UNCLASSIFIED

1 - 3

HW-30121

~~SECRET~~

AEC RESEARCH AND DEVELOPMENT REPORT

PLUTONIUM TRICHLORIDE: PREPARATION BY REACTION WITH PHOSGENE OR CARBON TETRACHLORIDE, AND BOMB REDUCTION TO METAL

By

W. B. Tolley

Metallurgy Unit
Applied Research Sub-Section

December 3, 1953

CLASSIFICATION CANCELLED

DATE MAR 15 1960

For The Atomic Energy Commission

H. F. Canale

Chief, Declassification Branch *ae*

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission by the
General Electric Company under Contract #W-31-109-Eng-52

Photostat Charge \$ 4.76 for
Access Permittees

Available from
Technical Information Service
P. O. Box 1001, Oak Ridge, Tennessee

This report was prepared as a scientific account of Government-sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights. The Commission assumes no liability with respect to the use of, or from damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

~~RESTRICTED DATA~~

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

~~SECRET~~

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

~~SECRET~~

-2-

HW-30121
Technology - Plutonium

INTERNAL DISTRIBUTION

Copy Number

1	F. W. Albaugh
2	O. F. Beaulieu
3	R. S. Bell
4	J. J. Cadwell
5	V. R. Chapman
6	V. R. Cooper
7	O. H. Greager
8	K. M. Harmon
9	T. W. Hauff
10	O. F. Hill
11	W. K. MacCready
12	J. E. Maider
13	W. M. Mathis
14	L. M. Meeker
15	W. N. Mobley
16	E. G. Pierick
17	T. Prudich
18	W. H. Reas
19	W. E. Roake
20	S. G. Smolen
21	W. B. Tolley
22	G. W. Watt, University of Texas
23	O. J. Wick
24	300 Files
25	Yellow Copy
26 - 29	Extra Copies

~~SECRET~~

~~SECRET~~

-3-

HW-30121

Technology - Plutonium

EXTERNAL DISTRIBUTION

Copy Number

30 - 33	Argonne National Laboratory
34	Armed Forces Special Weapons Project, Washington
35 - 37	Atomic Energy Commission, Washington
38 - 41	Carbide and Carbon Chemicals Company (ORNL)
42	Chicago Patent Group
43	Dow Chemical Company (Rocky Flats)
44 - 47	duPont Company, Augusta
48	duPont Company, Wilmington
49	Hanford Operations Office
50	Iowa State College
51 - 53	Knolls Atomic Power Laboratory
54 - 55	Los Alamos Scientific Laboratory
56	Massachusetts Institute of Technology (Benedict)
57	Patent Branch, Washington
58	University of California Radiation Laboratory, Livermore
59 - 73	Technical Information Service, Oak Ridge

~~SECRET~~

~~SECRET~~

-4-

HW-30121

CONTENTS

	<u>Page</u>
I. INTRODUCTION	5
II. OBJECTIVES	6
III. SUMMARY AND CONCLUSIONS	6
IV. DISCUSSION	7
A. The Preparation of Metal Trichlorides	7
1. Preparation of Cerous Chloride	8
a. Reaction with Carbon Tetrachloride	9
b. Reaction with Phosgene	11
2. Preparation of Plutonium Trichloride	12
a. Preparation of Reactive Plutonium(IV) Oxide	12
b. Reaction with Carbon Tetrachloride	12
c. Reaction with Phosgene	13
B. The Reduction of Metal Trichlorides	14
1. Cerous Chloride	15
a. Reduction Procedure	15
b. Iodine - Calcium Booster	15
c. Sulfur - Calcium Booster	16
d. Elimination of Booster	18
2. Plutonium Trichloride	20
a. Iodine - Calcium Booster	20
b. Elimination of Booster	21
C. Recovery of Plutonium from Slag and Crucible Waste	22
D. Corrosion of Materials of Construction by Phosgene	24
ABSTRACT	29
REFERENCES	30

~~SECRET~~

~~SECRET~~

-5-

HW-30121

PLUTONIUM TRICHLORIDE: PREPARATION BY REACTION
WITH PHOSGENE OR CARBON TETRACHLORIDE, AND
BOMB REDUCTION TO METAL

I. INTRODUCTION

Plutonium metal is currently prepared at HAPO by the reduction of plutonium tetrafluoride with calcium metal in an hermetically sealed bomb. An iodine-calcium thermal booster is employed, which serves the purposes of providing rapid internal heating and of lowering the melting point of the slag. The plutonium tetrafluoride is prepared by the reaction of gaseous hydrogen fluoride with plutonium dioxide at elevated temperatures according to the following equation.

