IE JAN 19 1971

ARH-SA- 72

CONF-101103--6

MASTER

A PYROCHEMICAL PROCESS
FOR THE REDUCTION OF
PLUTONIUM DIOXIDE TO METAL

R.E.FELT

MAY, 15, 1970

This Document was Prepared Under
AEC Contract AT (45-1)—2130

Atlantic Richfield Hanford Company
Richland, Washington

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

A PYROCHEMICAL PROCESS FOR THE
REDUCTION OF PLUTONIUM DIOXIDE TO METAL

Rowland E. Felt

Plutonium Process Engineering Section
Operations Support Engineering Department
Chemical Processing Division

ATLANTIC RICHFIELD HANFORD COMPANY

Richland, Washington

May 15, 1970

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or 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.

ABSTRACT

A pyrochemical process has been developed for reducing plutonium dioxide directly to metal with calcium and a salt flux. Direct oxide reduction eliminates several intermediate processing steps which generate waste streams requiring further processing. Waste recovery is nearly eliminated by this method of producing plutonium metal. The process has been demonstrated by producing 2,000 grams of plutonium metal. Further equipment development is required to make the process operational.

A PYROCHEMICAL PROCESS FOR THE REDUCTION OF PLUTONIUM DIOXIDE TO METAL

INTRODUCTION

The processes for producing plutonium metal have remained relatively unchanged for over 20 years. The conversion chemistry from nitrate to metal is well known, and few improvements have been made in the production processes.

Most plutonium metal production involves three basic steps: (1) conversion of purified plutonium nitrate to oxide, (2) fluorination of the oxide, and (3) reduction of the fluoride to metal with calcium. Elimination of Step 2, fluorination, by directly reducing oxide to metal would be a significant improvement. Fluorination with HF gas is a constant source of equipment and operating difficulty, and causes a significant release of neutrons by (α , n) reaction with fluorine. This creates an avoidable exposure of personnel to radiation.

A second source of concern is the cost of recovering the plutonium from waste streams generated by the current metal production process. Recovery of these wastes is a sizable contributor to the total cost of plutonium metal production. Thus, there is an economic incentive to look at new processes which would reduce or eliminate these expensive waste streams.

SUMMARY AND CONCLUSIONS

A new and different pyrochemical process has been developed for directly reducing plutonium dioxide to metal. The process permits semicontinuous production of plutonium metal with

plutonium dioxide and calcium as the starting materials. The advantages of this new process are: (1) the elimination of the oxide-fluorination step, (2) almost complete elimination of all waste recovery requirements, (3) a compact process requiring less equipment and maintenance, and (4) lower personnel radiation exposure.

The process has been demonstrated in the laboratory by producing over 2,000 grams of high-purity plutonium metal. Equipment for utilizing the process on a plant production-scale has been designed and is currently being installed. An economic evaluation of the effect of such a process on future operations was made and found to be favorable.

DISCUSSION

ECONOMIC INCENTIVES

Replacement of the existing metal production process cannot be justified without significant improvements in safety, ability to meet future needs, or operating costs. Since the current process is relatively safe, and future needs can be only anticipated, the justification for a new process must rest on current operating cost considerations. The uncertainty of future needs requires process versatility for handling a wide range of anticipated requirements.

A comparison of the current oxalate precipitation-bomb reduction process used at Hanford with the proposed pyrochemical oxide reduction process is shown in Figure 1, page 3. The most significant differences are the reduction in processing steps, and elimination of waste streams.

The waste streams generated by the current process are:

- Filtrate from plutonium oxalate precipitation step.
- Filter sweepings from the fluorinator off-gas filter.

FIGURE 1

PLUTONIUM METAL PRODUCTION

- Slag, crucible, and sand from the bomb reduction step.
- Pickling solution from the metal button pickling step.

The contribution of each waste stream to the overall recovery cost is debatable because of the differences in recovery modes. It is currently estimated that 20 to 30 percent of the capacity of the Plutonium Reclamation Facility at Hanford is required to handle current waste streams of the plutonium metal production facilities.

