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REVIEW OF MAJOR PLUTONIUM PYROCHEMICAL TECHNOLOGY

W. Scott Moser and James D. Navratil, Rockwell International,
Rocky Flats Plant, Golden CO 80402

SUMMARY

The past twenty years have seen significant growth in the development and application of pyrochemical technology for processing of plutonium. For particular feed-stocks and specific applications, non-aqueous high-temperature processes offer key advantages over conventional hydrometallurgical systems. Major processes in use today include : 1) direct oxide reduction for conversion of PuO_2 to metal, 2) molten salt extraction for americium removal from plutonium, 3) molten salt electrorefining for Pu purification, and 4) hydriding to remove plutonium from host substrates. This paper reviews current major pyrochemical processes from the classical calcination-hydrofluorination-"bomb reduction" sequence through new techniques under development. Each process is presented and brief descriptions of production equipment are given.

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1. INTRODUCTION

Plutonium processing operations are conducted at four government-owned and contractor-operated facilities in the United States: Los Alamos, Hanford, Savannah River, and Rocky Flats. Original operations were undertaken during the Manhatten Project in 1943 with the separation of plutonium from irradiated reactor fuel at Hanford, and with the purification and secondary recovery of plutonium at Los Alamos. Similiar facilities were subsequently installed at Savannah River and at Rocky Flats in the early 1950's. Today, although technological innovations have been steadily identified and implemented, all four locations remain active in plutonium processing and in the development of improved processes for this application.

A major area of evolution over the past twenty years has been the growing role of pyrochemical technology in the overall plutonium treatment scheme. Pyrochemical processes utilize oxidation-reduction reactions and differences in solubilities among coexisting phases to recover or purify plutonium at elevated temperatures. Classical treatment systems have comprised a host of low-temperature aqueous unit processes including dissolution and precipitation as well as ion exchange and solvent extraction. However, pyrochemical processes, which feature a complete absence of aqueous solvents, offer a number of significant advantages which have stimulated their development:

1) Reactor sizes are much smaller for pyrochemical processes, often an order of magnitude smaller than aqueous process equipment of comparable throughput.
2) The absence of moderating reagents and solvents alleviates many nuclear criticality concerns.
3) Pyrochemical processes readily accept metallic feeds and produce high purity metallic products.
4) Process designs permit recycle of many reagents and by-product streams, thus decreasing net waste disposal problems.
5) The use of smaller facilities, with high recoveries, short reaction times, and less waste results in lower unit operating costs.

Several papers [1,2,3] have presented details of the more recent pyrochemical developments. In this paper, we will review the major pyrochemical processes currently in use, including brief discussions of those originating in the early days of plutonium processing.

2. EARLY PYROCHEMICAL PROCESSES

Aqueous treatment technology has historically produced either peroxide or oxalate by precipitation from pregnant purified solutions. In both cases, subsequent calcination has been used to produce plutonium dioxide (PuO_2) suitable for further treatment.

Experimental work during the 1940's resulted in the first successful conversions of calcined oxide to plutonium tetrafluoride (PuF_4) [4] and tetrafluoride reduction to metal with calcium [5,6] . This combination of calcination, hydrofluorination, and "bomb reduction" represents the classical process for metal production. Although a number of metal conversion routes from various salts have been explored [6,7], this sequence still finds wide application today.

Calcination

The chief objective of calcination is conversion of peroxide and oxalate to PuO_2 suitable for hydrofluorination. In addition, removal of carbon, sulphur ($SO_4^=$), and nitrogen (NO_3^-) is also desirable. Calcined products of both oxalate and peroxide processing are found to be refractory to subsequent treatment if calcined above the 350-450°C range. Consequently, calcining processes for both materials are carried out at below or 450°C. Residence times at temperature vary as a function of feed batch size and equipment type. Conversion of peroxide to PuO_2 is essentially complete by 300°C; however, oxalate conversion proceeds through a variety of intermediates resulting in residual carbon in the PuO_2 product [8]. The approach to stoichiometric PuO_2 and elimination of carbon are encouraged by calcining in air and enhanced solid/gas mixing. In the presence of excess air, CO_2 and SO_2 account for the majority of non-air off-gas components. Both materials may be two-stage calcined with drying or drying/dehydration comprising the preliminary stage.

Calcining of peroxide and oxalate has traditionally been conducted in static bed reaction boats or rotary calciners, the latter representing current preferred practice. In static treatment, stainless steel or Inconel calcining boats are used and heat provided by laboratory front-loading electric ovens. Rotary calciners are of inclined tube design with counter-current flow and provide continuous treatment of sized feed batches. The calcining tube is approximately 4 inches in diameter and 6-8 feet in length. Feed solids are mixed by rotary rabble arms as they move downward by gravity. Calciner temperature reaches 450°C to achieve maximum sulphate removal.

Recent development of the direct oxide reduction process (described in a following section) requires ~~permits~~ re-calcining at higher temperatures to achieve improved carbon and other impurity elimination. High temperature re-calcining is conducted at 850°C for 4-6 hours in front-loading laboratory furnaces heated by electric resistance elements. Oxides are held in calcining boats of 2-2.5kg capacity, and are mechanically stirred at intervals during treatment. High temperature calcining achieves approximately one order of magnitude decrease in calcine carbon content [9].

Hydrofluorination and Bomb Reduction

Hydrofluorination of calcined oxides is carried out in the presence of excess oxygen to produce PuF_4 for reduction to metal. The process is typically conducted at 600-650°C using anhydrous HF according to the following overall reaction:

$$PuO_2(s) + 4HF(g) \longrightarrow PuF_4(s) + 2H_2O(g) \qquad (1)$$

For suitably reactive oxides, reaction (1) can be carried to nearly quantitative completion under these conditions.

