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PREPARATION OF PLUTONIUM METAL VIA THE CHLORIDE STATE

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and
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PREPARATION OF PLUTONIUM METAL VIA THE CHLORIDE STATE

By

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Richland, Washington

July 20, 1960

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PREPARATION OF PLUTONIUM METAL VIA THE CHLORIDE STATE

I. INTRODUCTION

The basic chemistry of the chloride route from plutonium nitrate to plutonium metal was known in 1944,(1)(2)(3) and has been variously studied since then.(4)(5)(6)(7)(8)(9)(10)

In general, however, fluoride has been preferred to chloride in plutonium metal preparation. An objection to a plutonium fluoride is the high neutron density resulting from intense alpha radiation of the fluorine atoms. By using a halogen of higher atomic number, the neutron exposure of personnel would be reduced more than by any reasonable shielding. Plutonium trichloride was the most promising substitute and would lessen the neutron radiation by a factor of 100 in the dry salt.

A second advantage of a chloride process is a matter of purity. The volatility of several metallic chlorides serves to remove or decrease these impurities in the halide powder and the metal.

The process selected(11) for further development was the continuous chlorination of plutonium dioxide powder by phosgene gas in a heated vibrating tube, followed by the conversion of plutonium trichloride to plutonium metal by heating with calcium in a hermetically sealed bomb.

This chloride route for plutonium metal preparation is one of many variations possible in a general method proceeding from nitrate solution, to oxalate and/or oxide, to halide, to the metal.(12)(13) This paper emphasizes the chloride process selected, and substantially neglects some excellent development work performed by my colleagues on steps before and after chlorination.

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II. EQUIPMENT AND PROCEDURES

A. Oxalate Preparation

A stream of about one molar plutonium nitrate solution and another containing one molar oxalic acid solution and 0.25 molar hydrogen peroxide were pumped steadily into a four-inch diameter precipitator. The peroxide served to convert the plutonium to the tetravalent state. An air-driven stirrer prevented settling of the oxalate precipitate and aided the overflow of slurry into a round bottom pan (Figure 1) in which a moving blade kept the slurry agitated. Vacuum (18 inches or more of water) applied to a rotating filter drum removed the filtrate from the pan and deposited the precipitate on synthetic fiber filter cloth. The wet plutonium(IV) oxalate was scraped from the drum and dropped into a calciner. Losses of plutonium into the filtrate tank were about two to five percent. After destroying excess oxalate with permanganate, this solution was recycled into the process by which the plutonium nitrate was prepared.

B. Oxide Preparation

The screw calciner (Figure 1) received the wet oxalate, $Pu(C_2O_4)_2 \cdot 6H_2O$, passed it through 30 inches of furnace, and converted it to free-flowing oxide in about twenty-five minutes. The two-inch diameter screw in this calciner was made of Hastelloy C. Within the 304 stainless steel furnace tube, the powder was pulverized in a device similar to a kitchen meat grinder. Usual calcining temperatures were 250 to 350 C.

C. Chloride Preparation

The chlorinator was in a gloved hood adjoining the calciner hood, but

[redacted]

there was no atmospheric flow between them. The chlorination hood was supplied with a dry atmosphere.

The plutonium oxide dropped from the calciner into the chlorinator through two ball valves which opened and closed on cycles timed to prevent gas flow between these units. Carbon dioxide entering the valves swept the phosgene downstream. A Teflon bellows isolated these valves from the vibration of the chlorinator. Intermittent vibration was achieved by an automatic timer and an F-115 Syntron Vibratory Feeder rated at six tons of sand per hour. The intensity of vibration was adjustable. Gases left the reactor at a tee about eight inches from the upper end. The filter housing and ceramic filter mounted at this point were subject to vibrations of the reactor. The vibrations served to clean the filter and empty this powder back into the chlorinator. As the powder vibrated down the Hastelloy B tube, it was heated during a forty-inch path to temperatures rising to 500 C (Figure 2). The temperature in the first 15 inches could become excessive and sinter the powder unless the electric heat was adjusted downward as exothermic heat increased. Phosgene gas entered at both ends of the tube after being preheated to about 200 C. Typical operating details of the chlorinator are given in Table I.

These conditions yielded about 98 percent plutonium trichloride, whereas powder flowing at 400 g Pu/hr showed about 80 percent conversion. The maximum throughput with acceptable product was not determined.

D. Metal Preparation

The preparation of plutonium metal by calcium reduction of plutonium trichloride was done in the same developmental equipment as was used for

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TABLE I

TYPICAL OPERATING DETAILS OF CONTINUOUS CHLORINATOR

Throughput Rate	250 g Pu/hr
Residence Time	30 - 40 minutes
Bed Depth	1/4 - 3/8"
Tube Inside Diameter	Oval, 1-1/4" x 2-1/4"
Heated Length	40"
Furnace Temperature	500 C maximum
Filter Temperature	350 - 400 C
Chlorinator Slope	4 degrees
Vibration Cycle	10 sec on, 25 sec off
Gas Pressure	1 - 20" of water vacuum
Phosgene Flow	6 mols per mol of PuO_2

plutonium tetrafluoride. The pressure bomb and lid with pressure gauge may be seen in Figure 3. Also shown are containers of iodine, calcium, and plutonium trichloride, a crucible in a can, and a typical plutonium metal button.

