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PLUTONIUM METAL AND ALLOY PREPARATION BY MOLTEN CHLORIDE REDUCTION

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Introduction

The pressure vessel or "bomb" method of preparation of plutonium metal (1, 2, 3) was first introduced in 1945. Plutonium fluoride is mixed with excess calcium and a "booster" of calcium and iodine and heated in a ceramic crucible in a sealed pressure vessel to convert the plutonium to the metallic form. This method of metal production continues to be used quite successfully at the present time. It is less well known that plutonium trichloride was reduced with good yields by the same technique during the 1945 process development. The tetrafluoride was chosen for routine metal production in preference to the chloride because yields were slightly higher in the fluoride system and because the chloride absorbed water much more rapidly. The presence of water during reduction of the salt significantly reduces the yield. Other methods of plutonium metal production have been demonstrated, but none have received wide acceptance as has the bomb reduction of the fluoride.

Two significant problems are encountered in use of the plutonium tetrafluoride reduction. One of these is the large number of neutrons generated by the alpha-neutron reaction which occurs when alpha particles from plutonium decay interact with fluorine atoms to form neutrons. The second problem is one of omission, i.e. no purification of the plutonium is achieved by the process.

There were several reasons for the work on reduction of plutonium chloride from molten salts reported here. The first goal was development of a chloride procedure to supplant the fluoride system and its neutron problem. Another goal was development of a system that did not require a pressure vessel. A third goal was selection of another reductant or procedure which would produce a reasonably high yield of plutonium metal but not reduce some of the more reactive impurities. Other goals were operation at lower tempertures, and simultaneous preparation of alloys during reduction.

Thermochemical Considerations

As a first approximation, one may predict equilibrium concentrations and energy release of a chemical reaction by comparing the free energies of formation of the reactants and the products. Table I is a list of approximate free energies of formation of compounds encountered in reduction of plutonium, either as reductants or impurities. It can be seen from values listed in this tabulation that the reduction of plutonium tetrafluoride by calcium will result in release of much more energy (37 kcal/g-atom of fluorine) than will the reduction of the chloride by calcium (19 kcal/g-atom of chlorine). Thus, while the fluoride reaction must be conducted in a steel pressure vessel to contain this vigorous reaction, a less sturdy container will contain the chloride reduction.

Comparison of free energies of formation of the fluorides of calcium, magnesium, plutonium and rare earth metals leads one to the conclusion that calcium will reduce magnesium and the rare earths if present in the plutonium-tetrafluoride, while magnesium used as a reductant should reduce plutonium to the metal, leaving rare earths in the salt phase. Similarly, one would predict partial reduction of plutonium from the chloride by magnesium, while rare earth impurities should remain in the salt phase. It might also be speculated that reduction of plutonium from a molten salt, leaving active metal impurities in the salt phase, can be accomplished by adding a slightly substoichiometric amount of reductant.

One may pursue similar lines of reasoning in selecting a container material for reductions from fused salts. Ceramic crucibles are often used for such active metal reductions, and one should select the most stable material available as a container. It can be seen from Table I that the most stable oxides are those of calcium and thorium, but calcium oxide ceramics deterioriate if exposed to moist air, and thorium oxide is a source of thorium impurity which is very difficult to separate from plutonium. In summary, free energies of formation are useful in the selection of reactants and containers, but many other factors must also be considered.

Experimenta Procdures

All of the experimens described here are reductions of plutonium trichloride either as the pure molten salt, in solution with molten sodium chloride, or in lithium chloride-potassium chloride eutectic. The reductants used were sodium, calcium, magnesium, lanthanum or cerium. The apparatus used for all reductions is shown in Fig. 1. It consisted of a quartz furnace tube (50 mm diam) that was closed at the top by a neoprene stopper penetrated by a quartz thermocouple well, a tube for evacuation and backfilling with argon, and a quartz reductant addition tube. When granular calcium was used as reductant, it was contained in the rotatable side arm of this tube so it could be added gradually. In those cases where the energy release was small, the reductant addition tube was replaced by a molybednum rod (0.0625 in. dia) that was used to suspend a bar of reductant metal. At the desired reaction temperature, the rod was advanced through the stopper penetration to add the reductant to the molten salt in the crucible.

