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TITLE

STATUS OF PLUTONIUM TRICHLORIDE PROCESS DEVELOPMENT (II)

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PLUTONIUM TRICHLORIDE PROCESS DEVELOPMENT (II)

By

H. H. Hopkins, Jr.

234-5 Development Operation
Research and Engineering Operation
Chemical Processing Department

August 14, 1959

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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STATUS OF
PLUTONIUM TRICHLORIDE PROCESS DEVELOPMENT (II)

I. INTRODUCTION

The development of a reduction step using plutonium trichloride instead of plutonium tetrafluoride in 234-5 Building processing was proposed early in 1958.⁽¹⁾ This process change was intended to reduce the neutron radiation associated with plutonium fluoride. Neutron dose estimates show that over half of 234-5 Building neutron exposure is associated with the fluoride process steps.⁽²⁾ Other measurements⁽³⁾ show that a 60-fold reduction in neutron flux could be realized by converting to a chloride process.

Progress up to September, 1958, was described in a document covering the chemical aspects of the development work, including batch preparation of trichloride.⁽⁴⁾ The present report summarizes work done on this process over the past year, emphasizing continuous preparation of plutonium trichloride in large-scale equipment, the reduction of this product to metal, and large-scale recovery of slag and crucible. This work is described in detail in three separate documents covering chlorination,⁽⁵⁾ reduction, ⁽⁶⁾ and recovery.⁽⁷⁾

II. SUMMARY AND CONCLUSIONS

Continuous chlorination of plutonium dioxide to plutonium trichloride has been demonstrated in large-scale equipment. Phosgene at 450 - 500 C is recommended as the chlorinating gas in Hastelloy B equipment. Rates are available from which to calculate the performance of larger-scale equipment. Ceramic off-gas filters have been tested and conditions developed for separating off-gas from entrained solids. A dew point of -20 C is recommended for process equipment to maintain dry powder. Hydration rates have been measured for higher dew points.

Plutonium trichloride can be satisfactorily reduced to metal in nickel-coated magnesia liners. Yields in the 97 - 99 percent range were easily obtained in tests up to a 700-gram scale. The impurity level has been satisfactorily low, generally less than 1000 ppm. Button densities ranged from 16.8 - 19.4 g/cc with low densities largely due to impurity carryover. Confidence is complete in the ability of this process to produce specification metal.

No hazards arose from water of hydration, even though all reductions were loaded in ordinary laboratory air. An atmosphere of -20 C dew point is recommended to insure good yields and long hood life.

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Corrosion in reduction vessels approximated that observed with fluoride.

Cemented magnesia liners or tantalum liners show promise as reusable liners for chloride reductions.

Flow sheets have been developed for preparing a recovery feed from chloride slag and crucible. Chloride is reduced to 35 ppm, below the 1000 ppm limit for Recuplex feeds. The chloride is removed by boiling with nitric acid while dissolving slag and crucible. A separate nitric-hydrofluoric acid treatment of the silica precipitate is necessary to keep waste losses to the solids below one percent. Two treatments reduce losses to approximately 0.01 percent.

III. DISCUSSION

A. Continuous Chlorination Of Plutonium Dioxide

1. Feasibility

Continuous chlorination of plutonium dioxide to plutonium trichloride has been demonstrated both in small and large vibrating tube reactors.⁽⁴⁾⁽⁵⁾ Phosgene was selected as chlorinating agent because of its greater reactivity, favorable off-gas behavior, and freedom from explosion hazard. Over 13 kilograms of plutonium have been processed to trichloride in the large demonstration Hastelloy B reactor. This reactor is shown in Figure 1, and the results from this unit are described in Table I. Purity data are exemplified in Tables II and III. It is seen that adequate purity is maintained across the chlorination step.

A flow sheet for chlorination is presented in Figure 2.

2. Process Discussion

The feed for the large-scale chlorination work was plutonium dioxide made by the oxalate process in the laboratory prototype continuous Task I equipment. The oxide, in all cases, was prepared by low temperature calcination (250 - 300 C). The oxide was fed directly into the chlorination equipment. These conditions resulted in the development work approximating very closely the proposed production equipment in residence times, environment, etc.