The pyrochemical process has no significant waste streams. The waste salt from the process contains the calcium oxide by-product and trace quantities of plutonium. The plutonium concentration in the salt could be small enough to permit disposal as contaminated waste rather than recover the plutonium.

The new process could use plutonium dioxide from two different sources. The oxalate precipitation process could be used for nitrate requiring additional purification. A direct denitration process to calcine nitrate directly to oxide in a screw calciner could be used on nitrate feed meeting necessary purity specifications.⁽¹⁾ Either of these processes could also be used to produce oxide, if necessary. This provides much of the versatility which future business needs will likely require.

PREVIOUS WORK

A logical extension of the bomb reduction of plutonium tetrafluoride with calcium and iodine was the reduction of plutonium dioxide in a like manner. Table I, page 5, shows a comparison of the heat of reaction, bomb ignition temperature, and slag melting point for several plutonium reduction reactions.⁽²⁾

The oxide slags have a higher melting point and result from a lower heat of reaction than do the fluoride slags.

TABLE I
REDUCTION OF PLUTONIUM COMPOUNDS TO METAL

Reduction Reaction	Heat Released (ΔH) Cal/Mole Of Plutonium	Ignition Temp C	Melting Temp C
$\text{PuF}_4 + 2\text{Ca} \rightarrow \text{Pu} + 2\text{CaF}_2$	149.5	600	1330
$\text{PuF}_4 + 0.2\text{I}_2 + 2.2\text{Ca} \rightarrow \text{Pu} + 0.2\text{CaI}_2 + 2\text{CaF}_2$	175.2	400	1320
$\text{PuO}_2 + 2\text{Ca} \rightarrow \text{Pu} + 2\text{CaO}$	52.4	900	2572

Because the heat of reaction is insufficient to melt the slag and allow the melt to consolidate, the bomb reduction procedure with plutonium dioxide yields finely-divided plutonium metal powder. Thompson tried reducing oxide directly with calcium, barium, and aluminum with various salt fluxes, but reported such reductions to be "impractical."⁽³⁾

The first demonstrated preparation of plutonium metal by oxide reduction was made by Knighton and Steunenber.⁽⁴⁾ Their process was a result of extensive work aimed toward developing a pyrochemical process for separating plutonium, uranium, and fission products of spent nuclear reactor fuels. Plutonium dioxide was reduced by a molten magnesium-zinc alloy in the presence of fluxes composed of alkali and alkaline earth halides. The most satisfactory reductions were obtained at 800 C with a magnesium concentration of about 10 wt percent in the liquid metal phase. Plutonium metal was produced by removing the magnesium and zinc using vacuum distillation.

The choice of salt flux affected the equilibrium distribution of plutonium between the salt and metal phases. A magnesium salt (MgCl_2 or MgF_2) was always a component of the salt flux; therefore, a small quantity of plutonium remained

in the salt flux as plutonium chloride, as illustrated by the metal-salt reaction

The quantity of plutonium chloride or plutonium fluoride remaining in the salt flux was controlled by the magnesium concentration in the zinc alloy. The distribution coefficient

$$K_D = \frac{\text{wt } \% \text{ Pu in flux}}{\text{wt } \% \text{ Pu in metal}}$$

is approximately 1×10^{-2} for a 10 percent Mg-Zn alloy.

The author made an improvement on this basic process by eliminating the magnesium salt from the flux.⁽⁵⁾ A salt flux of LiCl, NaCl, KCl, and NaF resulted in complete plutonium dioxide reduction to the metal phase. The system is not dependent on the magnesium concentration in the reducing alloy--therefore, alloys of 80 percent magnesium-20 percent zinc can be used. This results in more plutonium being reduced per unit mass of alloy, so there is less zinc and magnesium to remove from the plutonium in the distillation step. This process was developed and demonstrated on a kilogram-scale.