A calcium and iodine reaction was used to boost the temperature of the principal trichloride and calcium reaction. These chemicals were mixed and placed in a magnesia crucible in the stainless steel can. This crucible had been previously sand-packed and fused into the can by impregnating the magnesia with molten calcium chloride. The can was used to prevent the molten chloride salts of a reduction from fusing the crucible and sand into the bottom of the bomb. The slag and metal were

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eventually routed or broken out of the crucible, and the crucible was reused many times.

After a reduction bomb was charged and the lid bolted in place, it was leak-tested and purged at least two times with argon. Firing was initiated by heating in a 10 kc induction coil for about 15 minutes to a bomb skin temperature of about 700 C. Firing was normally indicated by an upward change on the temperature chart and by a sudden drop in pressure. Bomb pressures were usually 50 ± 30 psig and rarely exceeded 100 psig. About 200 psig was considered the maximum safe pressure. While the reduction charge was molten, the plutonium metal collected in the bottom of the crucible, essentially free of any slag and excess calcium.

The flow sheet in Figure 4 shows the relative amounts of chloride, iodine, and calcium. T. S. Soine(14) recently discussed the variables in the calcium reduction of plutonium trichloride. Plutonium metal was prepared in batches ranging from 30 to 1400 grams with good success. Slag and broken crucibles from the metal reduction step contained plutonium which had to be recovered. R. C. Smith(15) developed the techniques for dissolution of these wastes in nitric acid and recovery of the plutonium as nitrate solution. Small amounts of scrap plutonium metal, powders, and liquid were similarly recovered. Liquid and solid wastes from this recovery work were sent to underground disposal along with other contaminated wastes.

III. DISCUSSION AND RESULTS

A. Process Discussion

The optimum conditions of oxalate preparation required an 0.1 molar

[redacted]

[redacted]

excess of oxalic acid in the supernatant stream. Nitric acid in the plutonium nitrate stream was 3.5 to 5 molar. Under these conditions, the plutonium losses to the filtrate were smallest and the filter cake was easily handled. If these conditions were not maintained, the precipitate would not filter readily and/or would cling to the trough rather than fall freely into the calciner.

The oxide preparation was stopped short of conversion to the stoichimetric plutonium dioxide. The powder could lose about 10 percent of its weight on further heating to 1000 C. The objective was to produce a free-flowing powder which would be easily chlorinated. Calcining temperatures were varied from 150 to 400 C with noticeable changes in powder color shade. All of the oxide powder was readily chlorinated, so optimum temperature was not defined.

Prior to use of the chlorinator described here, several other chlorinating agents were tried. Hydrogen and hydrogen chloride, gaseous carbon tetrachloride, and chlorine-carbon monoxide mixture were all compared with phosgene and found less reactive. Use of phosgene permitted a choice of a hundred degrees lower temperature for an equivalent reaction rate, or else a higher chlorination rate at the same temperature as the other reagents.

The vibrating tube was selected as the reactor because of other local experience with vibrating tubes, and also because it has no moving parts exposed to high temperature and corrosive atmosphere. The minor nickel impurity found in the chlorinated powder indicates the possibilities of using moving parts and higher temperature in a Hastelloy B chlorinator.

As noted earlier, in Table I, the phosgene flow was six mols per mol

[redacted]

of plutonium, or three times the stoichiometric requirement. This may have been more than was necessary. Under the specified conditions, the principal and minor chemical reactions were as follows:

$$PuO_2 + 2COCl_2 \longrightarrow PuCl_3 + 2CO_2 + 1/2Cl_2 \text{ (principal).}$$

$$PuO_2 + COCl_2 \longrightarrow PuOCl + CO_2 + 1/2Cl_2 \text{ (minor).}$$

$$PuOCl + COCl_2 \longrightarrow PuCl_3 + CO_2 \text{ (minor).}$$

$$COCl_2 \longrightarrow CO + Cl_2 \text{ (minor).}$$

$$H_2O + COCl_2 \longrightarrow 2HCl + CO_2 \text{ (minor).}$$

The phosgene hydrolysis indicated in the last equation occurred when moisture entered with the plutonium dioxide or when moist air leaked into the gas exhaust system. Chlorination did not occur when air leaked into the reactor tube. Small air leaks were the cause of incomplete chlorination on several occasions. The partly-chlorinated powders from such runs were recycled through the chlorination step with good results.

The conversion of plutonium trichloride to the dioxide by high temperature air was utilized in the handling of some impure powders such as hood sweepings. Some of these were freed of chloride by heating in air at 400 - 500 C, then dissolved by acids in stainless steel equipment. These may also be recovered as mentioned earlier.

Most of the time the plutonium trichloride formed in lumps which were largely pulverized by the vibration in the tube and in the product receiver. The inside of the lumps were chlorinated and offered no problem in reduction to metal. When the reaction tube was plugged by the lumps, it was due to experimental conditions. Three things were done to eliminate any serious problem from plugging: (1) the best operating conditions were

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defined, (2) the chloride exit was made oversize to prevent interference with flow, and (3) the tube end was altered to permit easy rodding of the tube if a plug developed.