Cylinders of hydrogen fluoride are generally contaminated with a small amount of hydrogen which tends to reduce part of the tetrafluoride to an off-standard trifluoride. For this reason a small amount of oxygen is continuously introduced during the hydrofluorination reaction to prevent the side reaction. As a consequence, the atmosphere employed in the preparation of plutonium tetrafluoride contains water vapor, oxygen, and hydrogen fluoride, a system which has proved to be excessively corrosive to furnace equipment at 600 C, the operating temperature for the preparation of plutonium tetrafluoride.

A source of difficulty in the bomb reduction operation has been the use of an iodine-calcium booster. Before reduction each loaded bomb is evacuated and flushed several times with argon. During this purging procedure and during subsequent heating, some iodine is volatilized and deposits in and plugs connecting tubing, thus requiring additional maintenance.

Previous investigations⁽¹⁾ have indicated that plutonium trichloride can be prepared by several methods and that these trichlorides can be reduced to give metallic buttons. Since some reports⁽²⁾ indicate that the usefulness of plutonium trichloride as a compound for metal production is limited, a thorough investigation of its preparation and reduction on larger than a milligram scale had never been attempted.

~~SECRET~~

II. OBJECTIVES

The objectives of this investigation were to study various chlorinating agents and to determine the conditions for their use in the preparation of plutonium trichloride from the dioxide, paying particular attention to rates of corrosion of pertinent materials of construction. It was also within the scope of this investigation to determine the conditions necessary for satisfactory reduction of plutonium trichloride to the metal, directing special attention to the replacement or to the elimination of the troublesome iodine-calcium booster now employed in the reduction of plutonium tetrafluoride.

III. SUMMARY AND CONCLUSIONS

A number of chlorinating agents suitable for the preparation of plutonium trichloride from the dioxide were investigated. Phosgene and carbon tetrachloride vapor were found to be excellent chlorinating agents at temperatures of 350 and 450 C, respectively. Plutonium trichloride prepared by reaction with phosgene or with carbon tetrachloride has been reduced to the metal in an hermetically sealed bomb by reaction with calcium. Metal yields of approximately 97 per cent were easily obtained on a twenty gram scale when using an iodine-calcium booster. It has been demonstrated that a method for the reduction of plutonium trichloride without the use of a booster can be developed to give metallic buttons of high yield and purity.

A procedure has been developed to recover the plutonium remaining in the slag and crucible after a reduction of the trichloride. Plutonium can be precipitated as the hydroxide and washed essentially free of calcium and chloride ion. After washing, the chloride concentration is reduced to a value of less than 75 ppm which may permit plutonium hydroxide and other solids to be dissolved in concentrated nitric acid⁽³⁾ and reprocessed through Recuplex.

The corrosion of various materials of construction by phosgene was briefly examined. The corrosion rates of the Hastelloy alloys A, B, and C were found to lie between 1×10^{-4} and 2×10^{-4} inches/month at 300 C and between 1×10^{-4} and 4×10^{-3} inches/month at 450 C. The logarithm of corrosion rate plotted as a function of temperature appears to be linear over the temperature range of 300 to 550 C, the working temperature for plutonium trichloride preparation. Above 550 C the corrosion of most materials of construction by phosgene is excessive. These preliminary investigations indicate that several materials of construction are satisfactory for use with phosgene at the temperatures required for the preparation of plutonium trichloride.

IV. DISCUSSION

A. The Preparation of Metal Trichlorides

Plutonium is an extremely hazardous material to handle. Because of this, cerium, a "stand-in" which exhibits closely related chemical and physical properties, both as the metal and as the trichloride, was used for a large portion of the preliminary work. Table I gives a comparison of some of the physical properties of plutonium, cerium, and their trichlorides.