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In the vibrating tube chlorination reactor, a tendency for lump formation was observed at the entrance to the reactor where the hot reaction zone commences. In order to minimize lump formation, a more intense vibration is required than in a fluorinator. The cycle employed was 10 seconds on, 10 seconds off. This more intense vibration minimized the lump problem, but it did intensify the off-gas solids problem. Also, it was necessary to carefully adjust the vibration intensity to achieve even powder flow whenever equipment changes shifted the weight balance of the tube.

Another difference between chlorination and fluorination processes is that no air is used in the chlorination process. Leaks contribute oxygen which reverses the reaction and drives it back toward the oxide. No difficulty was found in keeping the apparatus leak-free.

The hood atmosphere was maintained dry (-20 C dew point) by a steady bleed of two cubic feet per minute of process dry air. No problems in powder handling or hydration were experienced.

TABLE I

PuO₂ CHLORINATION RATES - DEMONSTRATION CHLORINATOR

<u>Grams Pu/hr</u>	<u>Hrs' Operation</u>	<u>Chlorinator Length At 450 C Or Above, Inches</u>
83	4	21
113	2	21
295	3	21
268	2.5	21
260	1	21
192	2	21
209	1	14
173	2	14
115	4	14
170	3	14
322	1	21

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TABLE II

PLUTONIUM TRICHLORIDE IMPURITIES

A comparison of typical spectrographic analyses of oxide, chloride, and metal when the Hastelloy B demonstration chlorinator was used with phosgene at 500 ± 25 C. Values are parts impurity per million parts plutonium.

<u>Impurity</u>	<u>Oxide</u>	<u>Chloride</u>	<u>Metal</u>
Ag	5	2	L2
Al	Invalid due to Al in phosgene filter		
As	-	-	-
B	10	2	L2
Be	-	-	-
Bi	-	-	-
Ca	2000	500	200
Cd	10	-	-
Cr	200	20	10
Cu	50	50	20
Fe	2000	100	50
Ge	-	-	-
K	50	100	-
La	-	-	-
Li	-	-	-
Mg	200	200	500
Mo	-	-	-
Mn	100	100	500
Na	200	200	10
Ni	200	500	200
P	-	-	-
Pb	50	100	50
Si	50	50	50
Sn	20	-	-
Tl	-	-	-
V	-	-	-
Zn	20	L20	50

(L) Less than
(-) Not detected

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TABLE III

PLUTONIUM TRICHLORIDE IMPURITIES

A comparison of typical spectrographic analyses of nitrate solution, oxide, and chloride when the Hastelloy B demonstration chlorinator was used with phosgene at 500 ± 25 C. Values are parts impurity per million parts plutonium.

<u>Impurity</u>	<u>Nitrate</u>	<u>Oxide</u>	<u>Chloride</u>
Ag	L5	L2	2
Al	5		5
As	-	-	-
B	5	-	L2
Be	-	-	-
Bi	5	-	-
Ca	50		50
Cd	L10	-	-
Cr	1000	100	50
Cu	20	5	20
Fe	>2000	L100	50
Ge	20	-	-
K	500	59	100
La	-	-	-
Li	50	-	-
Mg	50	20	50
Mo	-	-	-
Mn	100	20	50
Na	1000	100	200
Ni	500	100	500
P	-	-	-
Pb	50	50	20
Si	10	20	20
Sn	5	L5	L5
Tl	-	-	-
V	-	-	-
Zn	200	20	L20

(L) Less than
(>) Greater than
(-) Not detected
No analyses for elements not listed

3. Materials Of Construction

Data by W. L. Walker of HLO show corrosion rates of Hastelloy B, Hastelloy C, nickel, etc., to be about one mil per month in phosgene at 500 C (Table IV). Contamination of chloride powder by the laboratory demonstration reactor was not indicated.

TABLE IV

CORROSION OF MATERIALS IN PHOSGENE*
Corrosion Rates In Mils Penetration Per Month

<u>Material</u>	<u>Furnace</u>			<u>Exhaust Gas</u>
	<u>400 C</u>	<u>500 C</u>	<u>600 C</u>	<u>90 - 100 C</u>
Hastelloy B	0.02	0.9	7.2	7.1
Hastelloy C	0.02	0.6	6.1	9.0
Nickel	---	0.6	4.4	11
Chlorimet-2	---	0.8	5.6	11
Ni-O-Nel	---	0.9	12	19

(*) Phosgene plus 50 percent water-saturated air.

