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A SUMMARY OF INVESTIGATIONS OF THE PLUTONIUM CHEMISTRY LABORATORY

AUTHOR

H. H. Hopkins, Jr.

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Plutonium Chemistry Laboratory
Research and Engineering Operation
Chemical Processing Department

November 1, 1965

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A SUMMARY OF INVESTIGATIONS OF THE PLUTONIUM CHEMISTRY LABORATORY

INTRODUCTION

This document contains a summary and directory of investigations performed in the Plutonium Chemistry Laboratory under the General Electric Company. The period covered starts with 1952, when the group was known as the Separation Technology Unit; and extends through 1965.

The compilation is based on, and includes, much of the earlier work prepared by H. W. Crocker, "Summary Of 234-5 Development Progress, January, 1951 - June, 1961," HW-61319 RD Rev 1, September 22, 1961 (Secret). The material has been reedited, brought up to date, and much duplication dropped.

The information is arranged by subject, and within each subject, chronologically. Progress and summary reports are distinctively offset for easy spotting. When an investigation appears next to a month, the reader may refer to the specific monthly report for further information. These are listed at the end of the report by number.

For most subjects, use of the summary and progress reports will provide a complete description of the material, and reference to monthly reports will rarely be necessary.

A. AQUEOUS CHEMISTRY

1. VALENCE ADJUSTMENT AND SPECTRA

HW-27837 J. F. Facer, Procedures For Hydrogen Peroxide Addition In Valence Adjustment For Plutonium(IV) Oxalate Precipitation. 7/29/53 (Secret).

1956

April Plutonium(IV) to plutonium(III) reduction studies using H_2O_2, hydroxylamine hydrochloride, with sulfamic acid as holding reductant. Solutions were 17 - 70 g/liter Pu and 0.8 - 2.5 M HNO_3.

HW-44744 M. N. Myers, Absorption Spectra Of Plutonium And Impurity Ions In Nitric Acid Solution. 7/31/56 (Declassified).

June Studies of plutonium(IV) to plutonium(III) reduction in HNO_3 solution using sulfamic acid and ascorbic acid. Effects of solution concentration.

HW-44987 M. N. Myers, Reduction Of Plutonium(VI) With Hydrogen Peroxide. 8/17/56 (Confidential).

September Ascorbic acid stability tests. Effect of sulfamic acid, nitric acid, and plutonium concentration.

October Ascorbic acid stability.

Use of ascorbic acid as Pu(IV) to Pu(III) reductant in HNO_3 solution. An ion exchange process. Effect of ascorbic and sulfamic acids. Adaptability of ascorbic-sulfamic bearing filtrate solutions to batch and continuous kills, temperature effects.

November Effect of semicarbazide and aminoguanidine as reducing agents for ion exchange process. Effects of sulfamic acid.

Preliminary study on reduction of Purex 2BP stream with sulfurous acid, ascorbic acid, and hydroxylamine sulfate. Initial studies with sulfurous acid fail to reduce the Pu in the 2BP stream.

December Effectiveness of hydroxylamine, ascorbic acid, aminoguanidine, and semicarbazide as reductants in high acid solutions. Effects of time and oxidation. Semicarbazide is slower, but more stable than others.

TBP strip experiments on Purex 2BP show ascorbic acid and hydroxylamine as effective reductants. Sulfurous acid ineffective.

1957

HW-52796 A. Brunstad and R. C. Smith, Reduction And Stabilization Of Plutonium Nitrate In Cation Exchange Feed And Product Solutions. 9/24/57 (Confidential).

Study of reduction of cation exchange feed to Pu(III): 0.05 M hydroxylamine sulfate, 0.05 M sodium bisulfite, and 0.1 M semicarbazide required 24 hours, 2.5 minutes, and 0.5 minute, respectively. Hydroxylamine sulfate treated solution is stable for two weeks, other for four days.

HW-51655 A. Brunstad, Oxidation Of Plutonium(III) By Sodium Nitrite. 7/19/57 (Declassified).

2. SOLUTION CONCENTRATION

1953

August Plutonium - red oil reactions.

October Evaporation of CCP.

1954

January Red oil and precipitation of peroxide or oxalate.

October Specific gravity measurements for plutonium nitrate-nitric acid solutions.

HW-38555 R. A. Pugh, Direct Concentration Of Redox Product Solution. 10/19/55 (Secret).

HW-38513 M. N. Myers, Concentration Of Redox Product With Increased Aluminum Concentration. 10/22/55 (Secret).

Concentration limits of oxalate filtrates containing

200,000 ppm Fe; 10,000 each Al, Cr, and Ni. A factor of three was found. Oxalate destroyed by concentration.

Concentration studies for Redox 3BP (product solution) containing 100,000 ppm Al. ANN precipitation noted at 130 g/liter Pu concentration.

HW-60280 R. E. Latta and H. H. Hopkins, Jr., Continuous Concentration Of Cation Exchange Product. 5/20/57 (Secret).

Solutions up to 150 g/l Pu, 7 M HNO_3, 0.8 M $SO_4^=$ stable at boiling temperature.

1960

February Plutonium nitrate was successfully concentrated from 250 g/l Pu in 3.6 M HNO_3 to 630 g/liter Pu in 6 M HNO_3. The solution was stable, pumpable.

October A plutonium nitrate solution of 253 g/liter Pu in 3.5 M HNO_3 was successfully concentrated to a stable solution of 782 g/liter Pu in 5.7 M HNO_3.

3. PLUTONIUM POLYMER

1957

HW-54203 A. Brunstad, Polymerization And Precipitation Of Plutonium(IV) In Nitric Acid. 12/17/57 (Unclassified).

Study of polymer formation in Pu(IV) nitrate solutions of low acidity. Effects of nitric acid concentration and temperature. Absorption spectra of Pu(IV) from 0.02 M HNO_3 to 14 M HNO_3.

1958

February Study of polymer formation as a purification process. Separation factors of 3300, 40, 1000, 5, 100, and 100 for Al, Cr, Cu, Fe, Mg, and Ni, respectively, based on initial impurity concentrations of 10,000 ppm. Effect of precipitation on fine particle formation.

1960

May

Solutions of plutonium nitrate containing less than 1 M HNO_3 have formed polymer during concentration studies. Solutions with > 1 M HNO_3 were free of polymer formation. Solutions were concentrated from 45 g/liter to 550 g/liter Pu.

September

Samples of plutonium polymer were formed by heating plutonium nitrate solutions. The H/Pu values varied from 15 for dry polymer to 2900 for settled polymer slurry.

4. SOLUBILITY

1956

December

Effect of 0.65 M $(NH_4)_2SO_4$ on sulfate precipitation in Task I feed solutions on standing at room temperature.

1959

October

Solubility of $PuCl_3$ in 1 M HCl at 24 °C was 554 g/liter Pu. SpG = 1.756.

HW-55357 H. D. Warren and A. Brunstad, Solubility Of Plutonium(IV) Sulfate In Nitric Acid Solutions. 3/14/58 (Unclassified).

Solution of 65 - 80 g/liter Pu, 5.4 - 6.8 M HNO_3, 0.05 M $SO_4^{=}$ stable at room temperature.

1963

August

Plutonium solubility in sump solution at pH = 2 was 0.017 g/liter and at pH = 10, <0.001 g/liter.

1965

RL-SEP-558 D. M. Creighton, Solubility Of Plutonium(IV) Fluoride In Nitric-Hydrofluoric Acid. 6/11/65 (Unclassified).

5. CONCENTRATED PRODUCT SOLUTION [AT-SOLUTION] STUDIES

1952

HW-18738 J. F. Facer and W. L. Lyon, Use Of AT Solutions Without Evaporation. 9/1/50 (Secret).

Sulfate effect.

1953

April Plutonium sulfate in AT-solution (brown vs. pink sulfates).

June Gas evolution.

HW-29635 C. V. Packer, Gas Pressure In Sealed Sample Cans, Concentrated Plutonium Nitrate. 10/14/53 (Declassified).

November, December Gas evolution from AT-solution.

1954

January Plutonium(IV)-(VI) changes during evaporation as a function of nitric acid concentration; sulfate studies - dissolution of red sulfate. Gas evolution studies.

1956

May Prevention of solid precipitation in solution shipment.

6. DIRECT CALCINATION

1959

HW-61766 C. J. Berglund, Direct Calcination Of Plutonium Nitrate Solution. 9/2/59 (Secret).

1960

March Cold testing of direct calciner unit shows off-gas condenser capacity of 0.8 liters/hour. Evaporation capacity of calciner is adequate.

May Approximately 4 kg of Pu as 240 g/liter Pu in 4 M HNO_3 has been continuously calcined in an agitated bed at 275 °C. Feed rate was 240 grams of plutonium per hour. Original bed material was fine particle size PuO_2 (10 μ). As runs progressed, the particle size of the PuO_2 increased to about 600 microns (visual estimate). Operational difficulties were filter plugging, cyclone plugging, and off-gas condensation in the cyclone and filter.

June — Additional runs made using feed 200 g/liter Pu, 4 M HNO_3. Bed temperature of 275 °C and agitator speed of 150 rpm.

Tapped density of PuO_2 formed was 6 g PuO_2/cc compared to 2 g PuO_2/cc for oxide from oxalate-type calcination.

July — Approximately 4 kg Pu (200 g/liter Pu in 4 M HNO_3) processed in the direct calciner. Median particle size of PuO_2 was 170 microns. Eighty-two percent > 105 microns, 15 percent 49 - 105 microns. Calciner operating troubles were leaking packing gland, feed pump, and plugged off-gas line to the cyclone separator.

August — Micro-photographs at 25X and 125X show that the particle size of the calciner bed has increased from 10 microns to 100 - 170 micron size. More uniformity of particle size was noted as runs progressed. Spectrographic analysis confirms that corrosion contaminants are not introduced into the bed during calcination.

September — Powder leakage through shaft seals was minimized by installation of vacuum gauge and control on calciner.

Nitrate content of product from three runs was 0.07% at an exit temperature of 400 °C. Screen analysis of product shows 76% > 105 micron, 100% > 49 micron. Off-gas entrainment remains a problem.

October — Powder entrainment in the off-gas was reduced to 25% in the calciner by installation of a two-inch diameter settling column on top of the calciner.

November — The three-inch calciner successfully processed 500 g/liter Pu solutions at a 500 g/hr rate. Entrainment of powder continues to be a problem.

1961

February — Studies on reactivity of direct calcined PuO_2 showed particle size and residence time in the calciner strongly affect the rate of chlorination of the material. A sample of two hours' calciner residence gave 85%

chlorination, while a 24-hour residence sample showed 65% conversion.

May — Reactivity of plutonium dioxide formed by direct denitration of plutonium nitrate can be improved by addition of oxalate or sulfate. Percent conversion from plutonium oxide to plutonium trichloride was 98% and 85% for oxalate and sulfate additions, compared with 60% for material without additives.

HW-69650 — H. H. Hopkins, Jr., by H. W. Crocker, *Impurity Levels In Plutonium Nitrate To Yield Acceptable Metal By Direct Calcination, Hydrofluorination, And Bomb Reduction.* 5/18/61 (Secret).

HW-69738 — R. J. Rasmussen, G. L. Stiffler, and H. H. Hopkins, Jr., *Parameters In The Conversion Of Plutonium Nitrate To Plutonium Trichloride By A Direct Calcination - Fluid Bed Chlorination Process.* 5/31/61 (Declassified).

HW-73765 — G. L. Stiffler and H. H. Hopkins, Jr., *A Vertical Calciner For Converting Plutonium Nitrate Solution To Plutonium Dioxide Powder.* 6/1/62 (Declassified).

HW-77846 — F. D. Fisher, *Reactivity Of Plutonium Dioxide Prepared By Direct Calcination Of Nitrate Solutions.* 10/15/63 (Secret).

1965

RL-SEP-674 — R. E. Felt, *Equipment For The Direct Calcination Of Plutonium Nitrate.* To be published *ca.* 12/15/65.

RL-SEP-675 — R. E. Felt, *Fluorination Reactivity Of Plutonium Oxide Prepared In A Screw Calciner.* To be published *ca.* 12/15/65.

7. PLUTONIUM PEROXIDE

1951

HW-19882 — W. L. Lyon, *Filtration Of Plutonium Peroxide Slurry.* 1/5/51 (Secret).

