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AUTHOR(S): DAVID F. BOWERSOX, DANA C. CHRISTENSEN, JOEL D. WILLIAMS

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Los Alamos National Laboratory
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APPLICATIONS OF MOLTEN SALTS IN PLUTONIUM PROCESSING

by

DAVID F. BOWERSOX, DANA C. CHRISTENSEN,
AND JOEL D. WILLIAMS

ABSTRACT

Plutonium is efficiently recovered from scrap at Los Alamos by a series of chemical reactions and separations conducted at temperatures ranging from 700° to 900°C. These processes usually employ a molten salt or salt eutectic as a heat sink and/or reaction medium. Salts for these operations were selected early in the development cycle. The selection criteria are being reevaluated. In this article we describe the processes now in use at Los Alamos and our studies of alternate salts and eutectics.

INTRODUCTION

Pyrochemical processes are defined as nonaqueous operations conducted at elevated temperatures. Records indicate that crude methods for producing some metals existed as early as 3000 BC. Copper, silver, tin, lead gold, iron and steel were made pyrochemically by 1000 BC. Pyrometallurgy is still employed to make iron, copper, zinc and nickel; however, the modern application most similar to the plutonium process is that used to produce aluminum.

Reductions of uranium and plutonium tetrafluoride to metal were developed by R.D. Baker and co-workers during the Manhattan project (1,2). However, most recovery of plutonium has been by aqueous methods developed after World War II. In the 1950s, proposals to build metal-fueled fast reactors led to studies of pyroprocessing spent fuels. In such cases, uranium and plutonium could be purified without altering their metallic states. With adoption of the concept of oxide fuels, development of pyrochemical reprocessing was no longer emphasized. However, the results from these earlier studies were adapted into our pyrochemical scrap recovery program. The recent proposal by Argonne National Laboratory of the Integrated Fast Reactor, which utilizes a metallic fuel, includes pyrochemical processing of spent fuels and the spent blanket (3).

At Los Alamos, high purity plutonium metal is prepared from process residues by the flow diagram shown in Fig. 1. The two major process steps to produce metal (usually still impure) are direct reduction of plutonium dioxide and conversion of oxide to fluoride by hydrofluorination followed by reduction. If the americium content is high, either step is followed by molten salt extraction. The impure metal is then vacuum cast to shape and converted to high purity metal by electrorefining. The complexity of the process is increased because residues and wastes must be treated to recover all of the plutonium.

The pyrochemical research and development section at Los Alamos was formed to demonstrate an integrated scrap recovery process and, as a result of this demonstration, to provide high purity metal for other programs. In our studies, we also study methods to:

- Develop and demonstrate improved pyrochemical processes,
- Decrease waste generation while increasing productivity,
- Establish and maintain an expertise in plutonium chemistry and in pyrochemical operations, and,
- Transfer applicable technology to others in the nuclear community.

In this report, the four major steps in processing plutonium by our methods will be described. Salts and eutectics in use and promising alternatives will be discussed.

MAJOR PROCESSES

Hydrofluorination and Plutonium Tetrafluoride Reduction--In the hydrofluorination and plutonium tetrafluoride reduction process, plutonium peroxide, oxalate, or low-fired (under 800°C) oxide is converted to the tetrafluoride by hydrogen fluoride gas. Plutonium metal is produced at high pressure by the high temperature reaction between the fluoride and calcium metal. A booster, such as iodine, initiates the reaction

$$PuF_4 + Ca + I_2 \rightarrow Pu + CaF_2 + CaI_2 \qquad (1)$$

at about 600°C. While the slag residue remains molten, the more dense plutonium sinks to the bottom of the crucible, and, upon cooling, the metal solidifies into a button.

The waste streams from this process are a calcium chloride-calcium fluoride slag, the reaction crucible, and magnesia sand, (which is reused). Any plutonium remaining in the slag or crucible is recovered by aqueous processing. Off-gases from the fluorination are scrubbed and discarded.

The relatively small volume of residue and waste constitutes a major advantage of this process. Little or no purification occurs during the processing. On the other hand, no impurities are introduced from the process. Therefore, if the feed material is sufficiently pure, the product metal is satisfactory for high purity applications. Yields are usually high, varying from 97 to 99%.

The high neutron radiation field generated by the (alpha,neutron) reaction is a major disadvantage in the process because it constitutes a hazard for the personnel. The high pressure system, the high temperatures of reaction, and the highly corrosive gas are also potential hazards. Finally, high-fired, refractory oxide does not fluorinate and cannot be reduced to metal by this process.

