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THE CONTINUOUS CHLORINATION OF PLUTONIUM DIOXIDE

By

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THE CONTINUOUS CHLORINATION OF PLUTONIUM DIOXIDEI. INTRODUCTION

Previous reports on the chlorination of plutonium dioxide describe numerous small-scale experiments and a few fair-sized batch preparations. The chemistry of chlorination by numerous reagents is covered, but no process had received sufficient study for large-scale preparation of anhydrous plutonium trichloride. The literature search revealed no extensive studies on chlorination rates, exhaust gas filtering, atmospheric requirements, reactor materials, etc. A program was undertaken to select a chlorination process, to develop the necessary information for defining operating conditions and equipment specifications, and then to demonstrate the operation of the process.

II. SUMMARY AND CONCLUSIONS

The conversion of plutonium dioxide to anhydrous plutonium trichloride has been thoroughly demonstrated on a large scale in both batch and continuous processes. Operating rates and process requirements were developed in demonstrating the continuous process. Phosgene gas at 450 - 500 C is found to be the most reactive agent. Safe handling of phosgene was demonstrated. Low corrosion rates on selected alloys indicate durability of equipment and satisfactory chloride purity. Ceramic filters and non-corrosive pipe for exhaust gases are specified.

Plutonium trichloride remains anhydrous in air at dew point -20 centigrade. Hydration rates for higher humidities are reported.

Neutron emission from plutonium trichloride is significantly less than from plutonium tetrafluoride.

III. DISCUSSIONA. Chlorination Of Plutonium Dioxide1. Feasibility

The chlorination of plutonium dioxide has been accomplished by numerous investigators^(1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11) utilizing a variety of reagents and conditions. Many of these chlorinations were exploratory, minute-scale experiments in plutonium chemistry. Some were moderately-sized batch chlorinations to provide plutonium trichloride for subsequent experiments. The present study was planned⁽¹²⁾ to develop a process which could be applied on a large scale. The process development was deliberately pointed to utilize procedures and equipment with which the investigators were already familiar.

An interim report⁽¹³⁾ and this final report summarize the work

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of numerous contributors (see Section V). The reduction of plutonium trichloride and recovery of chloride wastes are reported separately. (14)(15)

A chlorination process has been demonstrated on a large-batch scale and also developed into a continuous process. Over 52 kilograms of plutonium trichloride have been prepared during this investigation. Of this, about 19.7 kg were produced in continuous units demonstrating the feasibility of continuous chlorination. The plutonium trichloride quality was satisfactory and yielded good metal in bomb reduction tests. The metal produced from properly-prepared plutonium was of satisfactory purity.

2. Chlorination Chemistry

Conversion of plutonium dioxide to plutonium trichloride may proceed directly or stepwise via the oxychloride. Direct chlorination by carbon tetrachloride is indicated in equations a and b:

The difference in these reactions is in the by-product gases. Phosgene is known to be present; and, therefore, may itself chlorinate the oxide directly.

The presence of carbon monoxide in the system has also been detected. This, with the chlorine, offers a fourth means of direct chlorination of the oxide.

Equations "e" through "j" indicate stepwise chlorination reactions.

The carbon monoxide may be formed in the stepwise chlorination

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or by dissociation of phosgene.

These reactions are typical for the many reagents which chlorinate plutonium dioxide. These are the reactions of most concern in the selected chlorination conditions. At higher temperatures (800 C), a volatile PuCl_4 may be an intermediate. Where insufficient reducing agent is present, another oxychloride, PuOCl_2 , is theorized. As found in small batch studies, the principal reactions are direct formation of trichloride.

3. Small Batch Studies

Chlorination studies were limited to processes which showed most promise for application in a continuous process or to investigation of variables in these processes. Tolley⁽⁸⁾ tried four reagents and recommended both carbon tetrachloride and phosgene at temperatures lower than other investigators.⁽¹⁾⁽⁴⁾⁽⁶⁾

For small batch studies, N. S. Wing used a one-inch tube furnace and carbon tetrachloride. The carbon tetrachloride was warmed to 65 C (boiling point 76 C) by a water jacket, and carried as vapor in a stream of argon through the furnace, a trap, and a caustic bubbler.

Plutonium dioxide in numerous small batches was chlorinated to study optimum temperature, chlorination rates, powder density, hydration rates, etc. Results on the 5 - 100 gram scale were good. A temperature of 450 - 500 C for carbon tetrachloride was recommended.

When plutonium dioxide was treated with undiluted phosgene gas at the same conditions, the chlorination was more rapid than with carbon tetrachloride. The surface of the powder was chlorinated in ten minutes. At 400 - 450 C, the effectiveness of the phosgene was about the same as the carbon tetrachloride at 450 - 500 C.

Several batches of plutonium(IV) oxalate were successfully chlorinated with phosgene. On some batches, conversion to oxide may have preceded chlorination. On one batch of plutonium oxalate containing slightly-less water than the monohydrate, chlorination with phosgene was completed at temperatures below 250 C in reasonably short time. The trichloride was light greenish-blue, almost grey. One measurement of bulk density gave 1.6 g/cc.