Powder flow control in the vibrating tube was more a problem than merely lumps. The resonance of the tube was influenced by suspension points, powder load, filter housing weight, vibrator mounting, etc. Experimenting was necessary to eliminate standing waves which interfered with powder flow.

The vibrating tube served its purpose in producing high quality plutonium trichloride which was readily reduced to plutonium metal.

A study of the variables in the metal preparation(14) showed that good mixing of the charge was not always necessary. The charge could be unmixed if the plutonium trichloride was on top.

The presence of moisture in the reduction could lead to hazardous bomb pressures. It was found that 0.5 percent water was permissible in the trichloride. Because the reduction work was performed in a gloved hood at 40 percent relative humidity, the rate of hydration of the trichloride was of concern.

Several powder samples of 3/4-inch depth were exposed to air at controlled humidities. The rates of weight increase are shown in Figure 5. Less than 0.01 percent increase was observed in 100 hours at dew point -18 C. There was no evidence of hydration at dew points -20 and -28 C. The permissible time of exposure at various humidities may be approximated from the graphs. Hydration is accompanied by a powder volume increase and a change to bright-blue color. Relative exposed area is critical in the hydration rate.

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B. Gases

Phosgene has been used for over two years without harmful incident. Procedures for safe handling of hydrogen fluoride are adequate for phosgene. Some psychological resistance was experienced.

In cold weather, the phosgene cylinders must be allowed to warm to room temperature to provide the normal 30 psig pressure. The gas flow control valve was heated to eliminate liquifying the phosgene by the pressure drop from 30 psig to below atmospheric normal.

Exhaust gases from the process were filtered to prevent losses of entrained plutonium powders and contamination of the environment.

The gases from the calciner were kept hot through a cyclone which trapped some of the oxide dust. A filter of glass cloth and then a water vapor condenser further prepared the off-gases for release into the general laboratory vacuum system.

Exhaust gases from the chlorinator were filtered through a heated ceramic filter. Filter cylinders cut into five-inch lengths from products of the Carborundum Company and of the Selas Corporation were both used with such success that no efforts were made to use more expensive Hastelloy filters. At the flow rates used, pressure drop across a filter was near 9 to 10 inches of water. Filter characteristics are shown in Table II.

The filters permitted the "bleeding" of some fine dust until a cake formed. In 30 or 40 hours of test operation, there was less than 0.1 gram of plutonium pass either of these filters. When a filter was operated cold, it became plugged by condensation of volatile chlorides. When a filter was heated to 350 - 400 C, these chlorides passed through, and condensed beyond the filter.

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TABLE II

CERAMIC FILTER CHARACTERISTICS

	Carborundum	Selas
Grade	5	XF
Porosity	ca 0.25	0.29
Pore Size	ca 65 μ dia.	100 μ dia.
Wall Thickness	7/8"	3/16"
Material	"Aloxite"	Unglazed porcelain

Spectrographic analyses of these condensates showed significant amounts of the following elements (listed in approximate decreasing order of concentration): iron, phosphorus, molybdenum, chromium, zinc, boron, bismuth, aluminum, nickel, silicon, potassium, titanium, manganese, and sodium. Most (but not all) of these are explained by the volatility of their chlorides and carbonyls.

After a second filtration and cooling of the exhaust stream, the gases for disposal were found(16) to be phosgene, carbon dioxide, chlorine, hydrogen chloride, and carbon monoxide. The boiling points of these make it easy to separate the phosgene (B.P. 8.3 C) in a cold trap. Phosgene thus recovered was reused with success. The economics of this step have not been evaluated.

Direct release of the filtered exhaust gases to atmosphere via a large dilution with other gases in the exhaust stack appeared feasible, but was impractical for this development program due to the long run of PVC pipe needed to reach the stack. A second-best method of gas disposal was

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adopted.

The filtered gases were carried into the bottom of a sodium hydroxide scrubber tower by applying vacuum to the top of the tower. The caustic from a 25-gallon reservoir was recirculated continuously through the tower which contained graphite Raschig rings. The initial sodium hydroxide concentration was six molar. More concentrated solution was impractical due to carbonate precipitation in the tower. The caustic was discarded when yet 0.5 to 1.0 molar in NaOH due to impending carbonate precipitation. This scrubber effectively removed corrosive gases and permitted release of the remaining gases into the hood exhaust system.

C. Materials

Most of the problems in selecting materials for this process were due to the chemical reactivity of phosgene and hydrogen chloride. When dry and at room temperature, phosgene is safely contained in black iron, copper, monel, stainless steel, etc. When hot, none of these are satisfactory. Table III, taken from unpublished data of W. L. Walker, shows five materials suitable for use in phosgene at 500 C, but much less suitable at 600 C. The high corrosion rates at 90 - 100 C show the effect of moisture and phosgene (essentially hot hydrochloric acid) at condensation temperatures. Several non-metallic materials are satisfactory at this temperature. At room temperature, the corrosion of 304L stainless steel was much less.

Phosgene and plutonium trichloride were used for two years in one gloved hood where the air was usually 40 to 60 percent relative humidity, without serious damage to the 304L stainless steel.