A more recent oxide reduction process which combines the features of bomb reduction with metal-salt extraction was developed by Wade and Wolf.⁽⁵⁾ The process consists of bomb-reducing plutonium dioxide with calcium in a heated tungsten vessel. The resulting fused oxide-metal "clinker" is then contacted with molten calcium chloride at 1000 C. The calcium chloride dissolves the calcium oxide formed by the reduction. The excess calcium floats to the top of the salt flux, leaving molten plutonium in the bottom of the vessel. Agitation of the oxide "clinker"-salt mixture was found to be essential for the salt flux to dissolve the calcium oxide. Several equipment designs evolved from experimental difficulties, but no tests were made with the plutonium reduction apparatus which evolved from the experiments. Mechanical design and materials of

construction are still to be demonstrated.

Several attempts were made to substantiate the process of Wade and Wolfe as a workable process rather than an experimental result. The attempts were largely unsuccessful because of equipment problems.⁽⁷⁾ The major problem areas are considered to be:

- An operating temperature of 1000 C.
- Poor plutonium metal coalescence.
- Insufficient agitation of the molten mixture.
- Complex equipment design.

A workable process should result if these difficulties could be overcome.

SALT SYSTEMS

The role of the salt system in a pyrochemical reduction reaction is not always obvious. The salt flux should have most of the following properties:

- A melting point equivalent to the metal system.
- No retention of plutonium in any form.
- No reaction with the metal system to form new compounds.
- Low viscosity to permit plutonium metal to separate by density difference.
- Ability to dissolve or suspend the oxides formed by the reaction without becoming too viscous.
- Ability to wet the plutonium dioxide.
- The reducing metal must be partially solubilized to improve the reaction rate.

The system chosen for this process was the salt eutectic CaCl_2 , 20 mole percent CaF_2 .⁽⁸⁾ The data for this system are

shown in Table II.

TABLE II
SALT SYSTEM PROPERTIES (9)

	<u>CaCl₂</u>	<u>CaF₂</u>	<u>(CaCl₂, 20 mole % CaF₂)</u>
Melting point, C	782	1418	650
Density, g/cc: solid	2.15	3.18	2.32
molten (800 C)	2.07	-	2.19
Viscosity, cp (800 C)	12	-	12
Calcium solubility, mole % (800 C)	1.1	-	1-2
Calcium oxide solubility, mole % (800 C)	13	-	13.7

The calcium oxide solubility in the salt flux was reported by Argonne as 13.7 percent at 800 C, as shown in Figure 2, page 9.⁽¹⁰⁾ Measurements by the author verified this value, but also showed the formation of a material which was not soluble, but existed as a colloidal suspension. Further experiments showed that the addition of CaO to the eutectic salt flux lowered the melting point. At CaO concentrations greater than 25 percent, the melting point started increasing.

The quantity of salt flux required by the process is limited by the amount of CaO that can be contained without causing the flux to become so viscous as to prevent plutonium metal from settling out. The viscosity is not affected by adding CaO to the salt flux up to the solubility limit; but beyond this limit, the viscosity increases slowly. Thus, the flux containment limit is not reached until it contains approximately 25 percent oxide.⁽¹¹⁾ Above this point, the viscosity of the salt flux is sufficiently large so as to prohibit settling of the plutonium metal.

The oxide solubility and containment capability of the salt flux determines many of the system's operating parameters.

FIGURE 2
PARTIAL PHASE DIAGRAM OF THE $\text{CaCl}_2\text{-CaF}_2\text{-CaO}$ SYSTEM

Reducing the fluoride content would lower the (α , n) reactions between the salt and plutonium. A small quantity of fluoride appears to be necessary to "wet" the oxide by a mechanism not fully understood. Comparing the lower melting point of higher fluoride salts against greater oxide solubility of lower fluoride salts should produce an optimum salt composition.

An alternate salt system being considered is the CaCl_2 -23 mole % CaF_2 mixture where the oxide solubility decreases to 13 percent, but has a lower melting point of 670 C when saturated with oxide.

METAL SYSTEMS

The choice of an active metal to reduce plutonium dioxide to metal is limited to those metals which are more reactive than plutonium. These include cadmium, cerium, magnesium, strontium, lithium, aluminum, barium, and zirconium. The physical and chemical properties which constitute a good reducing metal are:

- Large, negative, free-energy of formation (ΔF) of metal oxide.
- Easy separation from or insoluble in plutonium metal.
- Limited solubility in the salt flux.
- Metal oxide compatible with the salt flux requirements.