August — Coupling with parent plant product solution.

September — Acid neutralization; plutonium peroxide from AT-solution (concentrated product solution) - 0.5 *M* sulfate.

HW-21691 W. L. Lyon, Laboratory Evaluation Of One And Two Cycle Peroxide Processing Of F-10-P-Solutions On The Basis Of Metal Purity Obtained. 7/19/51 (Secret).

October	Variations in bulk densities; purities from single peroxide strike; effect of fluoride upon lanthanum separation.
November	Bulk density variations; disposal of methanol wash.
December	Bulk density variations; reaction of supernatants with alcohols; lanthanum separation.

1952

January	Neutralization by various agents; precipitation from concentrated plutonium solutions.
February	Effect of total nitrate concentrations; temperature variations.
March	Purity data for peroxides.
April	Decontamination factors for peroxide precipitations.
September	Precipitation from cleanout solutions containing manganese ion.

1953

February	Decontamination factors for peroxide precipitation.
March	Effect of manganese ion.

1954

HW-30558 R. A. Pugh, Laboratory Study Of Causes For High Solubilities Of Plutonium Peroxide. 1/6/54 (Secret).

February	Effect of fluoride and phosphate on formation of peroxy-complex.
August	Sulfate elimination; addition of phosphate, oxalate; temperature and acid effects.

1956

March	Continuous precipitation from 1.3 M HNO_3, 0.05 M sulfate, 50 g/l Pu solution at 20 °C feasible with 50% H_2O_2. Effects of sulfate concentration.

8. PLUTONIUM(III) OXALATE

1951

July, August	Study of process variables; coupling to Redox and Recuplex extraction process product solution.

1953

October	Plutonium(III) oxalate precipitation from Redox product solution.

1957

March	Precipitation of continuous ion exchange product at 55 °C. 1 M oxalic acid resulted in filtrate of 0.5 g/liter Pu with solids formation.

9. PLUTONIUM(IV) OXALATE

1952

January	Precipitation from 3BP (parent plant product) solution; also from concentrated plutonium solution.
February	Precipitation from synthetic 2BP (product); filter boat tests, cake-washing, filtration rates, etc.
May	Coupling studies, solubility vs. acidity; plutonium-uranium separation; supernatant treatment - boiling, platinum, hydrogen peroxide.
June	Purity data, effect of filtration; UX_1 separation; supernatant kill - platinum.

[redacted] DECLASSIFIED

HW-25844 J. F. Facer and M. N. Myers, Filter Media For Plutonium(IV) Oxalate. 9/11/52 (Secret).

September Effect of oxalic acid concentration.

October Rate of oxalic acid addition; separation from lanthanum, iron, nickel.

1953

HW-28168 K. M. Harmon, The Precipitation Of Plutonium(IV) Oxalate In Task I, Nitric Acid Tolerances, Reactor Dimensions. 5/26/53 (Secret).

Task I prototype studies.

August Temperature effects; aluminum addition; 0.06 M oxalate prior to pre-reduction; Task I prototype.

October Effect of anions; effects of stirrer speed; precipitation of solution after partial neutralization; filter cloth tests.

1954

February Glycol in the oxalate precipitation; dissolution of plutonium oxalate in aluminum and iron systems. Plutonium fluoro-oxalate.

HW-31186 J. F. Facer and K. M. Harmon, Precipitation Of Pu(IV) Oxalate. 3/30/54 (Secret).

June Agitation studies including use of air lift; interference by manganese ion; filter cloth evaluation; and mercury separation.

1955

HW-35727 J. F. Facer, Plutonium(IV) Oxalate Precipitation In The Task I Prototype. 3/7/55 (Secret).

Batch precipitation of concentrated Redox and AT solutions in Task I prototype.

March Hg limits on Task I nitrate feed of 1,000 ppm; Hg corrosion of the gold components of filter boats.

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May	DF's of 6.6 and 10 for Zr-Nb and Ru-Rh from Redox PR solution in oxalate precipitation. Stability of Dynel SD-9 cloth to oxalate precipitation.
June	Batch precipitation studies.
HW-40274	R. L. Beede, Separan 2610 As Task I (Oxalate Precipitation) Flocculant. 12/5/55 (Confidential).
1956	
March	Effect of versenes and fluoride on Zr-Nb DF across oxalate precipitation.
HW-45700	R. L. Beede, Continuous Plutonium(IV) Oxalate Precipitation, Filtration, And Calcination Process. 9/27/56 (Secret)
April	Calciner operating temperature limits. Effect of temperature on calciner capacity.
May	Degradation of Dynel SD-9 filter cloth in Task I process solutions.
November	Continuous Task I operation with 120 g/liter Pu in 5 M HNO_3 containing 0.65 M $(NH_4)_2SO_4$ showed no significant effect.
1957	
January	Purex product 146 g/liter Pu, 6 M HNO_3, 0.8 M $SO_4^=$ did not show precipitation after one-week storage. First cold runs in new continuous Task I unit used cerous nitrate (50 g/liter Ce) feed, 1 M oxalic acid strike solution. Calcined at 300 °C with 15 minutes' residence. Throughput 250 g/hr.
February	Continuous Task I cold run was made under identical conditions of the first run. Rocker arm agitator modifications.
May	Operability and capacity of continuous Task I unit demonstrated in hot runs. Purex 2BP feed 75 - 100 g/liter Pu in 4 M HNO_3, 500 g/hr, 1 M oxalic acid, loss to filtrate 1 - 3%. Precipitation directly in filter pan.
June	Continuous Task I runs using Redox 3BP as feed, 95 g/liter Pu in 4.5 M HNO_3, 500 g/hr, 1 M oxalic acid,

[redacted]

	loss to filtrate 5%. Calciner residence time studies at 350 °C. Fe impurities 300 ppm.
July	Continuous Task I runs.
August	Operation of continuous Task I on extended period. 25 kg Pu, 10% waste loss, Dynel SD-9 cloth superior. Product acceptable for fluorination and reduction.
September	Spectrographic results of the oxide produced in the sustained runs of August demonstrate the higher quality of oxide produced in continuous processing equipment. Runs demonstrate use of continuous Task I precipitation reactor with overflow of slurry into filter pan. Effects of flow control on cake quality.
October	Continuous Task I runs demonstrate suitability of simultaneous reduction-precipitation process. Calciner surge capacity tests.
November	Calciner surge tests were continued. Surge capacity 70% above normal steady state operating capacity. Test of cyclone separator and filter on calciner off-gas system.

1959

March	Effect of titanium and vanadium on Z-Plant processing. Aluminum oxide filter media tested with plutonium(IV) oxalate slurry. Study of plutonium oxalate and filtrate densities.
April	Particle size distribution in plutonium(IV) oxalate slurry. 10 - 100 micron size range. Water content of filtered plutonium oxalate cake.
May	Purification study by the continuous oxalate process flow sheet using 200 g/liter Pu in feed.
August	Effect of elevated precipitation temperatures for con-

[redacted]

tinuous plutonium(IV) oxalate formation is being investigated. Larger particle size of the precipitate was noted in runs at 50 °C compared to room temperature. Waste losses low in both cases.

HW-62060 L. K. Mudge, Influence Of Temperature On The Continuous Precipitation Of Plutonium(IV) Oxalate. 9/23/59 (Secret).

Variation in precipitation temperature for continuous plutonium(IV) oxalate did not affect purity of the precipitate.

1961

July Boron separation factor of 4 - 20 across oxalate precipitation.

1962

January Gallium separation factor 5 or better; mercuric ion 18.

1965

RL-SEP-550 M. H. Curtis, Laboratory Tests Of Filtration Characteristics. 6/9/65 (Unclassified).

10. OXALATE DESTRUCTION

1951

HW-21616 R. A. Pugh, Treatment Of 234-5 Building Concentrated Oxalate Waste Solutions For Recycle. 7/6/51 (Secret).

1954

HW-33666 RD K. M. Harmon, Supernatant Kill In Task I. 11/4/54 (Secret - Draft).

1955

March Valence adjustment studies on oxalate filtrates.

May Valence adjustment studies on oxalate filtrates.

[redacted]

June	Effects of ferric ion on valence adjustment studies for oxalate filtrates.
September	Chemical kill of plutonium oxalate demonstrated with $KMnO_4$ and H_2O_2.

1956

May	Investigation of conditions for batch and continuous killing of oxalate filtrate. Studies on stability of Dynel SD-9 filter cloth in oxalate precipitations.
HW-46711	C. J. Berglund, Evaporative Kill Of Oxalate Supernatants. 11/30/56 (Confidential).

1957

January	Pu nitrate solutions containing sulfamic acid or semi-carbazide, reoxidized and concentrated by a factor of five in a continuous kill. Feed solution was 6 M HNO_3, 0.05 M semi-carbazide, 11 - 50 g/liter Pu. Feed solution slowly added to boiling solution to safely accomplish the kill.
July	Filtrate from continuous oxalate precipitations treated by continuous chemical kill using $KMnO_4$ at 45 °C. Permanganate leg of the "U" column operated satisfactorily. Peroxide leg (1" diameter) reaction too vigorous at 10% or $2\frac{1}{2}$% peroxide concentration. Increased diameter of peroxide leg is required.
October	Evaporative kill experiments indicate manganous ion addition needed as catalyst, due to low amount of iron in filtrate.
November	Evaporative kill studies indicate a 21-minute decomposition half-time. Small amount of solids can be tolerated in the evaporative kill process.

11. PLUTONIUM TRIFLUORIDE PRECIPITATION

1956

HW-49147	C. J. Berglund, Continuous Plutonium Trifluoride Precipita-

[redacted]

[redacted]

tion: Progress Report. 3/18/57 (Confidential).

April	Continuous precipitation and filtration of PuF_3 from HNO_3 solution HF as precipitant. Effects of alcohol wash and filtrate loss. Attempted precipitation of PuF_3 from HNO_3 solution using fluosilicic acid. No precipitation noted. Effect of complexing strengths of Pu(III) and Pu(IV) on fluoride.
June	Studies on PuF_3 precipitation from high-purity plutonium nitrate using HF precipitant.
September	Effects of reducing agents, and precipitation data included.
October	Continuous precipitation from nitrate solution using 3 M HF. Feed reduced with SO_2 + ascorbic acid. Separation factors 10, 20, 10, 4 for Fe, Ni, Cr, Mg.
December	PuF_3 dried at 600 °C showed no weight change on standing 17 days.

1957

March	Continuous ion exchange product subjected to PuF_3 precipitation using 1 M excess fluoride. First strike slow filtering, 0.2 g/liter Pu in filtrate. Second strike, spiked 1000 ppm Dow Separan 2610; fast filtration, 0.05 g/liter Pu in filtrate.
April	Small-scale continuous precipitation runs, feed 50 g/liter Pu, 5 M HNO_3, precipitant 3 M HF. Valence adjustment with semicarbazide. Separation factors 125, 147 for Al and Fe. Slurry degrades upon standing overnight.

12. PLUTONIUM TETRAFLUORIDE PRECIPITATION

1955

October	Aqueous precipitation of PuF_4 from Pu(IV) nitrate solution using HF and ammonium fluosilicate.
November	Precipitation of PuF_4 from Pu(IV) nitrate solution using hydrofluosilicic acid and HF.

[redacted]

1956

January	Precipitation of PuF_4 from 40 g/liter Pu and 5 M HNO_3 with 4 M HF. Fe and Al separation factors of 10 - 20 for initial levels of 10,000 and 100,000 ppm respectively. Effects of washing on cake quality.
February	Studies on drying of the PuF_4 precipitate.

13. DOUBLE SALT PRECIPITATION STUDIES

1953

November	Precipitation studies; large-scale strike.
December	Precipitation studies.

1954

January	Double salt precipitation; 300 gram reduction.
February	Calcium-thorium fluoride precipitation.
March	Separation factors for the calcium double salt.
April, May	Large-scale operations.
June	Plant-scale operations.
Unreported	Decontamination factors for zirconium, niobium, and separation from sulfate.

14. CATION EXCHANGE CONCENTRATION

1956

November	Initial testing of semi-continuous Higgins-type columns.
December	Equipment testing results. Flow control problems on continuous equipment.

[redacted]

1957

January — Mechanical testing of hydraulic ram, conductivity probe, and pumps.