TABLE I

SOME PHYSICAL PROPERTIES OF PLUTONIUM AND CERIUM

	<u>Reaction in Air</u>	<u>M. P. -°C</u>	<u>B. P. -°C</u>	<u>Density</u>	<u>MW</u>	<u>$-\Delta F_{298}^{\circ}$ Kcal/mole</u>
Cerium	pyrophoric	645	1400	6.9	140.13	0
Plutonium	pyrophoric	632 ± 7	3235 ± 19	19.6 (α phase)	239.0	0
CeCl ₃	deliq.	822	2000	3.92	246.5	243
PuCl ₃	deliq.	760 ± 5	1767	---	345.5	219

1. Preparation of Cerous Chloride

The methods considered for use in the preparation of cerous chloride are listed in Table II. (4)(5)(6)(7)

TABLE II
METHODS OF PREPARING CEROUS CHLORIDE

	<u>Temp., °C</u>	<u>Time</u>
HCl + CeO ₂	600 - 800	Lengthy Preparation
HCl + Cl ₂ + CeO ₂	600 - 800	Lengthy Preparation
S ₂ Cl ₂ vapor + CeO ₂	700 - 800	Lengthy Preparation
Hexachloropropylene refluxed with Ce ₂ (C ₂ O ₄) ₃	185 - 195	18 - 20 hours
CCl ₄ vapor + CeO ₂	700 - 800	---
COCl ₂ vapor + CeO ₂	600	---

The first two methods involving gaseous hydrogen chloride at elevated temperatures were not evaluated experimentally since excessive corrosion of furnace parts by hydrogen chloride was expected. A laboratory investigation was made on the other four methods of preparation. With sulfur monochloride, temperatures necessary for reaction were high, 600 to 800 C. Difficulty was experienced in handling the monochloride and in the prevention of sulfur depositing at the cold junctions of the furnace tubing. Hexachloropropylene refluxed with cerium(III) oxalate for 18 hours failed to yield a satisfactory trichloride. Furthermore hexachloropropylene was found to be quite corrosive to stainless steels at room temperature and therefore is difficult to handle in metal furnace equipment. For these reasons the experiments with hexachloropropylene and sulfur monochloride were discontinued and emphasis was placed on the use of carbon tetrachloride and phosgene as the reactants.

a. Reaction with Carbon Tetrachloride

Metal chlorides were prepared by a solid phase-gas reaction between metal oxide and carbon tetrachloride vapor. Approximately 150 grams of oxide were used in each run and the efficiency of the preparation was determined on the basis of completeness of conversion, the time and temperature required for the preparation, purity of product, and the physical properties of the resulting trichlorides.

Argon saturated with carbon tetrachloride vapor was passed over cerium dioxide heated to the desired temperature in a tube furnace. A lineal flow rate of one half foot per minute was employed. The data for the preparation of cerous chloride with carbon tetrachloride are presented in Table III.

TABLE IIICHLORINATION OF CERIUM DIOXIDE WITH CARBON TETRACHLORIDE

<u>Time, hr.</u>	<u>Temp., °C</u>	<u>Product Cl/Ce Mole Ratio</u>
3	750 - 950	1.66
10	350 - 625*	2.81
10	525	2.59
10	600	2.84
* 350	1 1/2 hours	no reaction
425	1 hour	very slight reaction
500	1 hour	very slight reaction
550	4 hours	50 per cent converted, grey colored
625	2 1/2 hours	white product, high conversion

Several 800 gram batches of cerous chloride were prepared with carbon tetrachloride. More than twenty hours were required for the preparation of a product of 94 per cent conversion at temperatures of 550 to 600 C.

Since cerium trichloride is deliquescent, it was desirable to obtain some data on the rate at which water is absorbed. Extremely high reduction bomb pressures would result if the chloride was appreciably hydrated. As indicated in Figure I, after fifty minutes exposure to laboratory air of about 40 per cent relative humidity (which should be ample time for removal of the trichloride from the furnace, weighing it, and preparing the bomb for reduction) the amount of hydration is low and should offer no difficulty during the reduction operation. An 800 gram batch of cerous chloride which has been kept in a stoppered bottle for over nine months with continual sampling for reduction purposes has shown negligible hydration.

FIGURE I
RATE OF HYDRATION OF CEROUS CHLORIDE

b. Reaction with Phosgene

Phosgene is an extremely toxic material; inhalation of air containing 50 ppm phosgene over an extended period of time is usually fatal. Therefore, all work with phosgene was done in a well-ventilated hood with a series of ethanol and hydroxide traps to remove any excess phosgene after reaction with cerium dioxide.⁽⁸⁾ Phosgene reacts with the alcohol to form diethyl carbonate, a yellow liquid which is infinitely soluble in the alcohol. The sodium hydroxide precipitates the hydrogen chloride formed during the esterification.

Phosgene from commercially available cylinders was passed at a rate of approximately one half lineal foot per minute over cerium dioxide which was heated to the temperature desired in a quartz furnace tube. The data obtained for the preparation of cerous chloride with phosgene are presented in Table IV.