[redacted]

TABLE III

CORROSION OF MATERIALS IN PHOSGENE(a)(b)

Corrosion Rates In Mils Penetration Per Month

Material	Temperature 90 - 100 C	400 C	500 C	600 C
Hastelloy B	7.0	0.02	0.9	7.2
Hastelloy C	9.0	0.02	0.6	6.1
Nickel	11	-	0.6	4.4
Chlorimet-2	11	-	0.8	5.6
Ni-O-Nel	19	-	0.9	12
304L Stainless	68.5	67	-	-

(a) Phosgene plus 50 percent water-saturated air, flowing at two liters/hour.

(b) Unpublished data by W. L. Walker, Hanford Laboratories Operation.

The attack of steel by phosgene and trichloride powder at room conditions is through hydrolysis and the formation of hydrogen chloride. The effect of various humidities was investigated as a means of limiting corrosion.

At a relative humidity of 40 percent or higher, thin films of powder deliquesced (formed puddles). This is a corrosive situation. A group of test coupons showed that corrosion decreased as humidity decreased. At dew point -20 C, there was negligible corrosion to test coupons of 304 stainless steel when in contact with plutonium trichloride. A dry atmosphere of -20 C dew point or better is readily available with commercial

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supply units. Such an atmosphere serves to prevent both corrosion and hydration of powder from carrying moisture into the reduction step.

A number of materials were tested in phosgene and are classified loosely in Table IV as useful or unsuitable for use in this program. Classification is subject to change with change in environment. For example, although "Krene" bags are unsuitable in phosgene, these bags gave satisfactory service on the chlorination hood because phosgene was generally confined to the process lines.

D. Product Quality

The quality of the final product is tied to the qualities of the intermediates. Some impurity concentrations in the process are shown later. Significant impurity removal was achieved in the precipitation of plutonium oxalate from the nitrate solution. Impurities in the oxalate may be assumed to correspond to those in the oxide.

The plutonium oxide was of olive-green color, entirely free of lumps, and of particle size about one micron or less. Its bulk density was approximately 1.5 - 2.0 g/cc. Normal plutonium content was 80 - 85 percent.

The plutonium trichloride color was various shades of greenish-blue when 90 percent or more chlorinated. When chlorination was incomplete, the oxide present was visible as a brownish tinge. From this color, a trained person may estimate the unchlorinated portion with accuracy of a factor of two.

Laboratory analyses of the chlorinated powder was approached in the following two ways:

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TABLE IV

MATERIALS TESTED FOR USE IN PHOSGENE

Temperature	Useful	Unsuitable
500 C	Nickel	Gold
	Hastelloy B	Platinum
	Hastelloy C	Inconel
	Glass	Baker 413
	Vycor	304L Stainless
	Porcelain	
	Quartz	
	Ni-O-Nel	
	Chlorimet-	
	Asbestos	
200 C	Teflon	
	Kel-F	
	304L Stainless (for short life)	
25 C	PVC (rigid)	Krene (plastic bag)
	Saran	Tygon or Nalgon Tubing (plasticized PVC-PVA)
	Polyethylene	
	Neoprene	Silicone Rubber
	Koroseal	Gum Rubber
	Nylon	Krylon Paint
	Monel (dry)	Brass (moisture present)
	Black Iron (dry)	Aluminum or Al-Di
	Copper (dry)	Zinc (galv. coating)

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An unweighed sample was analyzed for plutonium and for chloride content. The results were expressed as a ratio, Cl/Pu. This served to confirm that the material was primarily $PuCl_3$ (Table V). This expression was insensitive to trace amounts of unchlorinated powder. The analytical method failed when oxide in the sample failed to dissolve as in Runs 22 and 23. In these runs, a much higher chlorinator flow rate was attempted.

TABLE V

ANALYSES OF PLUTONIUM CHLORIDE POWDERS

Run Number	Ratio Cl/Pu	Percent Water Insoluble
16 previous runs	Average 2.99	-
17	2.96	-
18	2.62	-
19	2.94	-
20	2.99	-
21	2.98	-
22	2.97	8
23	2.98	13, 12.4
24		3.7, 4.7, 7.4
25		0.03, nil
26		Nil, 1.5
27		Nil, 1.5
28		Nil, nil
29		2.9

The second analytical approach was more satisfactory for detection of unchlorinated powder. A weighed sample was stirred into water, and the insoluble portion determined. The percent water insoluble included all of the PuO_2 and most, if not all, of any PuOCl. This method has not been thoroughly investigated, but the agreement between some duplicate samples are seen in Table V. The trichloride from numerous other runs was not analyzed in the laboratory, but the water-insoluble content was visually determined to be less than five percent by comparison with other samples.

The bulk density of plutonium trichloride varied from two to three g/cc. The average particle size was found to be 4.1 and 6.1 microns in two determinations by a Fisher Sub-Sieve Sizer.

The trichloride powder may be safely stored indefinitely at room temperature in containers sealed against moisture. Glass jars with Neoprene-lined caps were adequate, whereas paper-lined caps or polyethylene jars permitted water vapor to reach the powder. The powder is not stable against oxidation at room temperature if moisture is present. The greenish-blue trichloride turns to the bright-blue hexahydrate; and after about four days, an oxide layer is visible on the surface. At higher temperatures, the oxidation in air is more rapid.

