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HW-SA-2880

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CONVERSION OF PLUTONIUM NITRATE TO PLUTONIUM TETRAFLUORIDE VIA THE CONTINUOUS OXALATE-FLUORIDE METHOD

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January 25, 1963

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I. INTRODUCTION

The batch plutonium(IV) oxalate precipitation, filtration, calcination, and hydrofluorination process used to be a standard method for conversion of plutonium nitrate solution to plutonium tetrafluoride powder suitable for reduction to plutonium metal.(1)(2)(3) Problems encountered in the industrial use of the batch process included (1) lengthy time cycle, (2) non-uniform product, and (3) high processing costs due to operation and maintenance on the numerous batch processing units.

Continuous processing offers the advantages of uniform product and low unit cost due to higher throughput rates, lower operating and maintenance cost, and elimination of multiple batch processing units.

This paper describes the continuous conversion process and equipment developed in laboratory studies.(4)(5) This continuous process has since been scaled up and adopted for plant production of plutonium tetrafluoride.

Due to the toxicity of plutonium, all process equipment described here is in sealed glove boxes.

II. EXPERIMENTAL PROCEDURE

The principal chemical reactions for the process are presented in Figure I. Prior to or during precipitation, the plutonium solution is treated with hydrogen peroxide to convert any Pu(VI) and Pu(III) present to the (IV) valence state.

The stream of 0.1 - 1 M plutonium(IV) nitrate solution is pumped concurrently with a 1 M oxalic acid solution at ambient temperature into a four-inch diameter agitated precipitator vessel to precipitate the plutonium(IV) oxalate hexahydrate. An air-driven agitator maintains the precipitate in a slurry form for overflow from the precipitator into the filter pan. The plutonium nitrate and oxalic acid solutions are fed into the inner tube section of the precipitator to prevent short circuiting of unprecipitated plutonium out the overflow line.

A 2 - 20 inch vacuum (Hg) is applied to the rotary filter drum to remove filtrate and deposit the plutonium oxalate hexahydrate cake. As the drum revolves, a drop-wise wash (2 M nitric acid - 0.05 M oxalic acid) is added to the cake to remove any physically held impurities. A scraper removes the plutonium precipitate from the plastic fiber filter cloth (polyethylene or vinyl chloride-acrylonitrile) and deposits the solids in the discharge chute to the calciner.

Work Performed Under Contract No. AT(45-1)-1350
Between The Atomic Energy Commission
And General Electric Company

The filtrate, containing < 3 percent of the original plutonium and most of the metallic impurities, is treated for oxalate destruction and recycled to solvent extraction recovery facilities. The oxalate destruction is normally achieved by (1) contact with excess potassium permanganate followed with contact by dilute hydrogen peroxide to convert the excess permanganate and any manganese dioxide solids to soluble potassium and manganese nitrates, or (2) destruction of the oxalate ion by thermal concentration of the solution.

The damp plutonium oxalate hexahydrate cake exiting from the filter is fed into the screw calciner and converted to plutonium dioxide at 300 - 400 C. Air is introduced into the calciner to aid in carbon removal and insure complete calcination. An internal grinder pulverizes the material prior to completion of the calcination step. A free-flowing reactive plutonium dioxide powder is prepared using a 25-minute residence time in the calciner.

Plutonium dioxide exiting from the screw calciner is fed into a sloped vibrating tube hydrofluorinator. This reactor is lined with a noble metal (platinum or gold-platinum-palladium alloy) to prevent corrosion. The tube is periodically vibrated to attain powder conveyance through the unit. A mixture of hydrogen fluoride and oxygen flows countercurrent to the powder to effect the conversion to plutonium tetrafluoride. A residence time of 40 - 60 minutes at a temperature of 500 - 550 C is required to attain complete conversion to free-flowing non-hygroscopic plutonium tetrafluoride powder. The addition of oxygen to the gas stream is necessary to convert any hydrogen present in the hydrogen fluoride to water, thus eliminating reduction of part of the plutonium tetrafluoride to plutonium trifluoride. Hydrofluorination off-gases are filtered through a porous Teflon filter prior to disposal to waste via a water aspirator. Figure 2 shows the flow diagram of the continuous conversion process.

Reduction of the plutonium tetrafluoride to metal was performed by the conventional bomb reduction method using calcium metal and a calcium-iodine heat booster.(6) The plutonium tetrafluoride, calcium and iodine are thoroughly mixed and then charged into a steel reactor equipped with a ceramic reduction liner to minimize pickup of impurities. The reactor is sealed, heated by induction coils to approximately 400 C when the calcium-iodine reaction proceeds with liberation of heat to initiate the reduction reaction. The reduction is over in a few moments and the plutonium metal agglomerates and settles to the bottom of the reduction liner. The slag solidifies on top of the plutonium metal. Temperatures in the 1100 - 1600 C range are attained in the reaction, while reactor pressures of 30 - 100 psi are achieved. The plutonium metal is easily removed from the reactor after completion of a cooling period. Slag and crucible residues are recycled to recovery operations. The reduction flow sheet is shown in Figure 3.