From a long range view, a major change in this process would be replacement by a method employing plutonium trichloride as the intermediate reactant. Such a process might use controlled potential for metal separation by deposition rather than by chemical reductant. The new process would yield high-purity metal and eliminate the high radiation field.

In work at Hanford in the early sixties, the trichloride was produced and tested as an alternate processing route. However, corrosion problems and difficulty in obtaining high yields with refractory oxides led to adoption of a nitrate, aqueous system (4). We have produced plutonium trichloride from oxide on a 100 g scale and reduced the product to metal with calcium under several conditions (5).

In the pyroredox process (6), plutonium trichloride is produced in a potassium chloride melt by the reaction of zinc chloride with impure plutonium metal. The reaction is

$$2\ Pu + 3\ ZnCl_2 \rightarrow 2\ PuCl_3 + 3\ Zn. \qquad (2)$$

The zinc button, which contains the less reactive impurities, is mechanically separated from the salt and transferred to waste. The salt is then contacted with calcium to produce metal:

$$2\ PuCl_3 + 3\ Ca \rightarrow 3\ CaCl_2 + 2\ Pu. \qquad (3)$$

The impurities more reactive than calcium remain in the salt, which is discarded or recycled. The impure metal, which contains significant amounts of calcium, is further treated and electrorefined to produce high purity plutonium. This process would be applicable to lean plutonium streams; at present, it is used for recovering plutonium from spent anodes produced by electrorefining.

<u>Direct Oxide Reduction</u>-- Most scrap containing plutonium can be converted to oxide by burning in air at an elevated temperature. In the direct oxide reduction process (DOR), this oxidation is carried out at 800°C to ensure removal of carbon and organic impurities. This produces high-fired oxide which cannot be hydrofluorinated. However, the oxide can be reduced to metal in a solvent salt system by the addition of a strong reducing agent (7). In the DOR, the reaction is

$$PuO_2 + 2\ Ca \rightarrow Pu + 2\ CaO. \qquad (4)$$

The reaction begins at about 825°C in a large excess of molten calcium chloride salt. The salt melt provides both a heat sink and a solvent for the calcium oxide produced as a by-product. As shown by the phase diagram, Fig. 2, the oxide is soluble up to about 20 mol per cent (m/o) (8). The metal button, containing 97-99% of the feed plutonium, is mechanically separated from the

The fused salt block is counted to ensure a low plutonium content and discarded as low level waste. The metal button is transferred to the next processing step. The volume of spent salt is the largest residue formed in the integrated process. Studies have been shown that it can be regenerated to calcium chloride and recycled. The chloride-oxide mixture is melted and maintained at 850°C while chlorine is bubbled through the liquid melt. Under our operating conditions, the reaction:

$$Cl_2 + 2CaO,CaCl_2 \rightarrow 2CaCl_2 + O_2 \qquad (5)$$

proceeds until the salt contains less than 0.1% oxygen (9). Approximately 5 kg of spent salt is converted to usable chloride in less than two hours. The regenerated melt is purged with argon, transferred and cast for recycle.

Plutonium metal produced with the regenerated salt is comparable to that produced with first-pass salt. By recycling, very little plutonium is discarded in spent salt and residue volumes are significantly decreased. Salt has been cycled up to ten times with no detectable buildup of impurities. Yields averaged 98%. Potential waste reductions of 80% are calculated by utilizing regeneration and recycle.

The standard DOR process produces an impure button containing magnesium, which may be caused by the reaction of the magnesia crucible wall with calcium in the melt:

$$MgO + Ca \rightarrow CaO + Mg. \qquad (6)$$

This reaction can be minimized by adjusting the process parameters such as stirring rate, excess calcium, and operating temperature. Tests employing boron nitride crucibles have also been promising.

The calcium chloride salt was initially chosen, along with calcium as the reductant, because the oxide by-product is soluble in the salt. Similar solubility has been reported in the lower melting calcium chloride-calcium fluoride eutectic. We are currently comparing data such as yields from experiments employing either regenerated calcium chloride or a fluoride eutectic with the results of the reference DOR utilized in the integrated processes. Metal has been produced in the fluoride eutectic system at temperatures below the melting point of calcium. At these temperatures, reaction with the crucible wall is minimized and thus magnesium metal generation is reduced. (10). The lower temperature should also increase furnace life. The salt/metal interface is also very well delineated and salt occlusion in the metallic phase has not been observed. Additional data are being collected.