At Los Alamos, a static bed reactor has been used for production operations [10]. Downward flow of HF gas through a cylindrical packed bed boat is used. The static bed boat is contained in a Hastelloy C externally heated furnace shell. A rotary hydrofluorinator is in use at Rocky Flats. An inclined screw conveyor design and counter-current flow of oxide and HF is used. The reactor has three temperature zones ranging from 350°C at the solids inlet to 650°C at the solids outlet. Nitrates and picked-up moisture are removed in the low temperature end while sulphates are eliminated at the high temperature discharge end. In both static bed and rotary equipment, off-gases are passed to caustic scrubbing systems.

More recent work at Rocky Flats [11] has lead to the development of direct fluorination for production of PuF_4 as follows:

$$PuO_2(s) + 2F_2(g) \longrightarrow PuF_4(s) + O_2(g) \qquad (2)$$

Direct fluorination is carried out in a fluid bed reactor at approximately 300°C in 2-2.5kg batches.

The"bomb reduction" process produces plutonium metal from tetrafluoride according to the following thermite type reaction:

$$PuF_4(s) + 2Ca(s) \longrightarrow Pu(l) + 2CaF_2(l) \qquad (3)$$

In addition to high yields of plutonium metal, a major process objective is collection of a dense, coherent metal product. The process must be carried out such that reaction products are liquid and product metal can separate from the resulting calcium fluoride slag.

Ample energy is supplied by reaction (3) to provide high process temperatures sufficient for metal coalescence in most production scale systems: ΔH^{o}_{298} = -156.6 kcal/mole Pu. However, in small-scale or experimental reductions (below 500-1000g Pu), specific heat losses are large enough to require a booster reaction to maintain high process temperatures. The reaction most commonly used is:

$$Ca(s) + I_2(g) \longrightarrow CI_2(l) \qquad (4)$$

Typical iodine additions range from 0.3 to 0.5 moles I_2 per mole of plutonium, when required. Thus, a typical combined reaction for small-scale tests might be:

$$PuF_4(s) + 0.3I_2(g) + 2.3Ca(s) \longrightarrow Pu(l) + 0.3CaI_2(l) + 2CaF_2(l) \qquad (5)$$

for which ΔH^{o}_{298} = -196 kcal/mole plutonium. The presence of CaI_2 also aids by lowering the slag melting temperature by approximately 100°C.

Production operations use a 25% excess calcium addition above stoichiometric requirements. Reaction (3) initiates at 550-600°C, and charge temperatures are expected to peak at 1600-1700°C, although temperatures over 1900°C have been reported [12] . Internal reactor pressures reach over 100psig at temperature peaks. Production batch sizes typically exceed 1500g and no booster is required. The recovery of plutonium to metal product is 97 to 99% at purities normally exceeding 99.8%Pu.

The "bomb reduction" reactors are induction heated and constructed of a magnesia crucible fitted within a steel reactor can, or "bomb". Both prefired/sintered MgO crucibles and slip-cast crucibles have proved satisfactory. Mixed reactants are loaded into the crucible, the reactor evacuated and argon purged, and the heating cycle commenced. For small-scale reductions, reactor heating continues beyond initiation of the thermite reaction to permit effective metal/slag separation. In larger runs, process energy generation is sufficient. The success of a reduction run is also particularly sensitive to heat-up rate.

Too rapid a rise in temperature initiates reaction only at the charge outer shell and subsequent heat dissipation to the center yields poorly consolidated product. After reduction, the "bomb" is cooled, the crucible removed and broken to free the contents, and the metal product cleaned by acid pickling.

Recent improvements to the "bomb reduction" process have included addition of PuO_2 to the PuF_4 reduction feed [13,14], thus decreasing hydrofluorination requirements. Feed mixtures of 25-30% PuO_2 have performed successfully and resulted in significant production increases.

3. RECENT PYROCHEMICAL PROCESSES

The compelling advantages of pyrochemistry over aqueous systems in certain applications and shortcomings in early pyrochemical processes have stimulated a number of major process developments and improvements since the early 1960's. Direct oxide reduction (DOR), molten salt extraction (MSE), and hydriding have been developed and currently play a key role in production systems. Likewise, plutonium electrorefining (ER) has reached production-scale operation and undergone significant scale-up and improvements. These processes and their applications are described in following sections.

Direct Oxide Reduction

Direct oxide reduction (DOR) is a pyrochemical technique for the production of plutonium metal by direct calcium reduction of PuO_2. DOR bypasses the conventional hydrofluorination step and thus addresses three major process problems: 1) α-neutron reactions associated with fluorine, with resulting shielding, personnel exposure, and handling problems; 2) corrosion resulting from the use of HF gas; and 3) aqueous recycling requirements for CaF_2 slag, and crucible parts.

Early attempts at DOR failed to produce consolidated metal products [5,7,15,16] until the importance of a molten salt phase for mass transfer nad take-up of reaction products was appreciated. Follow-up work with various molten salt additives achieved growing degrees of success [17], until the first practical reductions to plutonium metal were reported in 1968 [18] and 1969 [19]. The process, as developed to date [1,2,20,21], is carried out in the presence of a molten $CaCl_2$ salt phase according to the following overall reaction:

$$PuO_2(s) + \underline{2Ca}(l) \longrightarrow \underline{2CaO}(s) + Pu(l) \qquad (6)$$

where underlines denote solution in molten $CaCl_2$. Calcium and its oxide are both soluble in $CaCl_2$. Thus, the salt provides two important functions: 1) a transfer medium for calcium to the reaction site, and 2) a mechanism for calcium oxide removal from the reaction site. Vigorous stirring is essential for successful reduction, and direct reaction of calcium with PuO_2 probably does occur to some extent. The insolubility of plutonium in the Ca-CaO-$CaCl_2$ system permits final metal consolidation.