III. EQUIPMENT

A. Precipitator And Feed System

The glass precipitator vessel is four inches in diameter by twelve inches high with a one-inch diameter overflow line located eight inches above the bottom of the vessel. The vessel is provided with a one-inch diameter sleeve for solution entry to prevent short-circuiting of any unprecipitated plutonium to the overflow point. The residence time in excess of 10 minutes in the vessel permits adequate particle growth for filtration. An air-driven agitator was used to keep the slurry in suspension.

Diaphragm metering pumps were used to control the plutonium nitrate and oxalic acid solution flows. Flow rate accuracy was ± two percent for the flow ranges of 1 - 5 liters per hour.

The precipitator is critically safe for the plutonium oxalate slurry, as well as solutions.

B. Filter

The 18-inch diameter by 3-inch thick polyethylene filter is fitted into a 5-inch wide by 8-inch deep filter pan. The filter pan was fabricated from 304L stainless steel. The solid polyethylene filter block is equipped with a filter fabric fitted to the periphery. Each filter section is equipped with filter cloth support studs. Solution outlet holes are drilled from the eight filter sections to the filtrate removal wear plate near the hub of the filter. The vacuum is adjustable for the top and bottom halves of the filter. The filter is of critically safe design. A rocker arm agitator maintains the overflow slurry in suspension during the filtration step. Both agitator and filter drum speed are adjustable. The plutonium oxalate cake is removed from the filter by a scraper and deposited in the calciner. The precipitator and filter designs are presented in Figure 4.

C. Calciner

The 2-inch diameter by 36-inch long critically-safe calciner is heated with two half-tube furnaces (≈ 2000 watts total). The furnace shell, fabricated from 304L stainless steel, is trough-shaped with a flat top (insulated to a depth of three inches) and is three inches high. Thermocouples record the shell temperature at selected points. A grinder is located 12 inches downstream of the cake inlet point to pulverize any lumps. The screw has a two-inch pitch, and is fabricated from 304L stainless steel. The calciner screw is driven by a gear motor at approximately one rpm. The filter-calciner assembly is in Figure 5. Figure 6 is an open view of the calciner.

D. Hydrofluroinator

The hydrofluorinator is constructed from materials which are resistant to hot moist hydrogen fluoride. The inconel reactor tube is eight feet long and has a two-inch inside diameter. The unit is sized to prevent nuclear criticality when completely filled with powdered plutonium compounds having a bulk density of 2.47 g/cc. The highest plutonium compound bulk density that has been measured for the materials involved is the plutonium oxide density of approximately 2.20 g/cc. The tube is mounted on a four degree slope. The tube is lined with an 0.01 inch layer of gold alloy (65 percent gold, 15 percent platinum, 25 percent palladium). The ends of the liner are equipped with 0.01 inch flanges of the gold alloy. All welding on the liner is with gold. The gas inlet and exit lines are gold alloy tubing for a length of six inches. The hydrofluorinator is shown in Figure 7.

The vibration system consists of two Model F-21 "Syntron" vibratory feeders equipped with a Model FC-21-2 control unit. The electric vibrators are located approximately nine inches from either end of the reactor tube. A 60 cycle, 0.01-inch amplitude vibration is used in normal operations.

The gas metering system consists of a monel rotameter, control valve, and tubing up to the reactor connection which is gold alloy. The hydrogen fluoride gas is heated to 165 C to eliminate presence of polymer at the metering point.

The off-gas stream is filtered through a Teflon filter and then carried to a waste sump by a water aspirator.

IV. DISCUSSION AND RESULTS

A. Oxalate Preparation

Plutonium nitrate solutions of from 30 - 250 g/l in plutonium were processed in the continuous unit. Most precipitations were done with 100 - 150 g/l solutions. In the precipitation process, the nitric acid and oxalic acid concentrations are controlled to maintain the final slurry 1.5 to 4.5 M nitric acid and 0.10 - 0.16 M in oxalic acid. Acidities below 1.5 M resulted in poor separation of impurities and formation of small cake particles which are difficult to filter. Slurry acidities above 4.5 M resulted in pasty cakes, plugged filters, and high plutonium losses to the filtrate. Excess oxalic acid less than 0.10 M or greater than 0.16 M resulted in higher plutonium losses to the filtrate. Deviations from room temperature (25 C) did not affect the precipitation process.(7)

By maintaining the acidity and excess oxalic acid in the recommended range, plutonium losses to the filtrate were controlled at less than three percent of the total plutonium processed. The experimental runs were normally less than five hours in duration. Longer runs would result in lower losses to the filtrate due to the elimination of frequent startup periods which cause higher plutonium losses from leakage of solids through the filter cloth. Metering pumps were used for solution flow control in the precipitation step. More precise flow control would contribute to lowering of the plutonium losses to the filtrate.

