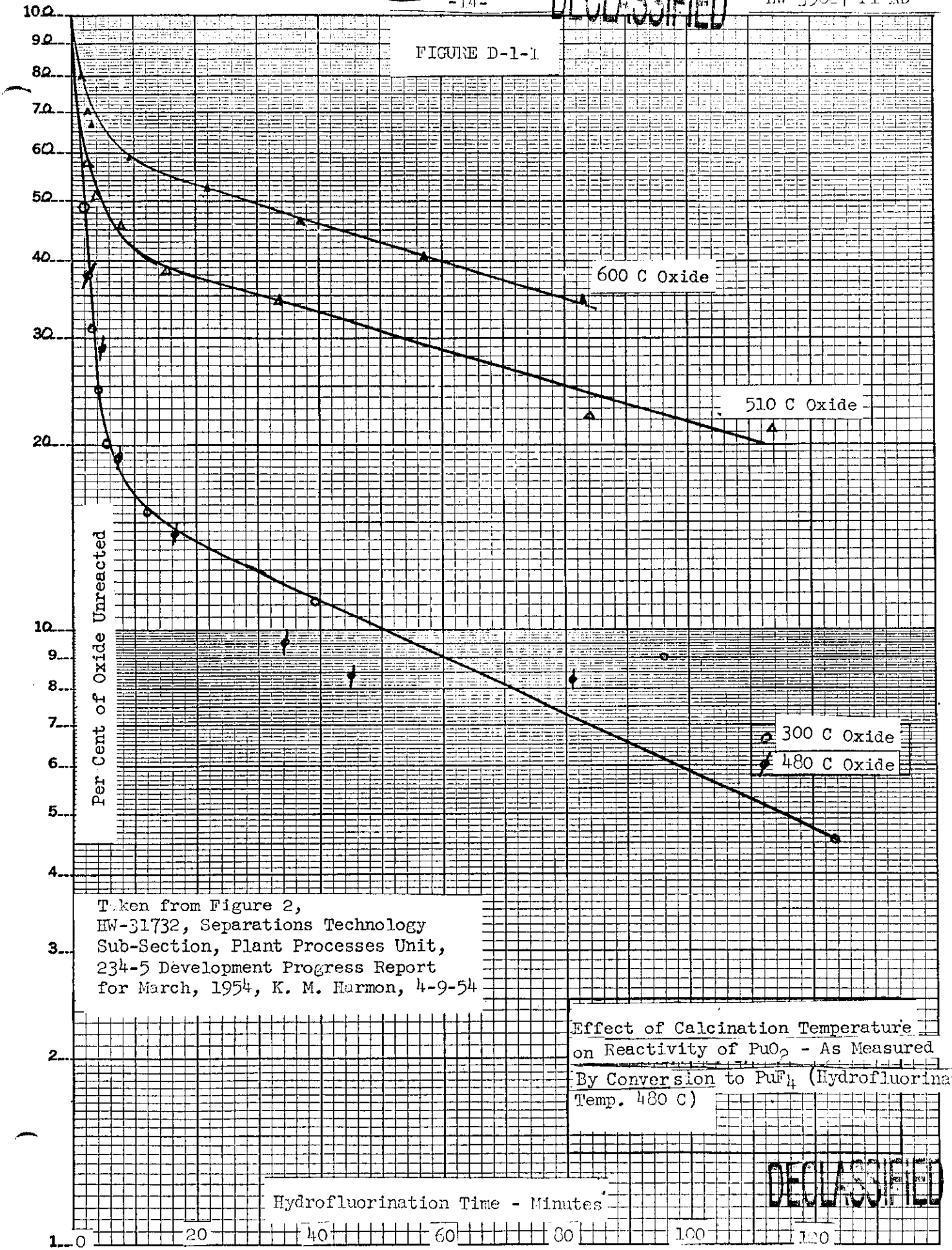
2. Plutonium(IV) Fluoride-PuF_4: Preparation with HF and O_2

a. Process

Plutonium(IV) fluoride may be produced by treating plutonium(IV) oxide, plutonium(III) or (IV) oxalate, plutonium peroxide, and other compounds with a mixture of anhydrous hydrogen fluoride and

FIGURE D-1-1



Taken from Figure 2,
HW-31732, Separations Technology
Sub-Section, Plant Processes Unit,
234-5 Development Progress Report
for March, 1954, K. M. Harmon, 4-9-54

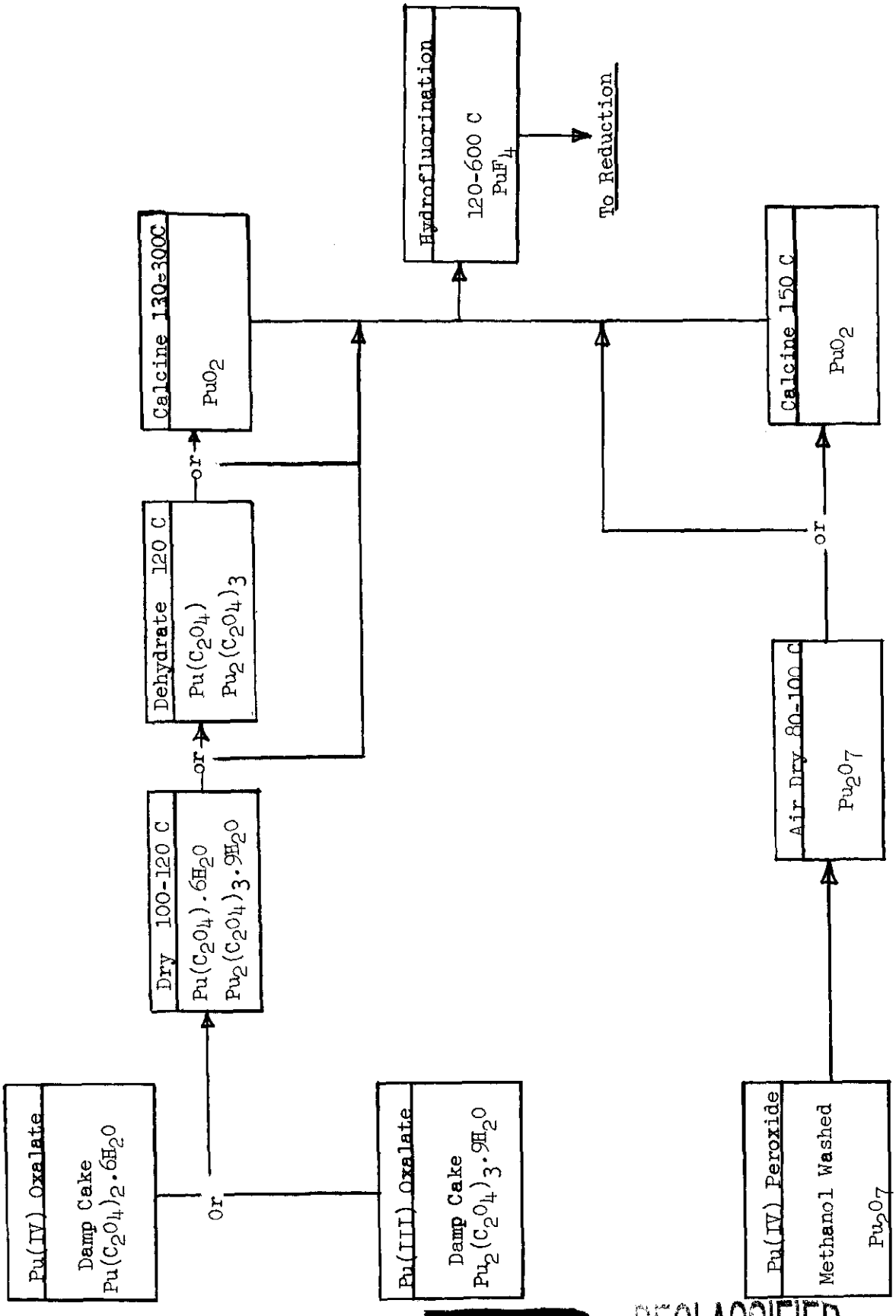
Effect of Calcination Temperature on Reactivity of PuO_2 - As Measured By Conversion to PuF_4 (Hydrofluorination Temp. 480 C)

oxygen (see Fig. D-2-1). The oxygen is used to prevent the formation of plutonium(III) fluoride by the action of the hydrogen which is normally found in commercial hydrogen fluoride. (Plutonium(III) fluoride, if formed, may be converted to the tetrafluoride by exposure to HF and O_2. The reaction rate increases with temperature and, up to 25 volume per cent, with oxygen concentration. For rapid conversion, the reaction temperature should at least equal the original hydrofluorination temperature.)

The hydrofluorination reaction is exothermic. With some compounds (e.g. the peroxide), the reaction will start at room temperature, but in order to obtain the anhydrous fluoride, the reaction temperature should be at least 400 C. Temperatures of 450 to 600 C are commonly used. Laboratory measurements of reaction rates, using thin powder layers, showed wide variations among samples from different batches of oxide and gave the principal conclusion that 1) if a distinct calcination step is carried out, the maximum temperature should be kept below 480 C, and 2) the hydrofluorination temperature should at least equal the calcination temperature. Hydrofluorination of oxides heated to temperatures greater than 600 C is frequently very slow.

At the conclusion of the hydrofluorination process, the powder is cooled to a temperature below 300 C before exposure to HF-free air, to prevent reaction with oxygen or water vapor.

FIGURE D-2-1



FLOW SHEET FOR HYDROFLUORINATION

b. Equipment - General

The commercial preparation of plutonium(IV) fluoride has, thus far, been carried out in batch equipment. A continuous hydrofluorination unit, however, has been under test since December, 1954, with excellent results.

The principal equipment problems are associated with the containing and handling of the gas streams, which are highly corrosive. The reaction chamber and the off-gas system, for instance, may be exposed to liquid or vapor containing water, hydrogen fluoride, oxygen, and nitric acid, at temperatures up to 600 C. The more common materials of construction include the noble metals, Hastelloy C, teflon, and fluorothene.

c. Batch Process

Figure D-2-2 shows 1) a typical furnace temperature schedule for the hydrofluorination of plutonium(IV) oxalate in a filter boat and 2) typical corresponding cake temperatures. For a given furnace cycle, the cake behavior may vary widely, being a function of moisture content, cake depth, and precipitate quality. As a result, the practice of starting HF flow at some definite time during the cycle rather than at a measured cake temperature may result, in some cases, in exposing a damp cake of oxalate to the HF and, in others, of not starting hydrofluorination until calcination is nearly complete. This, generally, is not important, although the variability may have a noticeable effect on fluoride quality where a short cycle (such as that