February — First continuous cation hot run completed. Steady state not achieved because of excessive gassing. Run conditions:

XAF	35 ml/min	Dowex 50W-X8 resin
XCS	2.1	
XAS	2.0	10-minute cycle
XCIS	5.0	Feed concentration 8.3 g/liter Pu
XAX	2.0	Product concentration 25 to 70 g/liter Pu. Waste losses ≈ 1%

Effects of feed reductants discussed. Elutant was 6.4 M HNO_3, 0.3 M sulfamic or semicarbazide.

March — Workable flow sheet was demonstrated in a continuous, two-week-long "hot" run of cation column. Run conditions:

XAF	39.5 ml/min	10-minute cycle
XCIS	5.0	Dowex 50W-X8 resin
XAS	2.0	Feed 2.5 to 7 g/liter Pu
XCS	2.1	Product 35 to 75 g/liter Pu
XAX	2.0	Waste loss 0.1%

Most promising feed reductant was 0.1 M NH_4HSO_3.

Effects of plutonium polymer formation during feed preparation.

Most promising eluant 5 M HNO_3-0.33 M sulfamic acid.

Higher product concentration may require cooling of XC column.

Stability of cation exchange product: oxidation of XCP dependent on solution acidity. Oxidation rate 0.2 to 5%/day. Effects of other reagents discussed.

Adjustment of Purex 2BP to 7 M HNO_3 resulted in oxidation to Pu(IV) within two minutes, for anion exchange feed.

[redacted]

15. ANION EXCHANGE CONCENTRATION

1957

April Tentative flow sheet demonstrated in a continuous hot anion exchange run.

Run conditions:

Resin Dowex 1-X4 (nitrate form) 5-minute cycle
Feed concentration 6 g/liter
Product concentration 45 g/liter Pu
Column temperature 50 °C

Effect of column temperature, feed flow rates, etc., discussed.

May Continuous runs with Purex 2BP as feed solution showed anion exchange to be superior to cation process for purification and decontamination.

1. Anion Zr-Nb DF of 28, Ru-Rh DF of 2.0
   Cation Zr-Nb DF of 3, Ru-Rh DF of 3.0.
2. Total gamma DF of 3 for both anion and cation.
3. Anion reduces silicon 10 to 20 fold, silicon not removed in cation process.
4. Anion: separation factors for (Cr, Cu, Fe, Mn, Ni, Ph) of 5 to 20, and (Al, Ca, K, Mg, Na) of 100.

Cation removed only slight amounts of light metals, none of the heavy metals.

June Changes made to permit sustained anion exchange runs at high throughput with Dowex 1-X4 anion resin.

July Operation of the anion exchange system on a Purex flow sheet in the temperature range of 50 to 70 °C and feed acidity range of 5 to 7.2 $\underline{M}$ HNO_3 was satisfactory. Flow rates up to 30% greater than the 54 mg $Pu/min/cm^2$ required by flow sheet were used. Product concentration was near the 58 g/liter equilibrium value. The ratio of XSW to XAX appears to depend on the volume of resin pushed. Satisfactory resin push was attained with 10 psi pressure. Zr-Nb DF = 250, Ru-Rh DF = 30 when adequate scrub flows are used. Appreciable FP's accumulate on the resin and are difficult to remove. Metallic separation factors varied from 5 to 100. Effects of temperature control, acidity, and column dimensions are recorded.

16. PLANT FEED SOLUTION STUDIES

1954

February	Plutonium phosphate precipitation in F-10-P (parent plant product solution).
December	F-10-P filtration and stabilization.
Unreported	ANN in 3BP - concentration effects.

1956

February	Effects of filtration and precipitation on removal of Zr-Nb from Purex PR solution. DF of 1.2 obtained.
March	Studies on use of silica gel or Dowex-1 column for Zr-Nb removal from Purex PR solution (DF's of 3).
May	Solids in concentrated Purex PR solution - Pu polymer, silica, iron, phosphorus. Dissolution procedure.
	Concentration of Purex 2BP.
July	Solids in Redox L-3 to L-4 valve. Ru, Zr, Nb, Al, Cr, Cu, Fe, Ni identified.
August	Study on solids in Purex tube bundle - primarily silica.
	Study on precipitation in Redox E-1, E-3 vessels.
	Studies on solids in Redox L-3 to L-4 valve.
October	Study of solids found in Purex concentrator. Contained high silica and iron. Si/Pu ration of 1/5 in solids.

1957

March	Purex concentrator solids. Black flint-like material

[redacted]

from Purex product concentrator contained mostly Si and Fe. Cr, Ni also detected, Pu was 1%.

1958

April	Solids in Purex ion exchange concentrator. Pu(IV) polymer and resin fines identified.

17. NEPTUNIUM PRECIPITATION

1958

August	Neptunium oxide (< 200 ppm metallic impurities) produced by oxalate precipitation and calcination. Bulk density was 2.7 g/cc. Effect of radiation buildup noted.

18. CORROSION

1952

December	Corrosion of alloys in HF-HNO_3.

1954

September	Haynes 25 for HNO_3-HF system. Elgiloy for HF-HNO_3 vapors.
October	Corrosion of Haynes 25 in HNO_3-HF solutions.
December	Stainless steel corrosion in slag and crucible solutions.

1956

September	Titanium corrosion in 8 M HNO_3, 130 g/liter Pu(IV), at boiling point 0.0003 ipm.
October	Corrosion of tantalum, titanium, 304-L stainless

[redacted]

[redacted]

steel in HNO_3-Pu solutions. Effect of sulfate ion. Ta and Ti superior.

HW-46779	A. Brunstad, Corrosion Of Stainless Steel, Titanium, and Tantalum In Plutonium-Nitric Acid Solutions. 11/27/56 (Unclassified).
December	304-L corrosion rate in boiling solution of 0.003 M oxalic acid - 5 M HNO_3 containing 1.5 g/liter Cr^{+3}, 0.00018 ipm.

1959

September	Corrosion of titanium and tantalum in HNO_3-HF-$Al(NO_3)_3$ system. Titanium corrosion rate was 3 mils/month, while tantalum was negligible.

1960

April	Corrosion tests of 309 SCb as welded, 309 SCb annealed, and 309 L welded and annealed stainless steel samples in Recuplex dissolver solution gave corrosion rates in excess of 0.035 ipm in all cases. Test duration was 150 hours.

19. MISCELLANEOUS

1954

January, March November	Filtration of aluminum nitrate.

1958

HW-56349	H. D. Warren and A. Brunstad, Turbidimetric Microdetermination Of Sulfate In Plutonium Solution. 3/14/58 (Unclassified).

[redacted]

1965

RL-SEP-823 H. T. Fullam, Thermal Stability Of Anion Resin In A Vented System. To Be Published ca. 12/15/65 (Unclassified).

B. DRY CHEMICAL CONVERSIONS

1. CALCINATION OF OXALATE

1952

September	Drying of plutonium(IV) oxalate: 150 °C, lumps, 300 °C for calcination; thermal decomposition of plutonium(III) and (IV) oxalate.
October	Plutonium(IV) oxalate drying procedure - glowing boat; temperature measurements.
December	Drying of plutonium(IV) oxalate (130 °C - hexahydrate).

1953

February	Plutonium(IV) oxalate decomposition - exothermic reaction.
May	Calcination of plutonium(IV) oxalate.
September	Calcination of plutonium oxalate.
October	Thermal decomposition of plutonium oxalate.

1954

February	Infra-red drying and calcining of oxalate.
March	Decomposition of plutonium(IV) oxalate; reactivity of PuO_2.

1956

April	Operating temperature range of 300 to 400 °C for

[redacted]

continuous Task I calciner determined from laboratory tests.

2. HYDROFLUORINATION OF PLUTONIUM PEROXIDE

1951

HW-21751	W. L. Lyon and B. Weidenbaum, *The Use Of Plutonium Peroxide For The Preparation Of Plutonium Tetrafluoride.* 7/26/51
October	Effect of air leakage.

3. HYDROFLUORINATION OF OXIDE

1950

HW-18796	J. F. Facer and W. L. Lyon, *Direct Hydrofluorination Of Plutonium(III) Oxalate.* 9/11/50 (Secret).
HW-19771	J. F. Facer and W. L. Lyon, *Gas Composition For The Direct Hydrofluorination Of Plutonium(III) Oxalate.* 10/26/50 (Secret).

1951

HW-20164	J. F. Facer and W. L. Lyon, *The Preparation Of Plutonium Tetrafluoride By Direct Hydrofluorination Of Plutonium(III) Oxalate.* 2/1/51 (Secret).

1952

July	Summary of dry chemistry and reduction data.
September	Cake depth vs. hydrofluorination rates.
October	Tolerance to laboratory air - 37% relative humidity.
November	Hydrofluorination of erupted boat load; tolerance to laboratory air. Analysis by conversion to oxide.

[redacted]

[redacted]

1953

October Direct hydrofluorination of oxalate - PuF_3 production.

1955

HW-36173 W. S. Figg, Continuous Task II Program - Plutonium(IV) Oxalate Calcination And Hydrofluorination Studies. 4/12/55 (Secret).

August Study on SiC filters as replacement of platinum frits for Task II.

December Continuous PuO_2 hydrofluorination studies, processing rate 0.4 kg/hr, $PuF_{3.72}$, reduction yield of 98.6% on PuF_4 product.

1956

HW-43953 M. N. Myers, The Use Of Freon-12 In The Conversion Of Plutonium(IV) Oxalate To Plutonium Trifluoride. 6/27/56 (Confidential).

HW-45917 R. L. Beede, Conversion Of Plutonium Trifluoride To Plutonium Tetrafluoride With Oxygen-Hydrogen Fluoride Mixtures. 9/27/56 (Secret).

September Simulated operation of plant reactor tested by conveying powder in a vibrating oval tray.

1957

January A plastic (Teflon and fluorothene) rotary feed valve replaced inconel feed screw to eliminate corrosion in continuous hydrofluorinator.

HW-65536 RD H. W. Crocker, Continuous Hydrofluorination Of Plutonium Oxide. 11/13/57 (Secret - Draft).

[redacted]

4. FREONATION AS A FLUORINATION METHOD

1952

July	First work.
December	Additional results.

1953

February	Two deep cake runs.
April	Work abandoned: corrosion, polymerization.
December	Corrosion in freon.

1956

HW-43953	M. N. Myers, The Use Of Freon-12 In The Conversion Of Plutonium(IV) Oxalate To Plutonium Trifluoride. 6/27/56 (Confidential)

5. PROCESSING OF METAL TURNINGS

1951

August, September	Hydrofluorination.

1955

September	Recovery of alpha phase turnings by controlled oxidation--fluorination.
October	Controlled oxidation of metal turnings in argon and oxygen, subsequent fluorination in Freon-12.
	Direct conversion of metal turnings to PuF_3 with argon and Freon-12.

[redacted]

6. HYDROGEN FLUORIDE ABSORPTION

1951

HW-23019 G. E. Benedict and K. M. Harmon, Removal Of Hydrogen Fluoride At Low Concentrations In Air Streams By Activated Charcoal And Sodium Fluoride. 12/2/51 (Restricted).

1952

HW-24495 K. M. Harmon, Removal Of Hydrogen Fluoride From An Air Stream By Adsorption In A Dorex Charcoal Filter. 5/16/52 (Secret).

HW-25771 K. M. Harmon, Capacity Of Marble Chips To Absorb HF Gas. 9/29/52 (Unclassified).

HW-26092 G. E. Benedict, Use Of Counter-Current Caustic Scrubber Column For Removal Of HF From Hydrofluorination Off-Gases. 11/3/52 (Secret).

7. CHLORINATION AND $PuCl_3$ PROCESS

1958

April Chlorination rate study for conversion of PuO_2 to $PuCl_3$ with CCl_4. Effect of temperature on rate and powder density.

June Chlorination rate study for conversion of PuO_2 to $PuCl_3$ with CCl_4. Reaction products identified as C_6Cl_6, C_2Cl_4, C_2Cl_6, CO_2, CO, Cl_2, $COCl_2$.

July Large-scale batch chlorinations of PuO_2 by $COCl_2$ continued. Effect of calcination temperature of PuO_2 on chlorination rate. High temperature chlorination (600 °C) introduced unknown residues in off-gas.