An agitator speed of 200 rpm was found to give the best slurry suspension. Lower speeds resulted in insufficient suspension, while higher speeds resulted in excessive splashing.

A pressure drop of approximately two to fifteen inches of mercury across the filter cloth was normal for most operations. The filter cloth was backflushed when higher pressure drops occurred from filter plugging. The rocker arm agitator in the filter pan was operated at 60 rpm to provide adequate slurry agitation. Drum filter rotation was normally 6 - 12 rph. The plutonium(IV) oxalate hexahydrate cake exiting from the filter is tan in color and has a bulk density of approximately 0.6 g/cc.

Typical operating conditions for the process are in Figure 8.

B. Filtrate Handling

The chemical destruction of excess oxalate was utilized for most of the experimental runs to get the filtrates into a form suitable for recovery by solvent extraction. The excess oxalic acid and plutonium oxalate solids from a volume of filtrate were destroyed by adding excess (0.17 volume) 4 percent potassium permanganate. The excess permanganate and any manganese dioxide were then destroyed by the addition of 0.1 volume of 10 percent hydrogen peroxide. The oxalate-permanganate reaction was carried out at 45 C.

Work was also done on the heat destruction of oxalate.(8) In this method, the filtrate was heated in an evaporator to destroy the oxalate present and reduce the volume of filtrate to be recycled to solvent extraction recovery units.

C. Calcination

Calcination of the plutonium(IV) oxalate was performed in the screw calciner at 300 - 400 C. Calcination at this temperature permitted rapid conversion, as well as formation of a reactive plutonium dioxide powder suitable for conversion to plutonium tetrafluoride. The plutonium dioxide formed in the calciner was not stoichiometric plutonium dioxide, but contained some residual moisture and intermediate compounds. The oxide was normally 80 - 85 percent plutonium. Temperatures below 300 C resulted in incomplete conversion, while operation above 480 C produced unreactive powders. The olive-green plutonium dioxide has a bulk density of 1.5 to 2.0 grams/cc. Particle size ranged down to one micron or less. The off-gas from the calciner was filtered through 40 micron filters to retain plutonium solids prior to condensation and disposal. No corrosion was observed in the calciner during the processing period.

A residence time of approximately 20 to 25 minutes (calciner screw speed of approximately one rpm) was found to be adequate for conversion of the plutonium(IV) oxalate to the oxide.

D. Hydrofluorination

The hydrofluorinator can be coupled to the calciner through two ball valves operated by an electric timer and equipped with an internal argon purge. This method was investigated and proved satisfactory for isolating halogen gases from adjacent operating equipment. However, in the continuous process investigations, the hydrofluroinator was located in another glove box and could not be coupled in this manner to the calciner.

The vibratory method of bed movement was selected because of mechanical simplicity and prevention of powder entrainment in the off-gas system. During normal operations, no visible powder entrainment could be detected when observing the tube interior with a strong beam of light. Plutonium collected on the off-gas filter confirmed the entrainment to be less than 0.2 percent.

Powder flow rate was independent of the angle of tube tilt and depth of powder over the ranges studies, 2 to 10 degrees and 0.1 to 0.5 inches, respectively. Maximum vibration intensity was used in the study. The vibratory reactor system is sensitive to weight distribution and required proper weight alignment to eliminate the formation of stationary powder waves which stopped powder flow through the tube. Once properly aligned, no further difficulties were observed.

Plutonium dioxide prepared at temperaturesbelow 400 C was readily hydrofluorinated at 500 - 550 C in the reactor tube. A 98 percent conversion of the oxide to a free-flowing plutonium tetrafluoride powder was attained. Percent conversion was measured by converting samples of the plutonium tetrafluoride to plutonium dioxide at 1000 C (constant weight plutonium dioxide) and back calculating to the percent conversion.

E. Product Quality

The continuous conversion process provides a free-flowing plutonium tetrafluoride product of low impurity level which is suitable for reduction to plutonium metal. Utilization of the plutonium(IV) oxalate process results in a high degree of separation for plutonium from such impurities as aluminum, iron, and chromium. Typical impurity concentrations, expressed in parts per million impurity per million parts of plutonium, for the complete conversion to metal are presented in Figure 9.

IV. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contributions of R. L. Beede, C. J. Berglund, and W. S. Figg in the experimental work on the continuous processing system.