Three different crucible materials were used. Reductions performed in tantalum gave the best yields of coalesced plutonium, but the product could be recovered only by leaching away the salt and excess reductant with water or dilute nitric acid, followed by dissolution of the plutonium with hydrochloric acid. Magnesium (10% titania) crucibles were satisfactory for most reductions and had the attractive feature of allowing mechanical separation and recovery of salt and metal

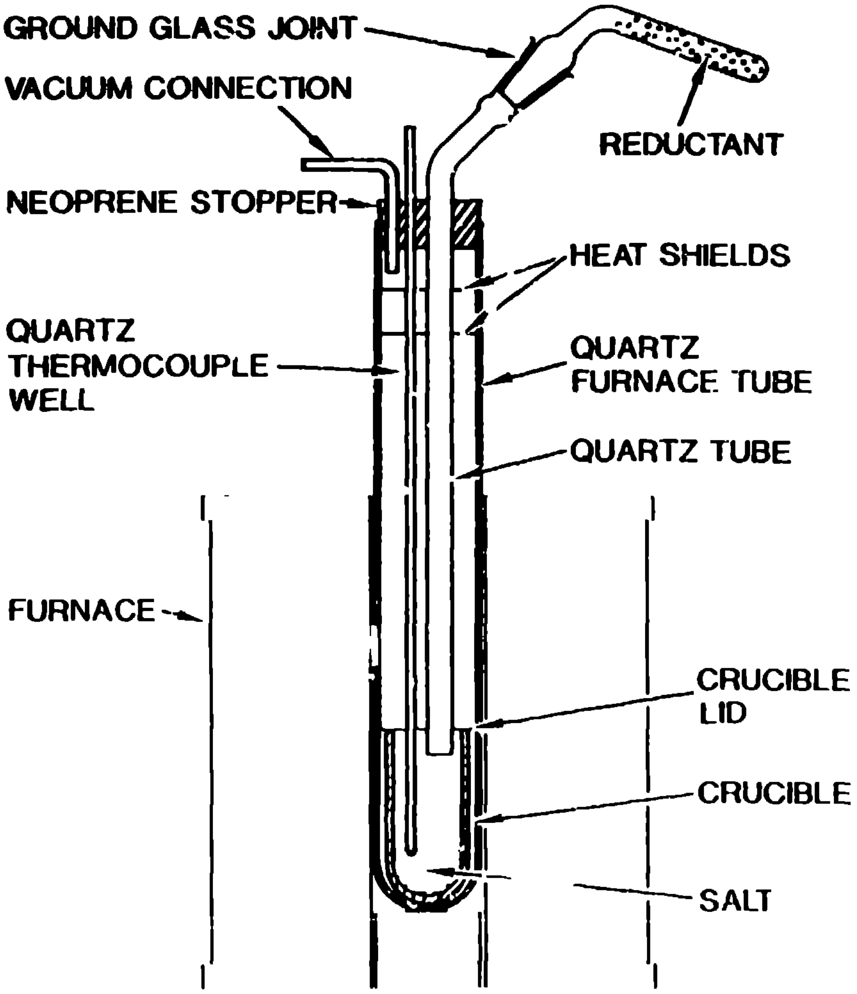

Figure 1. Apparatus used for reduction of plutonium chloride in molten salts on the 5-20 g scale.

products. Plutonium yields were generally slightly lower for reductions performed in these crucibles because of formation of small metal beads and an occasional "grey salt" phase. Quartz crucibles were generally found to be unsatisfactory because of reaction with the reductant or product.

To perform reductions, the salt containing 10-20 g plutonium in the form of the chloride was placed in a crucible which had been previously outgassed in-vacuo at the anticipated reduction temperature. The loaded crucible was quickly transferred to the quartz furnace tube, and the tube was closed and evacuated. When the reductant addition sidearm was to be used, the furnce tube was filled with argon, the sidearm removed, loaded with reductant, replaced, and the system was again evacuated. The furnace tube was placed in the resistance-heated furnace and evacuation was generally continued until the salt was molten. Evacuation was then discontinued, argon was admitted to a pressure slightly below ambient, and heating was continued until the desired reduction temperature (up to 850°C) was reached. The reductant was then either added slowly in the case of high energy release reactions, or quickly for low energy release reactions. The system was held at this temperature for a few minutes and the furnace power was then switched off. One notable departure from this procedure was the reduction with sodium. In that case the sodium and salt were mixed in the curcible at room temperature and then heated.