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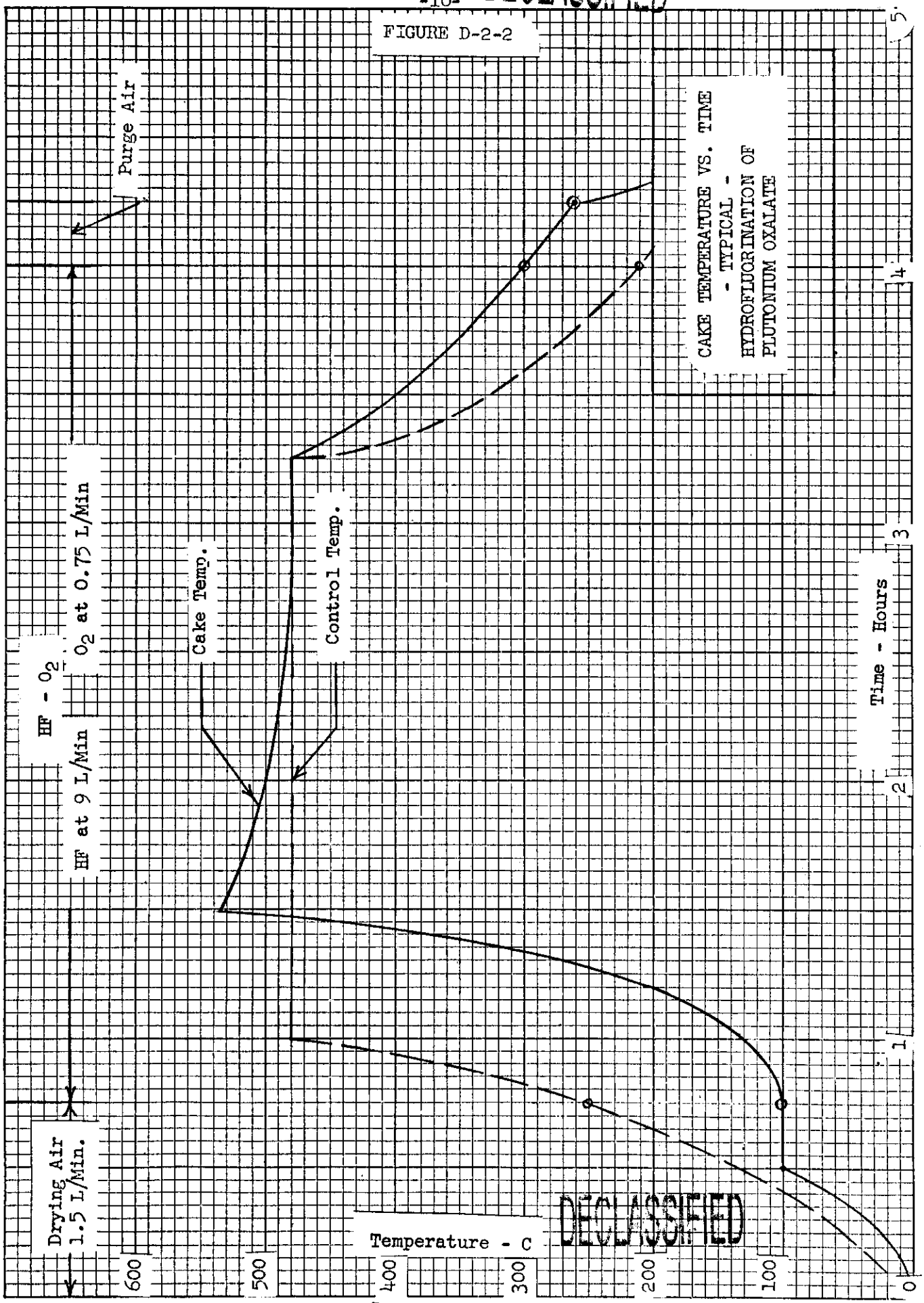
FIGURE D-2-2



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pictured) is employed. A denser fluoride is produced from plutonium(IV) oxide than from direct hydrofluorination of the oxalate.

Use of a porous-bottom boat, as a filter to collect the precipitate and as a reaction vessel which permits the reactant gases to be pulled through the cake, has given the shortest time-cycles. When a pan-type boat is employed, the reaction may be limited by slow diffusion of HF into the cake.

Figure D-2-3 shows the Time-Temperature diagram of a typical flowsheet for the direct hydrofluorination of plutonium peroxide. To prevent spattering and to give an easily-powdered fluoride, the peroxide precipitate is usually given an alcohol wash in the wet chemistry operation, and air dried at 75-80 C before the boat is brought to the hydrofluorination furnace.

The hydrofluorination cycle consists essentially of a low temperature hydrofluorination period ($\lesssim$180 C) and a high temperature period (500-600 C). Hydrofluorination is nearly complete during the low temperature part of the cycle. It is important that the peroxide cake not be allowed to decompose appreciably prior to hydrofluorination, because the decomposition product is not readily converted to the fluoride. If a high temperature oxide is formed, hydrofluorination at 600 C for several hours may be necessary.

d. Continuous Process Equipment

Processes for the continuous calcination of plutonium(IV) oxalate and hydrofluorination of plutonium(IV) oxide have been

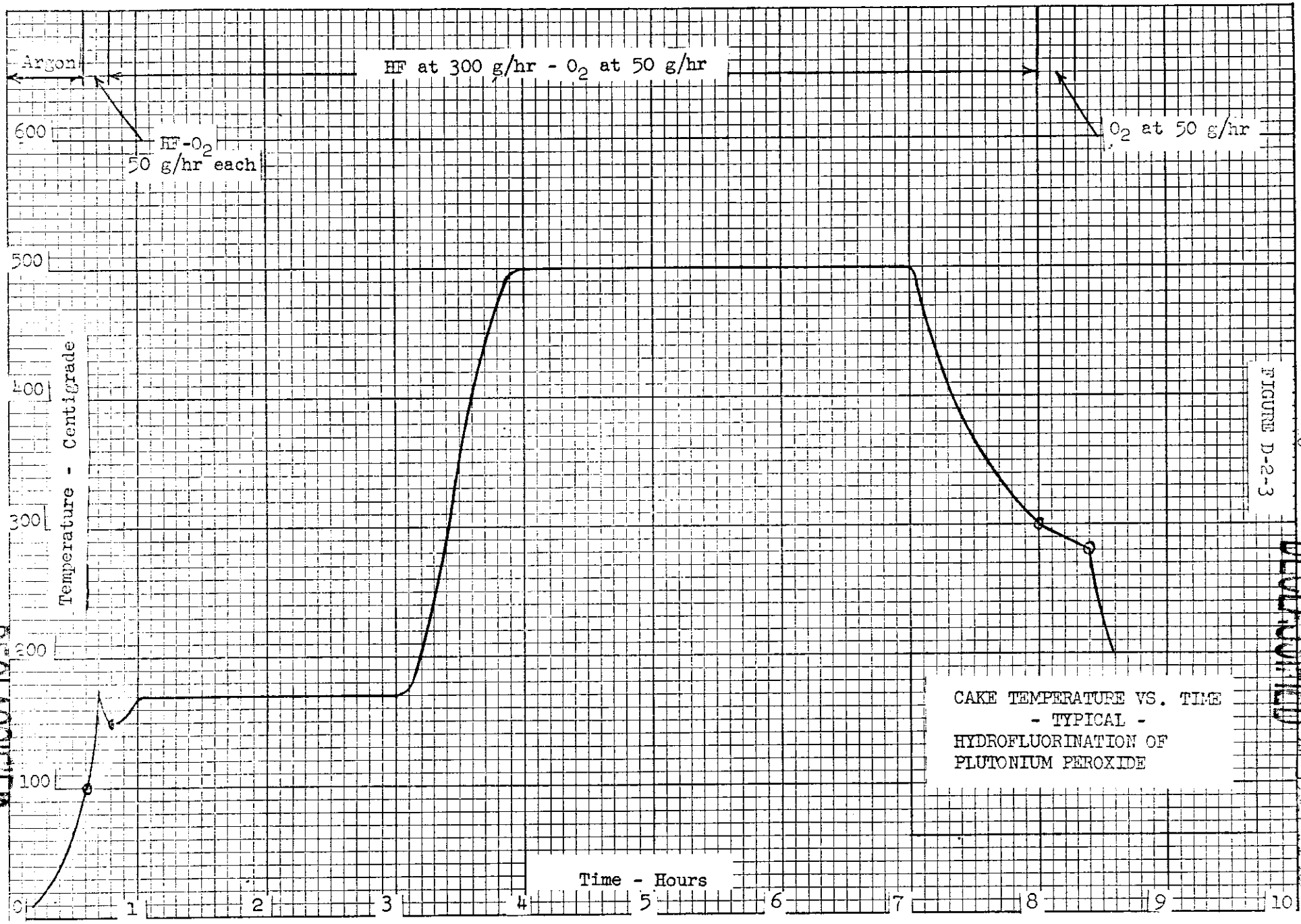


FIGURE D-2-3

CAKE TEMPERATURE VS. TIME
- TYPICAL -
HYDROFLUORINATION OF
PLUTONIUM PEROXIDE

demonstrated at HAPO. The calcination equipment consists of a stainless steel trough (heated from below by electric furnaces) containing a slowly rotating screw which drags the damp oxalate from the feed point, to the oxide hopper at the other end. An average residence time of 20 minutes, with the trough at 400 C, was found sufficient for calcination.

The continuous hydrofluorinator is illustrated in Figure D-2- 4. In this unit, an adjustable-speed screw-conveyor feeds the plutonium dioxide powder from a hopper into a two-inch, i. d., electrically-heated (to 500 C) reactor tube, eight feet long, which is isolated from the screw-conveyor assembly by a teflon bellows. Spring-mounted solenoids, one at each end, periodically vibrate the tube and cause the powder to flow through it and into a removable hopper. The powder residence time is controlled by the relative duration of the "on" and "off" vibration periods. A residence time of at least 45 minutes has been found necessary and is obtained in this equipment by "on" and "off" times of about 15 seconds and six minutes, respectively. Preheated hydrogen fluoride and oxygen are fed to the hydrofluorinator, counter-current to the flow of the powder bed.

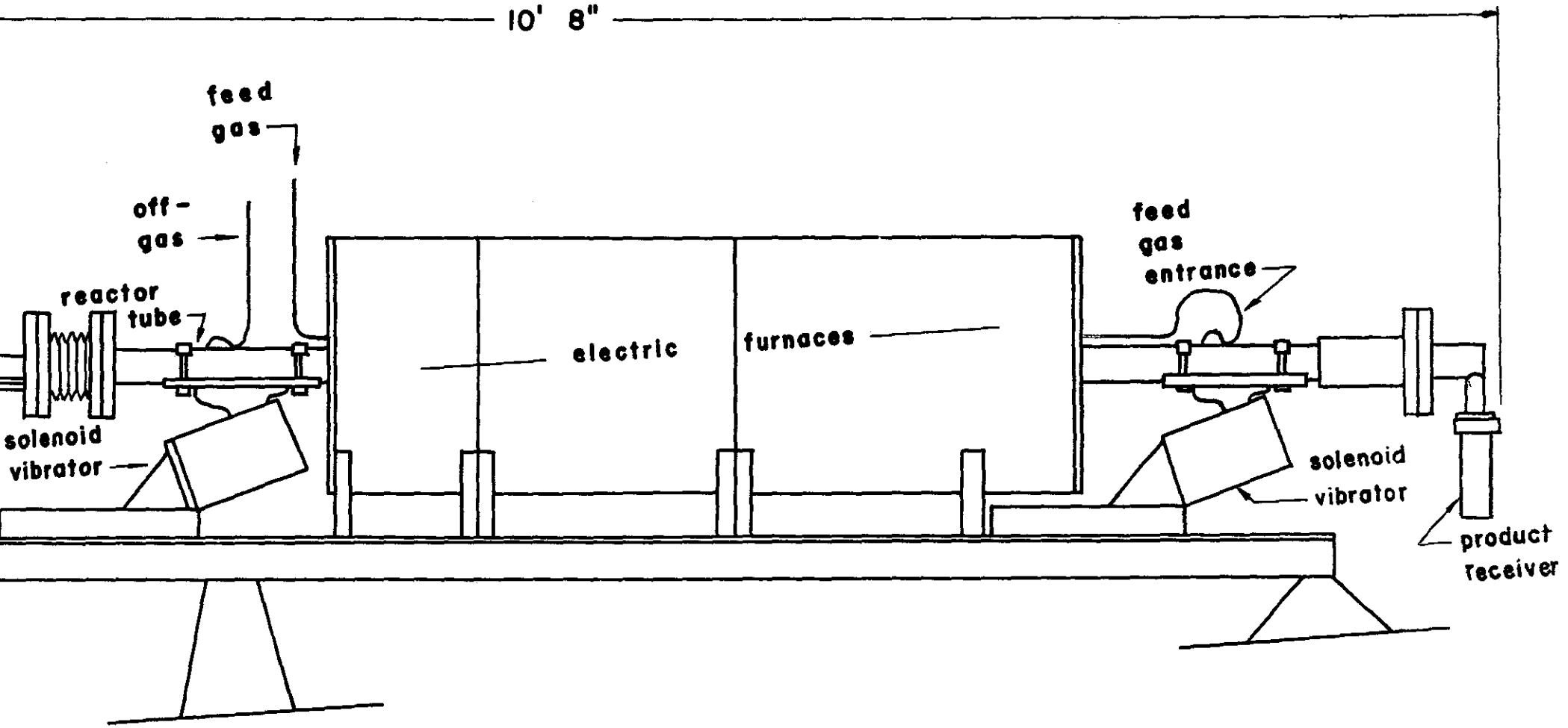
Attempts to directly hydrofluorinate the oxalate failed, as a result of solids caking in the reaction zone and oxalic acid, freed by metathesis, plugging the off-gas line.