V. REFERENCES

(1) Harmon, K. M., and J. F. Facer, The Precipitation Of Plutonium(IV) Oxalate In Task I, HW-27563. April 3, 1953 (Secret).

(2) Harmon, K. M., and J. F. Facer, Precipitation Of Plutonium(IV) Oxalate, HW-31186. March 30, 1954 (Secret).

(3) Harmon, K. M., and J. F. Facer, Plutonium(IV) Oxalate Precipitation In Task I Prototype, HW-35727. March 7, 1955 (Secret)

(4) Beede, R. L., Continuous Plutonium Oxalate Precipitation, Filtration, And Calcination Process, HW-45700. September 27, 1956 (Secret).

(5) Crocker, H.W. and C. J. Berglund, Unpublished Data, September, 1956.

(6) Harmon, K.M. and W. H. Reas, Conversion Chemistry Of Plutonium Nitrate, HW-49597. April 11, 1957.

(7) Mudge, L. K., Influence Of Temperature On The Continuous Precipitation Of Plutonium(IV) Oxalate, HW-62020. September 23, 1959 (Secret).

(8) Berglund, C. J., Unpublished Data. September, 1956.

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FIGURE 1

PROCESS CHEMISTRY

Precipitation

$$Pu(NO_3)_4 + 2\ H_2C_2O_4 + 6\ H_2O \rightarrow Pu(C_2O_4)_2 \cdot 6\ H_2O + 4\ HNO_3$$

Calcination

$$Pu(C_2O_4)_2 \cdot 6\ H_2O \xrightarrow[300\ C]{} PuO_2 + 6\ H_2O \uparrow + 2\ CO_2 \uparrow + 2\ CO \uparrow$$