Plastic materials' resistance tested in phosgene atmosphere.

HW-57498 H. H. Hopkins, Jr., Status Of Plutonium Trichloride--Process Development. 9/17/58 (Secret).

The status of the $PuCl_3$ program. Flow sheets for

[redacted]

[redacted]

preparation of the compound, reduction to metal, and recovery schemes are included.

November — PuO_2, previously heated to 1800 °C, was chlorinated to $PuCl_3$ in five hours using $COCl_2$ at 450 °C.

Study of hydration rates of $PuCl_3$ completed over range 2 to 75% relative humidity. A discussion and graph are included.

December — Samples of $PuCl_3$ from batch and continuous processing were found to have four and six micron particle size, respectively.

Large-scale batch conversions of PuO_2 to $PuCl_3$ by $COCl_2$ were made for reduction studies.

1959

January — Continuous chlorination of PuO_2 by $COCl_2$ in the 1" diameter tube operated at 70 g/hr on an extended run.

Run conditions:

Powder bed depth:	3/8"
Residence time in furnace:	45 minutes
$COCl_2$ flow:	200% excess
Temperature:	500 °C.

Effects of temperature and flow rates on the conversion are included.

Pu/Cl ratio = 2.7.

$COCl_2$ retention in cake: $0.02 \, \frac{\text{moles } COCl_2}{\text{mole } PuCl_3}$

Corrosion studies in $COCl_2$ system over 100 to 500 °C range. Hastelloy B and C most promising materials.

HW-59749 — L. F. Lust, The Analysis Of Exhaust Products In The Chlorination Of Plutonium Oxide With Phosgene. 3/24/59 (Confidential).

A summary of off-gas studies.

June — Chlorination of PuO_2 from direct calcination of plutonium nitrate solution.

[redacted]

Elimination of lump formation in the large continuous chlorinator.

August Demonstration chlorinator operated at 320 g Pu per hour. Off-gas filter and scrubber operation problems encountered. Equipment corrosion is low. Analysis of $PuCl_3$ product shows 97% conversion of the PuO_2 feed to halide. Operating temperature was 500 °C.

HW-61570 H. H. Hopkins, Jr., Status Of Plutonium Trichloride - Process Development (II). 8/14/59 (Secret).

HW-62967 R. W. Legan, Reprocessing Of Off-Standard Plutonium Trichloride Powders. 12/7/59 (Confidential)

Mixtures of PuO_2 and $PuCl_3$ (high impurities) best handled by oxidation to PuO_2 and dissolution in HNO_3-HF.

Hydrated or wet $PuCl_3$ can be dried adequately in phosgene atmosphere by heating from 80 °C to 180 °C and completing chlorination at 450 °C.

1960

January "Aloxite" filters in the vibrating tube off-gas system are giving adequate dust filtration. Some powder caking problem noted.

February Improved $PuCl_3$ preparations obtained by better control of each of the three furnace section in the vibrating tube unit.

The use of $PuCl_3$ from the vibrating tube unit has resulted in occasional low-density Pu button formation--cause unknown.

I&EC, Vol. 53, Page 453, June, 1961 M. J. Rasmussen and H. H. Hopkins, Jr., Preparing Plutonium Metal Via The Chloride Process.

August Plutonium dioxide from direct continuous calcination showed lower reactivity toward chlorination than oxide from calcined oxalate. In 20-minute chlorination tests, PuO_2 from oxalate yielded 3% insolubles; and from direct calcined nitrate, 30 to 60% insolubles.

October Five kg of plutonium chloride were prepared in the vibrating tube reactor. Chlorination was 96% complete

[redacted]

at a 250 g/hr plutonium rate.

1961

May — Formation of volatile chlorides by phosgene at 500 °C results in separation factors of 8, 4, and 100 for aluminum, iron, and gallium, respectively, from plutonium.

Ammonium chloride is not an effective chlorinating agent for plutonium oxide at 300 to 320 °C. Tests showed only 10% conversion in one hour.

1962

HW-72920 — H. H. Hopkins, Jr., by M. J. Rasmussen, Plutonium Trichloride Process Flow Sheet. 3/1/62 (Secret)

A comprehensive survey of the application of previous work.

HW-75970 — F. D. Fisher and J. G. Michaelson, Identification Of Acid-Soluble Material In $PuCl_3$. 12/29/62 (Unclassified)

HW-75971 — J. G. Michaelson, Preparation Of Plutonium Oxychloride. 12/29/62 (Unclassified).

1965

RL-SEP-673 — H. T. Fullam and T. S. Soine, Chlorination Reactivity Of Plutonium Oxide Prepared In A Screw Calciner. 8/13/65 (Unclassified).

A detailed study of reactivity.

8. FLUIDIZED BED CONVERSION

1960

January — The one-inch diameter fluid bed showed 50 to 70% conversion of PuO_2 to $PuCl_3$ during halogenation experiment at 450 °C.

[redacted]

[redacted]

February — Fluid bed halogenations indicate PuO_2 from direct calcined nitrate has a much lower reactivity than dioxide prepared by oxalate calcination.

October — The two-inch diameter fluid bed.

1961

June — The demonstration fluid bed unit (two-inch diameter) has been assembled.

1964

HW-83235 — H. L. Brandt, Development Of Fluidized Bed Chlorination For Converting PuO_2 To $PuCl_3$. 7/10/64 (Unclassified).

A status report issued at termination of the program.

9. STIRRED BED REACTOR

1965

RL-SEP-414 — T. S. Soine, Stirred Bed Gas-Solids Reactor. 8/65 (Unclassified).

An improved batch reactor.

RL-SEP-722 — H. T. Fullam, Flat Bed Gas-Solids Contactor. 9/17/65 (Unclassified).

A new design of critically safe, continuous gas solids reactor.

10. PROPERTIES OF DRY COMPOUNDS

1957

April — A two-gram sample of PuO_2-UO_2 mixed crystal prepared by H_2 reduction at 900 °C of ammonium diuranate - plutonium hydroxide formed by an ammonium hydroxide precipitation from a mixed nitrate solution. Pu/U = 1.5.

HW-54405 — R. E. Latta, The Stability Of Anhydrous Plutonium Trifluoride

[redacted]

[redacted]

To Saturated Water Vapor At Room Temperature. 1/7/58 (Confidential).

1958

February	Radiation dosage study on high-exposure plutonium. Effect of increase in hard gamma radiation on dosage.

1959

October	After 98 days, the H/Pu ratio changed from 14.96 to 14.28 and 14.79 for the plutonium oxide - polyethylene and plutonium oxide - methyl methacrylate cylinders, respectively. No dimensional changes were noted.
November	Five batches (150 g) of $UO_2 \cdot PuO_2$ mixed crystal were prepared for reactor fuels use. Plutonium content ranged from 4 to 90 weight percent.

1963

January	Packed densities of compounds: PuO_2 (Line) 0.92, PuO_2 (direct calcination) 1.58, PuF_4 (Line) 1.86.

C. REDUCTION TO METAL

1. FLUORIDE REDUCTION STUDIES

1951

July	Reduction of PuF_3.
September	Bomb fusion of turnings.

1952

April	Slag melting points. Mixed calcium and magnesium.
May	Addition of sodium fluoride, calcium-magnesium.

[redacted]

calcium-strontium alloys.

July	Sintered PuF_4 reduction. Reductions in air.
August	Effect of air.
October	Reduction of PuF_3 from freon halogenation.

1953

HW-27488 K. M. Harmon, W. L. Lyon, Laboratory Evaluation Of Double Batch Size Reductions. 3/27/53 (Secret).

April	Reduction of low-temperature fluorides.
May	Blue fluoride reductions.
June	Use of a single crucible for different batch sizes.
July, August	Blue fluoride reductions - plant scale.
November	Large-scale reduction of calcium plutonium fluoride, small reductions, reduction of calcium fluoride, plutonium fluoride mixtures

1954

January	Test of new Task III [reduction] pressure vessel.
Unreported	Spectrochemical analysis of metal from double salt reduction.

1955

July	Studies on hot water pickling of reduction buttons

HW-39012 R. L. Beede, Laboratory Evaluation Of Nelco Calcium For Plutonium Tetrafluoride Reduction. 9/15/55 (Confidential).

Evaluation of Nelco calcium without redistillation or grinding.

1957

July — Nine hundred grams of "blue fluoride" were divided into two batches and reduced. I_2/Pu was 0.8, excess Ca was 0.6. Yields were 98%, metallic impurities < 550 ppm. This indicates poor reduction from wet precipitated fluorides are probably due to oxide formation on the powder surface.

1958

January — Study of calcium reactivity and pressure buildup associated with reduction in Task III. Effect of moisture and I_2 on PuF_4 and Ca mixtures at room temperature.

1965

RL-SEP-259 — R. S. Rosenfels, Status Of Reusable Reduction Liner Development. 1/27/65 (Secret).

Description of reusable ceramic reduction liner cemented into a metal can. Tests and evaluation

2. SULFUR BOOSTER

1951

HW-21897 — W. L. Lyon, Reduction Of Plutonium Tetrafluoride To Metal In Charges Containing Calcium And Sulfur. 7/26/51 (Secret).

1953

HW-27881 — W. L. Lyon, Laboratory Evaluation Of The Use Of Sulfur In Reduction. 5/1/53 (Secret)

3. GALLIUM ALLOY FORMATION IN BOMB REDUCTION

1952

HW-25402 — K. M. Harmon, W. L. Lyon, and M. N. Myers, Addition Of

[redacted]

70-58 Oxide In Task III [Reduction Step]. 8/15/52 (Secret).

1953

HW-28357	W. L. Lyon, The Preparation Of Plutonium Alloy Castings In The Reduction Crucible. 10/1/53 (Secret).

4. OXIDE REDUCTIONS

1956

January	Reduction of CeO_2 to metal using Ca plus I_2 booster. Effects of slagging agents noted.
May	Reduction of PuO_2 by Ca resulted in no segregation or coalescence of metal. Cerium oxide reduction by Ca resulted in metal beads (cerium) up to $\frac{1}{4}$" diameter.
June	Attempt to reduce 40 grams PuO_2 resulted in no visible metal formation.

1958

August	Reduction of CeO_2 to Ce with calcium in CaF_2-$CaCl_2$ eutectic.

5. PLUTONIUM TRICHLORIDE

1958

April	Effect of Si and B pickup by Pu from Glascast crucibles.
May	Large reductions (0.6 - 1.0 kg) of $PuCl_3$ investigated. Button quality acceptable. Slag soaking problem in large reduction. Effect of two nesting crucibles as slag container.
June	Nickel-coated MgO crucibles prevent slag soaking and

[redacted]

[redacted]

crucible sticking in reduction of $PuCl_3$ to Pu.

Acceptable reductions made with $PuCl_3$ containing up to 1% water.

1958

September — $PuCl_3$ stored 1300 hours at 8.5% relative humidity was reduced to metal with a 72% yield.

October — $PuCl_3$ formed at 600 °C required additional $Ca-I_2$ booster for good reduction to metal.

A mixture of 55% $PuCl_3$-45% PuOCl was reduced to metal by calcium with a 95% yield.

Study of optimum amount of water tolerated in $PuCl_3$ to 96% reduction to metal. 0.6% water can be tolerated.

December — Study of $PuCl_3$ reduction with elimination of the mixing step.

1959

January — A 30-g button was recovered when 50 g of Pu as $PuCl_3$ were dropped with calcium into a crucible at 800 °C. The semi-continuous reduction atmosphere was argon.

March — Study of steel-coated MgO crucible in $PuCl_3$ batch reductions.

HW-60151 — T. S. Soine, Calcium Iodide - Calcium Chloride System. 4/24/59 (Unclassified).

May — Test of reusable NaCl-KCl impregnated MgO crucible for $PuCl_3$ batch reductions 20 - 200 gram scale.

Test of reusable nickel-coated MgO crucible on 700-gram $PuCl_3$ batch reductions.

HW-61564 RD — T. S. Soine, Batch Reduction Of Plutonium Trichloride. 8/14/59 (Secret - Draft).