3. Dry Chemistry Development

In the search for a dry chemistry process which could compete favorably with the preparation of plutonium(IV) fluoride by

FIGURE D-2-4

PROTOTYPE REACTOR



hydrofluorination, the following preparations have been studied in the laboratory:

a. Plutonium(III) Fluoride -PuF_3

Plutonium(III) fluoride may, of course, be prepared under the same conditions as are used for the tetrafluoride, with the substitution of hydrogen for oxygen. Another procedure which shows promise if the remaining problems can be solved makes use of the reaction between plutonium(IV) oxide or oxalate with Freon-12 (CCl_2F_2). Under well-controlled conditions, the reaction to form plutonium(III) fluoride (producing CO_2, phosgene, and chlorine as by-products) goes to completion in a few hours. The best results thus far reported were obtained with 1) plutonium(IV) oxide which had been prepared at a temperature below 300 C, 2) a reaction temperature of about 400 C, and 3) oxygen-free Freon -12 (the presence of traces of oxygen stops the reaction). The reaction is exothermic and, unless carefully controlled, may cause a sufficient temperature rise to sinter the powder bed and prevent further reaction. The Freon-12 is non-corrosive at temperatures up to ca. 600 C, but in some experiments was found to polymerize with the formation of a solid, teflon-like product.

b. Plutonium(IV) Fluoride: Preparation with Ammonium Bifluoride

Plutonium(IV) oxide prepared by the thermal decomposition of plutonium(IV) oxalate at temperatures below 400 C has been converted to plutonium(IV) fluoride, in the laboratory, by the following pair of reactions:

1) the preparation of ammonium plutonium(IV) fluoride, $2PuF_4.NH_4F$, by heating a mixture of plutonium(IV) oxide and ammonium bifluoride (40 per cent excess over stoichiometric) at a temperature in the range of 50 to 250 C. The reaction is exothermic and goes to completion even at 50 C.

2) thermal decomposition of the double salt in a gettered argon atmosphere, with the volatilization of ammonium fluoride. The reaction proceeds rapidly at 300 C, but a temperature in excess of 500 C was required to produce a fluoride which could be reduced without excessive pressurization of the reduction vessel and with the formation of satisfactory metal.

c. Plutonium(III) Chloride - $PuCl_3$

Plutonium(III) chloride has been prepared in good yield by the reaction of plutonium(IV) oxide (prepared at a temperature below 400 C) both with carbon tetrachloride vapor and with phosgene. Reaction temperatures for the CCl_4 reaction were 450-500 C and for the $COCl_2$ reaction, 300-400 C.

E. Metal Reduction

Plutonium metal may be prepared in the massive state by reducing any of several plutonium halides with an appropriate alkali or alkaline earth metal (see Table E-1 for a list of some of the possible reactions). In practice, plutonium(IV) fluoride is used, principally because it is non-hygroscopic and thus may be handled and stored without the danger of the water pick-up which must be guarded against with the use of the chlorides or bromides. Successful reductions of plutonium(IV) oxide have not yet been made, the chief difficulty being the high

TABLE E-I

POSSIBLE REACTIONS FOR THE PREPARATION OF PLUTONIUM METAL

REACTION		ΔH at 291°K, Kcal/mol Pu	M.p. of slag, °C	B.p. of slag at 760 mm, °C
$PuO_2 + 2\ Ca$	$Pu + 2\ CaO$	-52.4	2572	2850
$PuO_2 + 2\ Mg$	$Pu + 2\ MgO$	-40.5	2500-2800	3600
$PuO_2 + \frac{4}{3}\ Al$	$Pu + \frac{2}{3}\ Al_2O_3$	- 9	2050	2250
$PuF_4 + 4\ Li$	$Pu + 4\ LiF$	-159.2	870	1676
$PuF_4 + 2\ Sr$	$Pu + 2\ SrF_2$	-154.8	1190	--
$PuF_4 + 2\ Ba$	$Pu + 2\ BaF_2$	-152.4	1280	2137
$PuF_4 + 2\ Ca$	$Pu + 2\ CaF_2$	-149.5	1330	2500
$PuF_4 + 4\ Na$	$Pu + 4\ NaF$	-122.2	980-997(1040)	1700
$PuF_4 + 4\ K$	$Pu + 4\ KF$	-113.4	880	1500
$PuF_4 + 2\ Mg$	$Pu + 2\ MgF_2$	-104.6	1225(1396)	2260
$PuF_4 + \frac{4}{3}\ Al$	$Pu + \frac{2}{3}\ AlF_3$	- 15	1040	--
$PuF_2 + 3\ Li$	$Pu + 3\ LiF$	- 62.0	870	1676
$PuF_3 + Ca$	$Pu + CaF_2$	- 54.8	1330	2500
$PuF_3 + \frac{3}{2}\ Mg$	$Pu + \frac{3}{2}\ MgF_2$	- 21.1	1225(1396)	2260
$PuCl_3 + 3\ K$	$Pu + 3\ KCl$	- 82.9	776(790)	1500
$PuCl_3 + 3\ Li$	$Pu + 3\ LiCl$	- 62.2	613	1353
$PuCl_3 + \frac{3}{2}\ Ca$	$Pu + \frac{3}{2}\ CaCl_2$	- 56.0	772	1925
$PuCl_3 + \frac{3}{2}\ Mg$	$Pu + \frac{3}{2}\ MgCl_2$	+ 0.2	708	1420
$PuBr_3 + 3\ K$	$Pu + 3\ KBr$	- 94.2	730	1380(1435)
$PuBr_3 + 3\ Li$	$Pu + 3\ LiBr$	- 63.4	547	1265
$PuBr_3 + \frac{3}{2}\ Ca$	$Pu + \frac{3}{2}\ CaBr_2$	- 55.5	765	1200(806-812)
$PuBr_3 + \frac{3}{2}\ Mg$	$Pu + \frac{3}{2}\ MgBr_2$	+ 1.8	695	--
$PuI_3 + 3\ K$	$Pu + 3\ KI$	-103.8	723	1420(1330)
$PuI_3 + 3\ Li$	$Pu + 3\ LiI$	- 62.0	446	1190
$PuI_3 + \frac{3}{2}\ Ca$	$Pu + \frac{3}{2}\ CaI_2$	- 59.9	575	718
$PuI_3 + \frac{3}{2}\ Mg$	$Pu + \frac{3}{2}\ MgI_2$	+ 2.9	>700 d.	--

melting point of the slag which would be produced. Laboratory reductions have been made successfully with gross quantities of some of the other halides. These processes are described below.

1. Reduction of plutonium(IV) fluoride is generally carried out in a refractory-lined, sealed container built to withstand the pressures (50 to 400 psig) and temperatures (ca. 1600 C) which develop (Figure E-1-1). A typical metal reduction flowsheet is shown in Figure E-1-2. Calcium metal, ca. 125 per cent of the stoichiometric requirement, is used as the reductant, giving the reaction $PuF_4 + 2\ Ca = Pu + 2\ CaF_2 + 157.6$ Kcal. Iodine, along with an equivalent amount of calcium, may be added to give a "booster" reaction,

   $Ca + I_2 = CaI_2 + 128.5$ Kcal,

   which provides additional heat and favorably alters the properties of the slag (see Figure E-1-3 for the CaF_2 - CaI_2 phase diagram). The "booster" ratio required to give high yields of plutonium metal depends on the size of the reduction charge, small-scale reductions requiring a higher booster ratio in order to compensate for relatively larger heat losses (Table E-1-I). For reductions of one kilogram or more of plutonium, the supplemental heat provided by a booster is less significant. However, the use of as little as 0.05 mole I_2 per mole of plutonium has been found to give slightly improved reduction yields and to facilitate the separation of the metal regulus from the slag and refractory in the subsequent cleaning operation.

   Metal reduction yields of 97 to 99 per cent are commonly obtained in this process. Yields are linked with metal surface appearance, both being adversely affected by the presence of oxygen, either free or as plutonium

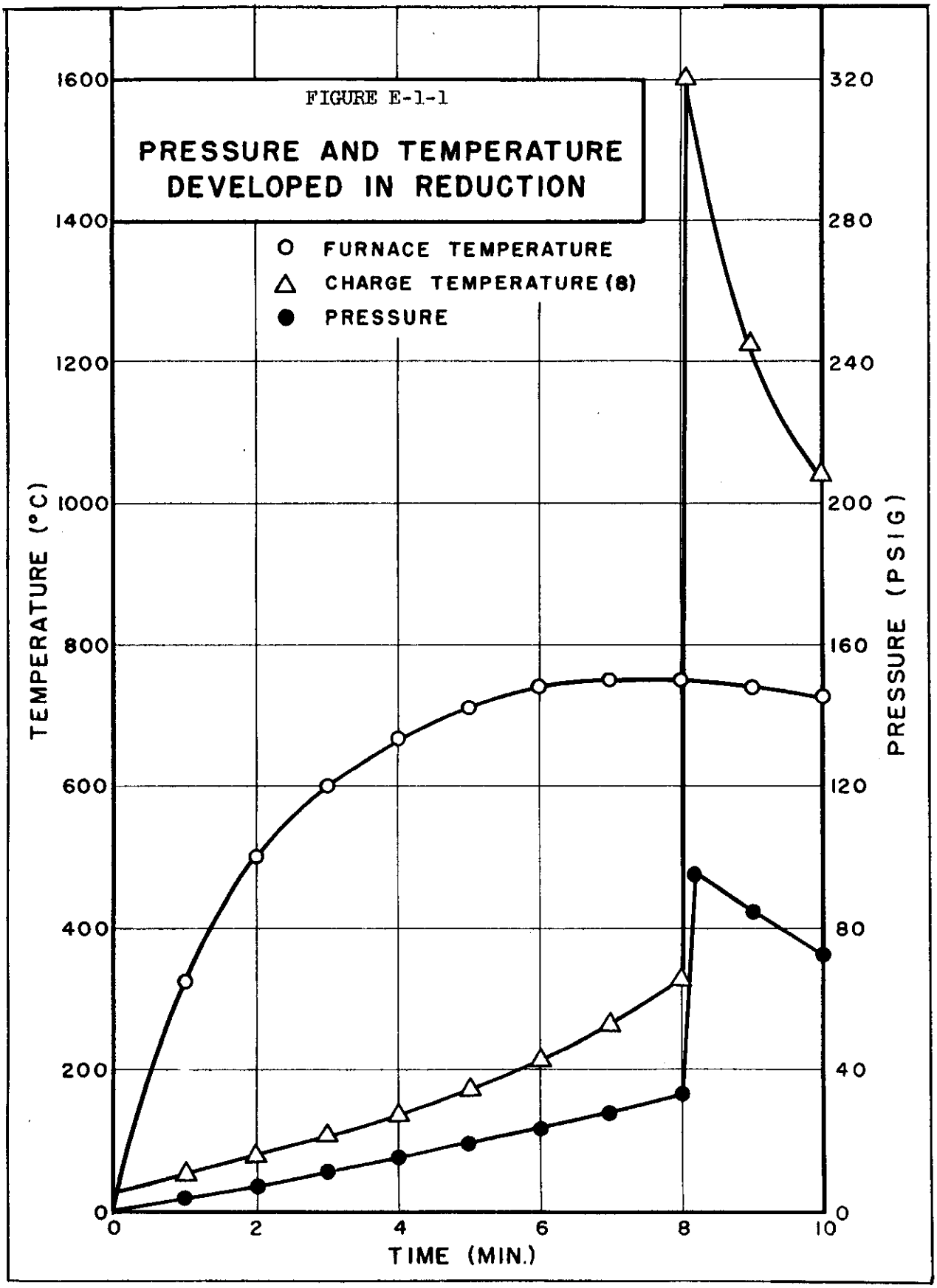
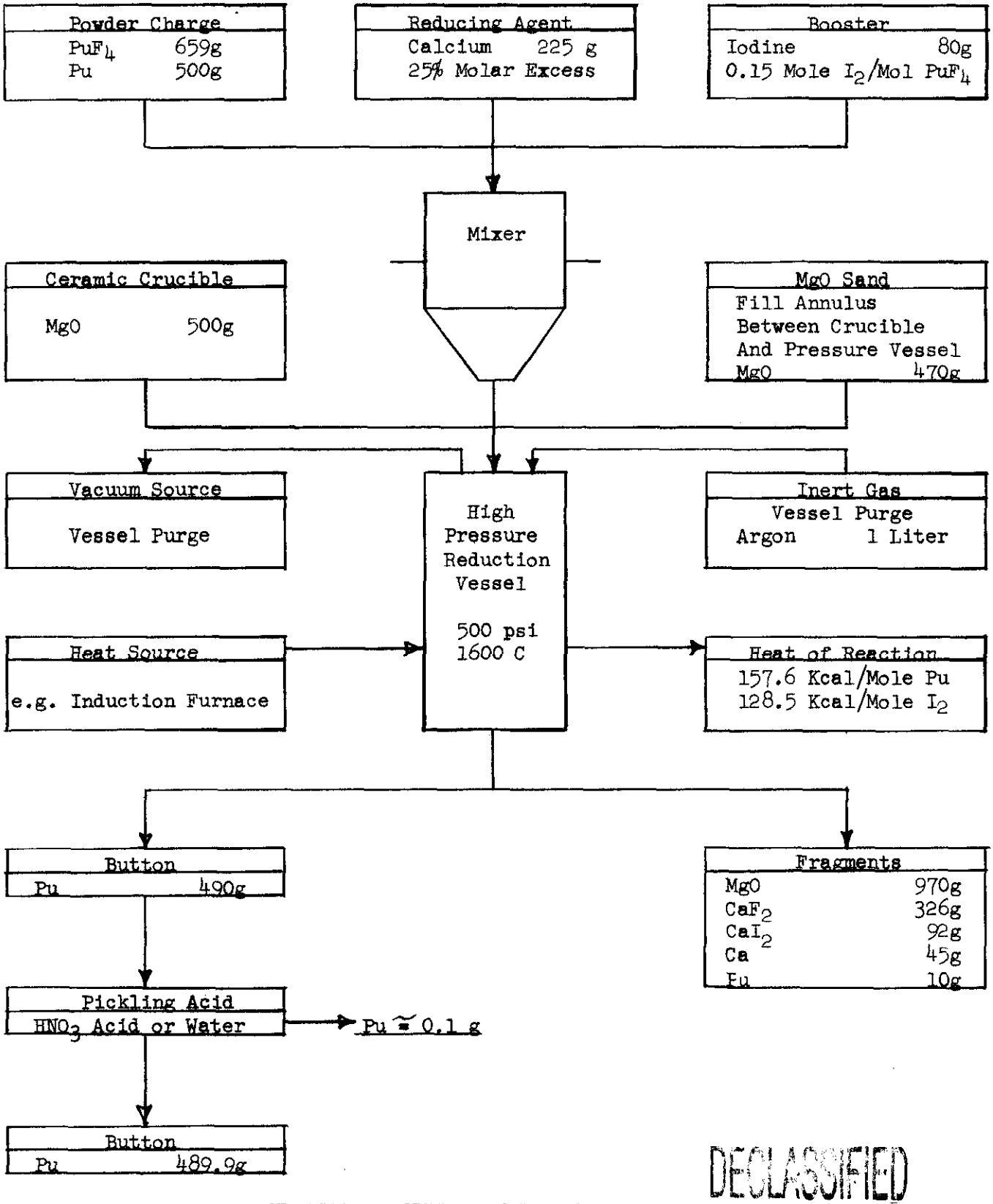