Hydrofluorination

$$PuO_2 + 4\ HF \xrightarrow[500\ C]{} PuF_4 + 2\ H_2O \uparrow$$

Reduction to Metal

$$PuF_4 + 2\ Ca \rightarrow Pu + 2\ CaF_2$$

$$Ca_2 + I_2 \rightarrow CaI_2$$

FIGURE 2

FLOW SHEET FOR CONTINUOUS CONVERSION TO PLUTONIUM TETRAFLUORIDE

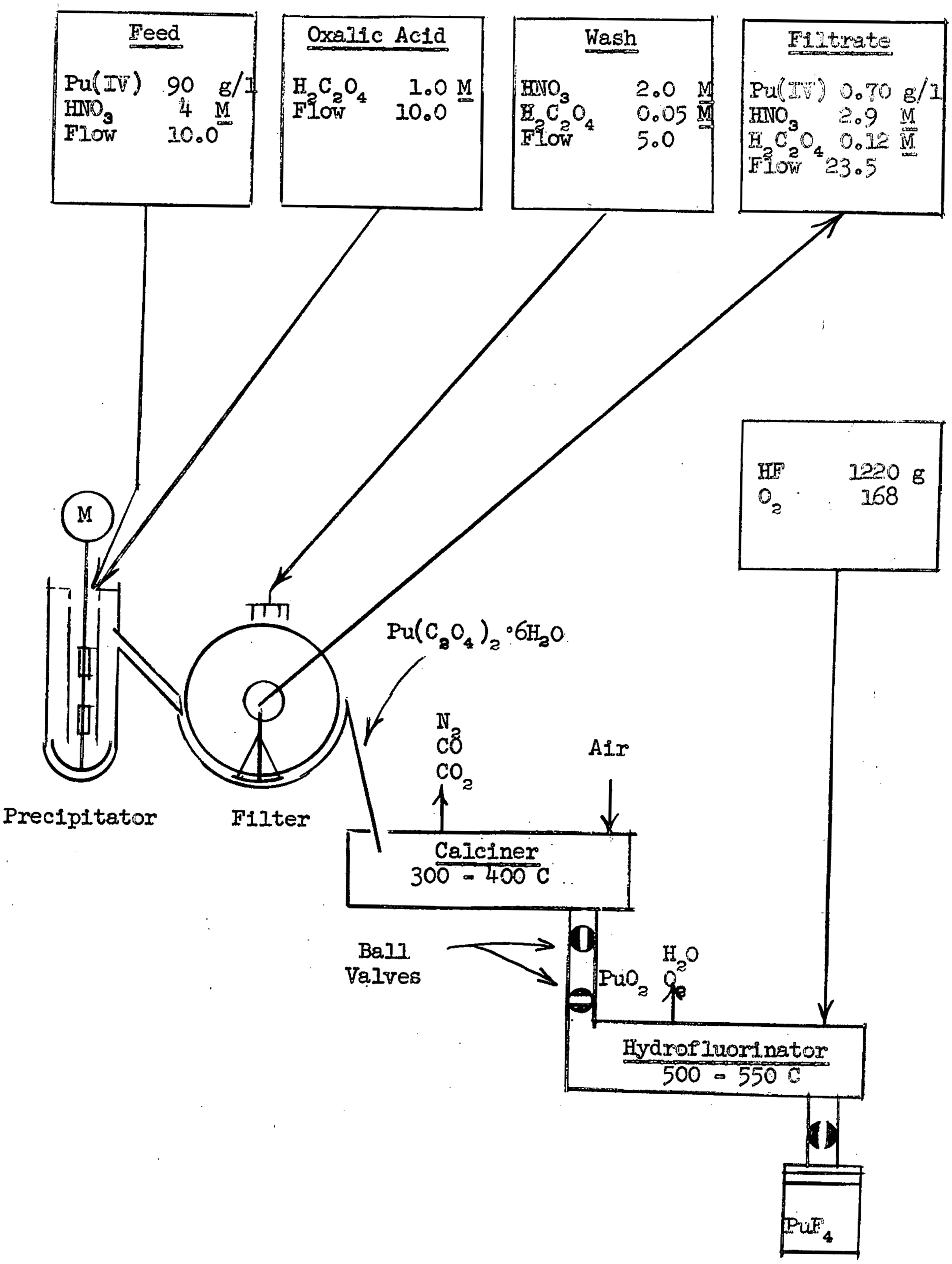

FIGURE 3

FLOW SHEET FOR BATCH REDUCTION OF PLUTONIUM TETRAFLUORIDE

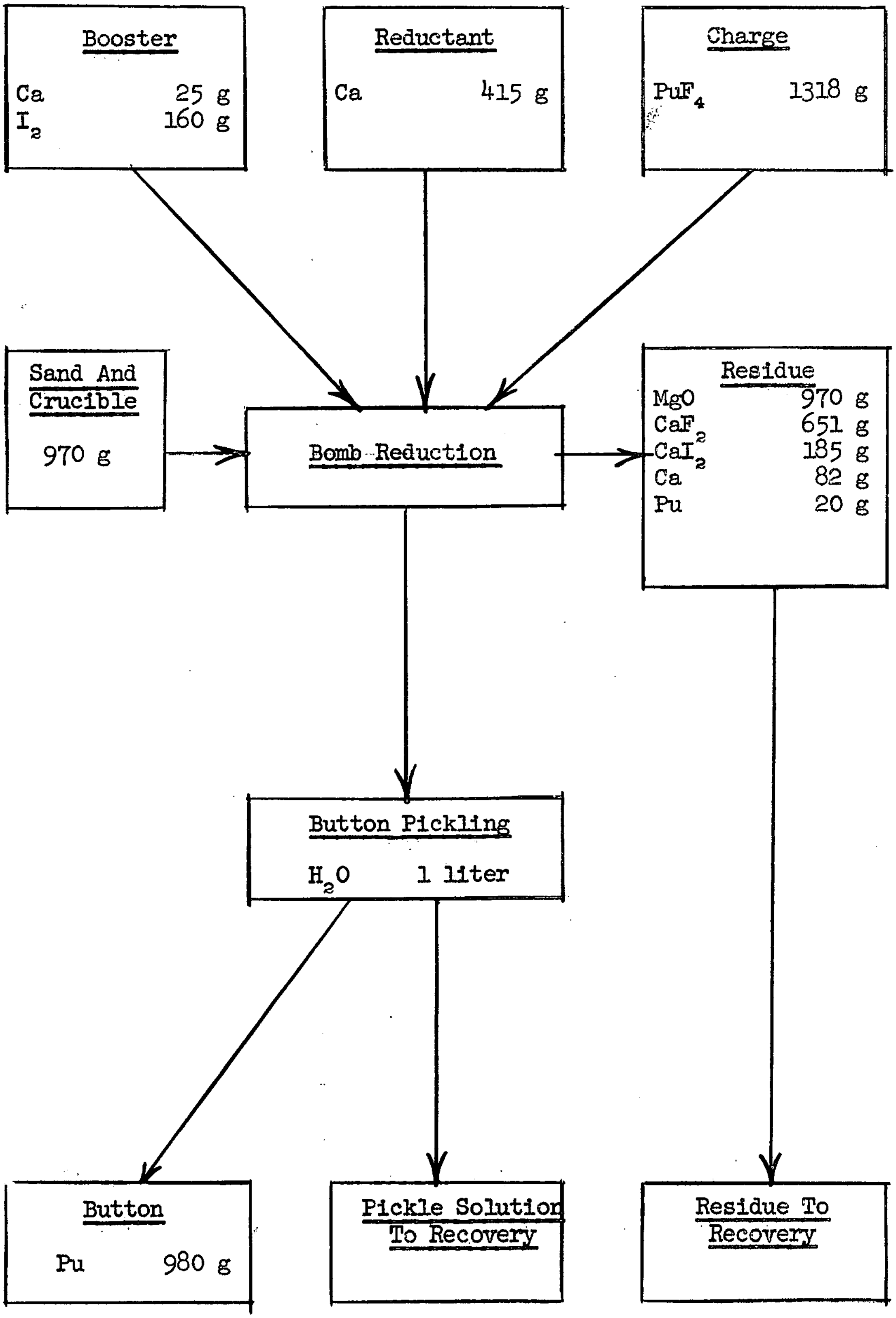

FIGURE 4

PRECIPITATOR - FILTER DESIGN