Plutonium trichloride was prepared by hydrochlorination of the hydride (4). Great care was exercised to limit exposure of the salt to air during handling and storage. Analytical reagent grade chlorides of sodium, potassium, lithium, lanthanum, and cerium were dried by heating in-vacuo before mixing with plutonium chloride. The desired mixtures of the salts were slowly heated to melting under flowing hydrogen chloride in quartz crucibles. The molten salts were sparged with hydrogen chloride for times of up to one hour, then sparged brifely with argon, and filtered through sintered quartz filters (5). Salts prepared in this way were stored under argon in desiccators until needed for use.

The reductants were added in a variety of shapes. Calcium was used as granules and as rods having diameters in the range of 3 mm to 10 mm. Sodium was introduced as cubes measuring approximately 1 cm on each edge. Lanthanum and cerium were used as bars having cross sections of about 5 mm by 5 mm. Magnesium and cerium-cobalt alloys were used as rods with diameters of about 5 mm. Surfaces of the bars and rods were cut under argon to remove any discoloration or oxide coating.

Qualitative Results

Qualitative evaluations of results of reduction experiments are listed in Table II. Reductions by granular calcium gave generally good results, but the addition of a calcium rod suspended by a molybdenum rod could not be controlled exactly enough to prevent severe spattering of the salt and cracking of ceramic crucibles. Reductions by sodium produced plutonium metal powder and some small shot. Magnesium reductions of plutonium chloride-20 wt% sodium chloride containing lanthanum and cerium chlorides having $LaCl_3/PuCl_3$ and $CeCl_3/PuCl_3$ mole ratios of about 0.03 proceeded quietly, but gave plutonium yields of only about 33% when only a slight excess of magnesium was used. When 240% excess mangesium was used, about 62% of the plutonium was reduced. Relative lanhanum and cerium concentrations in the metal product were lower than in the original salt by factors of 10 to 100. Lanthanum reductions proceeded smoothly and produced good yields with some separation of cerium from plutonium. Cerium and cerium-cobalt alloy reductions proceeded smoothly and produced good yields of alloys with plutonium.

Quantitative Evaluation of the Most Promising Reductions

Results of the reductions by granular calcium are shown in Table III. In reductions 1-1 through 1-5 the salt which was reduced was pure plutonium trichloride. These results are taken as an indication that the pure trichloride can be reduced to produce acceptable yields by reduction with 25% excess calcium if the reduction temperature is maintained high enough. The temperature of this system must be maintained well above the melting points of $PuCl_3$ (769°C) and $CaCl_2$ (782°C) long enough for the plutonium to coalesce into a regulus or button. The low yield of reduction 1-5 is probably due to the low maximum temperature. In reductions 2-1 through 2-9 the plutonium was put into the system as a mixture (premelted and filtered as a molten salt solution) of plutonium trichloride with 20 wt% sodium chloride. The eutectic temperature in this system is 450°C and the liquidus is about 480°. The liquidus of the product of reduction (calcium chloride-sodium chloride) is about 520°C. These low liquidus temperatures allow reductions to be conducted at much lower temperatures. This is shown by the good yield of reduction 2-1.

Reductions 2-6 through 2-9 show the results of reduction of plutonium chloride-sodium chloride by addition of near-stoichiometric amounts of calcium. The yields are seen to be very poor. This indicates reduction of the chloride by addition of substoichiometric amounts of calcium in an attempt to separate plutonium from impurities will not be a viable process.

Table IV shows the results of reduction of plutonium chloride (20 wt% sodium chloride) by suspending a bar of lanthanum in the molten salt at temperatures and for times listed here. The yields may be acceptably high for a process that gives a good separation from impurities such as cerium and americium, but recovery of the remaining plutonium from the salt would require significant effort. The decontamination factors for cerium in reductions 3-3 and 3-4 are of interest for separation of plutonium and rare earth fission products. It is also interesting to note that although excess lanthanum was suspended in the molten salt, the concentration of this metal in the plutonium product is only 0.13 wt%.