In the reduction step, about 97 - 99 percent of the plutonium collected as a metal button which had a density of 19 g/cc or higher. Impurities in the metal usually total less than 0.2 percent (Table VI). The totals indicate within a factor of two the general level of impurities at each step of the process. The rise and fall of nickel impurity indicate the corrosion of the chlorinator tube and the partial separation of metal from impurities in the reduction step. The iron

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TABLE VI

TYPICAL IMPURITIES IN CHLORIDE PROCESS

Parts Impurity Per Million Parts Plutonium Determined By Emission Spectrograph

Impurity	Nitrate	Oxide	Chloride	Metal
Ag	L5	L2	L5	L5
Al	L50	L50	L5	L5
As	-	-	-	-
B	L10	L5	L5	L2
Be	-	-	-	-
Bi	-	-	-	L[illegible]
Ca	50	10	20	5
Cd	20	-	-	-
Cr	1,000	200	50	50
Cu	20	10	10	10
Fe	5,000	300	70	200
Ge	-	-	-	-
K	200	50	100	-
La	-	-	-	-
Li	-	-	-	-
Mg	100	50	50	100
Mo	-	-	-	-
Mn	50	50	50	50
Na	500	200	200	L10
Ni	200	100	500	200
P	-	-	-	-
Pb	20	50	20	10
Si	50	50	50	20
Sn	5	5	-	L5
Tl	-	-	-	-
V	-	-	-	-
Zn	L20	20	L20	L20
Total	ca 7,000	ca 1,100	ca 1,100	ca 700

L = Less than
\- = Not detected

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values result from the chloride volatilization and the effect of using steel equipment in metal preparation and sampling.

The relatively-high purities found, together with the demonstration of a workable process, lead to the conclusion that plutonium metal preparation via the chloride state is a practical method. The exposure of personnel to neutrons may not decrease by a factor of 100; but on a single comparison of equal amounts of plutonium, the fluoride was shown to emit neutron radiation 64 times that of plutonium trichloride.