Phosgene is supplied in black iron. Copper, iron, monel, and stainless steel are suitable for supply lines.

Exhaust lines must be Hastelloy C up to the off-gas filter (350 C). Beyond this point, inexpensive replaceable materials may be used.

Plastics suitable for use with phosgene include Teflon, rigid PVC, polyethylene, Saran, and Kel-F. Rubbers are unreliable for process lines. Asbestos gaskets may be used.

Hoods may be 304L stainless providing a dry atmosphere is maintained (-20 C dew point). The trichloride powder absorbs water slowly at higher humidities; and at dew point +15 C, test samples show some pitting and intergranular attack. Maintenance of low humidity is doubly important where phosgene leaks may occur.

Recall that one laboratory stainless hood has been used for over a year and a half with phosgene and no humidity control. Corrosion is visibly severe, but the hood is still usable. The reduction hood (with no humidity control), in which trichloride has been used for

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an equal time, is in good condition--although staining is evident.

Objects of brass and zinc are attacked first in phosgene hoods of high humidity, and must be avoided.

B. Chlorination Off-Gas Disposal

Off-gas filters must be provided to prevent loss of plutonium in the off-gas stream. Selaas XF filters at 350 - 400 C worked well. As fingers, these ceramic filters were broken. As cylinders with metallic support, the filters were not damaged by vibration. In operation, less than 0.5 g Pu passed the filter in 42 hours.

The off-gas filters are operated at elevated temperatures to avoid plugging with volatile chlorides. Since the chlorination process removed aluminum, iron, and molybdenum from the plutonium stream, the off-gas filters are maintained at a temperature sufficient to pass these chlorides (325 C). They are condensed in a cold trap.

Corrosive off-gases from the chlorination step have been successfully neutralized in scrubbers containing 20 percent sodium hydroxide. Use of stronger caustic resulted in the formation of solid carbonates in those batch chlorinations where carbon dioxide was a major by-product. Equations describing the chlorination step and the caustic absorption step are given below:

C. Plutonium Trichloride Stability

1. Oxidation

Anhydrous plutonium trichloride is stable for an indefinite period at room temperature in a dry or inert atmosphere. Oxidation to dioxide appears after about four days in moist room air of 40 - 50 percent relative humidity at room temperature. At 100 - 150 C in air (humidity unknown), the powder oxidizes overnight. Oxidation proceeds rapidly in air at 400 C or higher.

2. Hydration

Anhydrous plutonium trichloride is hygroscopic, so must be kept in a dehumidified atmosphere or sealed container. A screw-cap glass jar with waxed paper or polyethylene gasket in the cap is not suitable protection at 40 percent relative humidity. Replacing the paper gasket with Teflon, Neoprene, or other moisture-impervious material will suffice if tightly closed. In the laboratory, a desiccator containing "Drierite" (dew point -62 C) proved convenient. A dehumidified atmosphere should be dew point -20 C or better for indefinite storage. Hydration rates as a function of dew point have been carefully studied.⁽⁵⁾

Thin films of the trichloride powder are deliquescent (form wet puddles) at relative humidities greater than 40 percent. Deliquescence was observed after 20 minutes at 52 percent relative humidity.

D. Reduction Of Plutonium Trichloride

1. Feasibility

The reduction of plutonium trichloride to pure metal can be carried out with good yields by the same general type of process as is now used, including mixing, purging, firing, knockout, and pickling. The equipment includes the same type of pressure vessel; but different crucibles, or liners. Use of the present size of plant equipment is enabled by the high density of the powder, 2.6. However, the humidity of process hoods where chloride powder is handled should be maintained at -20 C or lower to insure maximum yields. A flow sheet for the reduction of plutonium trichloride

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is shown in Figure 3.