The original fluoride reduction work considered all of these potential reductants. Calcium appeared to be the best choice, primarily because of its low melting point and the viscosity of the slag produced. For oxide reduction, none of the slags formed by any of the active metals has a sufficiently low melting point to permit plutonium metal separation from the slag. For this reason, the addition of a molten salt flux is needed to lower the reaction temperature to a workable level.

Batch reduction of oxide in a salt flux, as contrasted with the bomb-reduction technique, permits metals other than calcium to be used. The use of magnesium-zinc is a good example. However, the plutonium must be separated from the reducing metal alloy. Separation by distillation has been demonstrated with magnesium-zinc, but requires conditions of temperature and pressure that are difficult to engineer for routine production use.

The separation requirement becomes an important factor in selection of a metal reductant. Barium and calcium are both insoluble in molten plutonium.⁽¹²⁾ Since plutonium metal and calcium metal are immiscible at all temperatures, separation of the two metals is easy and there is no alloy formation. The density of plutonium (19.7 g/cc) and calcium (1.55 g/cc) span the nominal density of any molten salt flux (2 to 2.5 g/cc). This permits the salt flux to act as a separation barrier through which the plutonium metal sinks as it is produced, while the calcium remains dissolved in or floating on the salt.

Calcium metal also has a limited solubility in the salt flux, which is a definite advantage. Reaction between calcium and plutonium oxide suspended in the salt flux is much more rapid if the calcium is dissolved in the flux. Slow reaction rates occur if physical interface contact is required between a coalesced metal phase and the suspended oxide in the salt phase. Physical mixing becomes very important when such interface contacting is required. By dissolving calcium in the salt flux, the reaction rate is almost instantaneous and is not limited by interface fouling and mixing problems.

The solubility of calcium in the salt flux does, however, present potential control problems. At 800 C, the solubility is approximately 1 to 2 percent. The viscosity of the salt flux increases rapidly as the metal solubility limit is

approached. Thus, excess calcium added to the process would produce a highly-viscous melt and cause non-coalescence of the plutonium metal.

REDUCTION PROCESS

The newly-developed reduction process shown in Figure 3, page 13, efficiently produces coalesced plutonium metal from plutonium dioxide at 800 C within the solubility and viscosity limitations noted above. The experimental tests have demonstrated a workable combination of operating parameters as summarized in Table III, page 14.

The plutonium dioxide is added to the calcium chloride-20 mole percent calcium fluoride salt flux at 800 C to a concentration of 20 weight percent. The salt flux becomes viscous and difficult to stir at any higher concentrations. Solid granules of calcium metal are then added to the plutonium dioxide-salt mixture at a controlled rate. The calcium readily dissolves in the flux with slight agitation, and immediately reacts with the suspended plutonium dioxide. The temperature of the melt increases because of the exothermic reaction between the dissolved calcium and suspended plutonium dioxide.

Agitation is not an important factor in this process. Because the calcium readily dissolves in the salt flux, the vigorous agitation typical of solid-liquid contact operations is not required. Non-dependence on mechanical stirring is a significant benefit because of a reduction of corrosion and containment materials problems.

Sufficient calcium is added to the melt to reduce the plutonium dioxide completely. Because viscosity increases rapidly, it is important to keep excess calcium to a minimum. Additional plutonium dioxide charges can be added to the system with the same concentration constraint as the first charge. When the reductions have been completed, a small