September — Cause of variable button density remains unknown. A 700-gram size reusable MgO crucible has been used

[redacted]

[redacted]

	successfully eight times.
October	Reusable crucible used 12 times before cracks in ceramic liner caused failure. Reductions of $PuCl_3$ containing > 13% insolubles result in poor yields.
November	Experiments confirm that large amounts of PuOCl adversely affect $PuCl_3$ reduction to metal. Work on $BaCl_2$-impregnated reusable crucible shows lowered chemical attack on ceramic liner during reductions.
1960	
January	Reductions of $PuCl_3$ from vibrating tube chlorination gave > 99% yield and button densities of > 19.2 g/cc.
February	Reduction of $PuCl_3$ from vibrating tube unit gave occasional low density buttons. Traces of H_2, O_2, and N_2 were detected in button analysis, but no correlation evident.
April	Reusable crucible developed by cementing a ceramic crucible into a steel can with a mixture of sodium fluoride and calcium fluoride (MP = 810 C). Successful reductions were made in the unit. Reduction products were removed by drilling with a hole saw. Two $PuCl_3$ reductions were made in a tantalum crucible. Some tantalum oxide formation was noted on the crucible. Metal removal was no problem.
June	Tests on 500-g scale show 5% PuO_2 content in $PuCl_3$ gives 97% yield - 19.2 g/cc metal density, while 10% PuO_2 content reduced yield to 67% and metal density to 19.1 g/cc.
Paper Presented At NW Regional Meeting, ACS 6/16, 17, 1960	T. S. Soine and H. H. Hopkins, Jr., Active Metal Reduction Of Plutonium Trichloride

[redacted]

[redacted]

1961

October	Carbon in metal from chloride process averaged 160 ppm.
HW-72268	G. A. Saltzman and T. S. Soine, Calcium Reduction Of Plutonium Trichloride In A Fused Salt System. 1/12/62 (Confidential).

6. ELECTROWINNING

1958

April, May	Container studies started to determine suitable material for the NaCl-KCl-$BaCl_2$ melt at 800 °C. Zircon, stabilized zirconia, high-density alumina, nickel-coated MgO show promise. Studies used argon and H_2-HCl atmospheres.
June	Initial solubility study for $PuCl_3$ in NaCl-KCl-$BaCl_2$ melt. Container study continued using system of $CeCl_3$, NaCl-KCl-$BaCl_2$ melt, and Ce in argon at 800 °C. Effect of melt penetration and sticking noted.
July	Thoria, Pyroceram, and molybdenum crucible tests in the NaCl-KCl-$BaCl_2$ melt, argon, H_2, HCl system at 800 °C.
August	Description of newly-installed continuous electrolytic equipment. Tests of crucibles in a mixture of plutonium metal, $BaCl_2$-KCl-NaCl melt, and $PuCl_3$ in argon at 800 °C. Alumina crucible was most promising. Effect on other materials is recorded.

1959

July	Seven "hot" tests made with electrodeposition equipment. Successful plutonium deposits on cathode. Cell integrity problems noted. Cells tested were zirconia and alumina.
August	Electrodeposition tests resulted in 16 g Pu metal formation. Alumina cell contributed contamination to the metal product. Test of zirconia cell halted because of electrode shorting problems.
December	A magnesia cell impregnated with internal CaF_2 coating and nickel outside coating showed high resistance to flux and molten metal.

[redacted]

1960

February

Molybdenum and aluminum pickup in metal from process refractories.

Candling method of inspection reveals serious cracks and air bubbles in refractories which normal visual inspection cannot detect.

May

Corrosion tests of cell and electrode materials are in progress. Tungsten resistance to molten salts and molten plutonium was superior to molybdenum. Morganite (Al_2O_3) and 10% TiO_2-MgO cells were tested successfully in the two-phase system and molten plutonium, respectively.

June

Nickel-coated zirconia cell showed little corrosion attack in a four-hour run at 12% efficiency.

Nickel-coated magnesia-10% titania cell showed little corrosion attack in five-hour run at 22% efficiency.

Use of tantalum wire to connect molten product metal pool to cathode lead has reduced corrosion.

July

Runs using nickel-coated magnesia-titania cells.

August

Recent runs averaged 54 to 58% current efficiency, 23 to 31 amps operating current, and 100 to 200 grams plutonium product per run.

A foaming condition was eliminated by changing cell temperature, heat distribution, and molten salt composition. Cells and vent tubes (MgO-TiO_2 cells nickel-coated) are lasting longer than run duration. Run terminations caused by plugged off-gas line, plugged product overflow, and feed screw failure.

September

Run durations of 10 hours achieved. Plutonium production > 250 g/run. Cells were successfully exposed to molten materials > 12 hours without failure. Run terminations were due to product removal and molten salt overflow problems. Addition of a scraper-wiper has improved delivery of salts into the cell.

October

The 10-hour run reported in September resulted in a yield of 525 grams of plutonium with a current efficiency of 60.3%. Chief product contaminants were stainless steel corrosion product from accessary hardware.

November — A product purity run showed metal ion cleanup for elements with volatile chlorides.

Anode corrosion and vent tube (tantalum) corrosion at the salt-gas interface was evidenced in the runs.

December — One week of around-the-clock operation was attempted. Seven runs were made in the period. The longest run was 21 hours. Highest current efficiency was 41%. Vent tube replacement at 750 °C was demonstrated. BeO and $MgO-TiO_2$ refractory cells showed corrosion failure. ZrO_2 cell corrosion was not thoroughly tested. A limited test of a protected tungsten vent tube was promising.

1961

March — Improvement in hardware has reduced mechanical failures. Thermal shock tests have disclosed weaknesses in the nickel-coated cells.

A five-hour run produced 262 grams of plutonium. Run termination was not caused by equipment or failure. Run was at 30 amps. System response followed feed additions and voltage adjustments well.

April — An estimated 85 g/hr run was made. Improved flame spraying techniques have resulted in better nickel-coated ceramic cells.

1962

HW-75363 — M. H. Curtis, Continuous Electrowinning Of Plutonium Metal--Status Report. 10/26/62 (Confidential).

1963

January — PuO_2 dissolved fastest in melts with greater chloride ion activity.

HW-77591 — C. R. Becker and T. S. Soine, Screening Tests For Proposed Molten Salt Electrolytes. 5/10/63 (Confidential).

[redacted]

1965

RL-SEP-30 M. H. Curtis, Continuous Electrowinning Of Plutonium Metal--Progress Report. 4/65 (Unclassified).

A comprehensive, detailed summary of the significant work to date.

RL-SEP-244 T. S. Soine, Continuous Electrowinning Of Plutonium Metal, Scaleup Studies--Progress Report. (Unclassified).

A detailed description of large-scale tests performed from 1963-1964.

D. HIGH-PURITY PLUTONIUM METAL PROCESS

1957

May Two reductions to metal of purified PuF_3 were performed in CaO and CaF_2 crucibles. Button can be easily removed from CaF_2 crucible. High-purity CaF_2 crucibles are now available. Main impurities were:

Run #6 Ca 20 to 40 ppm, Ni 10 to 100, Fe 150, density 19.54.

Run #7 Al 8 to 20, Fe 50 to 200, Mg 10, density 19.36

June High-purity reduction (Run #8) with CaF_2 crucible using calcium with 60 ppm C resulted in 25% yield. Major impurities: Fe 69 ppm, Mg 100, Mn 10, Na 10, C 80.

HW-54578 R. E. Latta, Laboratory Production Of Pure Plutonium. 1/15/58 (Secret).

1958

February Metal button dissolved, purified by peroxide precipitation and hydrofluorinated to PuF_4 for special radiation studies. Total metallic impurities 100 ppm.

[redacted]

E. RECOVERY PROCESSING - FEED PREPARATION

1. SLAG AND CRUCIBLE DISSOLUTION - FLUORIDE

1952

January	Dissolution of sulfur slags.
May	Corrosion rates for dissolution.
June	Analysis of filter cakes; removal of iodate-sodium nitrate addition.
July	Silica analysis.
August	Plutonium holdup from dissolution.
November	Dissolution of fluorides in ANN-HNO_3.

1953

May, June	Filtration of slag and crucible solution - alundum (Al_2O_3) plates.
November	Dissolution of calcium fluoride - calcium iodide - calcium sulfide slag.

HW-30015 R. A. Pugh and W. L. Lyon, Dissolution Of Slag And Crucible Residues For Plutonium Recovery. 11/1/53 (Secret).

1954

January	Silica in off-gas.
March	Aluminum-to-fluoride ratio.
April	Iodate formation.
June	Silica in off-gas
October	Slag and crucible dissolution - SCX-1 corrosion rates, Haynes 25 and stainless steel corrosion.

1955

HW-38753 M. N. Myers, Hydrogen Production In The Calcium And Magnesium - Nitric Acid Reactions. 8/19/55 (Declassified).

December	Oxidation of calcium metal in unreacted PuF_4-Ca mixtures to eliminate H_2 evolution during powder dissolution.

1958

February	Study of steel slag and crucible can dissolution in 8 $\underline{M}$ HNO_3-0.3 $\underline{M}$ HF.

1960

June	Teflon dissolver operated without apparent damage in 13 $\underline{M}$ HNO_3 - 0.25 $\underline{M}$ HF for 123 hours. Outside vessel temperature was 110 to 170 °C.

1961

January	A two-liter glass dissolver was used for continuous dissolution of plutonium-bearing slag and crucible residues. Slag and crucible feed rate was 175 grams/hour in a seven-hour run. This rate corresponds to the flow sheet rate for the proposed large-scale dissolvers. Iodine concentration in the dissolver overflow solution was 0.55 g/liter and 2.5 g/liter, respectively, as iodine and iodate. Substantial, but controlled, foaming was encountered. Undissolved solids heel was $\approx$ 10% of the feed volume. Gelatinous solids formed in the overflow solution after storage for several hours.
February	A 28-hour continuous slag and crucible dissolution was completed. Essentially all the plutonium dissolved at flow sheet rates. Iodine concentration in the dissolver overflow product was 0.7 g/liter and 2.0 g/liter as iodine and iodate. Foaming continues to be troublesome. The overflow solution contained some gelatinous solids. Dissolver solution diluted to column feed specifications gave an E_a^o of 16 for plutonium when contacting with 20% TBP-80% CCl_4.

[redacted]

March	A 32-hour run was completed. Plutonium recovery was quantitative. Dilution of dissolver feed acid eliminated formation of gelatinous solids in the product overflow solution. A solids heel of 8% remained at run end. Foaming occurs at each solids addition charge to the dissolver. Product solution adjusted to column feed specifications was contacted with 20% TBP-CCl_4. Four stages of extraction removed 98% of the plutonium.

HW-69515 H. W. Crocker, Continuous Dissolution Of Plutonium-Bearing Slag And Crucible Residues. 6/61 (Unclassified).

A comprehensive summary covering the continuous dissolution work. Process points are (1) adequate plutonium dissolution, (2) satisfactory plutonium extraction from the dissolver product solution, and (3) low iodine and iodate content in product solution. Problems were (1) vigorous reactions during solids addition and (2) small solids heel buildup in dissolver.

2. SLAG AND CRUCIBLE DISSOLUTION - CHLORIDE

1958

March	Synthetic ("cold") chloride slag and crucible recovery studies. Effect of chloride boiloff with nitric acid as part of the dissolution process.
April	Dissolution, I_2 removal and chloride removal, were effected by 13 $\underline{M}$ HNO_3 at boiling point on synthetic slag and crucible. High degree of chloride removal accomplished. Degree of silica coagulation not evaluated.
August	Flow sheet for chloride removal and slag and crucible recovery determined from "hot" runs. Plutonium recovery of 89%. Elimination of separate iodine removal period. Precipitation and redissolution of plutonium polymer from slag and crucible solution to perform purification and volume reduction.
September	Little effect noticed on aluminum slag and crucible cans due to long-term storage of chloride reduction slag.

[redacted]

HW-58021 R. W. Henkens, Precipitation Method For The Recovery Of Plutonium From Chloride Slag And Crucible--Progress Report. 10/30/58 (Declassified).

Description of an alternate recovery process involving hydrolysis and precipitation of plutonium. Low acidity for precipitation is obtained by distillation of acid and water until a molten salt residue remains. Material then diluted, filtered, cake dissolved for processing, and filtrate discarded. Volume reduction advantages.

Plutonium recovery of 99%.

December Nickel-coated crucible dissolutions were made with the standard flow sheet, chloride boiloff, followed by HNO_3-HF dissolution of residue, without difficulty.