TABLE IVCHLORINATION OF CERIUM DIOXIDE WITH PHOSGENE

<u>Time, hr.</u>	<u>Temp., °C</u>	<u>Product Cl/Ce Mole Ratio</u>
15	355	2.0
3	450	2.54
6	450	2.77
5	500	2.76
5	575	2.74
5	650	2.84

A high grade cerous chloride can be prepared with phosgene at a temperature 150 C lower and in one half the time required with carbon tetrachloride.

2. Preparation of Plutonium Trichloride

Carbon tetrachloride and phosgene were the only two materials evaluated in the laboratory for the preparation of plutonium trichloride.

a. Preparation of Reactive Plutonium(IV) Oxide

In the preparation of plutonium dioxide from the wet plutonium(IV) oxalate the temperature of the cake is often 125 to 250 C greater than the furnace temperature due to the exothermic nature of the reaction. Investigations have indicated that a difficultly chlorinated or fluorinated oxide results when the cake temperature exceeds 400 C during decomposition of the oxalate.⁽⁹⁾ In practice, on a nominal 50 gram scale, the optimum method for the preparation of a reactive plutonium dioxide is as follows: Plutonium(IV) oxalate is precipitated from plutonium(IV) nitrate solution and washed and slurried into a reaction boat. The oxalate is dried in a stream of air at 125 to 150 C for one hour. The temperature is then raised to 300 C for two hours to decompose plutonium(IV) oxalate to plutonium dioxide, being careful that the cake temperature does not exceed 400 C.

b. Reaction with Carbon Tetrachloride

Plutonium dioxide was observed to react with carbon tetrachloride more rapidly and at lower temperatures than does cerium dioxide. The same conditions were used with plutonium as were used with cerium. The data obtained are presented in Table V.

TABLE VCHLORINATION OF PLUTONIUM DIOXIDE WITH CARBON TETRACHLORIDE

<u>Time, hrs.</u>	<u>Temp., °C</u>	<u>Product Cl/Pu Mole Ratio</u>
1	450	about 2.0
4	450	2.90
4	450	2.98
4	475	2.88
3 1/2	500	2.91

All samples showed low conversion at one hour.

c. Reaction with Phosgene

In review, cerous chloride has been prepared by reaction with carbon tetrachloride at 600 C and with phosgene at 450 C. Since the temperature required to chlorinate plutonium dioxide with carbon tetrachloride was found to be 450 to 500 C, it seemed reasonable that phosgene might produce plutonium trichloride at temperatures between 300 to 400 C. This temperature range was investigated. As shown in Table VI, conversion at 300 C is slow. However, a satisfactory trichloride can be prepared at either 350 or 400 C within an hour and a half.

TABLE VI
CHLORINATION OF PLUTONIUM DIOXIDE WITH PHOSGENE

<u>Time, hrs.</u>	<u>Temp., °C</u>	<u>Product Cl/Pu Mole Ratio</u>
0.5	300	not sampled
1.5	300	not sampled
2.0	300	2.52
0.5	350	1.29
0.5	350	1.85
1.0	350	2.49
1.0	350	2.55
1.0	350	2.57
1.17	350	2.83
1.75	350	unreliable analyses (product good)
1.85	350	2.80
1.0	400	2.78
2.0	300	2.52
1.0 followed by	350	2.69

B. The Reduction of Metal Trichlorides

In the present method of operation in the 234-5 metal production building, plutonium tetrafluoride is reduced with metallic calcium. An iodine-calcium booster of 0.2 moles each of calcium and iodine per mole of plutonium is mixed with each reduction charge to obtain a satisfactory button yield. On smaller scale reductions the amount of booster is necessarily increased for good button formation because of the higher rate of heat loss and the much lower heat capacities of the small reduction bombs.

The intent was first to determine if the metal trichlorides can be reduced by methods similar to those now employed in 234-5 operations, and second, to show that some improvements can be realized in these reduction procedures by using plutonium trichloride instead of plutonium tetrafluoride.