The mechanism of reduction is not fully understood, although some reaction sequences have been suggested [1]. It has been well established that reaction (6) is carried to completion (ΔG°_{1000K} = -44.3kcal/mole Pu) provided: 1) sufficient $CaCl_2$ is available to dissolve product CaO, 2) excess calcium is present, and 3) adequate stirring is used. The reaction is typically carried out at 830-835°C, where the solubility of calcium oxide in $CaCl_2$ is approximately 18.5 mole% CaO [22]. Melt viscosities rise significantly beyond about 14 mole% CaO [1]. Consequently, salt-to-oxide weight ratios of 4:1 to 5:1 are normally used. Reduction batch sizes have grown from original small-scale work (<50g oxide), through 700g PuO_2 sizes, to current feeds of about 1kg PuO_2. The 700g oxide batches treated at Los Alamos [21] have used 50% stoichiometric excess of calcium and achieve greater than 99.5% process plutonium yields. Rocky Flats reductions at about the 900g PuO_2 level have used 25% excess calcium loadings and achieve yields above 98%.

The DOR process is carried out under an inert atmosphere in typical equipment shown in Figure 1. The reaction crucible is usually vitrified MgO and dual-impeller stirrers of solid ceramic or hollow tantalum designs have been used successfully. The reduction charge is loaded into the crucible and the furnace and crucible slowly raised to about 800°C to avoid thermal shock of the refractories. The reduction reaction is initiated by vigorous stirring and requires only about 10 minutes for completion. During reaction, a significant temperature spike occurs due to the exothermic nature of the reaction. Stirring is discontinued to permit metal consolidation, the reactor is allowed to cool, and products are broken out for recovery.

Major shortcomings of the stationary process equipment ~~in Figure 1~~ include: 1) the long turnaround times necessitated by slow heat-up, and 2) the generation of a waste stream of ceramics for reprocessing. The "tilt-Pour" furnace shown in Figure 2 is currently being evaluated for DOR and offers up to a 60% decrease in processing time without waste refractories. The use of metal construction in place of refractories may require the use of the lower-melting binary $CaCl_2$-CaF_2 salt and lower process temperature to minimize corrosion and product contamination.

Molten Salt Extraction

Americium - 241 grows into plutonium -239 by beta decay of plutonium - 241. Its removal is required to minimize impurity levels in metal and personnel exposure to gamma radiation during plutomium processing. The molten salt extraction process (MSE) was developed to remove americium from plutonium by reaction with $MgCl_2$ in a molten salt solvent.

Investigations on electrorefining and fuel processing during the early 1960's [23,24] suggested the practicality of partitioning americium between molten salts and plutonium or its alloys. Subsequent experimental work resulted in development of a molten salt process specifically for this application [25,26]. The current MSE process is based on use of $MgCl_2$ in a NaCl-KCl or NaCl-$CaCl_2$ solvent salt to extract americium from molten plutonium according to the following reaction:

$$\underline{Am}(l) + 3/2\underline{MgCl_2}(l) \longrightarrow \underline{AmCl_3}(l) + 3/2Mg(l) \tag{7}$$

where the underlines indicate solution in the chloride salt or feed metal. The equilibrium constant for reaction (7) is approximately 1.5×10^6 at 1000°K and favors americium removal subject to the effects of metal and salt composition (i.e. component activities). The analogous plutonium/plutonium chloride reaction has an equilibrium constant of about 3.3, showing that modest plutonium will also be oxidized but will then participate in americium oxidation to the chloride.

The transfer of americium into the salt phase can be treated as an extraction process. In this case, the distribution of americium based on thermodynamic and empirical knowledge may be coupled with the ratios of reacting phases, role of side reactions, and approach to equilibrium to exhibit the effects of process variables [1]. In recent process development work at Rocky Flats [27], chemical equilibrium data and experimental results were used to calculate distribution coefficients for Pu and Am as functions of $MgCl_2$ loading in salt. These results were then used with classical extraction process equations to show the impact of $MgCl_2$ loading, number of extraction stages, salt-to-metal ratios, and other variables on americium removal and have proved extremely valuable in guiding production operations. A sample plot [1,27] is shown in Figure 3.

The MSE process has been in production at Rocky Flats since 1967 and is currently conducted in a two-stage counter-current system to minimize salt requirements and maximize americium content of the salt. Plutonium metal is treated in 2 -2.5 kilogram batches in metal ~~round-bottom tantalum~~ crucibles within resistance heated furnaces. Loaded salt and metal are raised to an operating temperature of 750°C and flat-bladed stirrers are used to agitate the molten salt and metal for equilibration. After reaction, slow stirring is used to aid phase disengagement. The furnace is cooled and products are removed in a break-out area. The furnace uses an inert atmosphere cover to protect tantalum parts, plutonium, or salts from nitriding or oxidation.

(See Fig [illegible])

In the original process application 5-6 mole % $MgCl_2$ was used in the NaCl-KCl feed salt. Today, 30 mole % $MgCl_2$ salts are used. Both salts were capable of 90% americium extraction in 2-stage counter-current treatment. However, the high-$MgCl_2$ procedure requires only about one-tenth the amount feed salt, with a commensurate increase in product salt Am content. Both 35 mole % NaCl - 35 mole % KCl - 30 mole % $MgCl_2$ and 50 mole % NaCl - 26 mole % $CaCl_2$ - 24 mole % $MgCl_2$ are used for MSE. The NaCl-KCl-$MgCl_2$ system is used when conventional aqueous techniques are used for spent salt treatment. The NaCl-$CaCl_2$-$MgCl_2$ may be used when the salt is processed by pyrochemical methods.