Molten Salt Extraction--The more reactive elements such as americium, the rare earths, alkali metals and alkaline earth metals can be separated from plutonium by the molten salt extraction process (MSE). A ternary salt composed of a calculated quantity of an oxidizng agent and a eutectic salt is contacted with impure metal, (11). The more reactive elements, such as americium, along with some of the plutonium, are oxidized into the salt phase. Most of the plutonium remains in the heavier metal phase, and upon cooling forms a metal button. At Los Alamos, the MSE process is employed when the americium would not be sufficiently reduced by electrorefining, (generally greater than 1000 parts per million (ppm)). Magnesium chloride is used as the oxidizing agent in a sodium chloride-potassium chloride eutectic. The major reactions are

$$2\ Am + 3\ MgCl_2 \rightarrow 2\ AmCl_3 + 3\ Mg \qquad (7)$$

$$2\ Pu + 3\ MgCl_2 \rightarrow 2\ PuCl_3 + 3\ Mg, \text{ and} \qquad (8)$$

$$Am + PuCl_3 \rightarrow AmCl_3 + Pu. \qquad (9)$$

The americium and plutonium concentrations in the salt are dependent on the amount of oxidant added, the concentrations of the elements in the impure metal feed, the operating temperature, the number of contacting stages and the mode of operation. Under our operating conditions, 90% of the americium and 1-3% of the plutonium are transferred into the salt (12). This plutonium must be recovered before the salt is discarded to waste. The relatively high americium content of the salt is a radiation hazard. The americium is potentially valuable, and, if it were recovered, the salt could be recycled.

In extractions where plutonium trichloride was substituted for magnesium chloride as the oxidizing agent, more americium was extracted (12). In addition, magnesium was not introduced by the process. The reaction is

$$3\ \mathrm{Am} + 2\ \mathrm{PuCl_3} \rightarrow 2\mathrm{Pu} + 3\ \mathrm{AmCl_2}. \qquad (10)$$

The black salt formed during the extraction has been reported as containing divalent americium (12, 13). We plan to calculate the distribution constant for this reaction as a function of concentration and temperature. The americium and plutonium in the salt will be recovered either by aqueous or pyrochemical methods; for example, by controlled potential deposition.

Casting--Impure metal buttons from DOR or MSE are collected, placed in a tantalum pour crucible, and vacuum cast to fit into the anode compartment of our electrorefining cell (13). The buttons are heated inductively under vacuum until liquid and then bottom poured into a graphite mold. Under the operating conditions, metallic impurities such as sodium, calcium and magnesium are partially volatilized. Additional magnesium and calcium evaporate and form a dark coating on the container walls during casting. Thorium, americium, alkali metals, alkaline earth and rare earth metals oxidize preferentially and remain in the pour crucible. Insoluble impurities, such as oxides, carbides and some metals, float on the melt surface and also remain in the crucible as residue. These residues are burned in air and cycled back into the recovery stream.

Experiments will test the feasibility of replacing the casting operation with either a salt extraction or distillation separation step. The extraction would be conducted in a vessel with a diameter suitable for forming a right cylinder of metal to fit in the anode cup of the electrorefining cell. Calcium chloride and various salt eutectics are being tested in extraction experiments and results, to date,are quite encouraging.

Electrorefining-- At Los Alamos, electrorefining is the major process for converting impure plutonium metal to a high purity product (14). Impure metal is placed in the anode compartment within an electrorefining cell, (See Fig. 3), and a sodium chloride-potassium chloride eutectic containing magnesium chloride is added. The cell is assembled, placed under argon, and heated. The salt eutectic serves as an electrolyte for transport of ionic species. The magnesium chloride provides plutonium ion in the electrolyte prior to electrolysis by the reaction

$$Pu + MgCl_2 \rightarrow Mg + PuCl_3. \qquad (11)$$

Current is passed through the cell and plutonium is oxidized in the anode compartment:

$$\mathrm{Pu}\ (\text{impure}, \ell) \rightarrow\ = \quad \mathrm{Pu}^{+3} + 3\,e' . \tag{12}$$

The positive ions are transported through the molten eutectic to the cathode, where reduction occurs:

$$\mathrm{Pu}^{+3} + 3\,e' \quad = \quad \mathrm{Pu}\ (\text{pure}, \ell) . \tag{13}$$

The overall reaction is

$$\mathrm{Pu}\ (\text{impure}, \ell) \quad = \quad \mathrm{Pu}\ (\text{pure}, \ell) , \tag{14}$$

and pure liquid plutonium metal collects directly below the cathode shield in the annulus between the outer cell walls and the walls of the anode compartment. The elements less active than plutonium remain in the anode compartment, combining with residual plutonium to form a solid anode heel. This spent anode must be further processed to recover plutonium.

