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ACTIVE METAL REDUCTION OF PLUTONIUM TRICHLORIDE

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ACTIVE METAL REDUCTION OF PLUTONIUM TRICHLORIDE

Plutonium metal can be made efficiently via the fluoride route by reduction of plutonium tetrafluoride with calcium metal using the calcium-iodine reaction as a booster. As you probably know, atoms such as fluorine, with low atomic numbers, give rise to high neutron densities when exposed to alpha radiation. Since neutrons are difficult to shield, anyone working with or near the tetrafluoride will be exposed to this radiation.

One means of reducing this radiation would be to replace the fluorine atom with one having a higher atomic number. At the present time, the most likely candidate seems to be chlorine. The use of this salt would reduce the neutron intensity approximately by a factor of 100. The use of the trichloride has another advantage in that the chlorination process would provide another purification step due to loss of volatile chlorides. It has been shown that the trichloride can be produced in the same manner as the tetrafluoride.

It is the purpose of this work to investigate the reduction characteristics of plutonium trichloride.

Physically, plutonium trichloride is very similar to the tetrafluoride. Thermodynamically, it is less stable with respect to reduction by calcium. Chemically, it is hygroscopic and will have to be treated accordingly. Table I shows the chemistry involved.

TABLE I

CHEMISTRY INVOLVED IN PuCl_3 REDUCTION

1. $\text{Ca} + \text{I}_2 = \text{CaI}_2$.
2. $2\text{PuCl}_3 + 2\text{Ca} = 2\text{Pu} + 3\text{CaCl}_2$.
3. $\text{PuF}_4 + 2\text{Ca} = \text{Pu} + 2\text{CaF}_2 \Delta H_{291} = -149 \text{ KCal.}$
4. $\text{PuCl}_3 + 3/2 \text{ Ca} = \text{Pu} + 3/2\text{CaCl}_2 \Delta H_{291} = -56 \text{ KCal.}$

A bomb reduction involves the use of a steel pressure vessel lined with some suitable material to prevent contact between it and the reaction products. The reagents are mixed and sealed in the pressure vessel. This is then heated until the firing temperature is reached.

The variables that need to be investigated are: proper ratio of reductant and booster, allowable moisture content of reagents, correct heating rate, liner or crucible material, quality of feed material and atmosphere.

Magnesium oxide crucibles were chosen for the liners. These are readily available and have been used for plutonium fluoride reductions.

The optimum amounts of calcium and iodine were investigated on a 30-gram scale. This was found to range from 15 to 30 percent excess for calcium, and from 0.2 to 0.3 moles iodine per mole plutonium; 25 percent excess of calcium and 0.20 moles of iodine were set as standard conditions. For some special cases, 0.25 and 0.3 moles of iodine were used.

It was soon apparent that one of the main problems would be that of a good liner material. The slag formed by the reduction penetrated the crucible and essentially cemented everything to the inside of the pressure vessel. Apparently the reason that it works for fluoride reductions is that the calcium fluoride stays molten for such a short period of time that there is little penetration. The calcium chloride formed, having a lower melting point, has more time to penetrate the crucible.

Several different crucibles were tried in an effort to alleviate this problem. The most successful to date has been a magnesia crucible cemented into a stainless steel can with calcium chloride. The reduction products are then drilled from the crucible to the surface of the button, which, with a small amount of chipping, usually fall free. Magnesia crucibles flame sprayed on the outer surface with nickel, copper, and steel have also been used with some success. Tantalum has also been used to a limited extent.

The loaded pressure vessels were heated with a 10 KC induction heater. The best results were obtained when the lower portion of the vessel was heated.

Heating was done rapidly to lessen the formation of calcium iodide on the surface of the calcium.

The presence of moisture in the powder can either cause unsafe pressures in the bomb or it may hinder the reduction, and low yields will result. By adding water to the trichloride prior to reduction, it was found that 0.6 percent by weight was about the maximum that could be present and still maintain suitable reduction conditions. Before unsafe pressures were reached, 0.9 percent was added. With the higher amounts of moisture, the reduction was improved somewhat by adding additional calcium.

Another important variable is the quality of the plutonium trichloride used for reductions. Trichloride with chlorine to plutonium ratios of from 1.7 to 3.0 gave satisfactory reductions. A qualitative method of identifying good powder was to use visual inspection. The presence of

brown material indicated incomplete chlorination and low yields would often result. An attempt to define this quantitatively was made by submitting the trichloride to aqueous leach and determining the percentage of insoluble material. Plutonium trichloride is completely soluble in water while the oxide and oxychloride are not. It was found that the trichloride could contain up to above eight percent by weight of insoluble material and still give good reductions. Several attempts were made at reducing oxychloride, with little success. Any material that looked as though it had been sintered or chlorinated above 600 C (black powder) required a little extra booster to give optimum results.

The presence of lumps was not detrimental as long as they were not larger than one-half inch in diameter and did not comprise more than one-eighth of the total powder volume. One small-scale reduction was made with 90 percent lumps with very satisfactory results.

The temperature and pressure of a normal reduction vary slightly, depending on the size of the reduction. The outside wall temperature ranged from 550 - 650 and the pressure varied from 30 - 100 pounds.

The usual course of events is for the pressure to build up slowly during heating and then drop suddenly to near zero on firing.

The slag is usually white or light-tan with the excess calcium in the form of a cap on top of the slag. Any dark material usually signifies a poor yield. Table II shows the results of several mixed reductions.

TABLE II

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>
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

After trying the above conditions for a mixed reduction, study was started on the possibility of making satisfactory reductions without mixing the reactants. This would eliminate one step in the process and would minimize powder spread.