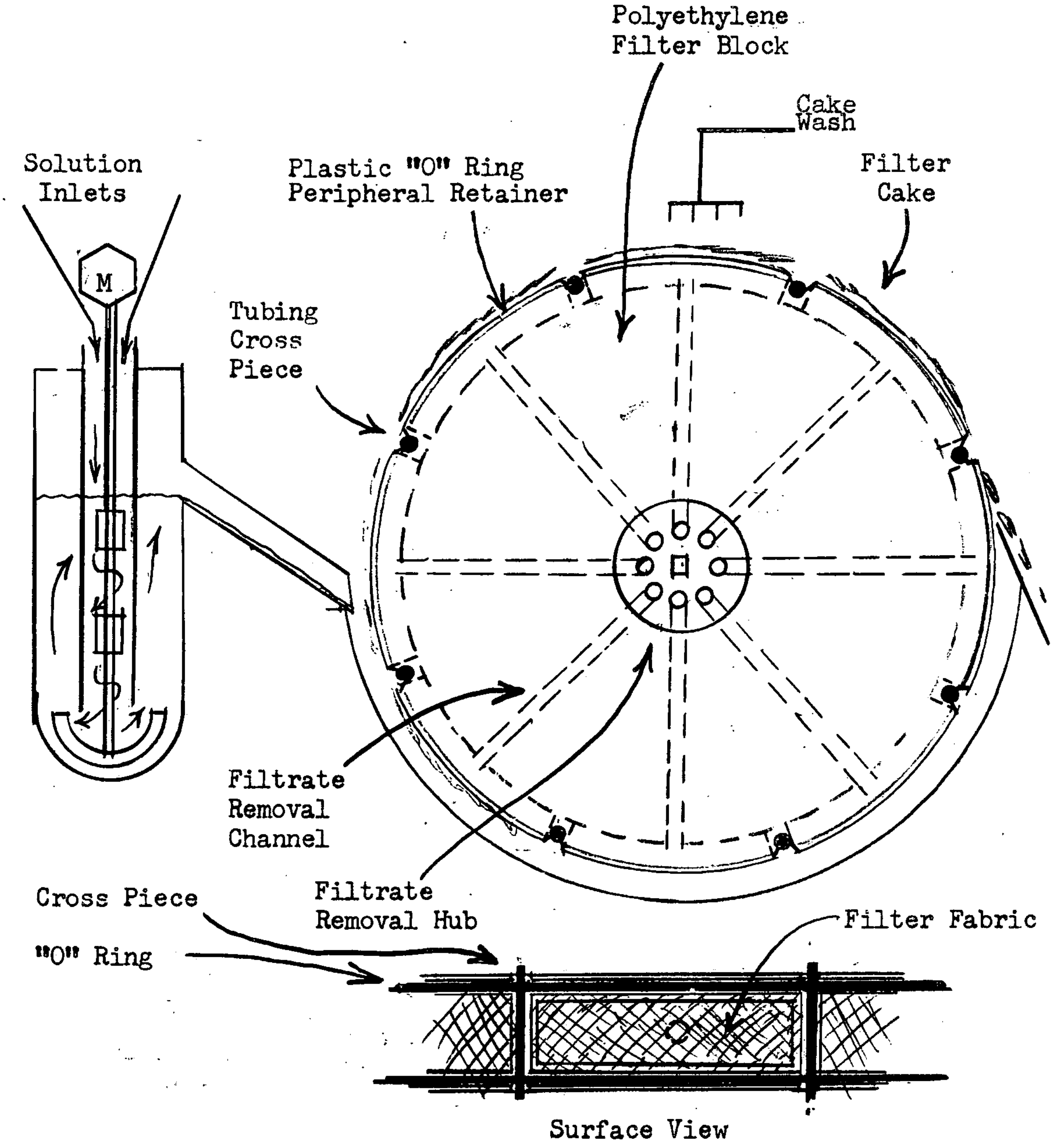

FIGURE 5

FILTER-CALCINER ASSEMBLY

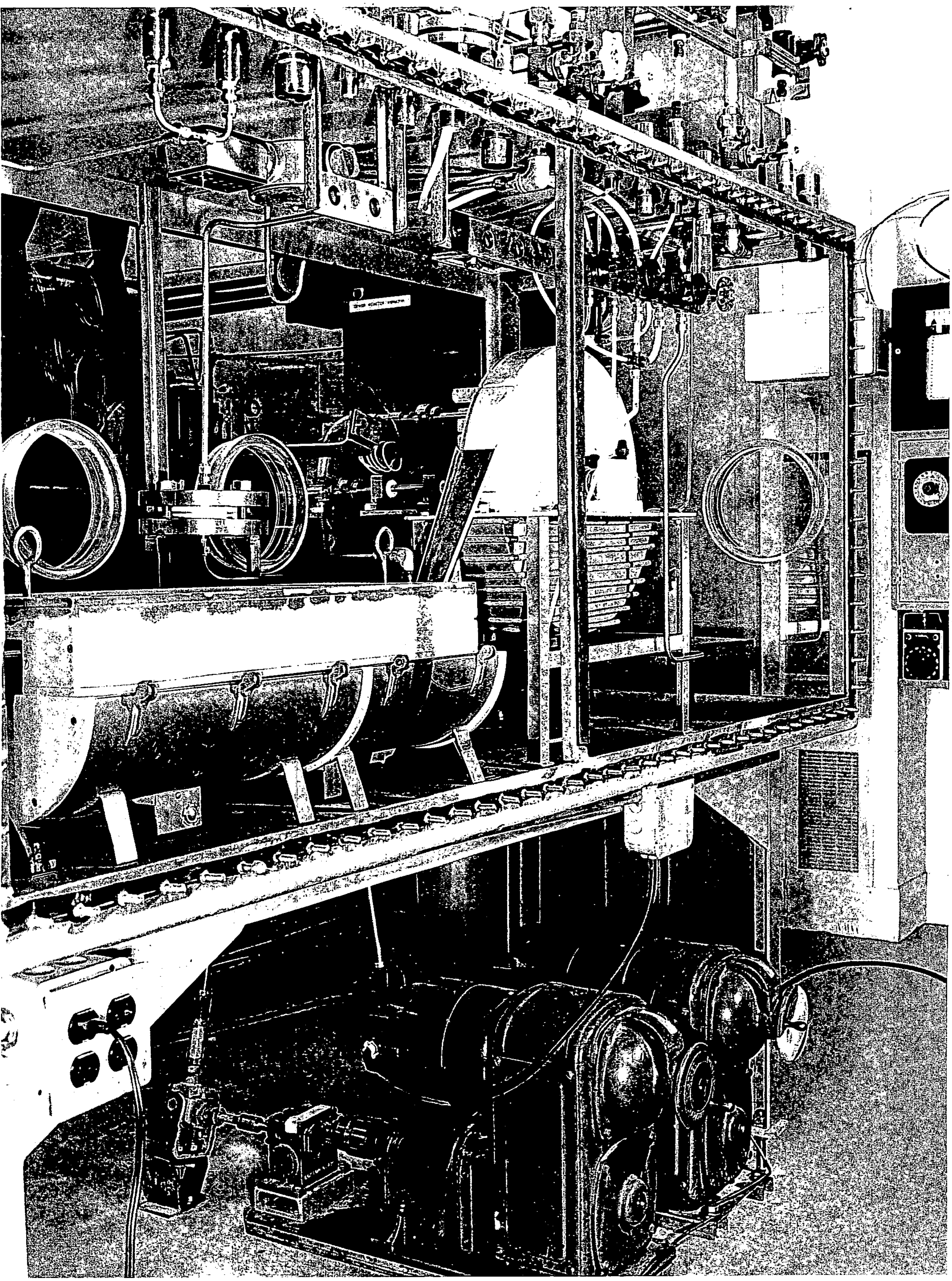

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FIGURE 6

CALCINER - OPEN VIEW

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FIGURE 7

HYDROFLUORINATOR

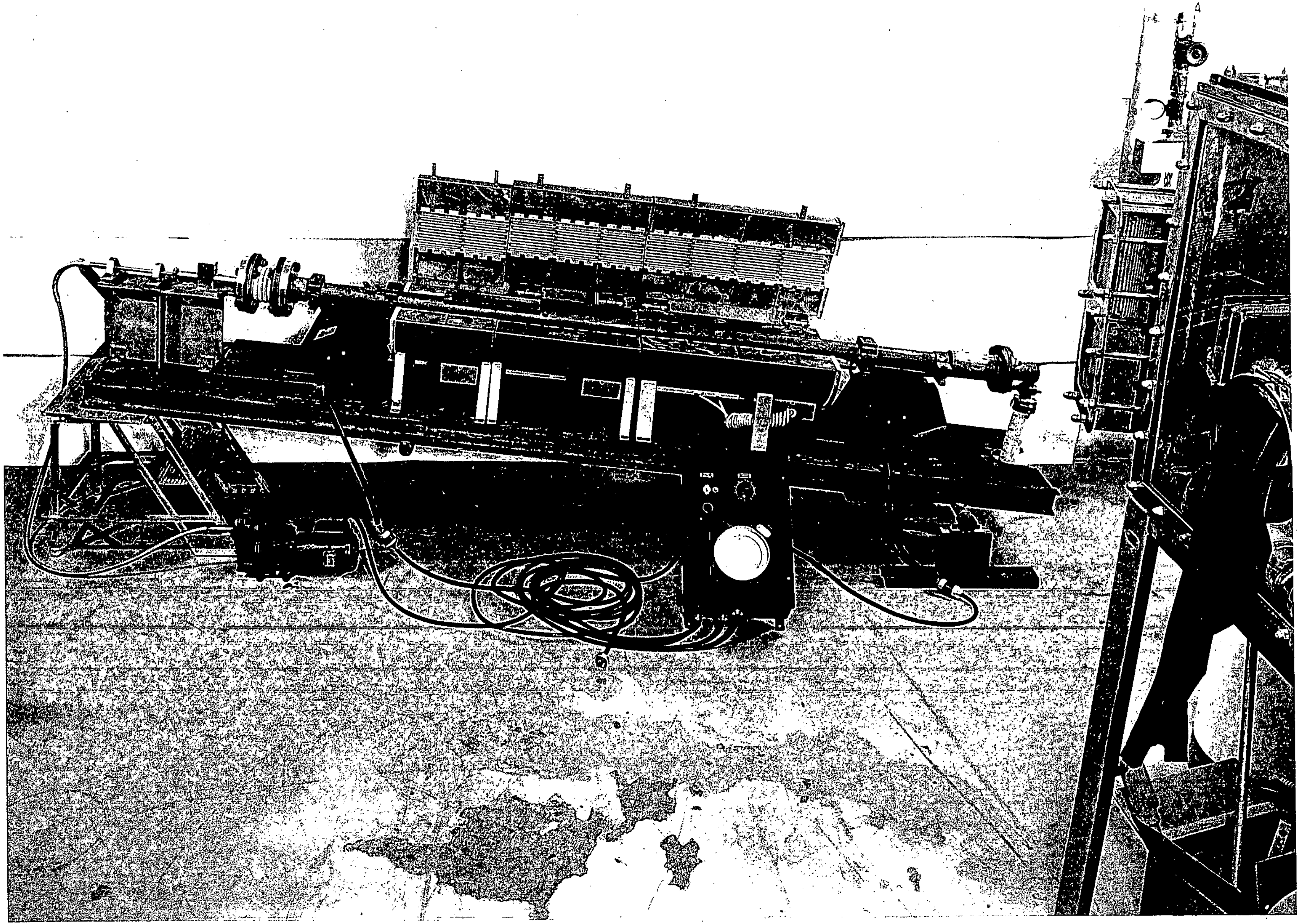

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FIGURE 8

TYPICAL OPERATING CONDITIONS