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FIGURE 1

SIMPLIFIED FLOW SHEET

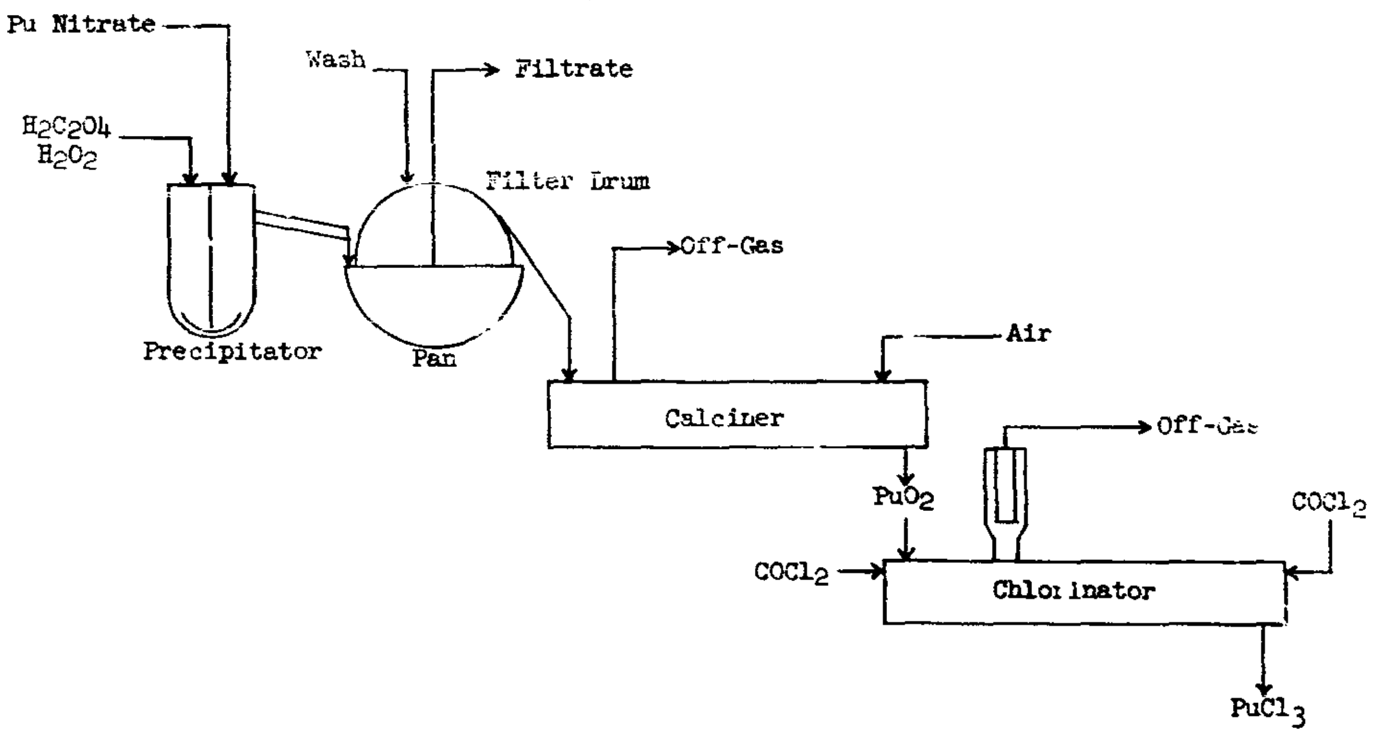

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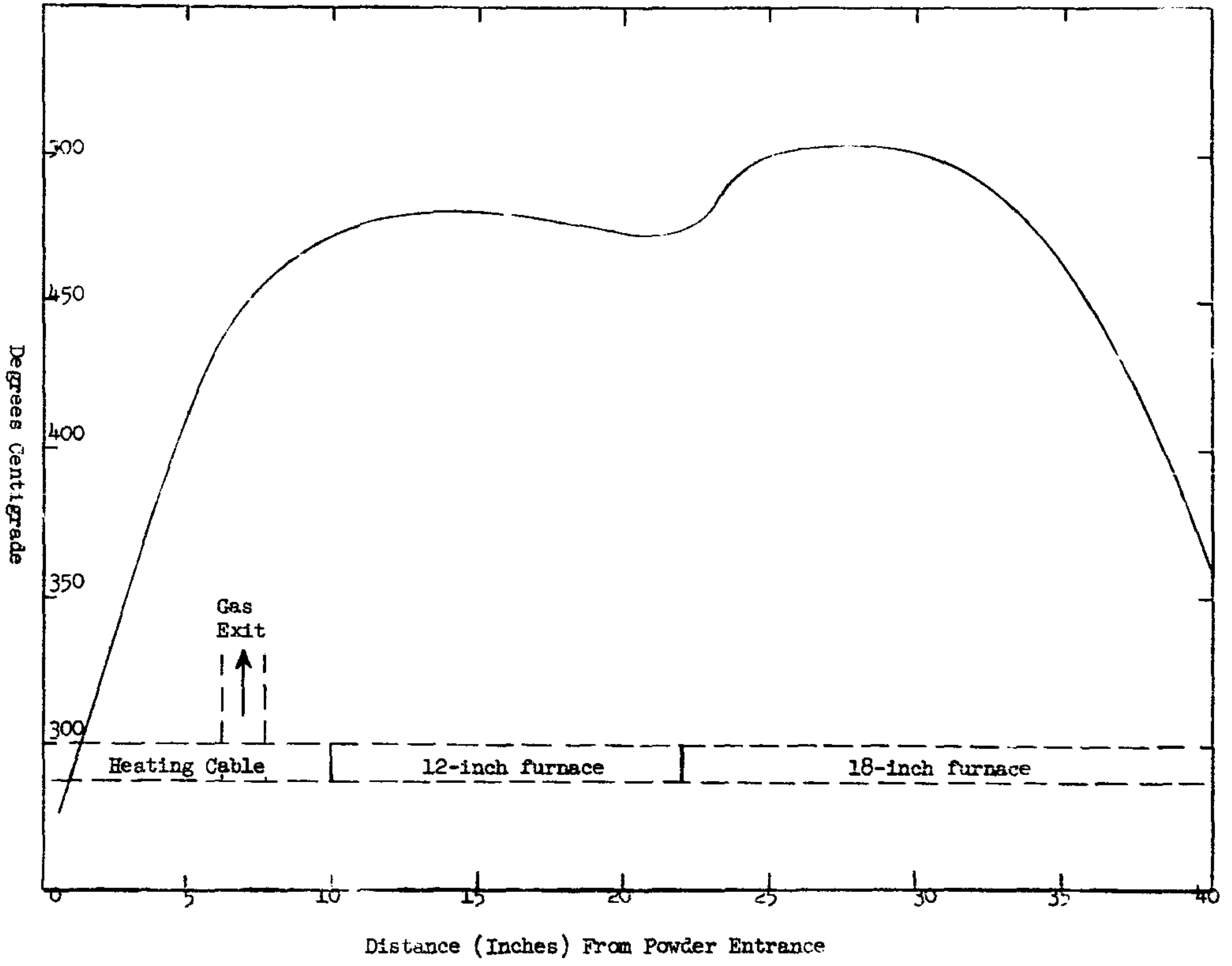
FIGURE 2