The results of reduction of plutonium trichloride (20 wt% sodium chloride) by heating with cerium to 675°C are shown in Table V. The low yield of reduction 4-3 is thought to have been caused by use of a lower temperature of reaction (655°C). Since cerium readily alloys with plutonium, it is not likely that high plutonium yields can be achieved in this system unless a product containing several per cent of cerium is acceptable. Lanthanum trichloride was present in the salt put into the reduction at concentrations sufficient to produce concentrations of 3-5 wt% in the metal product if it were reduced. The decontamination factors observed are of a magnitude that is of interest in processes used to separate plutonium from rare earths at this concentration level.

Results of reductions of plutonium chloride (20 wt% sodium chloride) by addition of a cerium-12.1 at % coblat alloy are shown in Tale VI. The goal of these reductions was to prepare a 20 at % plutonium-67.5 at % cerium-12.5 at % cobalt alloys in reductions 5-1 through 5-3 and a 50 at % plutonium-37.5 % cerium-12.5 at % cobalt alloy in redaction 5-4. The results of these reductions idicate the process may be feasible.

Summary

Satisfactory reduction of molten plutonium trichloride (pure and in combination with 20 wt% sodium chloride) by calcium, lanthanum, and cerium has been demonstrated on the 10-g scale. The yields were satisfactory for this scale of operation and it is indicated that these reductions may be useful for large scale operations.

Significant separations of plutonium from rare earth impurities was demonstrated for lanthanum and cerium reductions. Preparation of plutonium-cerium and plutonium-cerium-cobalt alloys during reduction was also demonsrated.

TABLE I

FREE ENERGIES OF FORMATION ON SELECTED FLUORIDES CHLORIDES, AND OXIDES AT 1000 K

(Values stated in kcal per gram-atom of anion)

Fluoride	-ΔF	Chloride	-ΔF	Oxide	ΔF
CaF_2	125	KCl	81	CaO	127
LiF	122	$CaCl_2$	78	ThO_2	123
LaF_3	121	NaCl	76	Ce_2O_3	122
CaF_2	120	$LaCl_3$	67	BeO	120
NaF	112	$CeCl_3$	66	MgO	118
MgF_2	111	$PuCl_3$	59	Al_2O_3	109
PuF_3	107	$MgCl_2$	58	Pu_2O_3	109
AlF_3	89	HCl	24	SiO_2	83
PuF_4	88	$CoCl_2$	23	H_2O	46

TABLE II

QUALITATIVE RESULTS OF REDUCTION EXPERIMENTS

Salt	Reductant	Result
$PuCl_3$(100%)	Ca, granular, 25% excess	(1)
$PuCl_3$-20 wt% NaCl	Ca, granular, 25% excess	(1)
	Ca, granular, no excess	(2)
	Ca, rod, 5 mm diam	(3)
	Na	(4)
	Mg	(5)
	La	(6)
	Ca	(7)
	Ce-Co	(7)
$PuCl_3$-65 wt% (LiCl-KCl)	Na	(4)
$PuCl_3$-NaCl-$CoCl_2$	Ce	(7)

RESULTS:

(1) High yield of coalesced Pu metal

(2) Poor yield, but significant separation of Pu from La and Ce

(3) Poor yield; reaction very difficult to control

(4) Poor yield; Pu product was a powder

(5) Very low yields; significant separation of Pu from La and Ce

(6) Good yields; significant separation from Ce; low La conc in Pu

(7) Good yields of binary or ternary alloys.

TABLE III

RESULTS OF REDUCTION OF PLUTONIUM TRICHLORIDE BY CALCIUM

No.[a]	Pu, g	Ca Excess	Crucible[b]	Ca Addition Temp, °C[c]	Max T, °C	Pu Yield, %	Remarks
1-1	25	25%	Ta	773-850	850	100	
1-2	11	25%	Ta	770-790	855	93	
1-3	17	25%	$MgO-TiO_2$	757-785	850	95	
1-4	16	25%	$MgO-TiO_2$	745-780	840	93	
1-5	22	25%	$MgO-TiO_2$	770-804	804	69	d
2-1	13	25%	Ta	700-715	715	99	e
2-2	10	25%	Ta	700-745	720	92	e
2-3	20	25%	$MgO-TiO_2$	520-565	860	99	
2-4	9	25%	$MgO-TiO_2$	575-590	850	99	f
2-5	12	25%	$MgO-TiO_2$	25	830	95	g
2-6	19	-1%	$MgO-TiO_2$	515-650	815	74	h
2-7	18	7%	$MgO-TiO_2$	530-575	855	76	h
2-8	13	-2%	Ta	700-735	850	76	
2-9	12	0%	Ta	690-730	955	64	

Notes:

a. The salt for Series 1 was 100% $PuCl_3$ and that for Series 2 was 80 wt% $PuCl_3$ 20 wt% NaCl.

b. The $MgO-TiO_2$ crucibles were 90% MgO-10% TiO_2.