1. Cerous Chloride

a. Reduction Procedure

A 50 gram size steel bomb with magnesia crucible liner was used for the reduction of the trichloride.* Magnesia sand was employed as a packing material between the bomb wall and the crucible liner to provide better heat transfer and to give the crucible more apparent strength, preventing its cracking during firing. Calcium was used as the reductant in all runs. The ground calcium was kept under argon except during weighing and transferring to the reduction bombs, since an oxide coating forms on the metallic calcium if exposed to air for long periods of time. The bombs were charged, purged with argon, and then were heated by induction until reaction occurred. Heating was continued at the same rate for two additional minutes. The time of firing and the temperature of the outside bomb wall were determined by means of a thermocouple in a well welded to the side of the bomb.

b. Iodine - Calcium Booster

When using a calcium - iodine booster bomb ignition usually occurs between 500 and 700 C with a rapid rise in temperature of 100 to 200 C observed upon ignition. When a pressure gauge was attached to the bomb the maximum internal pressure observed was 175 psig. On firing, this pressure drops instantly to 10 to 15 psig. Table VII shows the effect on the button yield of variations in the amount of iodine - calcium booster used in the reductions of cerous chloride. Button yields were high when using 0.4 to 1 mole of booster per mole of cerium, but dropped off appreciably when less than 0.4 mole iodine booster per mole of cerium was employed.

* See photograph, Figure 3.

TABLE VII

REDUCTION OF CERIOUS CHLORIDE WITH IODINE BOOSTER

20 grams scale
33 per cent excess calcium

<u>Booster Ca-I₂/Ce Mole Ratio</u>	<u>Product Cl/Ce Mole Ratio</u>	<u>Button Yield Per Cent</u>
1.0	1.66 (poor product)	86.0
1.0	2.81	98.0
1.0	2.59	99.0
0.6	2.59	94.0
0.6	2.84	99.4
0.4	2.84	97.7
0.4	2.59	96.7

c. Sulfur - Calcium Booster

Since iodine as a booster causes considerable difficulty in the plant operations, a sulfur - calcium booster was tested for the reduction of cerous chloride.

The heat liberated for slag melting is nearly the same using either booster. However, the sulfur forms high melting calcium sulfide which proves detrimental to the coalescence of the metal button. The data obtained for the reductions with a sulfur booster mixed with the charge are presented in Table VIII.

TABLE VIIIREDUCTION OF CEROUS CHLORIDE WITH SULFUR BOOSTER

20 grams scale
33 per cent excess calcium

<u>Ca-S/Ce Mole Ratio</u>	<u>Yield Per Cent</u>
0.00	0.00
0.2	18.1
0.4	67.0
0.5	69.7
0.6	58.7
1.0	0.00

Several reductions were carried out in a double crucible arrangement. The calcium and cerous chloride charge was placed in the inner crucible and a large amount of sulfur - calcium booster was packed around the charge crucible. The concentric arrangement was designed to prevent the calcium sulfide from being included in the slag and yet to provide heat to the charge for slag melting. The data obtained are presented in Table IX.

TABLE IXDOUBLE CRUCIBLE REDUCTIONS WITH SULFUR BOOSTER

10 grams scale
33 per cent excess calcium

<u>Ca-S/Ce Mole Ratio</u>	<u>Yield Per Cent</u>
1	0.00
2	37.1
4	40.2
4	32.2
8	23.3

One reduction was made using a combination of both procedures. Four moles of sulfur - calcium booster per mole of cerium were packed around the charge crucible which contained 0.5 mole sulfur - calcium booster per mole cerium mixed with the charge. The observed 33.7 per cent yield was no improvement over the yields obtained in the previous reductions. The use of sulfur boosters for reduction of cerous chloride or plutonium trichloride did not appear promising and further experimentation along this line was discontinued.

d. Elimination of Booster

In the cerium and plutonium trichloride systems the melting points of all reactants and products are much lower than in the fluoride systems. Since the chloride system is completely liquified at a temperature near 810 C, it proved feasible to perform reductions with no booster present by holding the temperature of the slag above 810 C for several minutes to allow the coalescence of a metal regulus.

A reaction bomb was designed and constructed twice the length of the normal fifty gram bomb and equipped with a copper water cooling coil to prevent melting of the copper gasket. The first charge was fired by heating the bomb in a pot furnace. A well-shaped button with a large calcium cap containing greater than one per cent cerium was obtained. All remaining charges were fired by induction heating. The temperatures were measured in a thermocouple well located on the bomb wall. It is estimated that the bomb well temperatures (prior to charge firing) are approximately 200 C higher than the slag temperature inside the bomb. Most charges ignited at temperatures between 600 to 900 C, however heating was continued until the well temperature reached 1150 C. This temperature was held for three minutes to insure melting of the slag. The lower portion of the bomb was well lagged with asbestos to obtain these high temperatures. Data obtained for the reduction of cerous chloride without booster are presented in Table X.