TEMPERATURE OF CONTINUOUS CHLORINATOR



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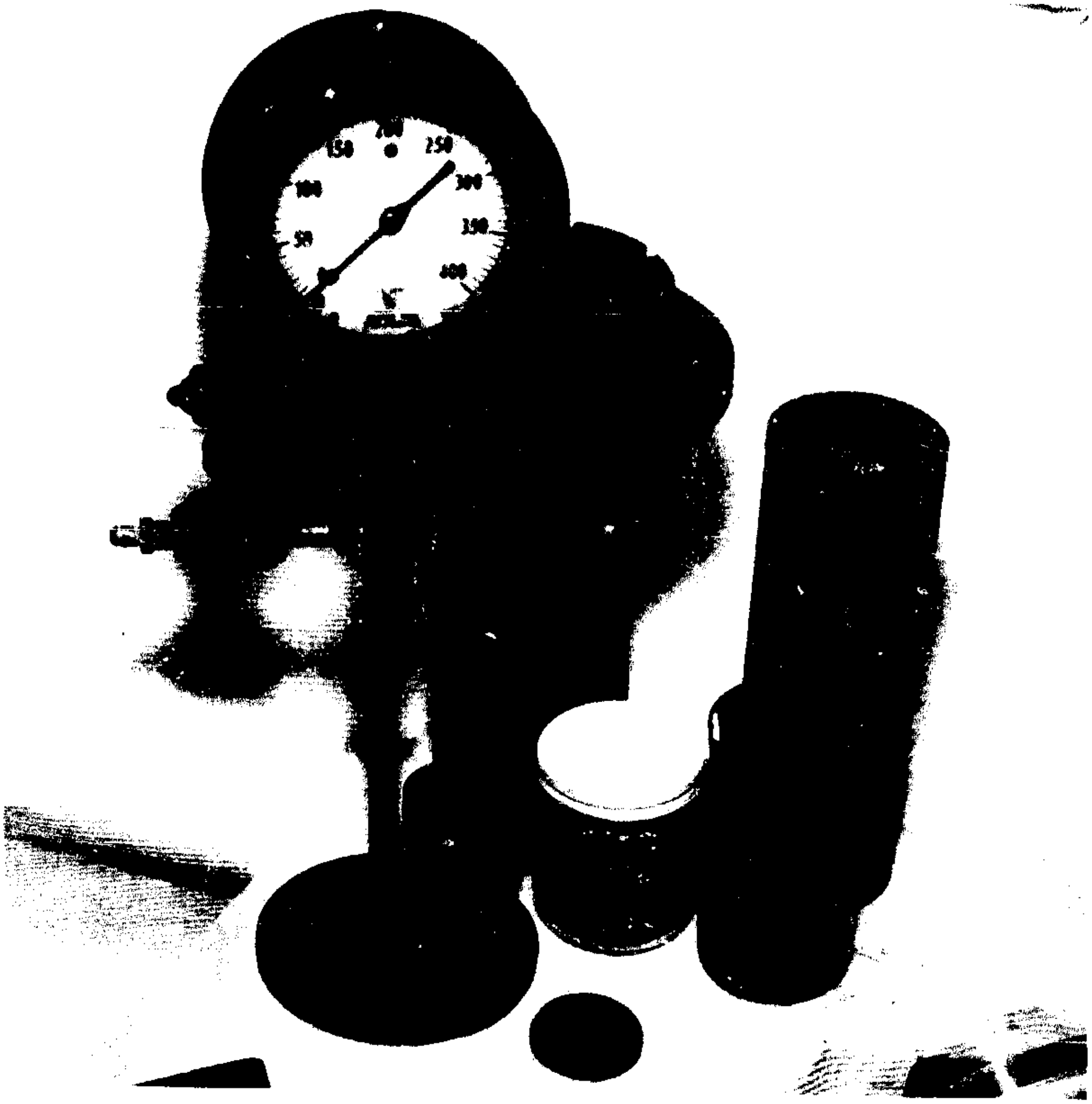