2. Process Discussion

Considerable attention has been focused on the possibility of pressurizing the mixer due to reaction of calcium and iodine with water of hydration from plutonium trichloride. Such pressurization has never been noticed in the laboratory work. In fact, chloride powder which has been properly stored over "Drierite" may be safely mixed and loaded in ordinary room atmosphere. The desiccant property of plutonium trichloride makes the charge less susceptible to reaction than tetrafluoride charges during mixing operations.

Numerous tests showed that hydration of plutonium trichloride occurs at a very low rate at a dew point of -13 C. However, storage at -20 C is recommended, since no hydration could be observed at this dew point. To test what would happen if water did accidentally get into a charge, a 700-gram reduction was carried out with 0.6 percent added water. A yield of 97 percent was obtained and a pressure of 130 pounds per square inch resulted.

Completely-chlorinated ~~powder~~ will result in the highest yields. However, as in the fluoride process, the reduction can tolerate a small quantity of oxide. Reductions can be carried out with 10 percent or less oxide in the trichloride. However, yields will be low by the quantity of oxide.

Loading a reduction vessel without mixing the charge was thoroughly investigated in hope of eliminating this dusty step.⁽⁶⁾ Placing the reductant and booster in the bottom of the crucible and adding the trichloride on top without mixing was successful on a 700-gram scale. Adding the trichloride to the reductant and putting the excess reductant and booster on top was also successful.

3. Metal Yield And Quality

Satisfactory yields are obtained as evidenced by Table V. Metal purity has been generally satisfactory with the metallic impurity level usually below 1000 ppm (Table VI). High impurities are associated with impure trichloride.

TABLE V

RESULTS OF PLUTONIUM TRICHLORIDE REDUCTIONS
WITH MIXED CHARGE

<u>Size Of</u> <u>Reduction</u>	<u>Number</u> <u>Of Runs</u>	<u>I₂/Pu</u>	<u>Average</u> <u>Percent Yield</u>	<u>Range</u>
30 grams	6	0.2	91	70 - 97
30 grams	13	0.25	95	93 - 99
700 grams	4	0.2	98	96 - 99*
700 grams	2	0.3	99	98, 100
1400 grams	3	0.2	93	86, 96, 97

Density has shown considerable variation in the laboratory (Table VII). However, usually more than one variable was being studied at once; and the laboratory buttons were not of optimum shape for density determination. Further work is indicated to determine the cause for the range of results.

A neutron count on one of the buttons gave an n/g/s of 55, a satisfactory value before casting.

4. Liner Materials

The requirements for the crucible or liner are much stricter for chloride reductions since the slag is extremely fluid at the temperatures involved. Thus, the slag easily penetrates standard magnesium oxide crucibles and the charge sticks in the pressure vessel. The most satisfactory solution to date has been to flame spray nickel on the outside of the magnesia liners. The nickel barrier retains the molten salt, whereas the magnesia assures purity of the plutonium metal. About 300 grams of nickel, or 30 mils, sprayed on an RCDS-1102 crucible stops chloride penetration and provides sufficient strength.

An attempt was made to develop a reusable liner. Three approaches to this end have been made. The first was to increase the thickness of the flame-sprayed coatings. This was not suc-