Product metal buttons normally carry excessive amounts of calcium or magnesium which must be removed. This is accomplished by vacuum casting at about 800°C.

Electrorefining

Impure plutonium metal from molten salt extraction, direct oxide reduction, or other sources~~, which does not meet foundry specification,~~ is purified by electrorefining (ER) using a molten salt electrolyte.

Successful electrochemical recovery of plutonium from metallic reactor fuels was reported in 1958 [28] and was followed by a 300g (Pu)-scale electrorefining process for making high purity metal at Los Alamos [29] in 1960. Subsequent work at Los Alamos [30-36], Rocky Flats [37-40], Hanford [41], and in other countries [42] has demonstrated the molten salt ER process in a variety of applications and has steadily improved the process by procedure and equipment modifications. Further understanding and evolution of the process has resulted in current production facilities in the 2 to 6 kg Pu range [43].

In plutonium electrorefining, impure molten Pu is placed in contact with a molten salt electrolyte. An initial concentration of Pu^{+3} in the electrolyte is established by either : 1) direct plutonium salt addition, or 2) inclusion of $MgCl_2$ in the salt mixture. In the latter case Pu^{+3} is provided by reaction (8):

$$Pu(l) + 3/2MgCl_2(l) \longrightarrow 3/2Mg(l) + PuCl_3(l) \qquad (8)$$

The impure plutonium is made anodic and a tungsten cathode or containment can is made cathodic. As current is passed, plutonium metal is oxidized at the anode to Pu^{+3} and taken up in the electrolyte, while Pu^{+3} is reduced to metal at the cathode, according to the following half-cell reactions:

$$\text{ANODE:}\quad Pu(l)_{\text{impure}} \longrightarrow Pu^{+3} + 3e^- \qquad (9)$$

$$\text{CATHODE:}\quad Pu^{+3} + 3e^- \longrightarrow Pu(l)_{\text{pure}} \qquad (10)$$

The calculated cell potential for (9) + (10), where the activity of Pu in the impure anode is 0.9 and temperature is 740°C, is only 0.003 volts. The overall potential required must include $I_x R_x$ losses in the cell circuit and any time dependent resistance (e.g. electrode polarization). So long as the cell driving potential does not exceed the decomposition of the salt chlorides, the electrolyte composition does not change.

The refining effect of an electrolysis process for a given impurity is a function of both ionic transport properties and thermodynamic properties (ie. activities in the salt phase). In the ER process, impurity elimination is controlled by the chemical activity of impurities in the electrolyte. Plutonium chloride acts as a salt-phase buffer to maintain low salt-phase activities for those impurities more noble (having less stable chlorides) than plutonium. These impurities, such as gallium or iron, are retained in the anode. Impurities such as americium are not retained in the anode, but are transferred to the salt as ions and are capable of being reduced at the cathode. On this basis, elements with chlorides less stable than $PuCl_3$ are expected to be retained in the anode and thereby removed from the plutonium being refined.

As electrofining proceeds, the concentrations of non-transferred impurities increase significantly in the anode, and eventually reach their solubility limits or begin precipitation of insoluble solid phases. These may ~~will~~ be relatively high-melting phases. They may float to the salt-anode interface and cause anode polarization by de-coupling the liquid anode-to-salt electron path. As polarization takes place, impurities are transferred to the salt and finally appear in the product, thus causing off-specification product. This effect limits practical anode depletions and highlights the importance of good salt/anode mixing or close process control to avoid impurity transfer at maximum anode depletions.

Production electrorefining is conducted at 740-750°C using equimolar NaCl-KCl electrolyte salt containing 3 mole % $MgCl_2$. At Los Alamos and Rocky Flats, electrorefining has been ~~is~~ conducted in stationary cells as shown in Figure 4. In these cells, a suspended tungsten cathode allows molten plutonium to coalesce and drip down to a collection ring in the bottom of the magnesia crucible outside the anode cup. Both salt phase and molten anode are stirred and a back-EMF technique is used to detect the onset of polarization and terminate ER runs before significant impurity carryover. At Rocky Flats, "tilt-pour" furnaces, as shown in Figure 5, are used for electrorefining. Typical charges consist of 2-2.5 kg of MSE or DOR metal. Metal of sufficiently high quality has been successfully produced with only the salt phase stirred. Metal is recovered from the stationary cell by crucible break-out and from the "tilt-pour" cell by casting. At Los Alamos, over the period 1964-1977, product yields (100 x Pu_{prod}/Pu_{feed}) of 75.2-84.7% have been achieved: average = 81.8% [44]. Product purities were well in excess of 99 9% Pu with feeds of 98-99% Pu, although 99.98% purities were achieved with 97% Pu feeds [44].

Hydriding

During plutonium processing, significant amounts of Pu are coated onto metallic and non-metallic substrates such as crucibles, tools, and equipment. This plutonium may be recovered for recycle without damage to the substrate by the hydriding process. The advantages of hydriding stimulated startup of a production prototype hydriding apparatus at Rocky Flats in 1972 [45, 46].

Gaseous hydrogen is reacted with plutonium in an oxygen-free vessel to produce plutonium dihydride by the following reaction:

$$Pu(s) + H_2(g) \longrightarrow PuH_2(s) \qquad (11)$$

The product hydride is ~~actually~~ non-stoichiometric but approaches PuH_2 composition. As the plutonium hydride is produced, it spalls off of the substrate and is collected. Product hydride may be either oxidized to PuO_2 for storage and further treatment or dehydrided by heating in vacuum to produce metal powder which is vacuum cast.