TABLE XREDUCTION OF CERIOUS CHLORIDE WITHOUT BOOSTER

20 grams scale
33 per cent excess calcium
Cl/Ce mole ratio = 2.80

<u>Time - Temp., °C</u>	<u>Per Cent Excess Calcium</u>	<u>Per Cent Yield</u>
15 min. at 900	33	89.8 ^(a)
15 min. at 882	33	0.00
8 min. to 960	33	90.2
1 min. at 960		
9 min. to 1100	33	94.7
3 min. at 1100		
8 min. to 1150	25	95.0
3 min. at 1150		
7 min. to 1115		
3 min. at 1115	10	92.9

(a) Charge fired in a resistance furnace.

Since operation on a plant scale with the exterior of the reduction bomb at 1100 to 1150 C would be difficult, and since the temperature of the charge probably does not exceed 950 C, an internally heated bomb designed to minimize heat losses might prove to be satisfactory for reduction of cerium and plutonium trichloride.

An internally heated bomb* has been built and tested. The heating element is a stainless steel sleeve wound with resistance wire which fits over the charge crucible. Three concentric heat shields of bright platinum were fitted loosely around the heating element. A thermocouple well is located just above the charge to indicate the time of firing and the approximate

* See photograph, Figure 3.

temperature of the slag. The whole assembly is enclosed in a metal bomb which can be held evacuated during the firing.

Four charges of cerium trichloride were fired using 33 per cent excess calcium. After the charges fired, the temperatures were raised to the extent indicated in Table XI and held for three minutes. No yield was obtained from the first reduction. The second and third gave rough buttons of fair yield. These poor yields were attributed to insufficient heating of the lower portion of the charge crucible where the button was formed. When this was remedied by relocation of the heating element, the fourth reduction produced a well-formed button of high yield.

TABLE XI

REDUCTION OF CEROUIS CHLORIDE WITHOUT BOOSTER
IN INTERNALLY HEATED BOMB

20 grams scale
33 per cent excess calcium
Cl/Ce mole ratio = 2.80

<u>Temperature, °C</u>	<u>Per Cent Yield</u>
600	0.00
800	85.8
900	87.5
900	93.8

2. Plutonium Trichloride

a. Iodine - Calcium Booster

Reductions of plutonium trichloride were made using the stoichiometric amount of calcium plus 33 per cent excess for reduction while varying the amount of iodine - calcium booster. Reductions of plutonium trichloride prepared with either carbon tetrachloride or phosgene gave essentially the same yields. The firing cycles found optimum with cerous chloride were used with plutonium trichloride. The data obtained are presented in Table XII.

TABLE XIIREDUCTION OF PLUTONIUM TRICHLORIDE WITH IODINE BOOSTER

20 grams scale
33 per cent excess calcium

<u>Booster Ca-I₂/Pu Mole Ratio</u>	<u>Product Cl/Pu Mole Ratio</u>	<u>Yield Per Cent</u>
1.0	2.98	93.2 ^(a)
0.6	2.90	97.7
0.6	2.48	97.8 ^(b)
0.6	2.79	96.2 ^(b)
0.4	2.81	96.8
0.3	2.91	89.3 ^(c)
0.2	2.91	89.1 ^(c)
0.3	2.88	98.8

(a) Ten gram reduction.

(b) Reduction of phosgene prepared material.

(c) Lumpy, off-color plutonium trichloride.

b. Elimination of Booster

The firing of plutonium trichloride charges without an iodine - calcium booster occurred between 700 to 900 C. The temperature was held at 1150 C for three to five minutes past firing. Although moderately successful reductions (yields of 70 to 90 per cent) were obtained on a twenty gram scale, it is anticipated that a satisfactory button of high yield can be obtained with further experimentation. Scale-up from 20 to 400 grams invariably results in more efficient reductions and higher button yields. It is therefore possible that good yields can be realized without a booster when using a 400 gram charge with little modification of the reduction equipment or the firing procedures now employed in 234-5 operation.

C. Recovery of Plutonium from Slag and Crucible Waste

Plutonium remaining in slag and crucible after a plutonium trichloride reduction can be returned to process through the Recuplex facilities, providing the chloride ion is first removed. To avoid corrosion of stainless steel equipment the solutions containing chloride must not be made acidic. The following procedure has been developed for lowering the chloride concentration to a value which might be tolerated in the Recuplex operation.