TABLE E-1-I

OPTIMUM RATIO OF IODINE TO PLUTONIUM TETRAFLURIDE
IN VARIOUS NOMINAL CHARGE SIZES FOR REDUCTION BY CALCIUM

Scale (Grams of Pu)	"Booster" Ratio (Moles I_2/mole PuF_4)
5	0.5
50	0.35
500	0.3
1000	0.15
1500	0.1

FIGURE E-1-2



TYPICAL FLOWSHEET - REDUCTION OPERATION

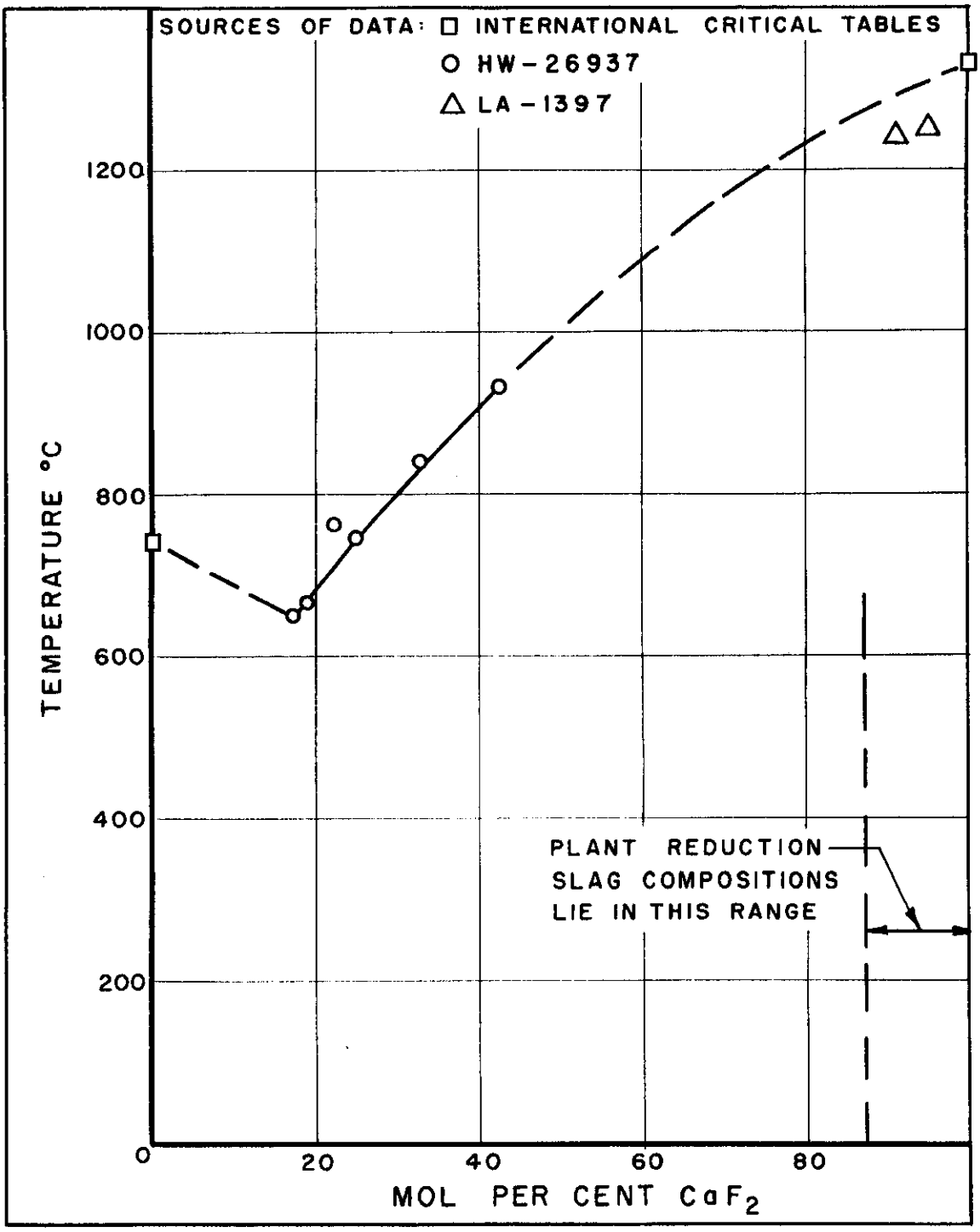


FIGURE E-1-3

POINTS ON THE CaI_2-CaF_2 PHASE DIAGRAM

oxide. Although oxygen exerts a deleterious effect, reasonably good yields may be obtained from plutonium(IV) fluoride containing up to 10 per cent plutonium oxide.

The pressure vessel may be heated either by induction or by a resistance furnace. The calcium-iodine reaction in a charge containing a "booster" starts at about 400 C, while a temperature of over 600 C is necessary to initiate the calcium-plutonium fluoride reaction.

2. Metal Reduction Development

Table E-2-I summarizes the laboratory results obtained in the bomb-type reduction of plutonium(III) fluoride (prepared by freonation), plutonium(III) chloride (prepared by reaction of plutonium oxide with phosgene or carbon tetrachloride), and calcium plutonium(IV) fluoride (prepared by precipitation and drying in an inert atmosphere). Calcium was used as reductant in all cases.

TABLE E-2-I

METAL REDUCTION DEVELOPMENT:
BOMB REDUCTION OF PuF_3, $CaPuF_6$, $PuCl_3$

Plutonium Compound	Plutonium Weight (grams)	Booster Ratio (Moles I_2/Mole Pu)	Reduction Yield (Per Cent)
PuF_3	20	1	97
	20	0.64	95.6
	20	0.5	94.0
	20	0.4	92.1
$PuCl_3$	20	0.3 - 0.6	96.2 - 98.8
$CaPuF_6$	30	0.8	93.2
	250	0.5	97.7

[redacted]

F. Plutonium Recovery

The high cost of plutonium and the relatively high process and mishandling losses involved in its chemical processing make waste recovery operations an important adjuvant to the production of plutonium metal. The principal sources of recoverable plutonium are filtrates from wet chemistry (1 to 10 per cent of the main-line throughput) and the solid, metal reduction wastes (1 to 15 per cent of the main-line throughput), with smaller quantities coming from metal button pickling, fabrication operations, equipment flushes, laboratory analyses, and various clean-up operations (see Figure F-1 for a simplified recovery flow diagram). After proper feed preparation, these materials are all amenable to recovery of their plutonium content by solvent extraction, either in a general purpose recovery plant or, (as has been demonstrated in the case of wet chemistry filtrates and other plutonium nitrate solutions which are relatively free of ionic contaminants) as recycle to a main separations plant.

1. Feed Treatment

Prior to their purification and concentration in the solvent extraction system, recoverable plutonium waste solutions are treated to eliminate:

(1) plutonium complexing agents, which would affect solvent extraction efficiency;

(2) surface-active materials, which would prevent stable column operation; and

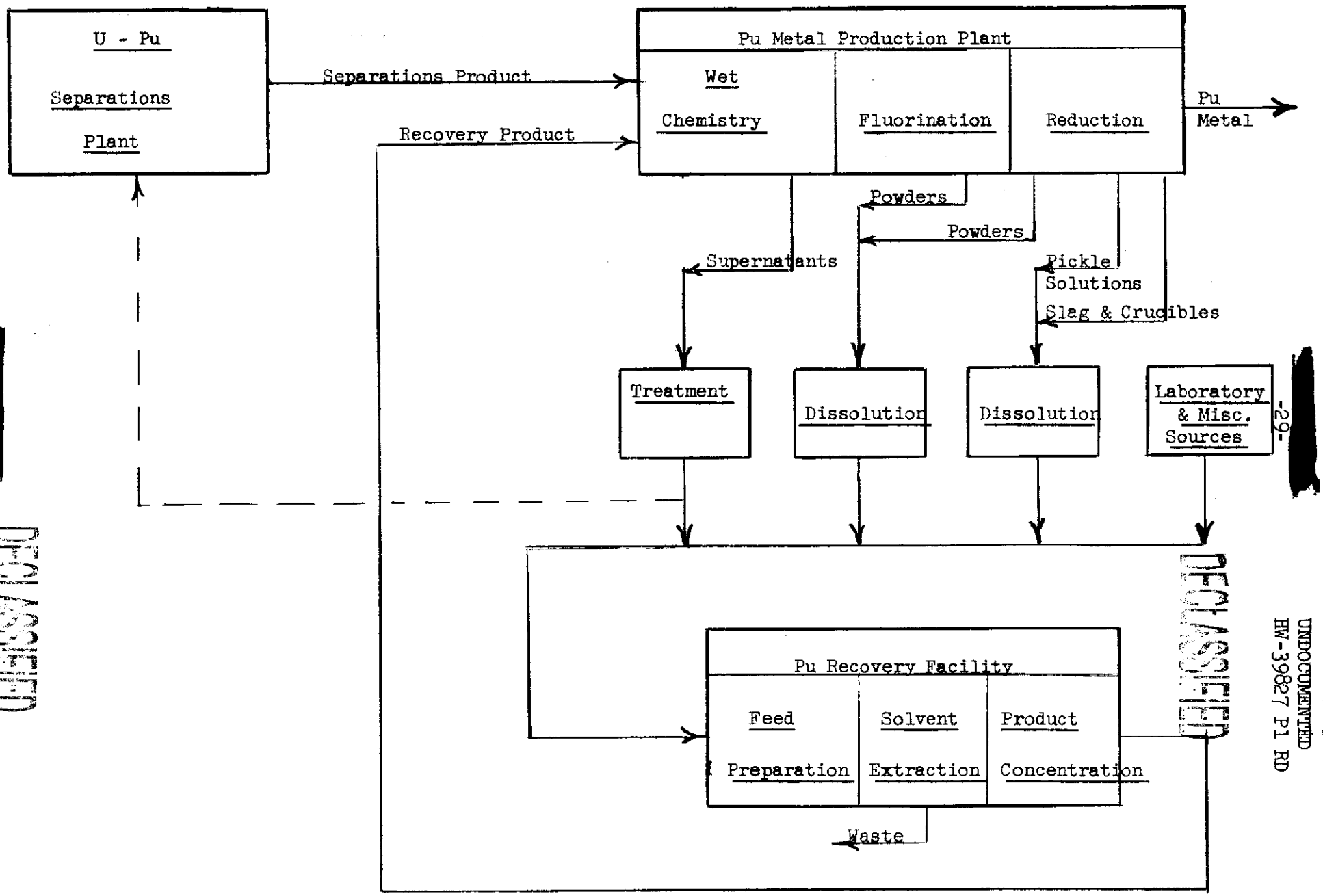
(3) ionic contaminants that would cause excessive corrosion in a nitric acid system.