Hydriding and oxidation are performed in reaction pans placed in closed horizontal cylindrical vessels. Hydriding is conducted at 100-400°C and 1-500 Torr of H_2 depending on the substrate and its plutonium loading. Oxidation is conducted in two stages, first at 300°C then at 500°C in O_2 gas. Both processes are limited by criticality constraints to 3 kg maximum batch sizes. Dehydriding is performed by adding heat and vacuum to reverse reaction (11). The reaction is carried out in a vacuum-tight furnace capable of achieving 700°C for decomposition. In all cases, exited hydrogen is disposed of by combustion.

4. AREAS OF CURRENT PYROCHEMICAL DEVELOPMENT

Following is a brief description of several areas of current process research and development activity.

Pyroredox

The pyroredox process is a three-step pyrochemical oxidation-reduction technique under development to separate impurity elements from plutonium. In the first stage, impure molten plutonium metal is vigorously mixed with a molten $ZnCl_2$ - $CaCl_2$ - KCl salt. Plutonium is oxidized by $ZnCl_2$ in preference to impurity metals forming less stable chlorides than zinc (e.g. Cr, Ga, Fe). An excess of $ZnCl_2$ is used to drive the oxidation according to the reaction:

$$Pu(l) + 3/2\ ZnCl_2(l) \longrightarrow PuCl_2(l) + 3/2\ Zn(l) \qquad (12)$$

The bath temperature exhibits a spike to about 700°C upon initiation of reaction. The remaining impurity metals are taken up by the zinc product, while impurity metals with more stable chlorides (e.g. Al, Am) are transferred to the salt phase with Pu. The salt and metal phases are cooled and separated.

In step two, plutonium is recovered from stage-one salt by reduction to metal with excess calcium by the reaction:

$$PuCl_3(l) + 3/2\ Ca(s\text{-}l) \longrightarrow 3/2\ CaCl_2(l) + Pu(l) \qquad (13)$$

The reduction temperature spike reaches about 700°C and bath temperature typically reaches over 800°C at termination of stirring. The cooled salt and metal phases are separated.

The reduction metal button is finally vacuum melted in step 3 to remove zinc and calcium.

Literature describing the process [47] indicates that development has reached the 2 kg scale. To avoid thermal shock, "tilt-pour" furnaces with metal crucibles are used for both oxidation and reduction steps. The use of high purity salts has been shown to minimize operating problems such as bath foaming and formation of insoluble impurities. Under good conditions, pyroredox will lower the impurity content of plutonium metal by about one order of magnitude at very high oxidation and reduction yields. The process has attractive applications as a primary plutonium purification technique and for treatment of ER anode heels for recycle.

Salt Treatment

A major development effort has been directed at recovery of plutonium and americium from spent pyrochemical salts to permit their discard or recycle. The NaCl - KCl - $MgCl_2$ salts from MSE and ER are currently processed by aqueous technology; however, recent pyrochemical techniques have shown significant promise for Pu and Am removal. Salts are treated at approximately 750°C in stationary or "tilt-pour" equipment to reduce $PuCl_3$ and $AmCl_3$ to metal with magnesium or calcium. When magnesium metal is used, addition is made via alloys such as Al - Mg or Zn - Mg. Reactions proceed as follows:

$$PuCl_3(l) + 3/2\ Mg(l) \longrightarrow Pu(l) + 3/2\ MgCl_2(l) \qquad (14)$$

$$AmCl_3(l) + 3/2\ Mg(l) \longrightarrow Am(l) + 3/2 MgCl_2\ (l) \qquad (15)$$

with all components in solution. Product plutonium and americium have been successfully collected by the zinc or aluminum solvent metal in a recoverable button. When calcium is used, reduction proceeds according to the following reactions:

$$PuCl_3(l) + 3/2\ Ca(l\text{-}s) \longrightarrow 3/2\ CaCl_2(l) + Pu(l) \qquad (16)$$

$$AmCl_3(l) + 3/2\ Ca(l\text{-}s) \longrightarrow 3/2\ CaCl_2(l) + Am(l) \qquad (17)$$

The thermodynamics of the process are determined by the relative stabilities of the metal chlorides. When calcium is used, magnesium is also reduced to metal by the following reaction:

$$MgCl_2(l) + Ca(l\text{-}s) \longrightarrow CaCl_2(l) + Mg(l) \qquad (18)$$

and acts as the plutonium or americium collector metal. Attempts at direct reductions using calcium metal on NaCl - KCl - $MgCl_2$ salts have not been completely successful to date, but offer the advantages that : 1) no solvent metal is required, and 2) $MgCl_2$ removal from the salt enhances Pu/Am removal. Calcium reductions of $CaCl_2$ - based salts have been successfully accomplished and have rekindled interest in alternative salt systems for ER and MSE.

The recycle of spent DOR salts is also an area of keen interest. Calcium oxide is contained at levels approaching saturation and prevents the re-use of untreated salts. Therefore, work is underway to convert CaO back to $CaCl_2$ using additive condensed-phase reactants or gaseous conversion such as

$$\underline{CaO}(l) + 2HCl(g) \longrightarrow CaCl_2(l) + H_2O \qquad (19)$$

where the underline denotes solution in $CaCl_2$. Direct chlorination is also under consideration, as are reaction/filtration sequences for this and other salts.

ACKNOWLEDGMENT

The processes reviewed in this paper are the result of many years of dedicated development work by a vast number of scientists, engineers, and technicians at Department of Energy facilities throughout the United States. A special acknowledgment is due these people for their technical efforts and thorough documentation from which this paper was drawn. This paper was prepared under the auspices of Rockwell International, Inc.,Energy Systems Group, on Department of Energy Contract No.