The chloride powder was successfully reduced to metal. Further investigation of oxalate chlorination was not pressed due to questions on disposal of the oxalate and on significance of the low density chloride.

Plutonium dioxide prepared by calcination of plutonium(IV)

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oxalate at 250 - 350 C was found to chlorinate more readily than if calcined at 400 - 500 C. For the latter, increased chlorination temperature was helpful. A test was made on oxide calcined at 900 C. About 30 grams of this was chlorinated in four hours by phosgene at 500 - 550 C. A small sample of oxide which had been ignited in the carbon arc of a spectrograph was also successfully chlorinated in four hours at about 525 C. These experiments indicate that chlorination may be useful on recovery of ignited wastes.

Normally there was no evidence of oxychloride in the products of phosgene and carbon tetrachloride chlorinations. Some batch chlorinations which were interrupted indicated little, if any, oxychloride between the dioxide and the trichloride with either of these two reagents. Deliberate attempts to produce oxychloride (PuOCl) with water vapor and a minimum of carbon tetrachloride indicated little or no oxychloride was formed. When some oxychloride was obtained (discussed later), some 10 grams of it were treated with phosgene at 470 - 500 C for nearly four hours. The analytical laboratory reported complete conversion of the PuOCl to PuCl_3 . These observations indicate that direct formation of trichloride is the most significant reaction of phosgene and carbon tetrachloride. Any amounts of plutonium oxychloride formed are readily converted to trichloride by phosgene.

Carbon monoxide and chlorine in equimolar mixtures were used on 10-gram batches of oxide. On one there was no apparent chlorination in three hours at 450 - 500 C. Two more hours at 525 - 550 C produced a dark, grey-green cake. A second batch was chlorinated at 500 - 550 C for almost three hours. Chlorination was complete on both. These gases required a higher temperature than is necessary with phosgene.

Hydrogen and hydrogen chloride, which were used in small-scale plutonium chlorination work, (1)(6) were tried here only once. A batch of 117 grams of plutonium oxide was treated with mixed hydrogen and hydrogen chloride at 450 C for three and one-half hours without success; then at 540 - 570 C for 14 hours, which removed all visible color of oxide. Laboratory analysis showed incomplete chlorination. X-ray diffraction study indicated much of the product was plutonium oxychloride, PuOCl . Further work with the hydrogen-hydrogen chloride reagents was discontinued due to the slow chlorination rate, incomplete chlorination, and the immediate hazard of hydrogen explosions.

4. Large Batch Chlorinations

Carbon tetrachloride having worked well on a small scale, was used for 300-gram batches before the small batch tests of phosgene were completed. It was while producing trichloride for reduction tests that the two reagents were more fully compared.

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A Pyrex powder vessel and a pot furnace (Figure 1) were loaded with 300 grams or more of plutonium dioxide. An excess of chlorinating agent passed through the powder, the supporting frit, and then to the trap and the caustic scrubbers. Problems with plugged exhaust lines were common with the large batches. Generally this was due to carbonate salt formation as the caustic approached neutrality.

With carbon tetrachloride, the plugging was also caused by collections of unidentified white solids in the trap and in the first scrubber. These were not water-soluble. When the exhaust gases from the chlorinator were scrubbed once with caustic, then passed through a cold trap at -50 C, several liquid fractions were formed. These were found to have boiling points of 8, 16 - 18, 22, 27 - 29, 74 - 75 C, and higher. One of the higher boiling components was a yellow viscous fluid and the second a wax-like film.

● Literature on various uses of heated carbon tetrachloride as a chlorinating agent indicate by-products of chlorine, phosgene, C_6Cl_6 , C_2Cl_4 , C_2Cl_6 , CO_2 , CO, and possibly others. A means for filtering and disposing of such a variety of by-products from a large-scale unit presented an extensive problem.

The few solids forming in the off-gas lines from phosgene chlorination were mostly water-soluble.

With both reagents, a problem of temperature control was experienced. In batches containing 300 grams or more of plutonium, about half resulted in exothermic reactions. The temperature rise started at 420 C. The temperature was partially controlled by interrupting the chlorinating reagent and turning off the electric furnace. About 10 percent of the batches resulted in excessive temperature (> 600 C), and the loss of a Pyrex vessel. It was not determined whether or not the observed heat rise was due to further calcination of the oxide prepared at 350 C.

The temperature of phosgene was given more study on 300-gram batches. Phosgene chlorinated the oxide slowly at 300 - 400 C. At 400 - 450 C, the reaction rate was good, and it continued to rise with temperature increase. Above 500 C, the powder contained more lumps and larger and darker crystals. At 600 C, the powder sintered into a hard cake. The reaction rate with phosgene through the range of 300 - 540 C is equivalent to the rate with carbon tetrachloride at 50 - 100 degrees higher. This is especially significant in the corrosion rates of metals. The excess of reagent required was roughly the same for both chemicals.

To summarize a comparison of the two reagents, phosgene permitted a choice of lower chlorinating temperature or higher reaction rate. By-products in the phosgene chlorination exhaust were fewer

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and less likely to interfere with gas filtering. The choice was phosgene, if it could be used with safety.