Solid wastes are dissolved and similarly treated.

a. Solutions. The recoverable waste solutions, of which filtrates from the various plutonium precipitation processes described in

FIGURE F-1

PLUTONIUM RECOVERY FLOW CHART



Section C are the most important stream, are listed in Table F-1-I, along with general methods of treatment prior to make-up as feed for solvent extraction.

b. Solid Reduction Wastes

The combined waste from the metal reduction operation (crucible fragments - usually MgO, containing 1-2 per cent SiO_2 as $MgSiO_3$; slag - CaF_2 and CaI_2, with plutonium as metal, oxide, and fluoride; and insulating, MgO sand) is the most important of the solid wastes, in terms both of quantity (2 to 8 kg of solids per kg of plutonium reduced) and plutonium content. The plutonium is primarily associated with the slag, but up to per cent has been found to be soaked into the crucibles. Handling problems generally make it desirable to combine all three materials in packaging for transfer to recovery, so that all three must be processed together.

The two principal dissolution flowsheets now in use are presented in Figures F-1-1 and F-1-2.

The principal chemical reactions involved in the process include:

(1) dissolution of calcium metal, to form hydrogen and/or oxides of nitrogen;

(2) dissolution of calcium iodide, with oxidation of the iodide to iodine by nitric acid (the oxidation to iodate may also occur, especially if the iodine-sparging system is inefficient or if the acidity is greater than 8-9 M);

(3) dissolution of calcium fluoride, with the formation of aluminum fluoride complexes as discussed below;

(4) dissolution of the bulk constituent of the material, magnesium oxide (during the initial heating of the system, a rapid exothermic reaction may occur at approximately 60 C; the reaction is apparently dependent upon the presence of iodine in the slag);

(5) coagulation of the silica to a stable form (in the presence of the fluoride ion of the "controlled fluoride" flowsheet silica is converted to the volatile fluosilicic acid and is then converted to a hydrated, dispersed form by the excess aluminum ion).

The major difference between the two flowsheets of Figures F-1-1 and F-1-2 lies in the active reagents employed to dissolve the plutonium oxides, plutonium fluorides, and plutonium metal present in the reduction wastes.

In the "aluminum nitrate-nitric acid" flowsheet, the active dissolution agent is 8-9 M nitric acid. Excess quantities of aluminum nitrate (2.5 Al/F mol ratio) are added to the dissolver with the nitric acid to complex the fluoride ion released from the slag and thus minimize vessel corrosion. The crucible materials, except the silica, are dissolved in approximately two hours, while the dissolution rate for plutonium oxide and metal is relatively slow. The plutonium dissolution efficiency varies from 40 - 80 per cent, so that the plutonium-bearing solids subsequently filtered from the solution must be further

processed to achieve a suitable overall recovery.

The active dissolution agents in the "controlled fluoride" flowsheet are 6-8 M nitric acid and the fluoride ion released from the slag. Controlled amounts of aluminum nitrate are added to complex a portion of the fluoride ion and achieve a balance between plutonium dissolution efficiency and vessel corrosion. Recovery efficiencies of up to 99 per cent are attainable, depending upon the total fluoride concentration, the Al/F mol ratio, and the combined iodine removal-oxide dissolution time. Two to three hours total exposure provides a high recovery when the total fluoride molarity is 0.2 - 0.3 and the Al/F mole ratio is 0.1 - 0.2, or when the fluoride molarity is approximately 0.6 and the Al/F ratio is 0.2 - 0.3. In the latter case, an increase in the Al/F mole ratio to 0.5 reduces the recovery to 60-75 per cent. Subsequent addition of aluminum nitrate to increase the Al/F mole ratio to 2-4 effectively complexes the fluoride ion, reducing the plutonium-dissolution and vessel-corrosion rates to those of the previous flowsheet. Acceptance of the high corrosion rate thus provides a sufficiently high recovery to eliminate further processing of the residual solids.

Since the emulsifying properties of silica in a solvent extraction system are largely eliminated by the coagulation treatment, the need to filter the solids from the dissolver solution is dependent upon the plutonium content of the solids and the type equipment employed during subsequent solution process steps. Satisfactory operation on a plant-scale basis

has been experienced during the processing of coagulated, but unfiltered, solution through pulse columns with 1/8-inch diameter plate perforations. Filtration may be desirable, however, for close-tolerance pumps, small diameter, plate perforations, mixer-settlers, etc. Filtration is necessary for further cake processing to recover undissolved plutonium.

Alumina block filters, sintered stainless steel filters, and cloth filters have all been employed satisfactorily. Filter aid precoats are generally employed with the block filters. Plugged units may be cleaned with hot caustic solutions.

c. Scrap Powder Wastes

Scrap powders result from normal spillage of process materials, mishandling during transit, and misfiring during reduction. The plutonium present varies considerably and may be as the fluoride, oxalate, and/or oxides. The reduction chemicals, calcium and iodine, may also be present. Dissolution of these materials is accomplished in a nitric acid-aluminum nitrate solution, which is suitable for subsequent solvent extraction. Precautions are necessary in the charging of calcium-bearing powders to prevent the uncontrolled evolution of hydrogen (such powders are frequently stored in an air atmosphere to permit calcium oxidation prior to recovery). Any iodine is distilled from the materials and the solution is boiled for up to eight hours under total reflux. The presence of plutonium oxide necessitates use of free fluoride ion (present in the fluoride powders and added as sodium fluoride to other powders) during the early part of the cycle.