TABLE III Notes Continued

c. The temperature range is due to heating by the energy released during reaction.

d. A metal fog was observed in the product salt. It probably was due to the low maximum system temperature.

e. The Pu product was analyzed for Ca and Ta. Results: 0.02% Ta; 0.12% Ca.

f. The Pu product was analyzed for Ca, Mg and Ti. Results: 0.01% Ca; 0.02% Mg; 0.1% Ti.

g. The calcium and salt were mixed at room temperature and heated.

h. Salts for batches 2-8 and 2-9 contained sufficient $LaCl_3$ and $CeCl_3$ to form a Pu metal product containing 3.2 wt% of each. The Pu metal was found to contain >0.07% La and 0.02% Ce in Reduction 2-6, and 1.1% La and 1.6% Ce in Reduction 2-7.

TABLE IV

RESULTS OF REDUCTION OF PLUTONIUM CHLORIDE BY LANTHANUM

					Conc. in Button, Wt%		
No.	Pu, g	$CeCl_3$, Wt %	Time at 700°C, Min.	Pu Yield %	La	Ce	Ce[a] DF
3-1	14	0	15	91	<0.007	---	--
3-2	20	0	25	90	0.27	---	--
3-3	15	3.5	35	94	0.09	0.38	10
3-4	17	2.3	35	95	0.17	0.09	27

[a] The decontamination factor (DF) for Ce is the Ce/Pu ratio in the salt divided by the Ce/Pu ratio in the metal product.

TABLE V

RESULTS OF REDUCTIONS OF PLUTONIUM TRICHLORIDE - 20 WT% SODIUM CHLORIDE BY CERIUM

No.	Pu, g	Pu Yield %	Button Comp[a] Ce, Wt%	Button Comp[a] La, Wt%	La[b] DF
4-1	15	93	27	<0.08	>35
4-2	18	91	16	2.09	50
4-3	19	88	14	0.04	116
4-4	16	90	1.1	<0.04	>750
4-5	16	90	2.6	<2.6	>240

[a] The remainder of the button was plutonium.

[b] The lanthanum decomination factor (DF) is the La/Pu ratio in the original salt divided by this ratio in the button produced.

TABLE VI

RESULTS OF REDUCTIONS OF PLUTONIUM TRICHLORIDE - SODIUM CHLORIDE BY CERIUM-COBALT ALLOYS

No.	Pu, g	Max Temp, °C	Time at Temp, Min	Pu Yield, %	Button Comp, at%		
					Pu	Ce	Co
5-1	7	775	5	98	20.7	66.6	12.7
5-2	6	560	40	97	19.8	67.4	12.8
5-3	7	645	10	93	19.5	67.8	12.8
5-4	16	715	15	93	49.3	37.8	12.9

Literature Cited

1. Baker, R. D., "Preparation of Plutonium Metal by the Bomb Method," Los Alamos report LA-473 (1946).
2. Maraman, W. J.; and Baker, R. D. in *Plutonium 1960* (E. Grison, W. B. H., Lord, and R. D. Fowler, eds.), pp. 202-215, Cleaver-Hume Press, Ltd., London (1961).
3. Baker, R. D.; and Maraman, W. J., in *Extractive and Physical Metallurgy of Plutonium and Its Alloys* (W. D. Wilkinson, ed.), pp. 43-74, Interscience Publishers, New York (1960).
4. Reavis, J. G.; Johnson, K. W. R.; Leary, J. A.; Morgan, A.N.; Ogard, A. E.; and Walsh, K. A. in *Extractive and Physical Metallurgy of Plutonium and Its Alloys* (W. D. Wilkinson, ed.), pp 89-100, Interscience Publishers, New York (1960).
5. Bjorklund, C. W.; Reavis, J. G.; Leary, J. A ; and Walsh, K. A., J. Phys. Chem. 63, 1959, 63, 1774-1777.