The safe use of phosgene has been demonstrated on this program for well over a year. Phosgene safety is discussed under VII, Appendix.

Chlorinations of plutonium dioxide with phosgene were scaled up to a one-kilogram batch size, the largest batch containing 1.1 kg of plutonium. The chlorination of kilogram-batches required 12 to 20 hours at temperatures of 430 - 550 C. The product was dark and caked at the upper region of these temperatures, but was light and free-flowing if the temperature was on the low side. The chlorination was slowest at the bottom and center of the batches due to shrinkage of the powder away from the vessel walls, resulting in channeling. If the chlorinations were interrupted, stirring of the powder helped eliminate the gas channeling.

Experience showed that complete chlorination required a two-fold excess of phosgene. This is, one mole of PuO_2 required six moles of COCl_2 . A flow sheet, Figure 2, gives material balances for this process. The flow sheet includes the caustic required to neutralize all exhaust gases. Caustic scrubbers were used in this program, but as is discussed later, gas dilution is recommended.

The feasibility of batch chlorination was well demonstrated with 59 batches of various sizes which contained nearly 25 kilograms of plutonium. A 400-gram batch size proved most convenient for an eight-hour operation. The plutonium trichloride produced was satisfactory in subsequent reductions, except for recognized off-standard preparations. The analyses of samples indicated average chlorination was 97.3 percent complete.

5. Continuous Chlorinator - Pyrex Reactor

A small continuous chlorinator was used to determine the feasibility of chlorinating plutonium dioxide in a continuous system. An electric vibrator moved powder down an inclined one-inch Pyrex tube passing through two 12-inch furnaces (Figure 3). An Eagle timer and a variac controlled the intermittent operation of the vibrator. Phosgene gas was metered and passed counter-current to the powder. Plutonium dioxide powder was fed by a Teflon rotary valve turned by a reduction gear motor. This, in turn, was operated intermittently by a timer and a variac.

Typical operating conditions were as follows:

Temperature (hottest point in chlorinator): 500 C.
Furnace length: 24" total, 18 - 20" at 450 C or above.
Residence time in furnaces: 45 ± 10 minutes.
Phosgene flow: 1.5 moles per hour, or 6 moles per mole PuO_2 .

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Powder bed depth: $1/4 - 3/8$ ".
Tube slope: 2 degrees.
Vacuum applied to chlorinator: $1 + 1/2$ " H₂O.
Vibrator operation: 1 second on, 60 seconds off, variac 120.
Oxide feed: Set at $1/2$ revolution per cycle.
1/2 revolution = 2 g Pu.
Timer: 2 minute cycle. Adjust only the off-time
for rate change.
Average rate: 57 g Pu/hr for 30 hours.

The glass permitted visual observation of the chlorination progress. For example, once it was observed that chlorination appeared incomplete on powder halfway through the furnaces. Increasing the temperature by 30 degrees resulted in a visible change in 10 minutes.

Air leakage into the chlorinator was a serious obstacle until discovered and corrected. Oxygen is incompatible with the chlorination reaction.

When rate or temperature tests yielded brownish-colored powder, this was recycled to complete the chlorination.

The glass reactor was operated under severe vibration and at temperatures up to 550 C. At this temperature the tube bent slightly under strain but was reheated and straightened. One tube was broken by a bump from a wrench after 275 hours of operating time. The replacement tube has not yet received that much usage.

Solids collected on the surface of the cold area of the reactor tube and in the off-gas line. They ranged in color from tan to very dark brown as a function of temperature. These proved to contain volatile chlorides which will be discussed later in the section on exhaust gas filtering.

The formation of lumps of chloride powder was a frequent occurrence. These were usually broken into small lumps by the action of the vibrator. Remaining lumps which entered the receiving jar were usually powdered by shaking the nearly-full bottle. Some lumps, being hard, entered the reduction operation in chunks up to marble-size, but gave no reduction problem. These lumps rarely showed incomplete chlorination on the inside. The lumps frequently interfered with the powder flow, but rarely plugged the reactor. Lump formation originated only at the entrance to the furnace where chlorination began (temperature about 300 - 400 C). Most of the plutonium trichloride was a free-flowing powder, light-greenish-blue in color.

Operation of this Pyrex chlorinator to date has produced 6.2 kilograms (as plutonium) of satisfactory plutonium trichloride.

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6. Continuous Chlorinator - Demonstration Reactor

A larger continuous chlorinator was prepared to further demonstrate the chlorination process. This unit, known as the demonstration chlorinator, is pictured in Figures 4, 5, and 6.

The Hastelloy B chlorination tube has an oval cross-section. Inside dimensions are 1-1/4" x 2-1/4", having 1" of flat surface and 3/4" radius bends. Total length is 49"--32" of it inside the two furnaces and end plates. The temperature is not uniform through the furnaces. Figure 7 indicates a typical temperature graph of the unit which shows about 21" at chlorination temperature of 450 C or above. Heating cable along the upper exposed tube (not shown) provided additional temperature control. Chromel-alumel thermocouples were located to record the hottest points in the furnaces, usually 525 ± 25 C. The corresponding hottest maximum chlorination tube temperatures are 500 ± 25 C.