FIGURE F-1-1

REDUCTION-CRUCIBLE DISSOLUTION
"ALUMINUM NITRATE-NITRIC ACID" FLOWSHEET

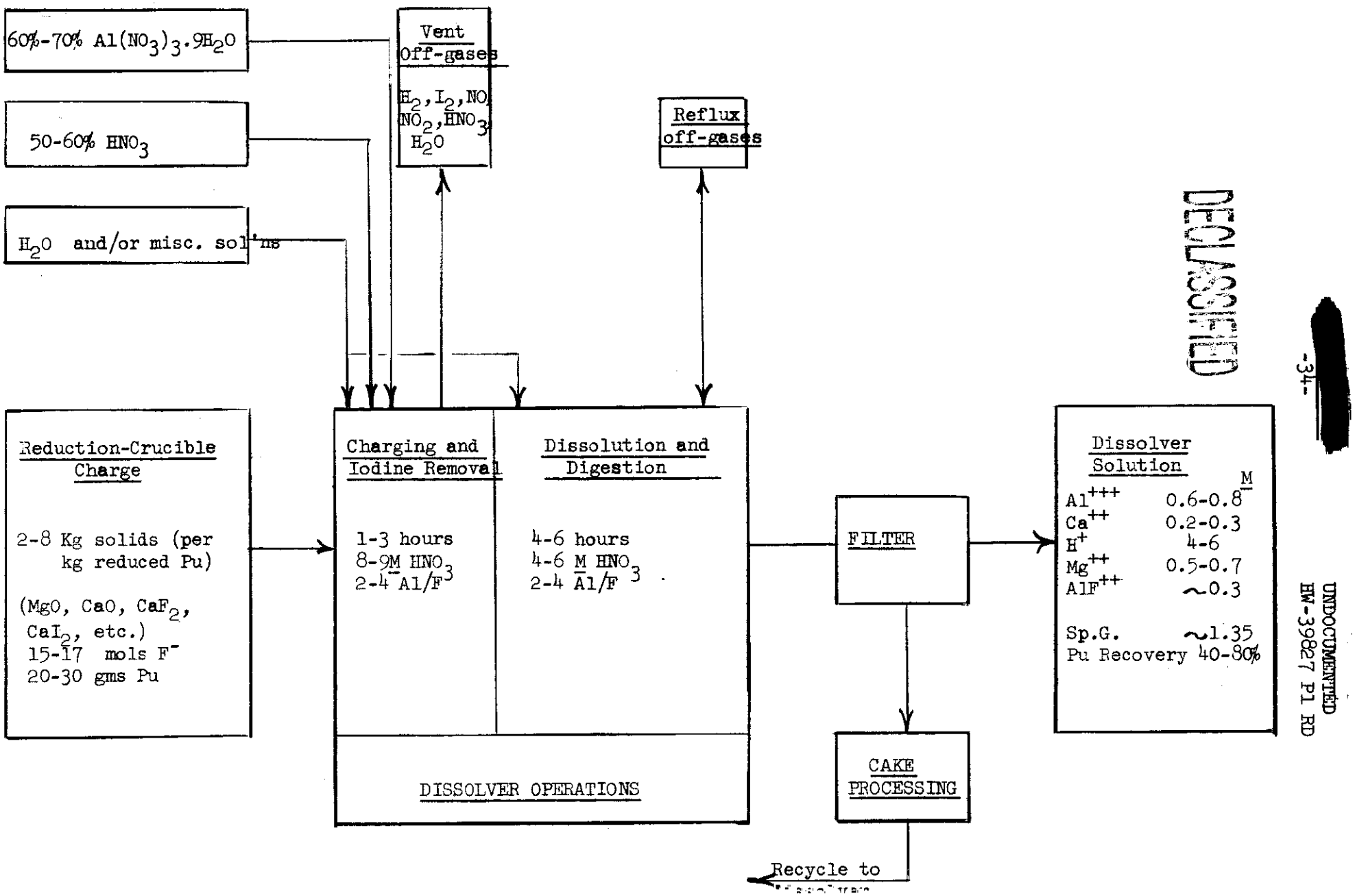


FIGURE F-1-2

REDUCTION-CRUCIBLE DISSOLUTION
"CONTROLLED-FLUORIDE" FLOWSHEET

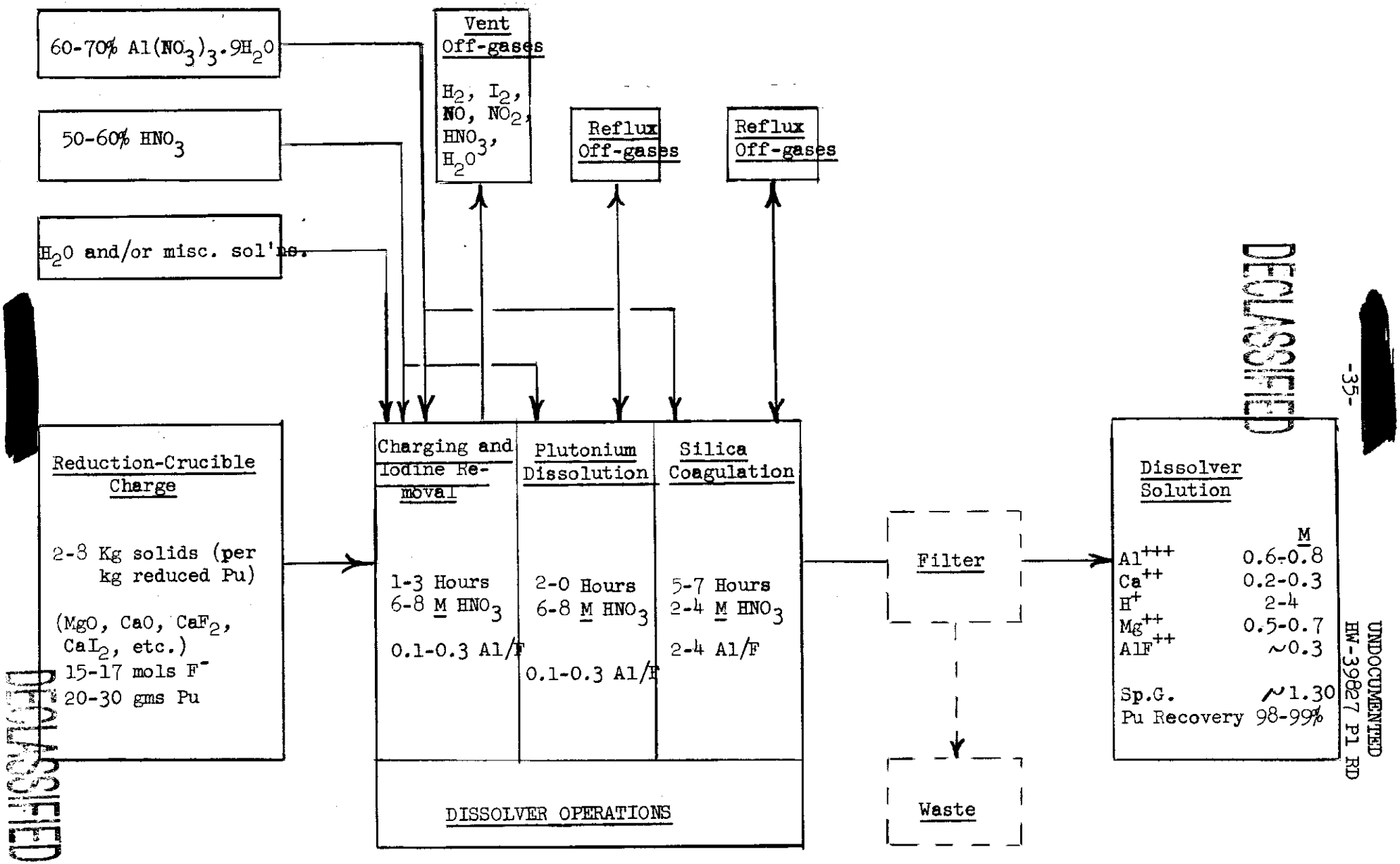


TABLE F-1-I

PREPARATION OF PLUTONIUM RECYCLE SOLUTIONS FOR SOLVENT EXTRACTION

Material	Principal Constituents	Treatment Needed	Methods	Remarks
Pu Peroxide SN	1-3 M HNO_3 5-15% H_2O_2 0.1-0.3 M $SO_4^=$ Assorted Metals	H_2O_2 Destruction	1. Heat kill: 1 Hr. at 70-80 C with 0.2 g/l Fe^{+3} 2. Oxidation of H_2O_2: $KMnO_4$, etc. 3. Addition of caustic to pH $\geq$ 5	Caution required Reaction violent Pu precipitates, Recoverable by Filtration
Pu(IV) Oxalate SN(a)	1-4 M HNO_3 0.05-0.15 M $H_2C_2O_4$ Assorted Metals	$H_2C_2O_4$ Destruction	Oxidation (MnO_4^- AT Room Temp; $CR_2O_7^=$ $\geq$ 65 C	Pu(III) may also be scavenged on CaC_2O_4, by add'n of CA^{+++} to 0.1 M HNO_3, 0.2-1M $H_2C_2O_4$
Pu(III) Oxalate SN	1-2 M HNO_3 0.6 M HI 0.2 M $H_2C_2O_4$	Iodine Removal $H_2C_2O_4$ Destruction	Boiling with conc. HNO_3, with addition of H_2O_2	
Pu Fluoride SN	1-5 M HNO_3 0.3-0.5 M HF	Kill corrosive effect of Fluoride	Addition of Al^{+3}	
Flush Solutions	Misc.	Depends upon reagents; Remove Solids	- - -	
Button-Pickling Solution	HNO_3 HI Assorted Metals	Iodide Removal	1. Process with other iodide-containing mat'ls. 2. Boil with conc. HNO_3	
Laboratory Wastes	Assorted	Removal of components which interfere with solvent extraction	- - -	

2. Solvent Extraction

The plutonium contained in the dissolved and/or treated recoverable waste streams is purified and concentrated in a solvent extraction system. Such a facility is basically similar to the main separations plants, involving feed preparation, two-phase contacting for extraction, scrubbing, and stripping, product concentration, solvent treatment, and waste disposal. A plutonium recovery plant, however, is smaller, simpler in construction, and requires fewer process steps. The low fission product content of the recovery streams permits contact maintenance and eliminates the need for high fission-product decontamination. Continuous partition and uranium processing are also eliminated, although uranium, which is present as a contaminant in wet chemistry supernatants, must be periodically purged from the system.

Two plutonium recovery flowsheets are presented in Figures F-2-1 and F-2-2, one involving simple extraction, scrubbing, and stripping, and the other product-refluxing. Tributyl phosphate is employed as the selective solvent in both flowsheets. Either flowsheet may employ kerosene-type diluent agents to provide a higher-than-water organic phase or carbon tetrachloride to provide a non-flammable, heavier-than-water organic phase.

a. Feed Preparation

Salting Agents

Aluminum nitrate and nitric acid are employed as plutonium salting agents, since the two reagents are required for the dissolution of the fluoride-bearing reduction-crucible and scrap-powder wastes. The following empirical equation provides a general correlation of laboratory data on the distribution of

plutonium(IV) between 15-20 volume per cent tributyl phosphate (in carbon tetrachloride) and the nitrate-salted aqueous phase.

$$\log(E_a^o)_{Pu(IV)} = \frac{1}{m}\left[1 - \frac{3/2\,[Pu_o]}{0.55}\right]\left[\log\left(\frac{SS}{B}\right)\right] + \log\left(\frac{TBP}{0.55}\right)$$

where: $(E_a^o)_{Pu(IV)}$ = distribution coefficient for plutonium(IV) = plutonium concentration ratio of the organic and aqueous phase.

m = slope of nitric acid parameter, Table F-2-I.

B = intercept of nitric acid parameter, Table F-2-I.

Pu_o = molarity of plutonium in the organic phase, Table F-2-II.

TBP = molarity of tributyl phosphate
= 0.55 for 15 volume per cent TBP
= 0.73 for 20 volume per cent TBP.

SS = salting strength of the aqueous phase =

$$\left[(NO_3^-) - 2(AlF^{++})\right]^{1/2}\left[\mu_{total} - \mu\, AlF(NO_3)_2\right]^{1/2}$$

μ = ionic strength =

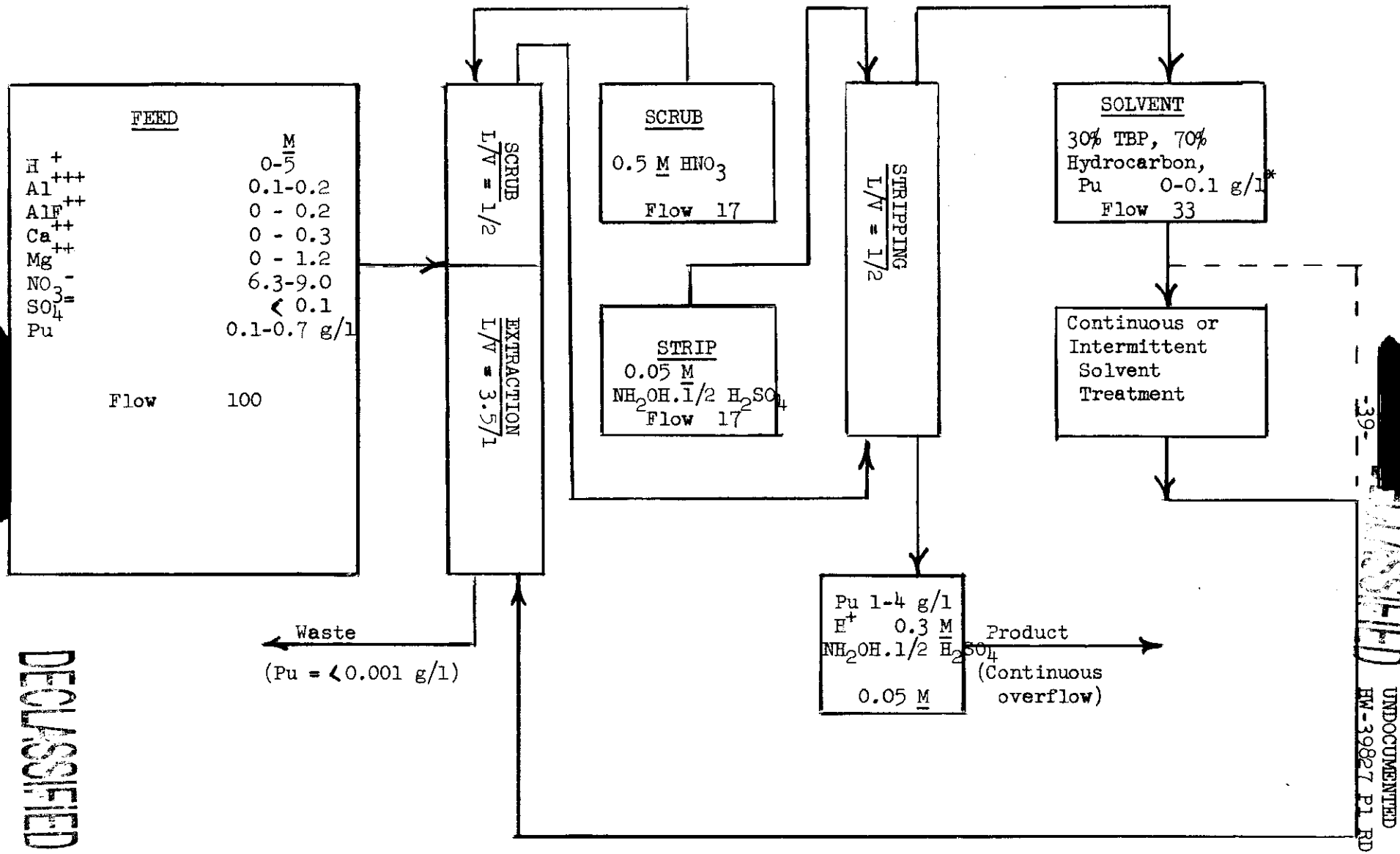
$$\left[9(Al^{+++}) + 4(Mg^{++}) + 4(CA^{++}) + (H^+)\ \text{etc.}\right]$$

The relative importance of aluminum nitrate and nitric acid is illustrated in Figures F-2-3 and F-2-4 for systems containing no other salts. The use of nitric acid as a salting agent provides a volume advantage, but is limited to lower concentrations by its eventually repressive effects on the distribution coefficient.

The use of the "salting strength" term in the empirical equation reflects the increased salting provided by the magnesium and calcium salts in the reduction-crucible solutions. Included in the "salting strength" is a term which expresses the repressive

FIGURE F-2-1

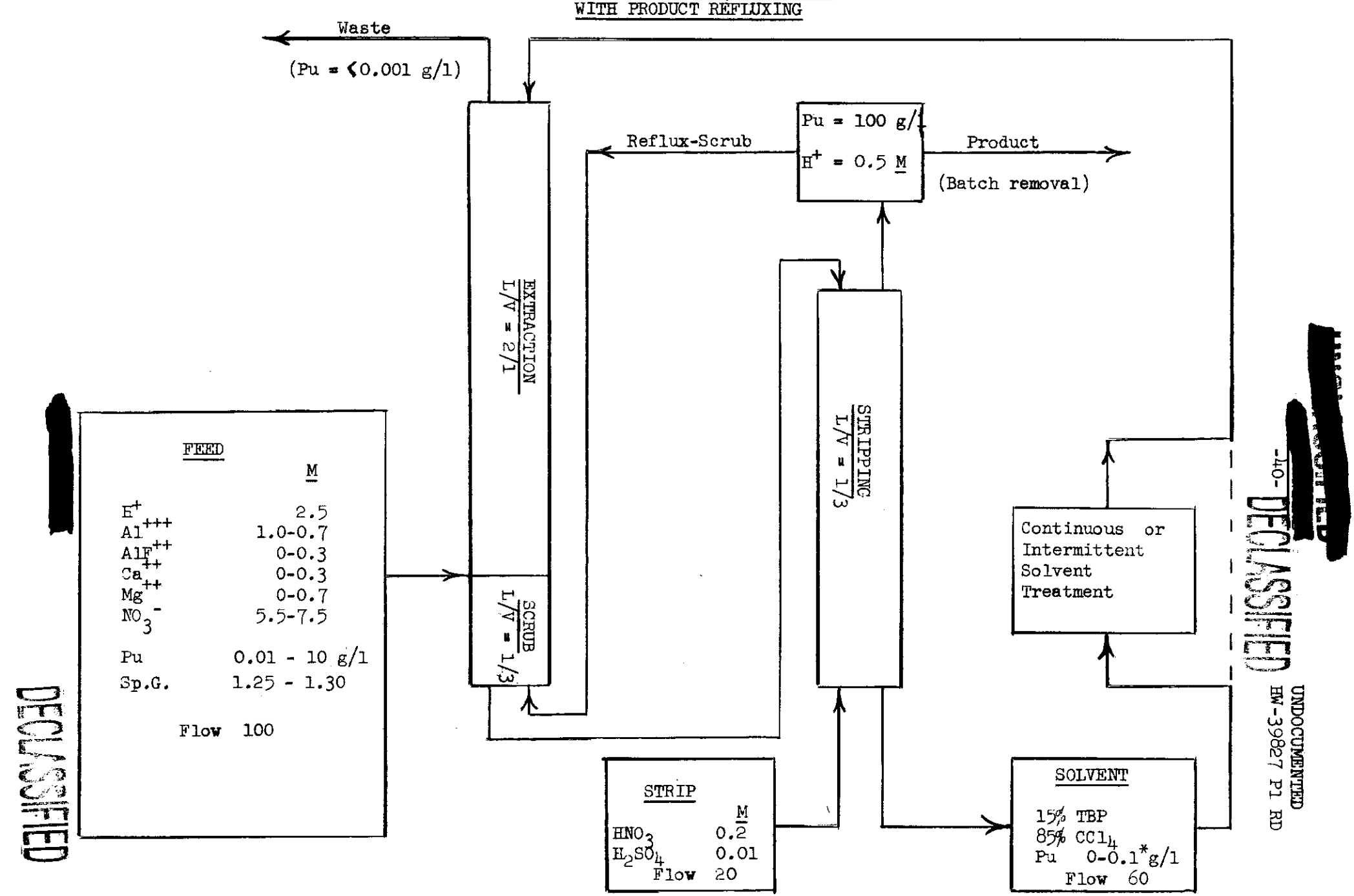
PLUTONIUM RECOVERY FLOWSHEET
WITHOUT PRODUCT REFLUXING



* Arbitrary limit for accumulation of "unstrippable" Pu prior to periodic solvent treatment.