Test of hydrolysis-precipitation flow sheet revealed difficulties caused by nickel in slag and crucible. Coprecipitation of Mg, Ca, and Ni, along with the Pu, and high waste losses to the filtrate occurred.

1959

January Test of reducing agents for Pu reduction to (IV) valence in hydrolysis-precipitation recovery method for nickel-coated MgO crucibles.

Large-scale (one crucible and slag) dissolver has been installed for chloride slag and crucible recovery development.

February Study of valence adjustment and precipitation parameters for hydrolysis-precipitation method of reprocessing nickel-coated MgO crucibles.

HW-61577 R. C. Smith, Recovery Of Plutonium From Chloride Slag And Crucible. 8/14/59 (Declassified).

September Dissolution of chloride slag and crucible containing fluoride with F/Al ratio of 1 was tested. Corrosion of glass equipment was negligible. Plutonium dissolution was not impaired, but solid residue was greater than normal.

[redacted]

1963

HW-77369 M. H. Curtis, Plutonium Recovery By The Quick-Leach Process. 4/26/63 (Unclassified).

HW-78655 M. H. Curtis, Plutonium Recovery From Chloride Button Line Wastes. 8/15/63 (Confidential).

3. OXIDE DISSOLUTION

1961

HW-68655 H. W. Crocker, Ammonium Bifluoride Fusion Of Ignited Plutonium Dioxide. 2/24/51 (Declassified).

> Average plutonium recoveries of 95% achieved. Approximately three hours are required for the process cycle. Applications of the process include recovery of plutonium from incinerator ash and metal or metal skulls.

4. METAL DISSOLUTION AND PRETREATMENT

1953

February Skull dissolution.

May, June Dissolution of reduction charges (caustic treatment).

1955

HW-34540 K. M. Harmon and R. C. Smith, Chemical Reactivity Of Plutonium Metal. 1/24/55 (Secret).

HW-39080 R. C. Smith and R. Wirta, Effect Of Ultrasonics On Dissolution Of Nickel In Nitric Acid. 9/20/55 (Unclassified).

HW-39880 R. C. Smith, Controlled Oxidation Of Plutonium Metal Turnings. 11/10/55 (Secret).

December Foaming problems in dissolution of alpha phase turnings.

[redacted]

[redacted]

1956

January	Dissolution of alpha turnings in HNO_3-HF mixture after initial caustic conditioning treatment.
HW-41464	R. L. Beede and C. C. Wheeler, Jr., Evaluation Of En-strip "S" For Stripping Nickel. 2/17/56 (Secret).

1957

HW-50597	A. Brunstad, [Nickel] Coating Removal With Dilute Nitric Acid. 7/31/57 (Secret).
	Optimum nickel coating removal was accomplished with 6.5 M HNO_3 at 70 °C in 15 minutes. Additional effects of acid concentration, time, and temperature are included.
September	Plutonium dissolved in 15 weight percent sulfamic acid solution. Concentrations 100 g/liter plutonium, in 0.3 to 1 M acidity, stable for three weeks.

1958

March	Initial tests of continuous dissolution of plutonium metal (10 g scale) in HNO_3. Effect of PuO_2 formation.

1959

April	Study of massive plutonium metal dissolution using sulfamic acid. Effects of final oxidation adjustment, plutonium sulfate, and plutonium polymer formation.
	Study of reactive alpha Pu skull passivation by caustic solution.
May	Study of reactivity of Pu-Al skulls during caustic passivation.
June	Problem of unusual reactivity of temperature cycled alpha Pu skulls.

[redacted]

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October	Studies on steam oxidation of plutonium skulls. Method produces a free-flowing easily-soluble (in 12.7 M HNO_3-0.2 M HF) PuO_2 powder. Oxidation was in argon at 150 to 250 °C.
November	A 300-gram skull was oxidized in 160 to 230 °C steam. The oxide dissolved in HNO_3-HF after one hour of refluxing.
December	Steam oxidation of skull material at 250 °C. Oxide product readily soluble. Massive metal oxidations proceed slower, and require vibration to remove oxide film.

1960

February	Dissolution of PuO_2 in 12.7 M HNO_3-0.05 M H_3PO_4 was 1/20 the rate in 12.7 M HNO_3-0.2 M HF. Low temperature PuO_2 from steam oxidation of metal was used for tests.
April	Experiments show 14 M H_3PO_4 will dissolve plutonium skulls at a rate equivalent to 12.7 M HNO_3-0.2 M HF. Residual solids in the solution can be readily dissolved in 16 M HNO_3. The H_3PO_4 concentration can be diluted below the Recuplex tolerance level. Mixtures of HNO_3-H_3PO_4 showed slow dissolution rates for skull material.
July	Final dissolution tests of PuO_2 from steam-treated skulls show 100% dissolution in 2 hours, 91% in 1 hour. Dissolution in 16 M HNO_3-0.2 or -0.25 M HF at boiling point.
HW-66431	R. C. Smith, Plutonium: Steam Oxidation And Oxide Dissolution. 8/12/60 (Confidential).

1961

HW-71526	E. L. Conner, Jr. and R. S. Kingsley, Nitric Acid - Hydrazine Dissolution Of Plutonium Metal. 10/22/61 (Secret).

[redacted]

[redacted]

1962

HW-72662	H. W. Crocker, Flow Sheets For Continuous Dissolution Of Plutonium Metal For Task I Processing. 2/19/62 (Secret).
HW-72242	R. S. Kingsley, Dissolution Of Plutonium Metal In Nitric - Hydrofluoric Acids. 3/15/62 (Secret).

5. INCINERATOR ASH

1956

December	Recovery of Pu from sandpaper and sweepings by ashing at low temperature followed by 6 M HNO_3-0.25 M HF leaching at boiling point. Pu recovery of 90%.

1959

June	A 97% conversion of plutonium in incinerator ash to tetrafluoride and nitrate solution was attained in a test. A ratio of four grams ammonium bifluoride to one gram ash was used. Fusion was at 200 °C. Filtration of the ash-bearing solution was very slow.

1960

November	Recovery of plutonium from ashes was tested using phosgene at 450 °C to convert the plutonium to $PuCl_3$. The temperature was raised to 800 °C to volatilize off the $PuCl_3$ which was collected in a cool vessel. 96.4% of the Pu was collected; 3.6% stayed in the ash.

1961

January	Ammonium bifluoride fusion of PuO_2 at 200 °C for one hour successfully converted the oxide to PuF_4. The molten salt mixture is readily soluble in 2 M ANN. On a 35-gram scale, 98% conversion was attained.
	Recovery of plutonium from synthetic ash spiked with PuO_2 in a preliminary experiment was 93% by the

[redacted]

[redacted]

fusion method.

1962

HW-72285 M. J. Rasmussen and H. W. Crocker, Recovery Of Plutonium From Incinerator Ashes. 1/15/62 (Unclassified).

September	Basic incinerator scrubber solution clarified by treatment with casein glue, acidification, and filtration.

F. RECOVERY - SOLUTION PROCESSING

1. Solvent Extraction - TBP

1952

February	Disengaging times for CAF-CAX as a function of specific gravities.
August	Effect of iodate, sulfate, and hydrogen peroxide on extraction coefficients.
September	Extraction coefficients. Solvent treatment.

1953

August	Life test of coated plates.
October	Testing pulse column plates and solvent stability.
November	Plate testing.

1954

January	Effect of oxalate; solvent decomposition.
April	Batch, counter-current runs; effect of oxalate.
July	Coefficients for Recuplex system; total reflux.
August	Coefficients for plutonium(VI).

[redacted]

September	Coefficients for 20% TBP; organic phase saturation; small column studies.
December	Coefficients for CC column - function of time.

1955

January	Study of decrease of E_a^o in the Recuplex stripping column when CCX is heated to 50 °C. Proposed uranium-plutonium partition flow sheet for Recuplex. Use pulse columns or a batch process in the solvent treatment tank.
February	Solvent decomposition studies, effect of plutonium concentration and solvent age.
March	Solvent damage studies, effects of CCl_4, formation of Cl^- corrodant. Plutonium distribution studies and an equation for scrub section of H-1 column.
May	Recuplex flow sheets C-9 and C-11 tested in laboratory columns.
June	Recuplex flow sheet C-11 studies. Solvent damage studies.
August	Valence studies on Recuplex concentrated CCP stream. Reactivity of H_2O_2 in feed makeup.

1957

December	Trimethoxyboroxine (TBM) was subjected to Recuplex-type extraction and stripping. 90% of TBM went to raffinate. TBM is a possible extinguishing agent for Pu fires.

1958

HW-55674	A. Brunstad, Emulsification And Precipitation In The Recuplex Columns. 4/9/58 (Confidential).

[redacted]

Investigation of Recuplex extraction column emulsification, stripping column precipitation. Effect of dispersed silica and TBP degradation products on extraction. Effect of fluoride on stripping.

Extraction coefficient studies on solutions from dissolution of steel slag and crucible cans.

August — Additions of "Mistron 28" to Recuplex sump cleanout solutions eliminated column emulsification problems during cleanout runs. Solvent was TBP-CCl_4.

1960

July — Extraction of HF by 20% TBP-80% CCl_4 studied at 8 M HF to 0.1 M HF range. Some extraction of HF noted. At 1 M HF in the aqueous phase, the H^+ concentration in the organic was 0.075 M. Contact of the organic with 5% Na_2CO_3 removed all the acid.

HW-68340 — R. S. Kingsley, H. W. Crocker, and H. H. Hopkins, Jr., Studies On The Reduction Of Recuplex Waste Losses. 1/31/61 (Confidential).

Study of ways of treating solvent and adding extraction capacity to reduce Recuplex waste losses.

Fresh 20% TBP-80% CCl_4 reduced the CAW to less than 0.05 mg/liter Pu. Presence of sodium nitrate in the CAW did not affect extractability.

A 1 M HF strip of the organic reduced the CCW to 0.1 mg/liter Pu. Organic which was HF-stripped was an effective extractant for CAW, giving E_a^o's of 10. Two stages of extraction using HF-stripped organic reduced the CAW to 1 mg/liter Pu.

1964

May — Iodine up to 0.1 M in solvent shown to have no effect on extraction or stripping.

November — Problems in column capacity when feed contains aluminum-complexed fluoride.

[redacted]

[redacted]

2. Solvent Extraction - DBBP

1957

August	Dibutyl butyl phosphonate (DBBP) results in more faborable extraction of the plutonium into the organic phase than TBP. However, stripping from DBBP has been poor. DBBP is more stable than TBP in aqueous HNO_3 solutions. Tetrabromoethane (TBE) as a density-increasing agent. Charts relating density to composition for the TBP-TBE-CCl_4 system have been prepared.
October	Satisfactory extraction and stripping were observed in batch tests using DBBP-TBE-CCl_4 solvent. The stripping agent was 0.05 M HNO_3-0.05 M $(NH_3OH)_2SO_4$.
December	Further extraction tests of DBBP-TBE-CCl_4 shows a decrease in distribution coefficient due to presence of TBE. Pentachloroethane, a high-density diluent (possible replacement for CCl_4) resulted in much lower extraction coefficients for Pu(IV) with TBP and with DBBP than found with CCl_4.

1958

HW-56606 RD A. Brunstad, Laboratory Evaluation Of Dibutyl Butyl Phosphonate And Tetrabomoethane For The Recuplex Solvent System. 7/1/58 (Declassified).

3. EXTRACTION WASTE PROCESSING WITH DBBP

1960

December	Use of 25% DBBP-75% CCl_4 gave E^a_S's averaging 160 for extraction of plutonium from CAW. Length of contact time was not critical. Three stages of extraction removed 99% of the plutonium from the CAW.

1961

January	Solvent of 35% DBBP-65% CCl_4 was effective through

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nine successive stages of extraction when contacting 3 mg/liter Pu solutions. Even the last stage reduced the plutonium concentration in the aqueous phase by a factor of 10.

The organic was washed in 1 M HNO_3 and stripped with 5% Na_2CO_3. Approximately 85% of the plutonium was stripped in four stages. Final pH of the organic was 10 to 12.

HW-69910 R. S. Kingsley and H. W. Crocker, Studies Of Dibutyl Butyl Phosphonate As An Extractant For Plutonium From The Recuplex Waste Stream. 6/15/61 (Declassified).