Powder was received and delivered through PVC ball valves (maximum observed temperature 60 C). A black Teflon bellows (Figure 6) (maximum observed temperature 160 C) isolated the receiving valve from the vibration used to move the powder through the tube. Inert gas bleeding into the system between two valves prevented the phosgene gas from working back into the calciner which provided the oxide powder. Phosgene gas, supplied from outside the building, was metered counter-current to powder flow and out through a ceramic primary filter (Figure 6), through a cooling trap and a secondary filter into a scrubber containing caustic. The top of the hood was provided with a water cooling jacket. Uncooled parts of the top reached a temperature of 52 C. Dry air supplied at about two cubic feet per minute kept the hood at -20 C dew point or better. Material entrance and exit were by plastic bag procedures.

There were several operating problems with this equipment. When the phosgene passed the control valve, the cooling from expansion was sufficient to liquify the phosgene. Heating the valve to 110 - 120 C corrected this problem.

Off-gas filters were originally ceramic fingers supported from one end by a ceramic flange or bead (Figure 6). Breakage of these caused several delays until the ceramic fingers were converted to cylinders and given metallic support through the center (Figure 8).

Filter housings were originally Pyrex glass pipe (Figures 5 and 6). After a few of these were broken, a factory-made "Double Tough" Pyrex Tee was successfully substituted. Subsequently, a Hastelloy C housing was fabricated. Another thermocouple and a heating cable were added to maintain filter temperature above 350 C.

Powder flow through the reactor tube was erratic. With every change of filter housing, the resonance of the tube changed and re-

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quired few vibration control settings to move the powder.

Powder lumps sometimes plugged the exit from the chlorinator. A plunger to break the lumps was installed. Lumps were most troublesome when a shutdown interrupted the progress and agitation of the powder.

At this writing, 13.5 kg of plutonium have been converted from oxide to chloride in the demonstration chlorinator.

Optimum operating conditions found to date are as follows:

Furnace temperature: TC 525 C; tube maximum, 500 C.

Filter temperature: 350 - 400 C.

Pre-furnace temperature: 350 C - 400 C.

Phosgene flow: 6 moles per mole of PuO_2 .

Powder flow: 0.8 moles, or 200 g Pu, per hour.

Powder bed depth: 1/4 - 3/8".

Powder residence time: 45 min. in furnace, one hour total.

Vibration: 10 sec. on, 10 sec. off, intensity setting 80.

Chlorinator slope: 4 degrees.

Chlorinator vacuum: 1 - 10" of water.

The flow sheet shown for batch phosgene chlorinations applies to the continuous operation (Figure 2).

Some of the chlorination rates observed to date are found in Table I.

7. Materials Of Construction

Chlorination tubes of Pyrex and of Hastelloy B have been used successfully at temperatures of 500 ± 25 C. According to recent tests of W. L. Walker (to be published), metallic chlorination tubes may be of Hastelloy C, nickel, Chlorimet-2, Ni-O-Nel, or Hastelloy B. All show nearly one mil per month corrosion in phosgene at 500 C (Table II). Any increase in temperature causes a sharp increase in the corrosion rate.

Ceramic filters show no deterioration in the exhaust gases. A ceramic cylinder held by metallic supports is durable and inexpensive. Presumably metallic frits would suffice, but these were not tested due to the cost of such filters.

The filter housing and filter supports (minimum temperature 350 - 400 C) must be of Hastelloy B or C or equivalent where in contact with the hot gases. Beyond the filter where powders cannot return to the chlorinator, corrosion rates of materials are less important. Where gases cool from 350 C to room temperature in a pipe (or possibly a cold trap), condensing metallic chlorides will likely plug the pipe unless these solids are removed. At about 100 C where water vapor

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TABLE I

PuO₂ CHLORINATION RATES - DEMONSTRATION CHLORINATOR

<u>Grams Pu/h</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

TABLE II

CORROSION OF MATERIALS IN PHOSGENE⁽¹⁾⁽²⁾
Corrosion Rates In Mils Penetration Per Month

<u>Material</u>	<u>Furnace</u>			<u>Exhaust Gas 90 - 100 C</u>
	<u>400 C</u>	<u>500 C</u>	<u>600 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

- (1) Phosgene plus 50 percent water-saturated air, flowing at 2 liters/hour.
(2) Unpublished data by W. L. Walker, HLO.

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from moist powder may condense, tests indicate increased corrosion (Table II). The most simple design could be replaceable stainless pipe where the gases cool. For the cold section of the off-gas line, rigid PVC or other plastic pipe is recommended.

Phosgene is supplied in black iron cylinders. The manufacturer recommends and sells an inexpensive control valve and cylinder adaptor which has copper tubing. Copper, iron, monel, and stainless steel are suitable as supply pipes. No leakage can be tolerated.