FIGURE F-2-2

PLUTONIUM RECOVERY FLOWSHEET
WITH PRODUCT REFLUXING



* Arbitrary limit for accumulation of "unstrippable" Pu prior to periodic solvent treatment.

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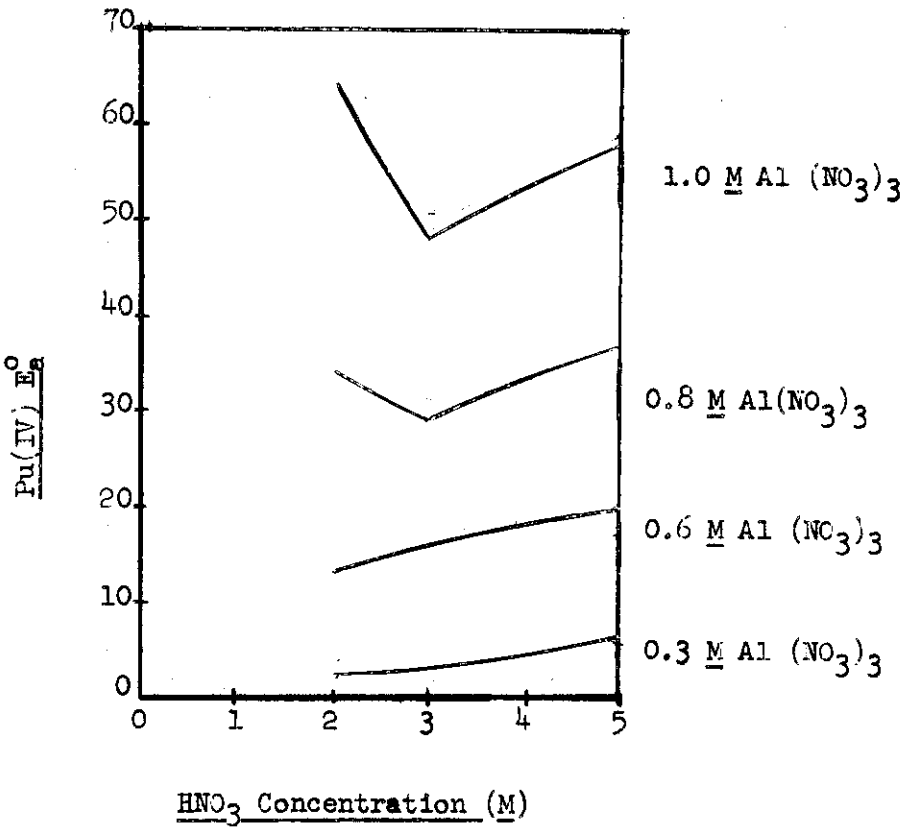

FIGURE F-2-3

EFFECT OF NITRIC ACID CONCENTRATION UPON PLUTONIUM(IV) DISTRIBUTION COEFFICIENT

For Pu(IV), HNO_3, $Al(NO_3)_3$ and 15% TBP-CCl_4 systems with organic phase Pu conc. of 1 g/l.

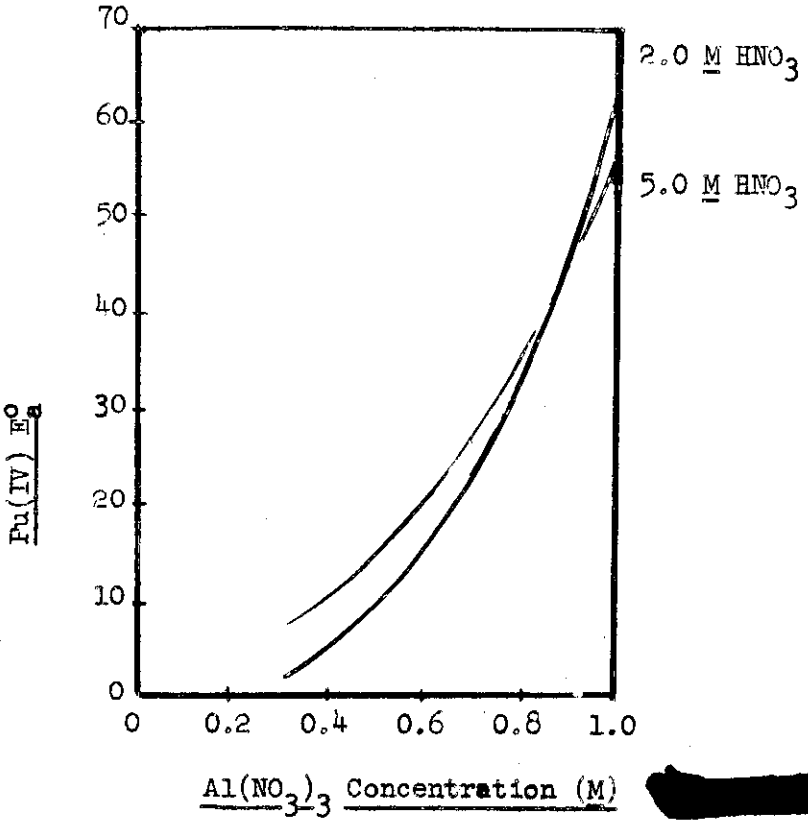

FIGURE F-2-4

EFFECT OF ALUMINUM NITRATE CONCENTRATION UPON PLUTONIUM(IV) DISTRIBUTION COEFFICIENT

For Pu(IV), HNO_3, $Al(NO_3)_3$ and 15% TBP-CCl_4 systems with organic phase Pu conc. of 1 g/l.

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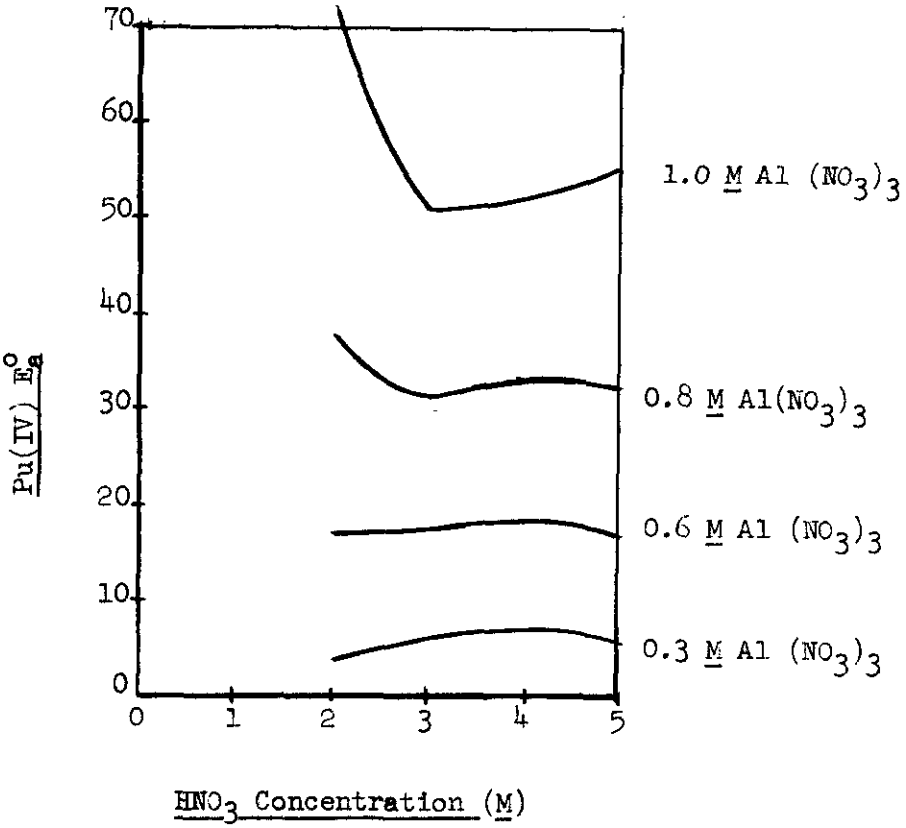

FIGURE F-2-3

EFFECT OF NITRIC ACID CONCENTRATION UPON PLUTONIUM(IV) DISTRIBUTION COEFFICIENT

For Pu(IV), HNO_3, $Al(NO_3)_3$ and 15% TBP-CCl_4 systems with organic phase Pu conc. of 1 g/l.

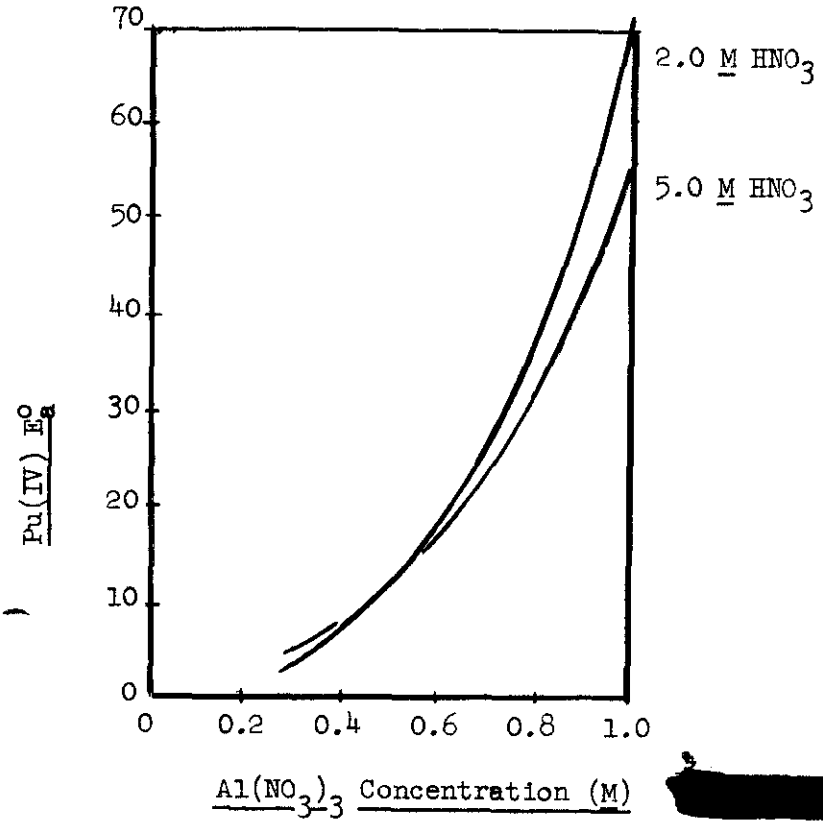

FIGURE F-2-4

EFFECT OF ALUMINUM NITRATE CONCENTRATION UPON PLUTONIUM(IV) DISTRIBUTION COEFFICIENT

For Pu(IV), HNO_3, $Al(NO_3)_3$ and 15% TBP-CCl_4 systems wit organic phase Pu conc. of 1 g/l.

effects of fluoride ion despite the presence of aluminum. Other plutonium complexing agents, such as sulfate and oxalate ions, also reduce the distribution coefficient, depending upon their concentrations and, in the case of sulfate ion, the acid concentration.