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TABLE VI

COMPARISON OF PURITY OF PLUTONIUM TRICHLORIDE POWDER
AND RESULTANT METAL

Impurity PPM of Pu	122*		124*		130*		133*		116*	
	200 gram		700 gram		700 gram		700 gram		700 gram	
	PuCl ₃	Pu	PuCl ₃	Pu	PuCl ₃	Pu	PuCl ₃	Pu	PuCl ₃	Pu
Ag	5	50	3	1	2	10	-	L2	5	L2
Al	400**	32	3000**	80	16	320	16	13	2000**	1300
As	-	-	-	-	-	-	-	-	-	-
B	2	5	2	-	2	L5	L2	2	1	L2
Be	-	-	-	-	-	-	-	-	-	-
Bi	-	-	-	-	-	-	4	-	-	-
Ca	250	25	500	50	21	3	16	13	800	200
Cd	-	-	2	-	-	-	-	-	-	-
Cr	20	50	31	20	100	20	20	5	35	10
Cu	100	50	100	500	50	10	10	10	35	20
Fe	50	200	70	100	200	50	58	L50	100	50
Ge	-	-	-	-	-	-	-	-	-	-
K	100	-	100	-	300	-	-	-	60	-
La	-	-	-	-	-	-	-	-	-	-
Li	-	-	-	-	-	-	-	-	-	-
Mg	1000	500	G5000	500	100	100	58	200	200	500
Mo	-	-	25	-	190	-	2000	-	10	-
Mn	100	50	100	50	140	100	20	50	150	50
Na	200	10	200	5	500	10	100	20	370	10
Ni	200	200	300	100	200	20	200	50	690	200
P	-	-	-	-	L200	-	-	-	-	-
Pb	100	5	100	20	50	20	L2	10	75	50
Si	20	100	70	20	2000	100	20	10	100	50
Sn	-	-	1	-	2	L5	L2	-	-	-
Tl	-	-	-	-	-	-	-	-	-	-
V	-	-	-	-	-	-	-	-	-	-
Zn	L20	L50	L20	-	50	-	-	-	L20	50

Legend:

- (*) Button number.
- (**) Off-standard trichloride powder.
- (-) Not found.
- (L) Less than.
- (G) Greater than.

No analyses for elements not shown.

TABLE VII

COMPARISON OF METAL DENSITIES WITH IMPURITIES
AND OTHER REDUCTION DATA (700-gram Scale)

Element	Button Number													M-4
	82	87	98	99	102	109	116	124	126	130	133	136	144	
Ag	2	2	5	2	2	2	2	1	50	10	2	1	2	-
Al	3	3	5	3	80	5	1300(3)	80	160(4)	320	10	130(4)	10	13
B	2	10	2	5	50	20	2	1	2	2	2	1	15	1
Ca	20	20	80	10	50	50	200	50	250	3	10	50	10	13
Cr	10	10	10	5	10	5	10	20	10	20	5	10	5	-
Cu	2	20	5	20	20	20	20	500	10	10	10	10	10	5
Fe	50	20	200	50	50	50	50	100	150	50	100	50	90	50
Mg	100	200	500	200	200	500	500	500	200	100	200	200	200	100
Mn	100	100	50	10	100	50	50	50	20	100	50	20	100	200
Na	2	2	2	2	2	20	10	5	10	10	20	1	2	-
Ni	50	50	20	10	200	50	200	100	100	20	50	100	400	40
Pb	2	5	20	20	50	50	50	20	10	20	10	10	10	-
Si	10	100	5	50	50	100	50	20	20	100	10	5	150	10
Sn	2	2	2	-	-	2	-	1	15	15	-	11	-	-
Zn	20	20	-	-	20	20	50	-	120	-	-	-	20	-
C	130	170	160	N.S.	N.S.	240	N.S.	290	N.S.	N.S.	N.S.	200	160	160
Cl/Pu Ratio	2.85	2.95	2.84	2.84	2.30	2.90	2.87	2.90	2.90	2.95	2.96	2.95	-	2.95
Density	19.36	19.31	19.17	19.05	18.42	18.96	16.68	17.83	17.42	16.33	19.35	18.55	18.77	19.27
Type of Reduction	B	B	S	S	S	S	S	B	B	B	B	B	B	M
Type of Crucible Coating	Ni	Cu	Ni	None	Ni	Fw	Ni(2)	Ni	Ni	Ni	Ni(2)	Ni	Steel(2)	Ni

(1) As Be, Bi, Cd, K, Mo, P, Tl, and V were not found in any buttons. No analyses for other elements.

(2) Crucibles impregnated with CaCl₂ after coating.

(3) Made from off-standard trichloride.

(N.S.) Not sampled.

(L) Less than.

(-) Not found.

(B) Ca and I₂ below PuCl₃.

(M) Ca and I₂ mixed with PuCl₃.

(S) Ca below with Ca and I₂ booster above PuCl₃.

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cessful because the crucibles continued to crack even with coatings over 100 mils thick.