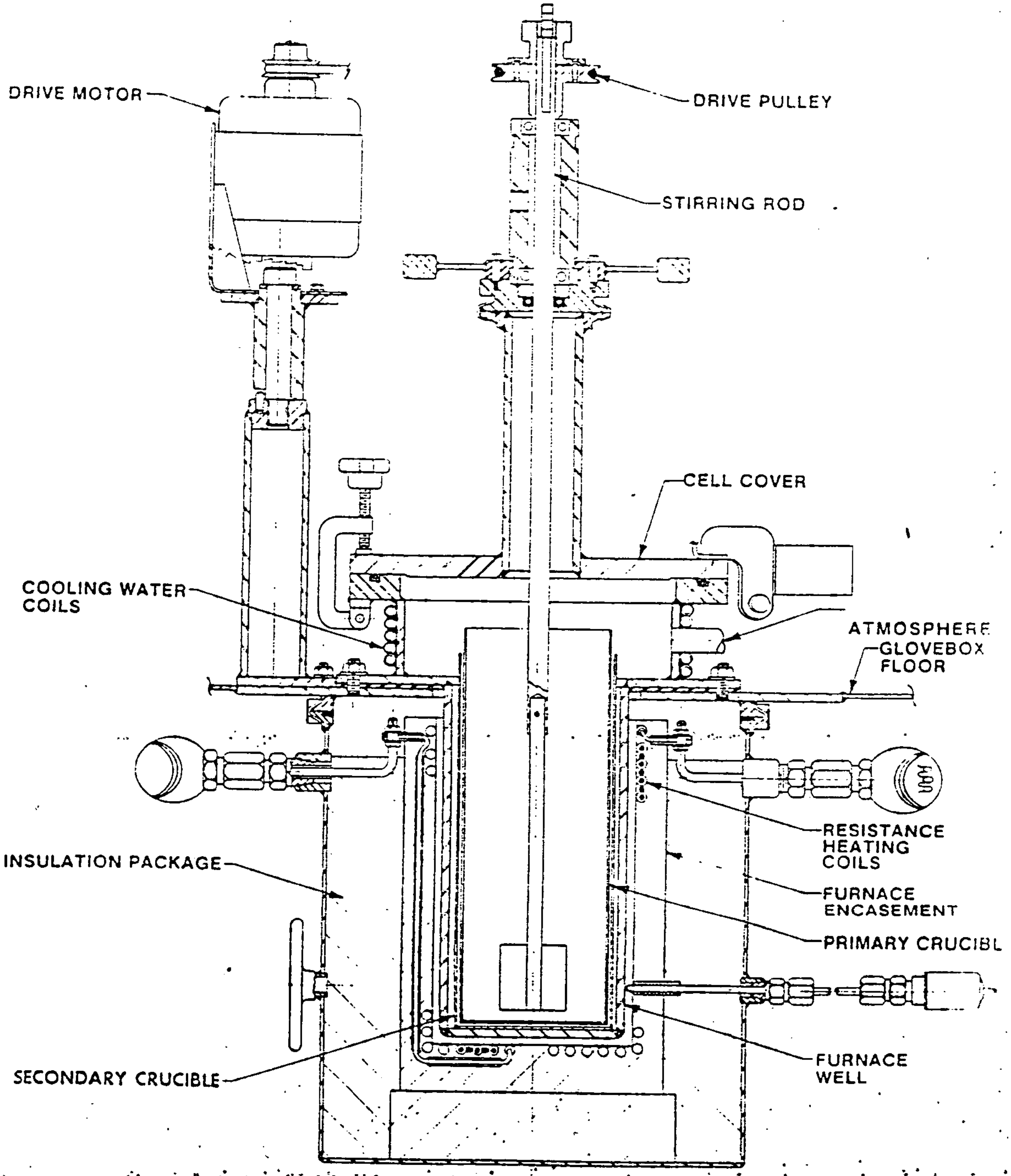

FIGURE 1: Stationary Furnace Used for Direct Oxide Reduction (with dual-impeller stirrer) or Molten Salt Extraction (as shown, with single-impeller stirrer) at Rocky Flats.