The free tributyl phosphate concentration affects the instantaneous distribution coefficient, as is indicated by the term involving the plutonium concentration in the organic phase (cf Table F-2-II). The E_a^o values reach a maximum at approximately one gram per liter plutonium in the organic phase and theoretically remain at the maximum value at lower concentrations. Both laboratory and plant data, however, indicate the E_a^o values decrease as the plutonium is depleted, presumably due to either plutonium complexing agents or plutonium valence states other than (IV). This effect is illustrated in Figure F-2-5, where theoretical and actual laboratory E_a^o values for a typical recovery feed are presented as a function of plutonium concentration in the organic phase.

Plutonium Valence

The presence of plutonium(III) or plutonium(VI) affects the overall distribution coefficient. Plutonium(III) is essentially inextractable, although in strong acid and concentrated salt solutions it may be oxidized and thus extracted. Plutonium(VI) is less extractable than plutonium(IV) as is illustrated by the data in Table F-2-III showing the ratio of distribution coefficients for plutonium(IV) and (VI) as a function of salting strength.

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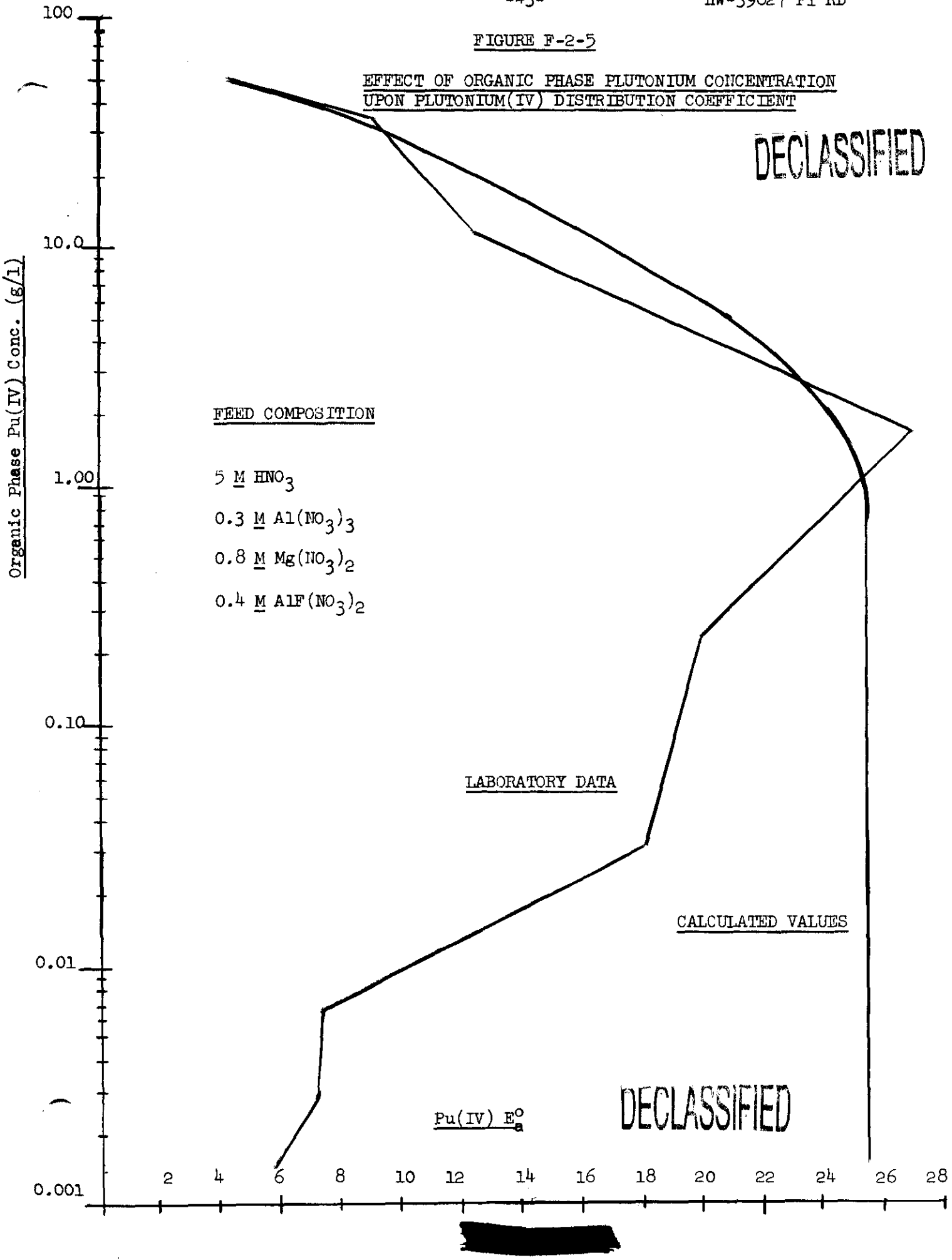
FIGURE F-2-5

EFFECT OF ORGANIC PHASE PLUTONIUM CONCENTRATION UPON PLUTONIUM(IV) DISTRIBUTION COEFFICIENT



[redacted]

Although high acid concentrations (>3 M) and high nitrate salt concentration (>5 M) favor the plutonium(IV) valence state, the plutonium(VI) content of dissolved reduction-crucible and scrap-powder materials may be as high as 20 per cent of the total. Moreover, treatment procedures for oxalate destruction result in the formation of plutonium(VI) in the wet chemistry supernatants. It may thus be desirable to include plutonium valence adjustment in the feed preparation step. For solutions not containing iron, hydrogen peroxide is an effective reagent. If the iron content of the solution is too high, a stabilized ferrous ion reagent (ferrous ammonium sulfate, sulfamic acid) followed by sodium nitrite may be employed to reduce the plutonium(VI) to (III) and then oxidize the plutonium(III) to (IV).

b. Column Performance

To achieve acceptable waste losses and product purity, six to ten equivalent theoretical stages are employed for extraction, one to four stages for scrubbing, and five to ten for stripping, the number depending upon the type flowsheet, the tributyl phosphate content of the solvent, the feed salting strength, and the presence of complexing agents and/or undesirable plutonium valence states. Various types of two-phase contacting equipment have been employed in plutonium recovery plants, including batch-contacting vessels, continuous pump mixer-settlers, packed columns, York-Scheibel columns, and perforated-plate pulse columns. Overall waste losses range from 0.05 to 0.5 per cent of the feed.

The simple flowsheet utilizes a low-acid scrub and strips plutonium from the organic phase by reducing the plutonium to the relatively inextractable(III) valence state. Product concentrations of one to four grams per liter are attainable with feeds of 0.5 - 1.0 gram per liter. In the reflux flowsheet, a major fraction of the product from the stripping column is recycled to the extraction column as the scrub stream, while plutonium is stripped from the organic phase by a dilute nitric acid solution. Product concentrations of up to 100 grams per liter plutonium are readily attainable with such a flowsheet.

The product-refluxing flowsheet provides a number of operational advantages. The high plutonium concentrations attainable eliminate the need for further concentration (by evaporation or ion exchange) prior to wet chemistry processing and thus minimize the amounts of extraneous materials (e.g. corrosion products, sulfate ion) present in the product solution. Moreover, the system is considerably more flexible, since a constant product concentration can be maintained despite the wide variations in feed concentrations that are experienced in a recovery plant.

On the other hand, the high plutonium concentrations involved in such a flowsheet result in some process disadvantages. The problem of plutonium fixation in the solvent due to tributyl phosphate degradation by alpha-particle bombardment is enhanced, causing relatively high plutonium concentrations in the organic raffinate from the stripping column (the complexing action of small amounts of sulfate ion in the stripping solution reduces

[redacted]

the plutonium concentration by factors of two to three). Extraction column waste losses are more sensitive to feed conditions since there is a highly concentrated plutonium inventory in the system. Adverse plutonium valence changes may occur within the system by virtue of plutonium(IV) disproportionation to plutonium(III) and (VI) in highly concentrated solutions. The mechanisms involved and methods of control are not as yet (December, 1955) completely understood.

c. Product Concentration

The plutonium solutions obtained from a product-refluxing recovery system are sufficiently pure (>95%) and concentrated for wet chemistry operations. It should be noted that the tributyl phosphate present in the product solution by solubility has no significant effect upon the precipitation cycle, subsequent cake properties, or plutonium solubility losses.

Product solutions from the non-reflux system require further concentration prior to wet chemistry operations. The available methods, steam-stripping (to remove tributyl phosphate) followed by evaporation and ion exchange are discussed in Sections and

d. Uranium Removal

The uranium present as a contaminant in the wet chemistry supernatants remains with the plutonium through the solvent extraction process and is thus returned to the main line. Since wet chemistry operations involve a uranium separation factor of 10-100 (for oxalate) or 100-1000 (for peroxide), a major fraction

of the uranium is returned to the recovery system and recycled again. If the uranium content of the virgin feed is great enough, the uranium accumulated in the recovery plant will eventually exceed the purity limit. Periodic removal of the uranium is therefore required. Recycle to the main separations plant of the individual wet chemistry supernatants from the precipitation of recovered plutonium may be the most convenient method of purging the system. Recovery systems involving ion exchange treatment of the product may utilize the resin column for uranium removal. An alternate method is periodic batch partition of the uranium and plutonium in the wet chemistry supernatants from recovered plutonium, employing the standard reduction of plutonium to the (III) valence state and extraction of uranium with tributyl phosphate for ultimate disposal to waste.

e. Solvent Treatment

Exposure of tributyl phosphate to plutonium results in the gradual breakdown of the solvent, the ultimate effects of which are discussed in Section . Removal of the prime solvent degradation product, dibutyl phosphate, may be accomplished, on either a continuous or a periodic batch basis, by contacting the solvent with dilute sodium carbonate (5-10 organic-to-aqueous volume ratio). If iodine is present in the solvent, dilute sodium hydroxide should be employed, since the carbonate solution does not effectively remove iodine.

To prevent the precipitation of plutonium hydroxide in systems where the plutonium concentration in the organic raffinate

is relatively high, the carbonate wash may be preceded by a plutonium-removal treatment, involving contacting the solvent with dilute oxalic acid (complexing the plutonium in the aqueous phase) or a stabilized ferrous ion reagent (reducing the plutonium to the aqueous-favoring (III) valence state). The plutonium may thus be recovered, while the carbonate wash is discarded.

f. Waste Disposal

Since the fission-product content of the recovery streams is relatively low, a number of methods for the disposal of the extraction wastes are available, depending upon the particular environment of the plant. The solutions may be partially neutralized and cribbed (whereby the plutonium is fixed by the ion exchange properties of the soil); they may be totally neutralized and stored indefinitely; or they may be scavenged (to remove plutonium) and the supernatants cribbed. The high salts content limits the volume reduction permissible by evaporation and may result in a thixotropic material upon neutralization.

TABLE F-2-I

NITRIC ACID PARAMETERS FOR PLUTONIUM DISTRIBUTION CORRELATION

HNO_3 Conc. (M)	HNO_3 Parameters* Slope (m)	Intercept (B)
2.0	0.230	2.75
2.5	0.255	2.83
3.0	0.265	2.98
3.5	0.260	3.20
4.0	0.245	3.58
4.5	0.225	4.10
5.0	0.185	5.00

* For equation ( ) correlating plutonium(IV) distribution between 15-20 volume per cent TBP in CCl_4 and a nitrate-salted aqueous phase.

TABLE F-2-II

ORGANIC PLUTONIUM PARAMETER FOR PLUTONIUM DISTRIBUTION CORRELATION

Organic Phase Pu Conc. (g/l)	Factor Value* $\left[1 - \frac{3/2\ Pu_o}{TBP}\right]$
1	0.990
5	0.934
10	0.886
12	0.864
20	0.773
30	0.655
48	0.455

* For equation ( ) correlating plutonium(IV) distribution between 15 per cent TBP in CCl_4 and a nitrate-salted aqueous phase.

TABLE F-2-III

EFFECT OF SALTING STRENGTH UPON PLUTONIUM(VI) DISTRIBUTION

Salting Strength	Distribution Coeficient Ratio $\frac{E_a^o \text{ for Pu(IV)}}{E_a^o \text{ for Pu(VI)}}$
3	2.3
4	2.7
5	3.0
6	3.3
7	3.6
8	3.8
9	4.0
10	4.2

[redacted]