The second attempt at a reusable crucible was to place a magnesia crucible in a stainless steel cylinder with a plate welded over one end. The volume between the crucible and cylinder is filled with magnesia sand. The crucible is then filled with calcium chloride and heated to about 900 C for 30 minutes. The calcium chloride binds the crucible to the can and results in a very strong container. The crucible obtained in this manner is similar to a flame-sprayed one except that it is much stronger. This is then used in a standard reduction pressure vessel. The crucible could be fused into the pressure vessel directly, but this would be harder to handle for recovery. After a reduction, the slag is drilled out and the plutonium button falls free.

This was done on a 30-gram scale and the crucible was used eleven times before it failed. The larger 700-gram scale one has been used once with no appreciable change in the crucible.

Another approach was to use tantalum. This has been done on a small scale (30-grams plutonium) both with and without a magnesia cup in the bottom to catch the metal. The slag was drilled out in both cases. When the cup was used, the button came free easily.

In bare tantalum, the plutonium wet the crucible enough to form the top of the button into a meniscus. This button was freed only after soaking in acid for a few minutes.

E. Recovery Of Plutonium From Slag And Crucible

1. Feasibility

Development work on a scale of 1.5 kg slag and crucible has shown that chloride can be adequately separated from slag and crucible solution by boiling with nitric acid. Table VIII describes a typical chloride slag and crucible; and Figure 4 describes the process. The silica solids must be treated to dissolve residual plutonium as is done in current recovery processing. Low waste losses are obtained with two treatments, as evidenced by Table IX.

Solutions from chloride slag and crucible recovery have been successfully processed by the solvent extraction plants for over a year.

TABLE VIII
SLAG AND CRUCIBLE COMPOSITION
1500-gram Charge

<u>Component</u>	<u>Weight - g</u>	<u>Moles</u>
MgO	708	17.5
CaCl ₂	395	3.5
CaI ₂	139	0.5
Ca	40	1.0
Ni*	196	3.3
SiO ₂	7	0.1
Pu	15	0.06

(*) Nickel-coated magnesia crucibles were used only part of the time.
Nickel would be present only in trace amounts without the coating.

TABLE IX
WASTE LOSSES FROM RESIDUE DISSOLUTIONS -
Recovery Flow Sheet

<u>Run Number</u>	<u>Total Plutonium</u>	<u>g From 1st Dissolution</u>	<u>Percent Of Total</u>	<u>g From 2nd Dissolution</u>	<u>Percent Of Total</u>
1 L	40.25	6.08	15.1	0.33	0.82
1 R	20.13	0.81	4.0	0.18	0.89
2 R	88.03	1.33	1.5	---	0.0
5 R	106.03	3.71	3.5	---	0.0
6 R	47.76	3.77	7.9	---	0.0
10 R	21.13	0.67	3.2	0.02	0.09
11 R	222.17	65.52	29.5	2.62	1.2
12 R	100.92	3.02	3.0	---	0.0
13 R	94.81	24.19	25.5	0.16	0.2
14 R	111.85	32.69	29.2	0.36	0.3
17 R	86.38	25.37	29.4	0.88	1.0
18 R	10.99	2.34	21.3	0.47	4.3
21 R	178.85	17.39	9.7	2.61	1.5
23 R	7.80	3.18	40.8	---	0.0
25 R	22.95	2.41	10.5	0.18	0.8
26 R	27.28	8.62	31.6	0.32	1.2
7+8+9	318.48	32.46	10.2	0.43	0.1
15+16	330.06	13.37	4.1	0.63	0.2
Average			15.6		0.70

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2. Storage

The chloride slag and crucible may be stored in the same manner as the fluoride slag and crucible, in covered aluminum or steel cans that are sealed out in plastic bags. These are held for processing in a slag and crucible storage box.

The slag and crucible must be placed in the cans immediately after reduction if exposure is to normal humidity. Otherwise, the calcium chloride will become moist. It is not necessary to seal-out the cans immediately, but this should be done within a few days. A slight puffing of bags may occur, but this reaches a steady state within a few days and presents no problems. Slag and crucible have been stored for thirteen months with no deterioration or pressure buildup.

3. Process Discussion

This work is more completely described in HW-61577.(7).