There are several methods of loading a reduction vessel without pre-mixing the constituents. The most desirable would be to place the plutonium trichloride in the vessel and then add the reductant and booster just prior to the reduction. This has an obvious disadvantage in that a

good portion of the heat from the booster would be dissipated upward and lost.

Another alternative would be to place the reductant and booster in the crucible first.

If neither of these is satisfactory, then feeding the reactants into the crucible simultaneously might prove successful. This would give a condition closely resembling a mixed reduction. However, this would require more intricate equipment and more diligent control of feed materials than the two previously discussed. Figure 1 illustrates the reductions involved.

Preliminary investigations on a small scale indicated that placing the reductant and booster on top of the trichloride had possibilities. When it was scaled up to 700 grams, only partial reduction resulted. At first it was thought that increasing the reaction area between the reductant and the trichloride might improve the yield. Using a crucible with about three times the cross-sectional area did not improve the results. Closer study of the problem showed that the calcium chloride formed probably floated the calcium away from the remaining trichloride. The only apparent solution to the problem is to alloy the calcium with some heavier metal such as zinc. This would hold it in contact with the trichloride.

Placing the reductant and booster below the trichloride gave reductions equal in quality to the mixed charge.

Simultaneous addition was simulated by pouring the reactants into the reduction vessel at the same time from separate containers. The results were almost identical to a mixed reduction. Table III gives the results of non-mixed reductions.

TABLE IV

COMPARISON OF DIFFERENT TYPES OF NON-MIXED
PLUTONIUM TRICHLORIDE REDUCTIONS

<u>Type Reduction</u>	<u>Size Reduction Grams</u>	<u>I₂/Pu</u>	<u>Yield Percent</u>
Ca and I ₂ on top of PuCl ₃ (5 runs)	700	0.30	70 (avg.)
Ca and I ₂ below PuCl ₃ (2 runs)	700	0.25	96 (avg.)
(5 runs)	700	0.20	98 (avg.)
Ca below PuCl ₃ with Ca and I ₂	600	0.25	94
booster above PuCl ₃	700	0.30	98
	700	0.25	99
Simultaneous	700	0.30	100
Ca and I ₂ poured into vessel simultaneously with PuCl ₃

Another step in the simplification of the reduction step would be the elimination of the iodine boosters. Several small-scale reductions looked very promising. Yields of better than 90 percent were obtained with 25 percent excess calcium. To date, only a few 700-gram reductions have been attempted with calcium only. They were all unsuccessful.

Both mixed and non-mixed tests sometimes resulted in yields of about 50 percent. It is felt that this is a matter of proper heating. Possibly the charge can be heated slower to make the entire contents up to temperature before firing. This would help make up for the loss of heat due to omission of booster.

The impurities in the metal buttons are usually below 1000 parts per million, as shown in Table IV. There is some purification across the reduction step. As a rule, such elements as calcium, potassium, and sodium are reduced by several orders of magnitude. Molybdenum is usually reduced to zero, and most of the other elements are reduced by 50 percent.

TABLE IV

COMPARISON OF PURITY OF PLUTONIUM TRICHLORIDE
POWDER AND RESULTANT METAL

	124		130		133		165		164	
	<u>PuCl₃</u>	<u>Pu</u>	<u>PuCl₃</u>	<u>Pu</u>	<u>PuCl₃</u>	<u>Pu</u>	<u>PuCl₃</u>	<u>Pu</u>	<u>PuCl₃</u>	<u>Pu</u>
Al	3000	80	16	320	16	13	20	20	5	8
Ca	500	50	21	3	16	13	74	2	80	2
Cr	31	20	100	20	20	5	50	<50	50	<50
Cu	100	500	50	10	10	10	30	10	10	5
Fe	70	100	200	50	50	<50	100	<50	<50	114
Mg	>5000	500	100	100	50	200	60	100	50	100
Mo	-	-	25	-	2000	-	-	<10	-	<10
Mn	100	50	140	100	20	50	50	<50	20	50
Ni	300	100	200	20	200	50	400	200	450	200
Si	70	20	2000	100	20	10	25	<50	90	<50
<u>TOTAL</u>	9624	1446	3943	770	2527	435	1159	599	1119	631

Densities of metal buttons from those reductions that were considered to be normal have been in the region of 19 g/cc or above, as shown in Table V. Low densities were usually encountered when the water-insoluble material amounted to more than eight percent of the feed material.

Figure 2 shows a proposed flow sheet for the reduction of plutonium trichloride.

TABLE V

COMPARISON OF METAL DENSITIES WITH IMPURITIES
AND OTHER REDUCTION DATA

<u>Button No.</u>	<u>Total Impurities</u>	<u>% H₂O Insoluble</u>	<u>Reduction Type</u>	<u>Crucible Type</u>	<u>I₂/Pu</u>	<u>Density</u>
M-4	600		Mixed	Coated	0.25	19.27
82	350		Bottom	Coated	0.0	19.36
98	900		Split	Coated	0.30	19.17
124	1450		Bottom	Coated	0.20	17.83*
133	410		Bottom	Reusable	0.2	19.35
168	939		Mixed	MgO	0.3	19.15
174	524		Mixed	Reusable	0.3	18.6
175	415		Bottom	Reusable	0.3	19.2
179	820	15	Bottom	Reusable	0.3	17.9
180	1600	15	Bottom	Reusable	0.3	17.7
174	890	8	Bottom	Reusable	0.3	19.07

(*) High aluminum from off-standard chloride

FIGURE 2

FLOW SHEET FOR BATCH REDUCTION OF PLUTONIUM TRICHLORIDE