FIGURE 3
PYROCHEMICAL REDUCTION PROCESS
FOR PRODUCING PLUTONIUM METAL

TABLE III
EXPERIMENTAL TEST RESULTS

Test No.	Metal Phase g		Salt Phase g		Temp C	Plutonium g		Metal Yield %	Test Conditions	Observations
1	Ca	5	CaCl ₂	15	1000	PuO ₂	5	32	PuO ₂ added to molten system using MgO-TiO ₂ crucible	Gas evolved, Ca badly oxidized.
2	Ca	5	CaCl ₂	26.5	1000	PuO ₂	10	-	Components layered, PuO ₂ on CaCl ₂ on Ca	PuO ₂ blown out of crucible by gases evolved.
3	Ca	5	CaCl ₂	30	1000	PuO ₂	10	77	PuO ₂ added to molten system	Gas evolved.
4	Ca	10	CaCl ₂	20	1000	PuO ₂	16	-	PuO ₂ added to molten system	Poor metal coalescence.
5	Ca	130	CaCl ₂ -20% CaF ₂	300	1000	PuO ₂	100	-	PuO ₂ added to molten system	Metal coated on crucible walls.
6	Ca	200	CaCl ₂ -20% CaF ₂	500	1000	PuO ₂	110	-	PuO ₂ added intermittently	Poor metal coalescence.
7	Ca	200	CaCl ₂ -20% CaF ₂	500	970	PuO ₂	118	-	Ta crucible--PuO ₂ added intermittently	Oxide reduced but metal did not coalesce. Apparent viscosity problem.
8	Ca	200	CaCl ₂ -20% CaF ₂	500	1000	PuO ₂	114	-	Ca added to molten salt, PuO ₂ added to molten system	Viscous melt--reason for high viscosity unknown.
9	Ca	41	CaCl ₂ -20% CaF ₂	750	800	PuO ₂	114	60	PuO ₂ mixed with salt, Ca added to molten system	Improved viscosity and metal coalescence.
10	Ca	48	CaCl ₂ -20% CaF ₂	750	800	PuO ₂	130	94	Ditto 9 except MgO-TiO ₂ crucible	Clean metal button, good coalescence. White smoke evolved.
11	Ca	100	CaCl ₂ -20% CaF ₂	600	800	PuO ₂	300	97	Ditto 10	
12	Ca	100	CaCl ₂ -20% CaF ₂	1200	800	PuO ₂	300	-	Ditto 10	Viscosity problem due to large PuO ₂ loading.
13	Ca	60	CaCl ₂ -20% CaF ₂	1200	800	PuO ₂	170	90	Ditto 10	
14	Ca	100	CaCl ₂ -20% CaF ₂	1200	800	PuO ₂	300	99	Ditto 10 but alternated Ca and PuO ₂ additions	System is working!
15	Ca	300	CaCl ₂ -20% CaF ₂	1400	800	PuO ₂	500	100	Ca and PuO ₂ additions ditto 14	System is working!
16	Ca	300	CaCl ₂ -20% CaF ₂	1400	800	PuO ₂	500	100	Ditto 15	System is working!

amount of excess calcium is added to assure complete reduction. The individual batch size is limited by the calcium oxide containment capability of the salt flux. The accumulated plutonium content from several reductions is limited by criticality considerations.

The salt flux containing calcium oxide is syphoned from the tungsten reduction crucible to a tungsten salt contacting vessel where it is treated with a calcium-30 percent zinc alloy. Any unreduced plutonium dioxide carried over by the salt flux is reduced during this second contact. The spent salt flux carrying the calcium oxide from the system can then be disposed of since it normally contains less than 0.1 percent of the plutonium added to the system. The plutonium concentration in the salt phase ready for discard is approximately 0.06 percent plutonium.

The calcium-30 percent zinc reducing alloy accumulates the small quantities of plutonium from the waste salt. When the plutonium concentration builds up to a 5 percent concentration, the alloy is syphoned to a metal distillation apparatus where the zinc and calcium are distilled from the plutonium. The metal distillate is recycled to the salt contacting vessel for further use. The plutonium metal product is incorporated with the primary metal product if it meets purity specifications.

The plutonium metal created by the reduction reaction forms into drops and settles to the bottom of the reduction crucible. From there, it is syphoned to a tantalum receiver vessel. The plutonium metal is allowed to cool and solidify in the receiver. An inert atmosphere of argon is maintained in all process vessels because of the reactive nature of plutonium and calcium. A solid ingot of plutonium metal is removed from the receiver and packaged for storage or shipment. The metal product should contain the same impurities as the

initial oxide feed; the process does not contain an impurity removal mechanism, and high-purity calcium and flux materials can be specified. The purity of oxide feed and metal product from several reduction tests are shown in Table IV.