Many plastics, such as Teflon, rigid PVC, polyethylene, Saran, and Kel-F, are suitable for use with phosgene. When plasticizers are present as in flexible tubing of PVC or PVA ("Tygon", "Nalgon", etc.) or in plastic bags such as Bakelite "Krene", the phosgene reacts with the plasticizer causing discoloration and deterioration. Polyethylene tubing and bags can be used in preference to the "Tygon" or "Krene".

Gum rubber, Neoprene, silicone rubber, and synthetic rubbers generally are unreliable unless the formulation has been tested and found satisfactory. Indeed, some have proven very suitable; particularly in dry atmosphere where the plasticizers, too, are less troublesome.

The preceding paragraphs apply to gaskets just as to tubing and equipment parts. Various asbestos gaskets have proven useful with phosgene on the hot equipment. An asbestos gasket which has absorbed phosgene may swell and become useless if exposed to water or moist air.

Hoods may be of 304L stainless steel, providing a dry atmosphere is maintained. The anhydrous plutonium trichloride is non-corrosive; but at humidities above dew point -20 C, it absorbs water and becomes corrosive. At dew point +15 C, the test samples showed significant corrosion. Where phosgene leakage in a hood is possible, the dry atmosphere (dew point -20 C or better) is of major importance. Should appreciable phosgene escape into a hood with moist air, the phosgene and moisture form a corrosive film of hydrochloric acid on the exposed surfaces.

The objects first attacked by phosgene in a hood where the humidity was allowed to rise, were those of brass or zinc. The brass parts of a balance, an electric cover plate, and laboratory clamps became wet and corroded. Tools sprayed with Krylon showed reaction with phosgene in air before "unprotected" tools were attacked.

B. Chlorination Exhaust Gas Disposal

1. Filtering

The primary purpose of filtering was to prevent loss of plutonium

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via the off-gas stream. Some filters improvised with glass wool and bottles were useful in preliminary work or as secondary filters. For primary filters, some commercially-available ceramics were tested by Rey.⁽¹⁸⁾

The filter housing and ceramic finger filter shown in Figures 5 and 6 were unsatisfactory due to breakage. The Pyrex pipe housing shown was replaced by a factory-made "Double Tough" Tee which proved durable. The beaded or flanged ends on the finger filters usually broke when tightened into place. This was probably due to the necessity of high temperature asbestos gaskets, which differ greatly from the soft rubber gaskets supplied. When the ceramic fingers were cut into cylinders and given a Hastelloy C support (Figure 8), the filter breakage was eliminated.

Ceramic filters were used first at low temperature, 50 C or less. A Selas XF filter plugged after 23 hours' use, and a Selas XFF lasted only 13 hours at low temperature.

The plugging was not due to buildup of dust on the filter, but to condensation of metallic chlorides volatilized out of the reactor. The oxide feed contained significant amounts of aluminum and iron at the time of these tests. The approximate boiling points of most chlorides and carbonyls which could pass a heated filter as vapor are as follows:

AlCl ₃	183 C	SiCl ₄	57 C
BCl ₃	12.5 C	CrCl ₄	257 C
FeCl ₃	319 C	Fe(CO) ₅	103 C
MoCl ₄	312 C	Ni(CO) ₄	43 C
MoCl ₅	268 C	SnCl ₄	113 C
WCl ₅	276 C	TiCl ₄	136 C
WCl ₆	337 C	ZrCl ₄	331 C

To permit aluminum chloride or ferric chloride to pass through the filter, a heating cable was wrapped around a Pyrex "Tee" filter housing to provide a temperature of 350 - 400 C. Thereafter, a new Selas XF filter was used at this temperature for 58 hours before it was removed to test other filters and filter housings. Vibration had not damaged the filter. The dust and volatile chlorides which had passed this filter in the last 42 hours of operation contained 12.4 percent plutonium. A generous estimate of the condensate and dust weight indicated that less than 0.5 gram of plutonium had passed the filter as dust or vapor. This is partially recoverable from a suitable cold trap following the filter.

The filter sample referred to above was also analyzed by spectrograph. Major constituents were iron and phosphorus (no explanation). Present in strong amounts were boron, molybdenum, chromium, and zinc. In lesser concentrations were aluminum, nickel, silicon, and titanium. Aluminum content of the oxide feed was less

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than 10 ppm at the time of these tests. Rey(18) reported success with back-flushing. This has not been sufficiently evaluated with plutonium dusts because chlorinator vibration removed any cake over 1/8 inch in thicknesses from the filters and dropped it back into the chlorinator.

2. Exhaust Gas Composition

Gas analyses work by Lust(19) during operation of the small continuous chlorinator indicated the following major constituents in the off-gases when operating with a four-fold excess of phosgene:

Volume Percent

COCl ₂	7-57
CO ₂	20-50
CO	10-20
Cl ₂	7-12
HCl	7-9

The wide variations in the phosgene and carbon dioxide values are normal because they vary with the degree of phosgene utilization at the time of sampling.

The carbon monoxide and some of the chlorine are products of phosgene dissociation. The hydrogen chloride is from phosgene hydrolysis due to residual moisture in the plutonium dioxide. Consumption of caustic in the scrubber is effected little by these side reactions of the phosgene.