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HW 66148

FIGURE 4

FLOW SHEET FOR BATCH REDUCTION OF PLUTONIUM TRICHLORIDE
Scale: 1 kilogram Pu

~75 to

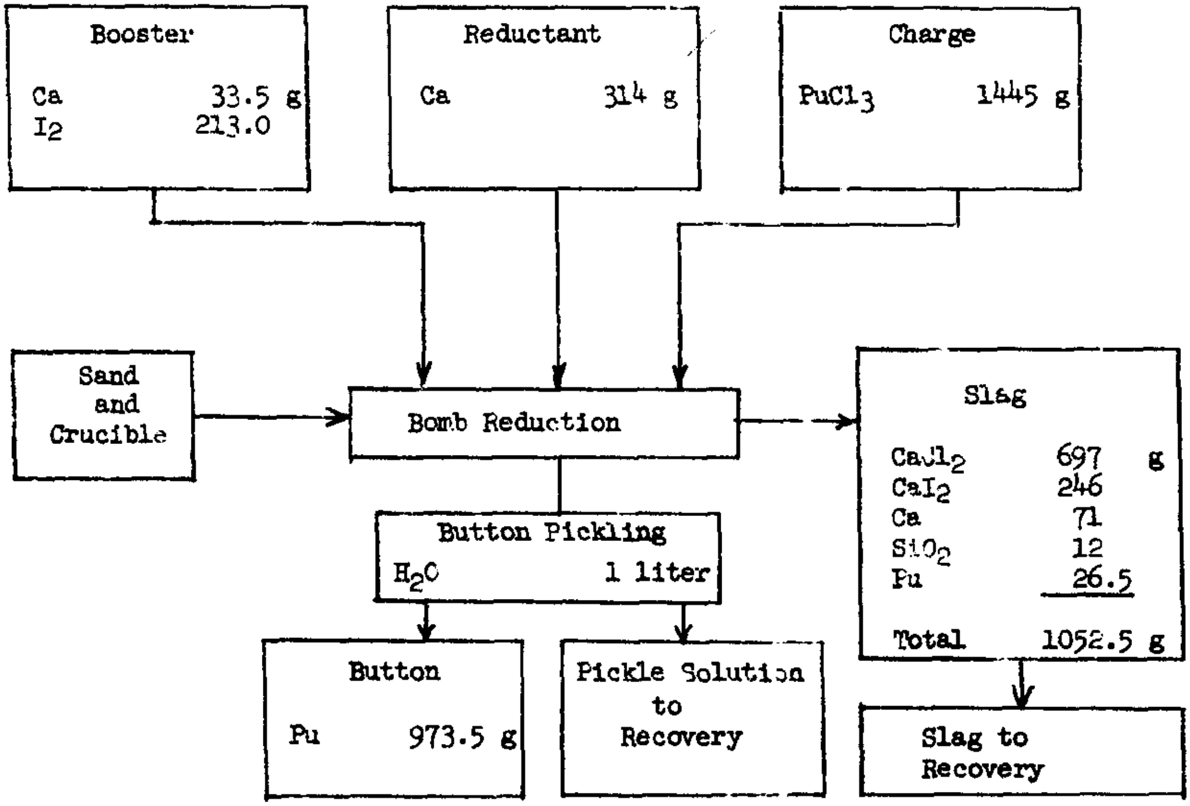

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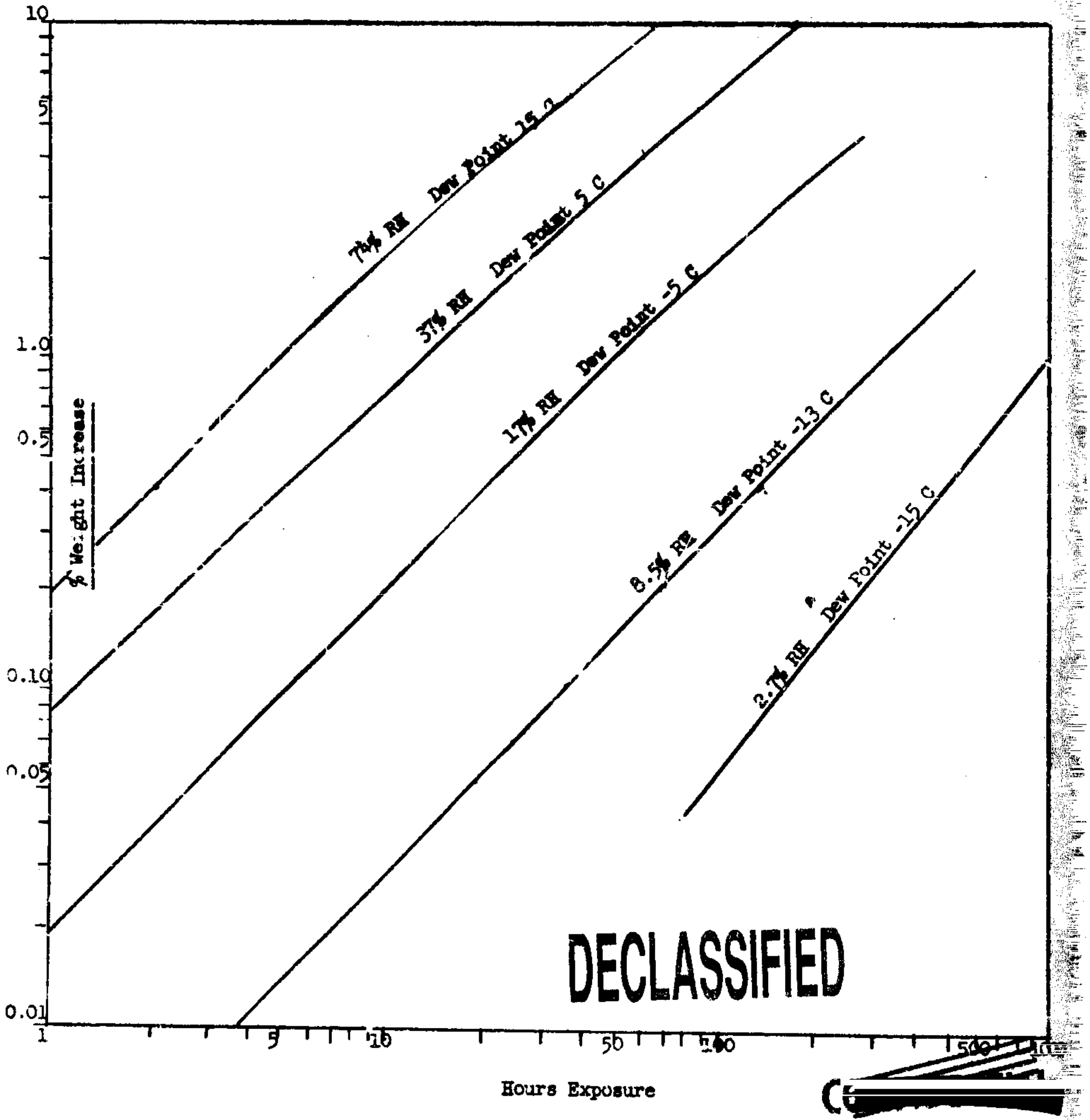
FIGURE 5

HYDRATION RATES OF PLUTONIUM TRICHLORIDE AT CONTROLLED HUMIDITIES



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