TABLE IV
AVERAGE PURITY OF PLUTONIUM DIOXIDE FEED AND METAL PRODUCT*
ppm

	<u>Al</u>	<u>Ca</u>	<u>Cr</u>	<u>Fe</u>	<u>Mo</u>	<u>Ni</u>	<u>Si</u>	<u>Ti</u>	<u>C</u>
Oxide Feed	200	10	100	590	100	100	450	500	480
Metal Product	250	500	100	300	100	150	500	500	300

(*) Data from Runs 11, 14, 15, and 16 of Table III, page 14.

Equipment designs for the process have been kept simple to assure reliable operation. Shear-formed tungsten crucibles are used for all contacting operations. Tantalum or tantalum-10 percent tungsten tubing is used for plutonium transfer; stainless steel is adequate for salt transfer. The contacting vessels and receiver vessel are heated by high-frequency induction heating. The transfer lines are heated by coiled electrical heating elements. Material transfers are made by syphons controlled by the pressure in each vessel.

The unique features of the process are:

- A low temperature oxide reduction (800 C) using a salt flux and calcium.
- A liquid phase reduction process in which the calcium reductant is dissolved in the salt flux.
- The production of a coalesced metal phase with minimum agitation.
- Simple and reliable equipment designs.

The new process has been demonstrated in the laboratory by producing over 2000 grams of high-purity plutonium metal.

Equipment for utilizing the process on a plant production-scale has been designed and is currently being installed.

REFERENCES

1. R. E. Felt. *Equipment For The Direct Calcination Of Plutonium Nitrate*, RL-SEP-674, General Electric Company, Richland, Washington. December, 1965.
2. S. M. Stoller and R. B. Richards. *Reactor Handbook, Volume II, Fuel Reprocessing*, 2nd Ed., Interscience Publishers, Inc., New York. (1951).
3. M. C. Thompson. *Reduction Of Plutonium Dioxide To Plutonium Metal*, DP-893, E. I. DuPont de Nemours and Company, Savannah River Laboratory, Aiken, South Carolina. July, 1965.
4. J. B. Knighton and R. K. Steunenberg. *Preparation Of Metals By Magnesium Zinc Reduction, Part II, Reduction Of Plutonium Dioxide*, ANL-7059, Argonne National Laboratory, Argonne, Illinois. June, 1965.
5. R. E. Felt. *Plutonium Metal Production BY Magnesium Reduction Of Plutonium Dioxide*, Atlantic Richfield Hanford Company, Richland, Washington. To be published.
6. W. Z. Wade and T. Wolfe. *The Production Of Plutonium Metal By Direct Reduction Of The Oxide*, UCRL-50403, Lawrence Radiation Laboratory, University of California, Livermore, California. February 22, 1968.
7. W. D. Domning, Dow Chemical Company, Private Communication. October 23, 1968.
8. M. Ishaque. *Liquid-Solid Equilibria In The Quaternary System Containing NaCl, KCl, CaCl₂, NaF, KF, and CaF₂*, Bull. Soc. Chim Fr., pp 127-138. (1952)

9. A. Seidell. *Solubilities Of Inorganic And Metal Organic Compounds*, D. Van Nostrand Company, Inc., Princeton, New Jersey. (1940)
10. R. C. Vogel. *Chemical Engineering Division Annual Report, 1968*, ANL-7575, Argonne National Laboratory, Argonne, Illinois, p 26. April, 1969.
11. J. K. Skinner and R. E. Felt. *Molten Salt Systems For The Direct Oxide Reduction Program*, ARH-808, Atlantic Richfield Hanford Company, Richland, Washington. August 29, 1968.
12. F. W. Schonfeld, et al. *Metallurgy And Fuels*, Series V, vol. 2, p 582.
13. R. E. Felt. *Process For Producing Plutonium Metal From Plutonium Dioxide*, ARH-IR-157, Atlantic Richfield Hanford Company, Richland, Washington. February 3, 1969.