3. Exhaust Gas Neutralization

It was necessary to neutralize corrosive gases from the chlorinator exhaust to protect the hood exhaust piping. These gases were absorbed in caustic.

The scrubber system (Figure 9) used for gases from the demonstration chlorinator was designed to include some recommendations of Rey(20). The upper portion was operated as a gas phase column and the lower, large diameter section was filled with the sodium hydroxide. Caustic recirculated from a 25-gallon tank, down the column, and back to the tank. Experience with this system proved that more operator effort went to the scrubber than to the chlorinator.

Off-gas treatment by a caustic scrubber neutralizes phosgene, hydrogen chloride (from moisture and phosgene), carbon dioxide, and chlorine. Carbon monoxide and nitrogen (air leakage) bubble through unchanged. An economic loss is experienced in the unnecessary use of caustic by the carbon dioxide, which need not be neutralized. The chemical reactions are the following:

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As the neutralization proceeded, the caustic normality diminished from six to about one, below which point carbonate precipitation threatened to plug the system. The chemical reaction warmed the system to 50 - 60 C.

4. Exhaust Gas Dilution

The most satisfactory disposal of corrosive gases from chlorination is by dilution. After the gases are filtered, and cooled to remove condensates, it is feasible to pass them through non-corrosive pipe such as rigid PVC direct to the stack. Where adequate dilution is available, the use of a caustic scrubber is thereby avoided.

5. Recovery Of Phosgene

Several trials were made to recover the excess phosgene leaving the chlorinator. Because phosgene liquifies at about 8 C, it is easily trapped in a bath of dry ice and alcohol, or one of ice and brine. Reuse of such recovered phosgene was satisfactory in subsequent chlorination, but was an inconvenience in the laboratory. The economics and safety of phosgene recovery, rather than any process difficulties, should determine the feasibility of said recovery.

C. Characteristics Of Plutonium Trichloride

1. Stability

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 100 - 150 C in air (humidity unknown), the powder surface oxidized overnight. Oxidation proceeds rapidly in air at 400 C or higher.

Dry plutonium trichloride which has partially oxidized may be re-chlorinated with phosgene. If water of hydration is present, the temperature should be raised slowly while sweeping the powder with the dry gas. The powder will melt and cake if the melting point (94 - 96 C) of $\text{PuCl}_3 \cdot 6\text{H}_2\text{O}$ is reached before this water is removed. Vacuum drying is also feasible.

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2. Color

The color of anhydrous plutonium trichloride, a greenish-blue, is an excellent indicator for the absence of the green-olive dioxide. As little as one or two percent dioxide is visually detectable, especially as a fine brownish dust settling on the top of the powder after shaking the container. When five percent or more dioxide is present, the greenish-blue chloride color is masked almost completely. Incomplete chlorination is indicated by any brownish appearance to powder or lumps. Color detection of oxy-chloride is not reliable because its color is similar to the trichloride.

The chlorination temperature (and probably other variables) influence the powder color. Chlorination at 400 C results in a light blue-green (almost grey) powder. Higher temperatures up to 600 C produce larger and darker crystals. Sintering is apparent after 650 C is reached. Upon hydration to $\text{PuCl}_3 \cdot 6\text{H}_2\text{O}$, the color becomes a bright blue.

3. 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.

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.

When trichloride powder in glass jars is exposed to humid air, the progress of hydration may be noted by the color change from blue-green to bright blue; i.e., from anhydrous to hexahydrate. Intermediate hydration steps are not evident, but may be formed under controlled conditions.⁽²¹⁾⁽²²⁾ Hydration slows, as a barrier of hexahydrate protects the anhydrous salt from the moist air.

Hydration rates are largely influenced by the physical arrangements of the apparatus. Diameters of the exposed powder surfaces primarily control the differences in hydration rates. A narrow, deep container would reduce the hydration rate below that of an equal weight of powder in a wide, shallow container. Containers were chosen to be miniatures of powder pans. The inside diameter of each "pan" was 0.94". Inside height was 0.85" with the powder

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added until 0.75" deep. Powder in these "pans" was exposed to controlled atmospheres of dew points -28, -20, -18, -15, -13, -5, +5, +13, and +15 degrees centigrade. These atmospheres were provided in ointment-jar desiccators containing sulfuric acid of known specific gravity. The relationship of dew point to sulfuric acid specific gravity⁽²³⁾ is given for 20 centigrade. The temperature was 20 - 23 C during the test period, but all values are based on the 20 C temperature.

Each portion of chloride powder originally weighed 17 ± 2 grams. Weighing to five significant figures was done in a dry atmosphere at intervals. Powder exposed to air of dew point -28 C and dew point -20 C showed no weight gain. At dew point -18 C, the weight gain, if any, was less than 0.01 percent in a thousand hours. At -15 C dew point, the gain was about 0.6 percent in 650 hours. At -13 C dew point, the gain was 0.5 percent in 200 hours. Powder containing 0.5 percent water has been successfully reduced. Additional data may be read from Figure 10.