The initial acid additions to the charge are of 12.7 M HNO_3 (60 percent). As the acid is added, heat of neutralization warms the solution up and most of the iodine boils off as ICl , a relatively-volatile compound. Carbon dioxide is used as an inert carrier gas. Elemental iodine formation is minimized by the concentrated acid, and iodine deposition in cool parts of the system is minimized. The off-gases pass through a condenser and then into a caustic scrubber to absorb residual iodine and chlorine compounds.

After all the acid is added and the reaction subsides, heat is applied to start boil-down. The progress of chloride removal is followed by the solution temperature. A solution concentrated to a boiling point of 140 C will contain chloride ion concentration of 0.005 M Cl^- , or 180 ppm. Concentration to 155 C decreases this to 0.001 M or less. The solution is a molten salt at this stage and must be diluted with 3 M HNO_3 before the temperature falls to 100 C. This chloride removal process is similar to the Darex process⁽⁸⁾; but the reflux and constant volume boiloff periods have been eliminated by taking the salt to a higher temperature.

The diluted chloride-free solution is filtered through "M" porosity frits. Approximately 16 percent of the plutonium is retained in the solids.

With the usual plutonium content of chloride slag and crucible, the silica residues from up to 35 runs could be accumulated in a stainless tank for leaching. The residues are leached with 12.7 M HNO_3 - 0.1 M HF by refluxing for two hours. The hot solution is made 0.29 M $\text{Al}(\text{NO}_3)_3$, refluxed an additional half-hour, cooled, and filtered through "C" porosity filters. One leaching reduces loss to the solids to 0.7 percent, two leachings to <0.01 percent. Examples of silica leaching data are presented in Table IX.

Titanium sparge tubes were used in the dissolver, and no evidence of corrosion was observed. This material is recommended for boiling nitric-hydrochloric acid mixtures, but contact with hydrofluoric acid must be avoided. Tantalum may also be used.⁽⁶⁾

The time cycle for this recovery operation, not including residue treatment, is about eight hours. This is approximately the same as for a fluoride slag and crucible dissolution. The dissolution of crucible is limiting in both cases.

IV. FUTURE WORK

Laboratory work over the past year has shown that plutonium trichloride can be prepared and reduced to specification metal in large-scale equipment. Further work will attempt to minimize the corrosive conditions, improve conversion efficiency, and refine the equipment to a high state of reliability in long runs.

A. Chlorination

The off-gas filtering system on the chlorinator has performed its filtering function well. However, the physical limitations of the experimental hood have prevented optimizing the setup for the filter housing. In the higher operating rate runs, some difficulty with powder packing in the housing was experienced. An optimum filter housing must be set up to show that powder can be directly recycled without buildup at the higher operating rates.

Further work should be done to find the range of acceptable vibration cycles, gas flow, and powder feed.

Direct chlorination of plutonium oxalate offers a possibility of operating at lower temperatures under less corrosive conditions. Rapid chlorination of oxalate at 250 C was observed in one isolated case.

Use of a screw feeder and drive in the chlorinator would eliminate

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the problem of critical balancing associated with vibratory tubes.. Dusting would be decreased. If operation at lower temperatures can be achieved as suggested above, the extra metal in the corrosive zone could be tolerated.

B. Reduction

Further work with reusable liners will be undertaken, emphasizing tantalum or magnesia cemented in steel liners. If successful in the chloride system, these may have application with fluoride.

Electrolytic reduction of plutonium trichloride is being pursued in an independent program. This program provided the original incentive for chloride work; and still provides the greatest long-range impetus.

C. Recovery Of Slag And Crucible

Recovery work will turn to all titanium equipment. Aluminum nitrate will be added to the feed to prove compatability. This addition is an insurance measure. Titanium is highly intolerant of fluoride solutions; and, hence, addition of a fluoride complexing agent is a desirable move for equipment protection--both to guard against an error in addition of the wrong acid, or an error in charging a fluoride slag during the plant transition from fluoride to chloride.

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FIGURE 1
DEMONSTRATION REACTOR

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Scale: 1 kilogram Pu

This flow sheet was developed for the one-reduction crucible. The reusable crucible is still in development stage.

FIGURE 3

FLOW SHEET FOR BATCH REDUCTION OF PLUTONIUM TRICHLORIDE

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