Extraction coefficients ranged from 160 to 250. The DBBP consistently removed 95% of the plutonium in one contact. Ninety volumes of CAW can be contacted by one volume of 25% DBBP-75% CCl_4 before exceeding a waste loss of 0.1 mg/liter Pu. A DBBP column flow sheet was developed.

1964

HW-81710 D. M. Creighton, Test Column For Recovery Of Plutonium From CAC-880 Waste Stream. 4/7/64 (Unclassified).

A solvent extraction process demonstration of the column operation is described.

June Cation distribution coefficients into 25% DBBP-75% CCl_4. Iron and calcium have significant distributions.

1965

RL-SEP-507 D. M. Creighton, W-2 Waste Recovery Column Stripping Studies. 6/1/65 (Unclassified).

4. WASTE SOLUTION TREATMENT

1952

April Neutralization of CAW; viscosities; settling characteristics.

[redacted]

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[redacted]

May	Viscosity of neutralized CAW.
November	Neutralization of CAW.

1954

October	Protective coatings for CAW crib.

5. ANION EXCHANGE

HW-73456	H. W. Crocker, Anion Exchange Flow Sheets And Equipment For Recovery Of Task I [Oxalate] Filtrates. 4/23/62 (Confidential).

6. SOLVENT PROCESSING

1958

March	Scavenging of Recuplex solvent by precipitation of PuF_4 from CAX (15% TBP in CCl_4) by HF or HF and NaF. Residual Pu in organic $\approx$ 0.01 g/liter.

7. SUMP WASTE WATER

1960

December	Approximately 80% of the plutonium was recovered from D-6 sump sample solutions by ion exchange. Five hundred column volumes of solution were processed in the 1" diameter x 19" high ion exchange bed. Dowex 50W-8X, sodium form resin, was used. Acidity of the feed was adjusted to 0.05 M HNO_3 and and also made 0.05 M NH_4HSO_3 prior to loading. Fine solids formed in the feed vessel during the run period.

1961

February	Samples of sump waste adjusted to a pH of 2 and 0.05 M $NaHSO_3$ were loaded onto Dowex 50W-8X. Less than 2%

[redacted]

[redacted]

plutonium breakthrough was noted after 500 column volumes throughput. Flow rate was 17 ml/min/cm^2. Elution with 1 M $NaHSO_4$ removed < 20% of the plutonium in six column volumes.

April — A concentration of 0.1 M NH_4HSO_3 is required to reduce the plutonium valence to (III) in sump wastes in one hour. Elution tests show 75% plutonium removal when using 3 column volumes of 3 M HNO_3-0.3 M HSO_3NH_2 followed by 3 column volumes of 6 M HNO_3-0.3 M HSO_3NH_2.

May — Recent tests indicate that pre-treatment of the sump solutions may not be necessary, as a run without adjustment chemicals showed the plutonium all to be in the (III) state. This was shown by complete elution with 6 M HNO_3-0.3 M HSO_3NH_2.

HW-70406 G. L. Stiffler, *The Removal Of Plutonium From 234-5 Building Sump Water.* 7/20/61 (Declassified).

G. NON-AQUEOUS PROCESSING

1. POWDERED METAL

1960

HW-64289 G. L. Stiffler and M. H. Curtis, *The Preparation Of Plutonium Powder By A Hydriding Process--Initial Studies.* 3/10/60 (Unclassified).

Plutonium powder was prepared on a 10-gram scale by the hydriding method. Studies made on sintering temperature encountered in hydriding process show sintering starts at 450 °C.

HW-66017 V. G. Eschen and M. H. Curtis, *Experimental Production Of Plutonium Powder By Mechanical Comminution.* 7/8/60

1961

HW-70931 E. R. Gilbert and M. H. Curtis, *Preparation Of Plutonium Powder By Hydriding--Delta Metal.* 9/6/61 (Secret)

[redacted]

2. METAL REACTIONS

1953

December	Reaction of plutonium metal in nitrogen or in CO_2.

1961

*December	Effect of oil, plastic, rubber, on corrosion of machined surfaces.

1962

*March	Corrosion of machined surfaces. CCl_4 a definite contributor. Lard oil more corrosive than a chlorinated oil.

1964

HW-81240	R. H. Bond, Corrosion Of Plutonium Metal When Stored In Containers Having Plastic Components. 3/6/64 (Secret). Radiation damage to plastics and corrosion effect.

3. NICKEL CARBONYL COATING

1952

November, December	Nickel carbonyl analyses.

1955

February	Nickel carbonyl coating studies. Eleven uranium pieces coated to one mil thickness.
March	Nickel carbonyl coating studies.
April	Nickel carbonyl coating studies, experimental data submitted for statistical analysis.

(*) Reports issued by Weapons Process Engineering.

[redacted]

4. ELECTROREFINING

1961

November	Porous ceramic anode not effective. Cell voltages measured.

1962

HW-73491	T. S. Soine, Continuous Electrorefining Of Plutonium--Progress Report. 10/5/62 (Confidential).

1965

RL-SEP-503	T. S. Soine, Batch Electrorefining Of Plutonium Metal: Progress Report. (Unclassified). A comprehensive summary and status report.

H. MELTING AND CASTING

1. MELTING UNDER FUSED SALT

1956

March	Effects of temperature and $CaCl_2$-CaF_2 composition on recovery of plutonium from alpha phase turnings by $CaCl_2$-CaF_2 slagging.

1957

November	Recovery of plutonium from skulls by vacuum melting - impractical on small or badly-oxidized fragments (10% yields). Vapor phase reduction with calcium was unsuccessful. Experiments started on melting skulls in $CaCl_2$-CaF_2 eutectic.
December	Glascast crucibles fired at 2300 °F will contain the $CaCl_2$-CaF_2 melt at 1000 °C. Magnesia, CaF_2, quartz, sodium silicate impregnated magnesia were

[redacted]

ineffective. Study of Ca reduction of PuO_2 in a $CaCl_2$-CaF_2 melt.

1959

January	Test on recovering Pu from skulls was successfully made by melting skulls with Ca-$CaCl_2$ at 1050 °C. Recovery was > 90%.
February	Recovery of skulls by calcium chloride salt bath.

1961

May	Batch reduction of skulls (93% plutonium) with stirred calcium, calcium chloride, sodium chloride, and magnesium chloride gave yield of 80 to 100%. Purification remains undetermined.

2. INGOTTING

1959

November	Use of salt plug for bottom pour casting crucibles is being studied. Lithium fluoride - calcium fluoride and sodium chloride - potassium chloride appear favorable on first tests. Attempts to boil off impurities in low-density button from $PuCl_3$ reduction were unsuccessful.
December	A tapered lithium fluoride - calcium fluoride plug did not contaminate plutonium metal. Plug erodes during casting.

1961

April	Experiments show high yields in dribble pour briquet melting operations.
*July	Four sequential briquet melting pours gave 93.6% yield.

(*) Reports issued by Weapons Process Engineering.

[redacted]

1962

*September Ingot purification by controlled freezing. Interim data presented showing C segregation. Photomicrographs.

1963

*January High and erratic nitrogen analyses of buttons. Ingot analyses.

HW-77040 RD R. H. Bond, The Plutonium Nitride Problem. 3/22/63 (Secret - Draft).

*February Nitrogen analyses across button. Effect of zone cooling on ingot.

*May Tantalum casting stack design for briquettes. Carbon in ingots. Button castings gave 97% yield.

1964

*December Limits of carbon separation by slow-freeze process as function of density.

RL-SEP-94 RD R. H. Bond, Data From Metal Purification Study. 12/11/64 (Secret - Draft).

1965

RL-SEP-360 R. H. Bond, Skull Formation During Casting--Correlation And Applications. 3/15/65 (Secret).

3. MOLD CASTING

1956

January Castings attempted in copper mold. Effect of temperature on incomplete pours.

(*) Reports issued by Weapons Process Engineering.

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[redacted]

September	Copper mold time cycle < 4 hours. Six runs completed, all metal passed purity specifications.
November	Problems associated with machining of castings. Design of new permanent mold.

1957

HW-48900 R. C. Smith, Casting Of Plutonium In Copper Molds - Interim Report. 1/17/57 (Secret).

Castings have been made with 3/8" ID ceramic tube to direct Pu metal from pouring crucible directly into desired side of copper mold. Diverting crucible is reused to decrease ceramic recovery. The decrease in turbulence and more direct flow eliminate cold shut formation.

February	Pours made with ceramic tube resulted in improved metal surfaces. Pours made with pouring crucible spout above center of diverter gave poor cast surfaces on metal. Pours made with a side-pour pouring crucible gave good cast surfaces.
May	New four-piece copper mold has solved breakout problem with delta metal. Folds are still present in casting. Alteration of mold and melt temperature, use of top pour, and ceramic diverters to direct metal flow away from center plate have not eliminated folds at metal surface. New gating method to be devised.
June	Gating the metal flow tangent to polar surface of mold has reduced formation of cold shuts on metal.
November	Metal surface satisfactory on pieces cast through a tantalum diverter at optimum temperature values.

1959

September	Tests conducted on three types of tantalum carbide as mold material candidates. Wetting and bonding of plutonium precludes their use as mold materials.
October	Chemical interaction and adhesion limit use of tantalum nitride as a mold material.

[redacted]

[redacted]

1960

September	Pyrolytic graphite was tested as a mold candidate material. Less severe physical damage occurred with pyrolytic graphite exposed to molten plutonium at 850 °C than with normal graphite.
October	Tests being conducted with lithium aluminum silicate as mold material for alpha and delta plutonium casting.
November	Lithium aluminum silicate shows heat shock and spalls in contact with molten plutonium.
December	Tantalum crucible, oxidized and coated with CaF_2, shows promise in tests as a casting mold.

1961

January	A dense, glazed, calcium fluoride test mold shattered when contacted with molten plutonium.

HW-69223 RD R. H. Bond, ZD-500 Ball Rod And Plug Rod Casting - November, 1960 through February, 1961. 4/7/61 (Secret - Draft).

March	A thin-walled tantalum crucible has been used routinely as an ingot mold for plutonium casting. No chemical or dimensional changes have been noted in the mold.
*May	Fiberglas fibers in the pouring crucible result in radiographic rejects.
*August	Investigation of sticking plug valves.

4. ALLOYING

1963

*August	Stirring-blending equipment for casting alloy ingots.
*September	Direct alloy blending. Vertical agitation.

(*) Reports issued by Weapons Process Engineering.

[redacted]

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*November Details of work on recovery of briquets using stirring before pour. Stringers necessitate a second ingotting.

1964

HW-83736 R. H. Bond, Preparation Of Delta-Stabilized Plutonium By Direct Alloy Blend Techniques. 9/21/64 (Secret - AWD).

I. AMERICIUM

1964

HW-81236 R. S. Kingsley, Americium Recovery - Interim Startup Flow Sheet. 3/6/64 (Unclassified).

HW-83075 R. S. Kingsley, Americium Recovery--Phase II Purification Flow Sheet. 7/10/64 (Unclassified).

1965

RL-SEP-518 R. S. Kingsley, Solvent Extraction Recovery Of Americium With Dibutyl Butyl Phosphonate. 6/4/65 (Unclassified).

A comprehensive study of solvent extraction process data.

RL-SEP-729 R. S. Kingsley, A Multi-Column Ion Exchange Purification-Concentration Process For Americium. 1965 (Unclassified).

J. U^{233} PROCESSING

1965

RL-SEP-712 H. T. Fullam, Summary Of U^{233} Studies In The Plutonium Chemistry Laboratory. 9/8/65 (Unclassified).

(*) Reports issued by Weapons Process Engineering

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[redacted]

K. CERAMIC DEVELOPMENT

1955

April	Test of MgO-5% CaF_2 crucible fabrication. Slip casting studies.
June	MgO-5% CaF_2 preparations.
July	Coated graphite molds prepared by spraying on MgO slurry.
August	Preparation of Al_2O_3, MgO, zirconia slip cast crucibles.

1956

November	Fabrication study on straight thermocouple wells produced from MgO. Essential dimensions and technique.