4. Other Characteristics

Anhydrous plutonium trichloride has a melting point of 763 C and a boiling point of 1770 C, although decomposition begins below 1500 C. Its vapor pressure is 0.012 mm Hg at 750 C.

Two particle-size observations were made on a Fisher Sub-Sieve Sizer. Average particle sizes were reported as 4.1 for a large-batch chlorination with phosgene at 500 C, and 6.1 microns for the Pyrex continuous-chlorinator using phosgene at 460 C.

Zachariassen⁽²¹⁾ has reported that the anhydrous salt has a hexagonal crystal having a calculated crystal density of 5.70 per cubic centimeter.

Bulk density of the powder is usually 2.6 ± 0.4 grams per cubic centimeter. Observations of bulk density are shown in Table III.

A sample of anhydrous plutonium trichloride was submitted to Hanford Laboratories Operation for the measurement of neutron emission rate. The reported answer⁽²⁴⁾ was tabulated in comparison with the tetrafluoride and plutonium metal as follows:

<u>Compound</u>	<u>Emission Rate</u>		<u>Average Neutron Energy, MEU</u>
	<u>n/sec/g Of Compound</u>	<u>n/sec/g Of Pu</u>	
Pu	96	96	1.9
PuF ₄	6800	8870	1.4
PuCl ₃	96	138	<u>ca 1</u>

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The fluoride neutron emission rate is 64 times that of the chloride in this observation. This may be significant in personnel exposure.

TABLE III

BULK DENSITY OF ANHYDROUS PLUTONIUM TRICHLORIDE

<u>Run Identity</u>	<u>Bulk Density g/cc</u>	<u>Remarks</u>
<u>Batch Chlorinator</u>	2.58	Average of 14 random samples
<u>Pyrex Chlorinator</u>		
30-1	2.28	
30-2	2.00	Average of 2.02, 1.95
30-3	2.32	
30-5	2.96	Average of 2.88, 3.04
30-6	2.99	Average of 2.96, 3.02
30-7	2.88	
30-8	2.79	
30-10	2.41	
30-10A	<u>2.85</u>	
	2.61	Average
<u>Demonstration Chlorinator</u>		
4-7-2	2.58	
4-28-2	2.40	
5-19	2.20	
6-15-1	2.36	
6-26	2.75	
6-15 and -16	<u>2.15</u>	
	2.41	Average

5. Purity

Laboratory analyses (Table IV) of the trichloride indicate an average chlorination of 97.3 percent of theoretical, corresponding to the formula $PuCl_{2.92}$.

The impurities in the powder are shown in Tables V, VI, and VII in relationship to the purity of the feed material and of the resulting metal. The chlorination step did not contaminate the

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powder to any troublesome extent. In the case of elements forming volatile chlorides, an improvement in purity is indicated.

The reduction of the trichloride to metal indicated the powder was satisfactory.(14)

IV. FUTURE WORK

Some additional runs on the demonstration chlorinator are needed to determine its maximum capacity. Heating of the upper end of the Hastelloy B tube and supplying part of the phosgene at that end would increase the effective length of the chlorinator.

Among various possible studies to further improve the process, there is one line of investigation which shows most promise. Dry plutonium oxalate was chlorinated by phosgene at a temperature of 250 C, 200 degrees lower than oxide chlorination. At this temperature, the addition of a screw drive through the chlorinator could certainly be tolerated without fear of corrosion problems. This would eliminate vibrator resonance and chloride lump problems by providing positive control of powder flow.

V. ACKNOWLEDGEMENTS

H. H. Hopkins, Jr., managed and guided this and other related studies. H. W. Crocker designed the chlorinators and the gloved hoods containing them. The provision of dry atmosphere for the Pyrex continuous unit is credited to R. H. Bond. Initial chlorinations were by N. S. Wing, now of Finished Products Operation Analytical Control. W. L. Walker of HLO Chemical Development performed the corrosion testing. George Rey, also of HLO Chemical Development, assisted in filter and scrubber testing and designs. L. F. Lust, now of HLO Analytical Laboratories, gave valuable help in the chlorination work. The oxide feed for the demonstration chlorinator was prepared by C. J. Berglund as needed.

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TABLE IV

CHLORIDE/PLUTONIUM RATIO BY LABORATORY ANALYSES OF PLUTONIUM
AND CHLORIDE ON UNWEIGHED SAMPLES OF PLUTONIUM TRICHLORIDE

<u>Run Identity</u>	<u>Cl/Pu</u>	<u>Remarks</u>
<u>Batch Chlorinators</u>	2.92	Average of 59 batch chlorinations.
<u>Pyrex Chlorinator</u>		
30-1	2.99	
30-2	2.81	
30-3	2.64	
30-4	2.78	
30-5	2.68	
30-6	2.70	
30-7	2.84	
30-8	2.84	
30-9	3.07	
30-10	2.78	
30-10A	2.90	
30-11	2.91	
30-13	<u>2.91</u>	
	2.83	Average of 13 Pyrex Chlorinator runs.
<u>Demonstration Chlorinator</u>		
4-7-1	3.04	
4-7-2	2.95	
4-17	2.96	
4-22	2.83	
4-28-1	2.92	
4-28-2	2.94	
5-4	2.95	
5-6	2.91	
5-13	3.09	
5-19	3.07	
6-4	3.03	
6-15	3.00	
6-16	3.08	
6-26	3.04	
7-8	3.10	
7-9	<u>2.94</u>	
	2.99	Average of 16 Demonstration Chlorinator runs
	<u>2.92</u>	Average of 88 samples of PuCl ₃

NOTE: Accuracy of each estimated at ± 10 percent.