Since 25 to 35 per cent excess calcium is used in the charges, the solutions from slag dissolution are always strongly basic and contain large amounts of calcium hydroxide. This calcium hydroxide is difficult to filter and tends to occlude chloride ion, preventing its subsequent removal by washing. At a pH of 10.5 to 11 calcium hydroxide is soluble while plutonium hydroxide precipitates. Addition of excess concentrated ammonium hydroxide provides a simple method of obtaining this pH range, eliminating the need for accurate measurements of acidity. Sulfamic acid is added, without making the solution acidic, until the calcium hydroxide dissolves. The pH is then adjusted to the value desired with excess ammonium hydroxide. Sulfamic acid is used instead of nitric acid to dissolve the calcium hydroxide since nitric acid precipitates free iodine, causing filtering difficulties.

Some difficulty has been experienced in filtering and washing the solids after pH adjustment. The fines from the magnesia crucible and magnesia packing sand hinder filtering. However, this difficulty is not critical, and, if necessary, centrifugation of the solids can be employed. Chloride ion concentration has never been consistently reduced to the values of 10 to 20 ppm first hoped for. Concentrations of chloride ion in the final solutions after dissolving all solids with nitric acid ranged from 11 to 120 ppm. It is anticipated that chloride concentration can be reduced to values less than 75 ppm with little difficulty on a plant scale. The factors considered limiting in the chloride removal are first, surface adsorption of chloride ion on magnesia fines and on the plutonium hydroxide precipitate, and second, the formation of difficultly soluble plutonium oxychloride which is not dissolved by the water leaching and therefore increases the chloride ion concentration in the final nitric acid solution which is to be sent to Recuplex. Since the average reduction yield of 20 and 400 gram reductions should equal about 97 and 99 per cent respectively, the concentration of chloride in the slag as unreacted plutonium trichloride or insoluble oxychloride should be greatly reduced in the large scale reductions. Should all the plutonium from a 20 gram reduction of 97 per cent yield exist in the slag as the oxychloride, the chloride concentration in the final solution to Recuplex would be about 180 ppm even though washing is completely efficient. In a 400 gram reduction of 99 per cent yield the chloride ion concentration would be about 60 ppm. If the oxychloride is actually the cause of the slightly high chloride contamination, scale-up should result in the reduction of chloride contamination by a factor of three or to chloride ion concentrations of 25 to 30 ppm. Extended slag recovery studies are necessary on plant scale before a final decision can be made as to the feasibility of this procedure for preparing the slag and crucible for plutonium recovery through Recuplex. The data obtained are presented in Table XIII.

TABLE XIIICHLORIDE CONCENTRATION IN FINAL SOLUTION TO RECUPLEX

<u>Washes</u>	<u>Volume</u>	<u>Calculated^(a) Chloride Concentration, ppm</u>	<u>Actual Chloride Concentration, ppm</u>
5	50	40.0	117
4	100	14.4	120
5	100	2.9	91
4	150	3.7	11
5	150	0.5	84
6	150	0.1	78

(a) Calculated on basis of dilution.

D. Corrosion of Materials of Construction by Phosgene

Phosgene vapor has been shown to be the best chlorinating agent of those tested for the preparation of plutonium trichloride from the dioxide. It was, therefore, within the scope of this investigation to examine the corrosive action of phosgene on various materials of construction. Metal samples were placed separately in quartz tubes and phosgene gas was passed over the heated samples at a rate of about one half lineal foot per minute for eight hours. The corrosion rate in inches per month was calculated from weight loss measurements. Temperatures were regulated to ± 5 C. Of the metals tested the Hastelloy alloys A, B, and C exhibited the lowest corrosion rates. Corrosion by phosgene between 300 and 550 C is relatively slow. Inasmuch as the operating temperatures during chlorination need never exceed 400 C, the use of these Hastelloys should prove satisfactory. The Hastelloy alloys A, B, and C will "age" when held in a temperature range of 600 to 1000 C. Aging will increase the ultimate tensile strength and improve the high-temperature properties of these alloys. However, this aging results in excessive precipitation along the grain boundaries and the

corrosion - resistant properties of the alloys are greatly reduced. When the logarithm of corrosion rate is plotted as a function of the temperature, as in Figure II, straight lines are obtained for Hastelloy alloys A, B, and C in the temperature range of 300 to 500 C. The corrosion rates of these Hastelloys, in this temperature range, may be estimated using the following formulas.

$$\text{Hastelloy A: } \log_{10} \text{ C.R.} = 0.00814 T - 6.36$$

$$\text{Hastelloy B: } \log_{10} \text{ C.R.} = 0.00615 T - 5.61$$

$$\text{Hastelloy C: } \log_{10} \text{ C.R.} = 0.01023 T - 7.03$$

C.R. is the corrosion in inches per month, and T is temperature in degrees centigrade. Above 550 C the corrosion rate increases excessively, possibly due to the precipitation along the grain boundaries at these elevated temperatures. Whether or not excessive corrosion would be experienced after long operation due to possible aging of the Hastelloy alloys at low temperature will have to be determined by more extensive corrosion tests. The corrosion data are presented in Table XIV.