1957

February	Nine-inch, coarse-mix, MgO chimneys made without use of hardened dies or other costly equipment. CaF_2 slip casting.
May	Development of routine method of alkaline slip casting of CaF_2 crucibles was demonstrated. Crucibles were smooth, and free of blisters. Effect of calcining temperature on slurry pH was investigated. Low CaO impurity did not affect stability of crucible.
June	Doughnut-shaped setter plates show promise in firing CaF_2. Crucible distortion experienced with circular setter plates.
July	CaF_2 (-48 mesh, calcined at 1200 °C) required 12-hour ball milling to attain best slip casting properties.

[redacted]

1957

August	Work is in progress on a four-compartment vibration-cast crucible. Cracks formed during firing at 1760 °C. Slip cast shells (from the I-4 pattern) appear to be more promising and will be tested.
September	Acceptable four-compartment I-4 vibration-cast crucibles were produced by eliminating Carbowax from the formulation and substituting magnesium sulfate solution. Blister-free slip cast CaF_2 crucibles were achieved by de-airing the slip by means of an evacuated desiccator and lowering the sintering temperature from 1100 to 1000 °C. Magnesia crucibles were impregnated with molten CaF_2 at 1400 °C. The crucibles thus treated were impervious to water, while ordinary crucibles are not.
October	Difficulties in fabricating four-place magnesia casting molds (CS-201) were overcome. A magnesia pouring crucible was successfully coated with 1/32" nickel. Glascast was used successfully for slip casting tensile specimen molds.
November	Plutonium tensile specimens cast in Glascast molds are fine-grained, superior strength. Surface impurities of B - 4 ppm and Si - 200, are low enough to warrant further testing.
December	Studies initiated to form Glascast shell mold. Glascast crucibles fired at 2300 °F developed for skull recovery employing $CaCl_2$-CaF_2 melt at 1000 °C.

1958

January	Problems of removing Glascast casting molds from plaster form overcome. CaF_2 crucibles fired using green MgO setter plates

[redacted]

[redacted]

	to prevent cracking.
March	MgO crucibles nickel-coated externally.
April	Method for slip cast MgO continuous reduction cell with integral drain tube and riser.
June	Vibration casting technique specifications completed.
July	Tests of impregnating MgO crucibles with salts to reduce porosity. Initial fabrication of MgO liners for Rokide Z-coated pressure vessel. Nickel-coated MgO crucible study.
GERL Report 59GL213	R. S. Rosenfels, Slip Casting Of High-Purity Calcium Fluoride Crucibles. October, 1959. Paper given at High Temperature Inorganic Materials Symposium.
October	Test of impregnating MgO crucibles with salts to reduce porosity.

1959

May	Test of H-7 pressed, sintered high-silica and I-10 $MgO-CaF_2$ investment-cast pouring crucibles.
June	Results of the H-7 and I-10 crucible tests in pouring applications. H-7 most promising.
August	Fabrication and firing problems of the RS-201 reduction liner have been solved. Thermal shock tests of CaF_2 crucibles show that coarse mix slip cast material survives shock from 1100 °C, while standard mix fails when shocked from 700 °C.
December	Three PuO_2 slip cast crucibles fabricated and fired at 1300 °C. Bodies were sound, shrinkage was ≈ 30%.

1961

HW-68910	R. S. Rosenfels, Slip Casting Of Magnesia-Titania Bodies. March 20, 1961 (Unclassified).

[redacted]

[redacted]

[redacted]

A condensed version appeared in the American Ceramic Society Bulletin Volume 43, No. 8, Page 566, under the title Dense Slip Cast Magnesia-Magnesium Titanate Ware.

A procedure was developed for slip casting cells of 90% magnesia-10% titania. The cells withstood a molten chloride eutectic at 800 °C for 1.5 hours. Casting variables studied were calcining temperature of titania, percentage of titania, sintering temperature, and oxidizing temperature.

Tests on $MgO-TiO_2$ slip casting have resulted in cells with only 0.8% porosity. A 10% fraction of -28 +100 magnesia, milled with -200 magnesia and calcined titania, was used. The bodies were of high density and were also glazed.

March Pouring crucibles were developed for specialty plutonium melting applications where a ceramic is required. The crucible, 88% coarse magnesia, 9% fluffy titania, and 3% fluffy calcium fluoride, were hard, dense, non-spalling, thermal shock-resistant, and are non-reactive toward plutonium.

1965

RL-SEP-647 R. S. Rosenfels and L. J. Adams, Methods Manual--Ceramic Shop. 7/30/65 (Unclassified).

RL-SEP-824 R. S. Rosenfels, Ceramic Cells And Stirrers For Electrorefining Of Plutonium Metal. To be published ca. 11/15/65 (Unclassified).

Brochure Specialty Products And Technical Services, Ceramic Shop, 234-5 Building, 200-West Area. To be published ca. 12/15/65.

L. PROPERTIES OF MATERIALS

1952

October Sintered stainless steel - porosities; resistance of rubber to nitric acid, hydrogen peroxide.

Corrosion of various materials in hydrofluorination off-gases.

[redacted]

[redacted]

[redacted]

1952

November	Porosities of platinum disks.

1953

August	Chemical resistance of Homalite.

1954

February	Fluorothene stability in process streams.
December	Filter cloth for aluminum nitrate filtration.

1957

July	A guillotine button cutter has been tested using aluminum buttons 1-1/8" thick. Twenty tons of force are required to cut the button.
August	The guillotine button cutter was put into use. Cutter was operated by a one-ton press, and worked well until damaged by maloperation.

1958

March	Test of Eastman Adhesive 910 for attaching Plexiglas port rings to Homalite CR-39 plastic.
May	Eastman 910 adhesive in use for attaching Plexiglas to Homalite CR-39 (Hood 9).
December	Test of radiation dose increase with plutonium concentration for solutions in polyethylene bottles. Effect of lead shields recorded.

1959

September	Test shows plastic bags (a co-polymer of polyvinyl chloride - acetate) contain 5.3% chloride.

[redacted]

1959	
October	Tests show majority of chloride from plastic bags remains in ash when burned at 700 - 900 °C.
1960	
January	A one-inch Jamesbury, PVC, ball valve operated for 407,000 cycles simulating PuF_4 powder transfer. No valve damage was noted during inspection. Lead oxide was used as a PuF_4 standin.
March	Distillation of polyethylene from plutonium oxide - polyethylene solids cylinders is feasible.
HW-65207	H. W. Crocker, Plutonium Oxide - Plastic Mixtures For Critical Mass Studies. 5/12/60 (Unclassified).
	Dimensional checks on plutonium oxide-polyethylene and plutonium oxide-methyl methacrylate cylinders revealed no warpage in 270 days time. Polyethylene cylinder diameters reduced 0.6% and thickness reduced 1% over this period. Methyl methacrylate cylinder diameters increased by 0.5% and thickness increased 0.4% over this period.
June	An Ecco "Gearchem" pump was operated for 970 hours pumping 232 g/liter Pu in 4 M HNO_3. Internal pump parts exposed to Pu for 48 days. No mechanical maintenance required other than infrequent gland adjustment.
July	PVC-coated gloves were tested in hood use. The gloves are stiffer than Neoprene, but have better resistance to organic. The seal between the plastic and glove body came apart in use, and the method of attachment to glove ports requires improvement.
December	A set of plutonium oxide-polystyrene pressed cylinders showed no gas release in a four-week period. The radiation resistance of the polystyrene is superior to the other plastics tested as fuel cylinder candidates.

H. H. Hopkins Jr

APPENDIX

SEPARATIONS TECHNOLOGY AND RESEARCH AND ENGINEERING MONTHLY REPORTS

1951

January	HW-20161 H
February	HW-20438 H
March	HW-20671 H
April	HW-20991 H
May	HW-21260 H
June	HW-21506 H
July	HW-21802 H
August	HW-22075 H
September	HW-22304 H
October	HW-22610 H
November	HW-22875 H
December	HW-23140 H

1952

January	HW-23437 H
February	HW-23698 H
March	HW-23982 H
April	HW-24337 H
May	HW-24605 H
June	HW-24928 H
July	HW-25227 H
August	HW-25533 H
September	HW-25781 H
October	HW-26047 H
November	HW-26376 H
December	HW-26720 H

1953

January	HW-27522
February	HW-27739
March	HW-27624 H
April	HW-28355
May - June	HW-28695
July	HW-29035
August	HW-29504
September	HW-29692
October	HW-30158

[redacted]

1953 (continued)

November	HW-30486
December	HW-30677

1954

January	HW-31078
February	HW-31336
March	HW-31732
April	HW-31956
May	HW-32070
June	HW-32189
July	HW-32818
August	HW-33156
September	HW-33750
October	HW-34072
November	HW-34161
December	HW-34147 H

1955

January	HW-34631 H
February	HW-35530 H
March	HW-35891 H
April	HW-36440 H
May	HW-36928 H
June	HW-37658 H
July	HW-38375 H
August	HW-38828 H
September	HW-39260 H
October	HW-39751 H
November	HW-40182 H
December	HW-40692 H

1956

January	HW-41205 H
February	HW-41702 H
March	HW-42219 H
April	HW-42626 H
May	HW-43137 H
June	HW-43938 H
July	HW-44580 H
August	HW-45115 H
September	HW-45707 J
October	HW-46432 J
November	HW-47056 J
December	HW-47675 J

1957

January	HW-48132 J
February	HW-48835 J
March	HW-49503 J
April	HW-50089 J
May	HW-50584 J
June	HW-51211 J
July	HW-51802 J
August	HW-52353 J
September	HW-52864 J
October	HW-53449 J
November	HW-53967 J
December	HW-54319 J

1958

January	HW-54821 J
February	HW-55215 J
March	HW-55571 J
April	HW-55914 J
May	HW-56218 J
June	HW-56602 J
July	HW-56972 J
August	HW-57238 J
September	HW-57640 J
October	HW-58051 J
November	HW-58305 J
December	HW-58711 J

1959

January	HW-59079 J
February	HW-59434 J
March	HW-59849 J
April	HW-60236 J
May	HW-60559 J
June	HW-60915 J
July	HW-61366 J
August	HW-61736 J
September	HW-62179 J
October	HW-62593 J
November	HW-62864 J
December	HW-63313 J

1960

January	HW-63706 G
February	HW-64089 G
March	HW-64576 G
April	HW-64991 G
May	HW-65169 G
June	HW-65935 G
July	HW-66271 G
August	HW-66646 G
September	HW-66958 G
October	HW-67252 G
November	HW-67459 G
December	HW-67985 G

1961

January	HW-68345 G	
February	HW-68700 G	
March	HW-69051 G	
April	HW-69443 G	
May	HW-69803 G	HW-69996*
June	HW-70182 G	
July	HW-70588 G	HW-70750*
August	HW-70918 G	HW-71073*
September	HW-71187 G	
October	HW-71577 G	
November	HW-71895 G	
December	HW-72154 G	HW-72420*

1962

January	HW-72551 G	
February	HW-72890 G	
March	HW-73193 G	HW-73171*
April	HW-73525 G	
May	HW-73884 G	
June	HW-74151 G	
July	HW-74505 G	
August	HW-74804 G	
September	HW-75145 G	HW-75070*
October	HW-75470 G	
November	HW-75702 G	
December	HW-76054 G	

(*) Reports issued by Weapons Process Engineering.

1963

January	HW-76443 G	HW-76372*
February	HW-76848 G	HW-76842*
March	HW-77138 G	
April	HW-77504 G	
May	HW-77795 G	HW-77755*
June	HW-78076 G	
July	HW-78484 G	
August	HW-78817 G	HW-78764*
September	HW-79097 G	HW-74078
October	HW-79480 G	
November	HW-79768 G	HW-79801*
December	HW-80243 G	

1964

January	HW-80672 G	
February	HW-81078 G	
March	HW-81620 G	
April	HW-82089 G	
May	HW-82526 G	
June	HW-83012 G	
July	HW-83508 G	
August	HW-83876 G	
September	HW-84354 G	
October	RL-SEP-52 G	
November	RL-SEP-112 G	
December	RL-SEP-197 G	RL-SEP-283*

1965

January	RL-SEP-282 G
February	RL-SEP-332 G
March	RL-SEP-405 G
April	RL-SEP-476 G
May	RL-SEP-509 G
June	RL-SEP-654 G
July	RL-SEP-618 G
August	RL-SEP-706 G