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TABLE V

PLUTONIUM TRICHLORIDE IMPURITIES

A comparison of typical spectrographic analyses of oxide, chloride, and metal when the Pyrex continuous chlorinator was used with phosgene at 450 - 500 C. Values are parts impurity per million parts plutonium.

<u>Impurity</u>	<u>Oxide</u>	<u>Chloride</u>	<u>Metal</u>
Ag	L2	L2	L2
Al	5	16	13
As	-	-	-
B	L2	L2	2
Be	-	-	-
Bi	-	-	-
Ca	5	16	13
Cd	-	-	-
Cr	20	10	5
Cu	10	20	10
Fe	200	50	L50
Ge	-	-	-
K	-	-	-
La	-	-	-
Li	-	-	-
Mg	50	50	200
Mo	50	-	-
Mn	20	20	50
Na	100	100	20
Ni	200	200	50
P	-	-	-
Pb	2	2	10
Si	20	20	10
Sn	L2	L2	-
Tl	-	-	-
V	-	-	-
Zn	-	-	-

(L) Less than
(-) Not detected

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TABLE VI

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 VII

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

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VII. APPENDIX

Phosgene Safety

Phosgene, or carbonyl chloride, formula COCl₂, was notorious as a war gas. Safety measures which are adequate for handling cylinders of hydrogen fluoride are fully adequate for phosgene. Complete protection of the eyes, nose, and mouth are required; but the skin is not damaged by occasional exposures to traces of phosgene gas.

Reliable fresh-air masks or Chemox masks are necessary when the phosgene concentration in air exceeds one part per million. Automatic warning devices are available to detect gas leakage at this level. A Davis phosgene analyzer was used for leak detection. Phosgene leakage may be detected by the distinctive odor of the gas which is noticeable at five parts per million or less. Concentrations of twenty-five parts per million for one-half hour or longer are dangerous. Phosgene is a primary irritant of the respiratory tract. Over-exposures cause coughing and tear formation. Edema in the lungs may not appear serious until four, or even six, hours after over-exposure.

Phosgene is supplied in cylinders in liquid form at a gas pressure of about 30 psi (gauge) at room temperature. The cylinders should never

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be heated to exceed this pressure. The boiling point is 8.2 C or 46.7 F. If the cylinder is not upright, the liquid, rather than gas, will flow when the valve is opened. Detailed valve instruction accompanies each cylinder.

Experience with phosgene has demonstrated that it can be used and handled with safety.

M. J. Rasmussen
M. J. Rasmussen

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Figure 1
BATCH CHLORINATOR

Powder Vessel: Modified Glass Frit

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FIGURE 2

FLOW SHEET, CHLORINATION OF PLUTONIUM OXIDE

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FIGURE 3

CONTINUOUS CHLORINATOR - PYREX REACTOR

- A. Motor to drive valve C. Controlled by Flexopulse (Eagle Signal Corporation, Moline, Illinois) and Motor Control (G. K. Heller, Baltimore, Maryland).
- B. Plutonium oxide reservoir.
- C. Powder valve.
- D. Powder trap and ceramic finger filter.
- E. Vibrator (Model 1-91-0002, Vita Pack Vibrator).
- F. Pyrex glass pipe, 1" I.D.
- G. Electric tube furnace (Type 70, Hevi-Duty Electric Company, Milwaukee, Wisconsin).
- H. Powder valve, manual.
- I. Chloride receiver.
- J. Phosgene entrance.
- K. Off-gases exit to scrubber.

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FIGURE 4
DEMONSTRATION REACTOR

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FIGURE 5
DEMONSTRATION REACTOR

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FIGURE 6
DEMONSTRATION REACTOR

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FIGURE 7

TYPICAL TEMPERATURE GRAPH OF DEMONSTRATION REACTOR

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FIGURE 8

SUPPORT FOR CERAMIC FILTERS

- A. Hastelloy C 3/8" diameter rod, nut, washer, and fiberglass gasket. Rod threaded for 3-1/2" to 6" filters.
- B. Hastelloy C 3/8" O.D. tubing, holes for gas exit.
- C. Elbow, 316 SS, 1/2" T, 3/8" male NPT welded to tubing "B", threaded into flange "E".
- D. Ceramic filter, 1-3/4" O.D.
- E. Hastelloy C flange.
- F. Pyrex pipe, 3" diameter, and pipe flange.

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Figure 9
EXHAUST GAS SCRUBBER SYSTEM

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FIGURE 10

**HYDRATION RATES OF PLUTONIUM TRICHLORIDE
AT CONTROLLED HUMIDITIES**

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