In electrorefining, the elements more reactive than plutonium concentrate in the salt, along with trivalent plutonium and plutonium shot (believed to be small uncoalesced metal product). This salt residue is heated to 800°C with calcium present as a reducing agent. The resulting plutonium-americium-calcium button is recycled into the production stream and the spent salt is discarded.

The purity of electrorefined buttons under our operating conditions is typically greater than 99.95%, and one-pass yields range from 75-80%. The yield depends on the purity of the anode metal. The process has been used to produce high purity metal for a number of years (15).

Our research has been concentrated on developing a solvent anode such as cadmium, bismuth or lead in which the plutonium in the anode dissolves and is oxidized to depletion (16). Experiments have been quite successful with little or no plutonium remaining in the spent anode. However, at temperatures above the melting point of the sodium chloride-potassium chloride eutectic the cadmium in the anode is volatilized. Some of this metal condenses in the product, and additional cadmium is lost to the walls of the reaction vessel. In addition to experiments with lead and bismuth solvent anodes, substitutions of lower melting eutectics, such as lithium chloride-potassium chloride, are being evaluated. Operating temperatures can then be dropped into the 675-700°C range.

Magnesium chloride is used to provide trivalent plutonium in the electrolyte upon initiation of electrorefining. This eliminates some, but not all, of the generation of sodium and potassium during electrolysis. However, this step adds magnesium to the anode, which is an impurity that may interfere with the maintenance of a liquid anode. Tests show that plutonium trichloride is a suitable substitute for magnesium chloride in the cell.

Residues would be reduced by recycling the spent anode (if it is a solvent anode) and the eutectic salt. Impurities would probably build up with recycle, and a regeneration step should be evaluated. Since the cost of storage of discards and residues is escalating, such a recycle could be quite beneficial.

SUMMARY AND CONCLUSIONS

The present integrated pyrochemical process for producing high purity metal from plutonium scrap has been used quite successfully at Los Alamos. Yields from a one-pass system are about 65-75%, and the residual plutonium is efficiently recovered by a series of secondary operations. However, yields can be significantly increased and residue generation reduced by altering the operating conditions. Many of these changes are related to the salts employed in the operations.

Considerations of other molten salts and eutectics are particularly interesting and potentially useful in the DOR process. The addition of calcium fluoride to the present calcium chloride system to form a lower melting eutectic produces a metal button that does not adhere to the salt. The reaction can apparently be carried out at lower temperatures, thus, possibly, reducing calcium reaction with the crucible wall. Further study of reaction parameters is underway.

A second area of concerted study in the DOR system is regeneration of the spent salt followed by recycle. Development tests are complete, and a demonstration has been initiated.

Further changes in casting could evolve from the present study of the DOR process. If DOR were combined, or followed by a salt extraction step or distillation process to remove magnesium and excess calcium from the impure metal button, casting might become unnecessary. This is particularly valid if a solvent anode operation, with no dimension requirements for the anode material, is adopted.

Lithium chloride-potassium chloride has been substituted for sodium chloride-potassium chloride in electroelectrorefining, and plutonium trichloride has been used in place of magnesium chloride. Results have been encouraging, but more study will be needed.

Recycle of both the solvent anode and the salt in electrorefining is feasible, and tests are planned. As impurities build up in both salt and the anode, some method of regeneration or purification, perhaps distillation, will needed. Semicontinuous operation and remote control of processing are also areas of interest.

Finally, nondestructive, in-line assay would be very useful in these systems and work has been initiated in this field.

On-going research and development programs in pyrochemistry at Los Alamos have been described in this report. As data are collected and evaluated, areas of concern, and concepts of the processes, will change. We are presently emphasizing development, but we are also interested in reaction mechanisms, salt purification and equipment design. We hope to learn more through interaction with the scientific community through related studies, and we plan to continue to report upon our programs.

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