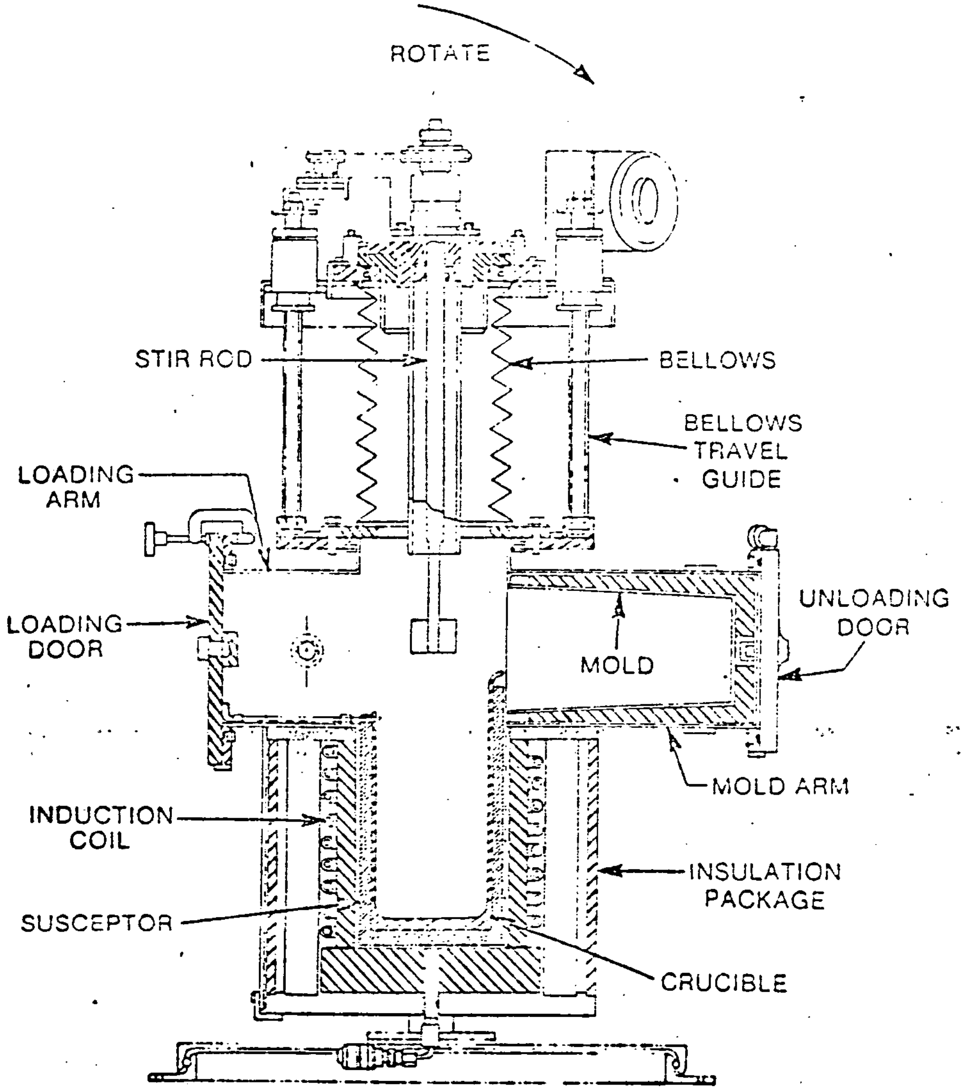

FIGURE 2: Tilt-Pour Furnace Used for Direct Oxide Reduction (with dual-impeller stirrer) or Molten Salt Extraction (as shown, with single-impeller stirrer) at Rocky Flats.

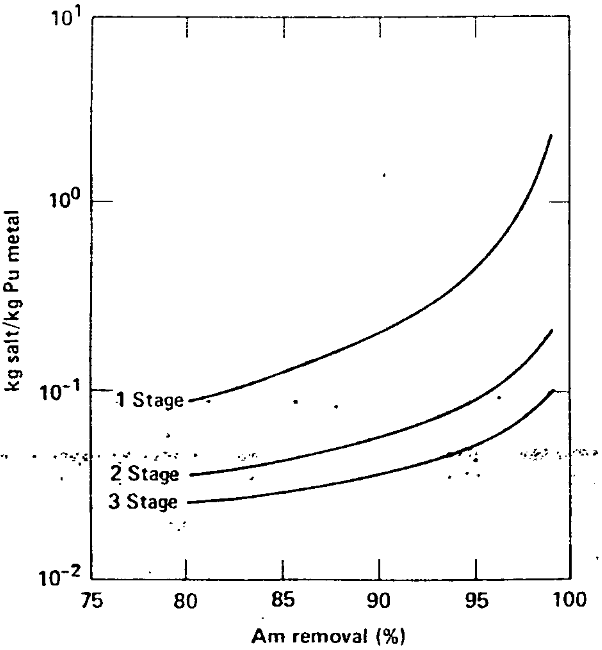

FIGURE 3: Yield Contours for Americium Extraction vs. Salt/Metal Ratio for Multi-Stage Counter-Current Extraction with Salt Composition: 30 mole % $MgCl_2$ - 35 mole % NaCl - 35 mole % KCl (after Coops[illegible], et.al. [1]).