Feed Stream: $Pu(NO_3)_4$, 90 g Pu/l, 3.5 - 5.5 M HNO_3

Precipitating Agent: 1 M $H_2C_2O_4$

Wash Stream: 2 M HNO_3 - 0.05 M $H_2C_2O_4$

Precipitation Temperature: 25° C

Loss to Filtrate: < 3 percent of total plutonium

Residence Time in Precipitator: 15 minutes

Calciner Temperature: 325° C ± 15° C

Residence Time in Calciner: 25 minutes

Hydrofluorination Temperature: 500° C ± 25° C

Residence Time in Hydrofluorinator: 50 minutes

HF Flow Rate: 680 g/hour

O_2 Flow Rate: 93 g/hour

Conversion to PuF_4: 98 percent

Plutonium Throughput: 0.25 - 0.5 kg/hr

FIGURE 9

TYPICAL IMPURITIES FOR THE CONVERSION PROCESS

	Nitrate	Fluoride	Metal
Ag	< 5	< 2	< 2
Al	8000	<50	<20
B	< 10	-	-
Ca	50	10	<10
Cd	20	-	-
Cr	1000	200	<10
Cu	20	10	
Fe	5000	300	200
K	200	50	10
Mg	100	50	50
Mn	50	50	50
Na	500	100	50
Ni	200	100	50
Si	50	50	10
Sn	5	5	5
Zn	< 20	<20	<20

(-) Not detected.

As, Be, Bi, Ge, La, Li, Mo, P, Pb, Tl, V, not detected.