WBT:ms

W B Tolley

W. B. Tolley

TABLE XIVCORROSION OF MATERIALS OF CONSTRUCTION BY PHOSGENE

<u>Metal</u>	<u>Temperature, C</u>	<u>Corrosion, inches/month</u>
Hastelloy A	300	1.2×10^{-4}
	350	3.1×10^{-4}
	450	2.0×10^{-3}
	550	1.8×10^{-2}
	600	1.6
Hastelloy B	300	1.8×10^{-4}
	350	3.3×10^{-4}
	450	1.5×10^{-3}
	550	7.6×10^{-3}
	600	1.3
Hastelloy C	300	1.1×10^{-4}
	350	3.3×10^{-4}
	450	3.7×10^{-3}
Hastelloy D	350	2.4×10^{-3}
	450	1.1×10^{-2}
Inconel	350	1.6×10^{-2}
Monel	350	1.5×10^{-3}
Haynes 25	450	1.4×10^{-2}
Tantalum	450	3.1×10^{-2}
Stainless Steel Type 309 SCb	600	1.6

FIGURE II
CORROSION OF HASTELLOY ALLOYS A, B, C, AND D BY PHOSGENE

FIGURE III

Internally Heated Bomb with
50 gram Crucible and Gasket

Normal 50 gram Size Bomb
Equipped with Pressure Gauge

Photograph Unclassified

ABSTRACT

Thirty gram batches of plutonium dioxide can be readily chlorinated by reaction with phosgene or carbon tetrachloride at temperatures of 350 and 450 C respectively. Plutonium trichloride prepared by either method can be reduced to the metal in an hermetically sealed bomb by reaction with calcium. On a twenty gram scale yields of approximately 97 per cent are obtained when a calcium - iodine booster is employed. It has been demonstrated that a method for the reduction of plutonium trichloride to the metal without the use of a booster can be developed.

Soluble plutonium in slag and crucible waste can be precipitated as the hydroxide at a pH of 10.5 to 11 and washed essentially free of chloride contamination. The concentrated nitric acid solution from dissolution of plutonium hydroxide and other solids contains less than 75 ppm chloride which may permit its reprocessing through Recuplex.

Of the materials tested the Hastelloy alloys A, B, and C were found to be the most resistant to phosgene corrosion. The corrosion of these alloys was found to lie between 1×10^{-4} and 2×10^{-4} inches per month at 300 C and between 1×10^{-4} and 4×10^{-3} inches per month at 450 C. The logarithm of the corrosion rate plotted as a function of the temperature appears to be linear over the temperature range of 300 to 550 C. Above 550 C the corrosion rate of all materials tested is excessive.

~~SECRET~~

-30-

HW-30121

REFERENCES

- (1) Garner, C. S., The Preparation of Plutonium Trichloride, LA-112, July 24, 1944. (SECRET)
- (2) Kennedy, W. J., and C. S. Smith, Special Report Presented at May Meeting with C. A. Thomas on Final Purification and Metallurgy of 49, p. 2. (SECRET)
- (3) Groot, C., H. H. Hopkins, and W. W. Schultz, Recovery of Plutonium from Slag and Crucible, HW-20817, June 15, 1951. (SECRET)
- (4) Ohya, Masakichi, Electrolysis of Metals of Cerium Family and the Preparation of Pyrophoric Alloy, Repts. Imp. Ind. Research Inst., Osaka, Japan, 7, No. 4, 1-30 (1926).
- (5) Heap, W., and E. Newbery, Chlorides of Cerium, Aluminum, Magnesium and Similar Metals, U. S. Patent 1,331,257, Feb. 17, 1920.
- (6) Christensen, E. L., Preparation of Anhydrous Plutonium Trichloride, LA-1431, October 15, 1952. (SECRET)
- (7) Garner, C. S., The Preparation of Plutonium Trichloride, LA-112, July 24, 1944. (SECRET)
- (8) Dyson, Malcolm, "Phosgene," Chemical Reviews, Vol. 4, (1927); p. 150-151.
- (9) Smith, R. C., and W. E. Roake, Plutonium Trifluoride; Preparation by Reaction with Freon-12 and Bomb Reduction to Metal, HW-30040, September 15, 1953, p. 8. (SECRET)

~~SECRET~~