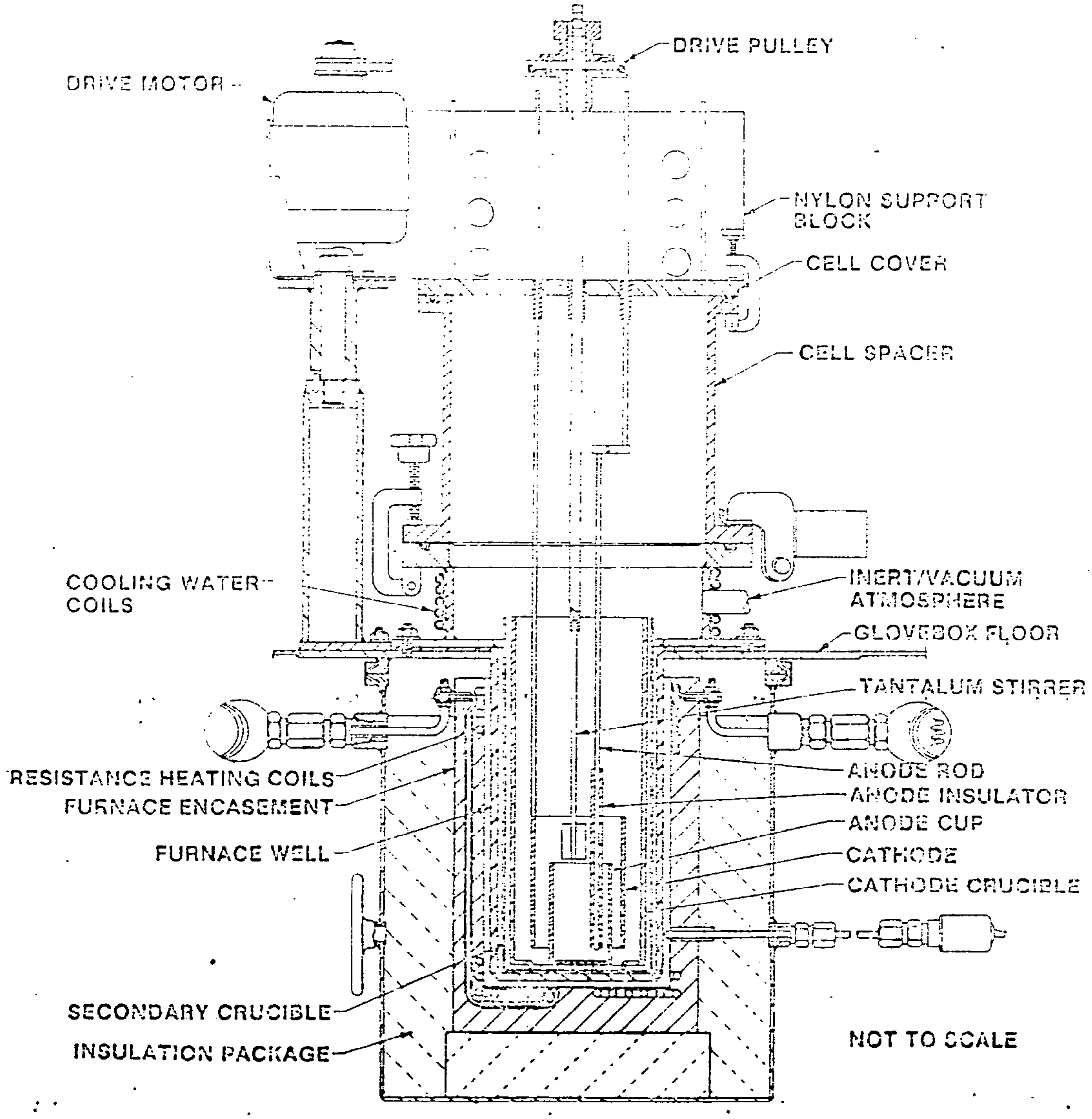

FIGURE 4: Stationary Furnace and Electrorefining Cell Arrangement Used For Plutonium Electrorefining at Rocky Flats.

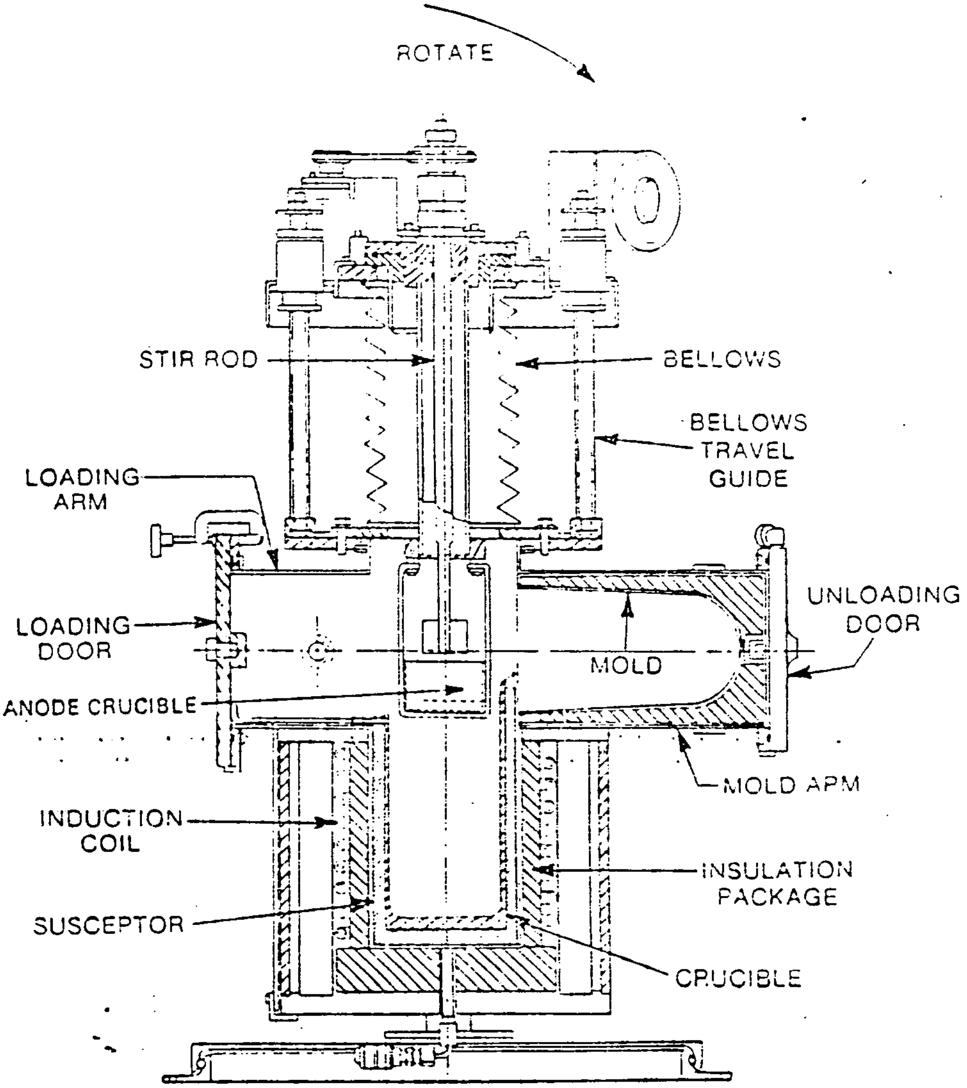

FIGURE 5: Tilt-Pour Furnace and Electrorefining Cell Arrangement Used For Plutonium Electrorefining at Rocky Flats.

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