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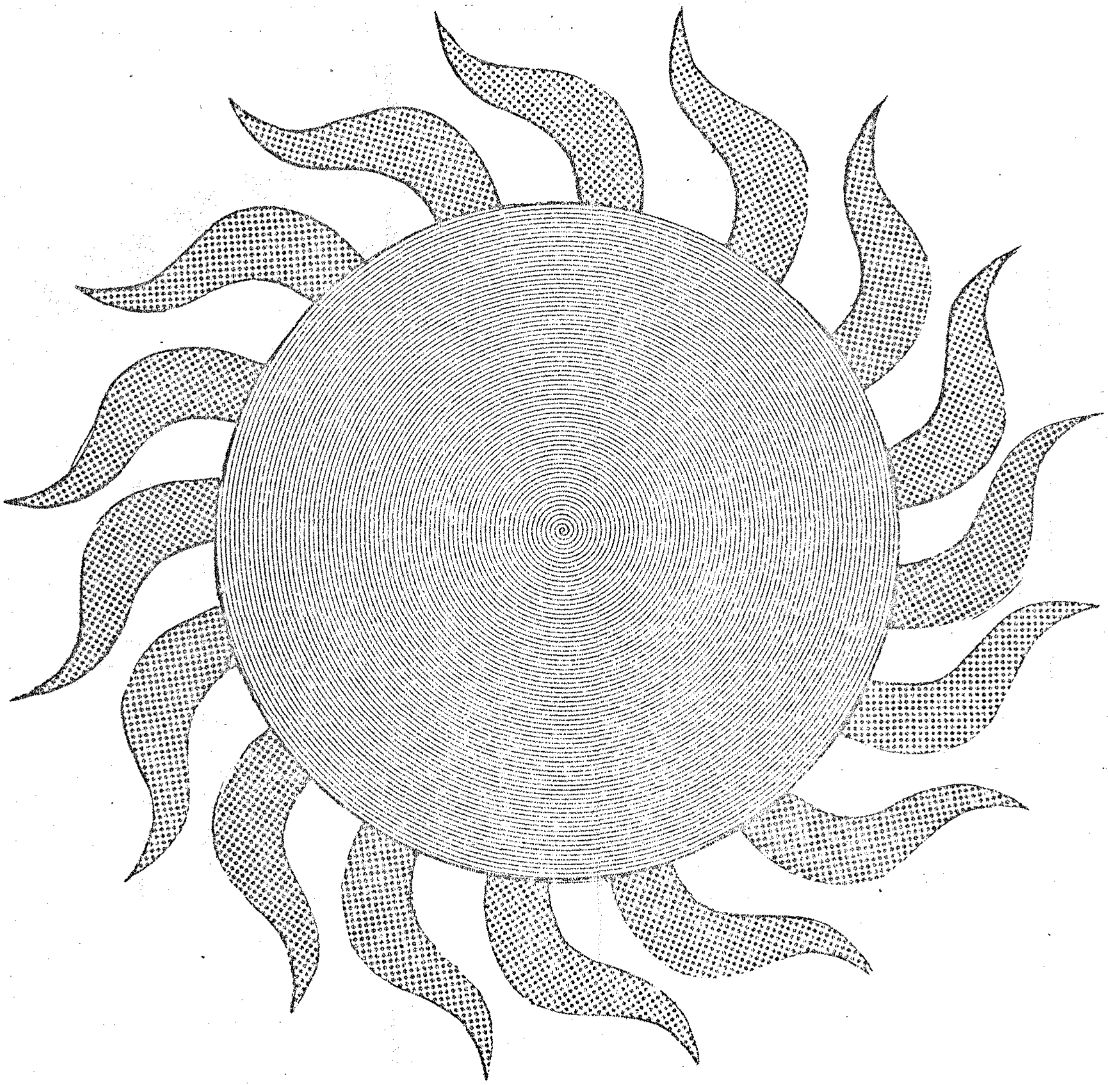

Pyrochemistry
At
Rocky Flats

PYROCHEMISTRY AT ROCKY FLATS

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INTRODUCTION

Pyrochemical and pyrometallurgical processes are utilized at Rocky Flats for plutonium recovery and purification. Many of these processes use molten salts and molten metals which are stirred together or equilibrated at 700 to 900 °C, resulting in chemical reactions. In one case, an electric current is also applied. These processes include molten salt extraction (MSE) for the removal of americium from plutonium; salt cleanup (SCU) for the recovery of the americium and plutonium from the MSE spent salt; direct oxide reduction (DOR) for the conversion of plutonium oxide to plutonium metal; and two plutonium metal purification processes, electrorefining (ER) and pyroredox. The above processes also come under the heading of "extractive metallurgy." There are other pyrochemical processes at Rocky Flats which will not be discussed here. These include the removal of plutonium metal from substrates using hydrogen (hydriding), the conversion of plutonium oxide to plutonium tetrafluoride (fluorination or hydrofluorination), the reduction of plutonium tetrafluoride to plutonium metal (bomb reduction), and the burning of Foundry casting skulls and other plutonium metal to plutonium oxide.

EQUIPMENT

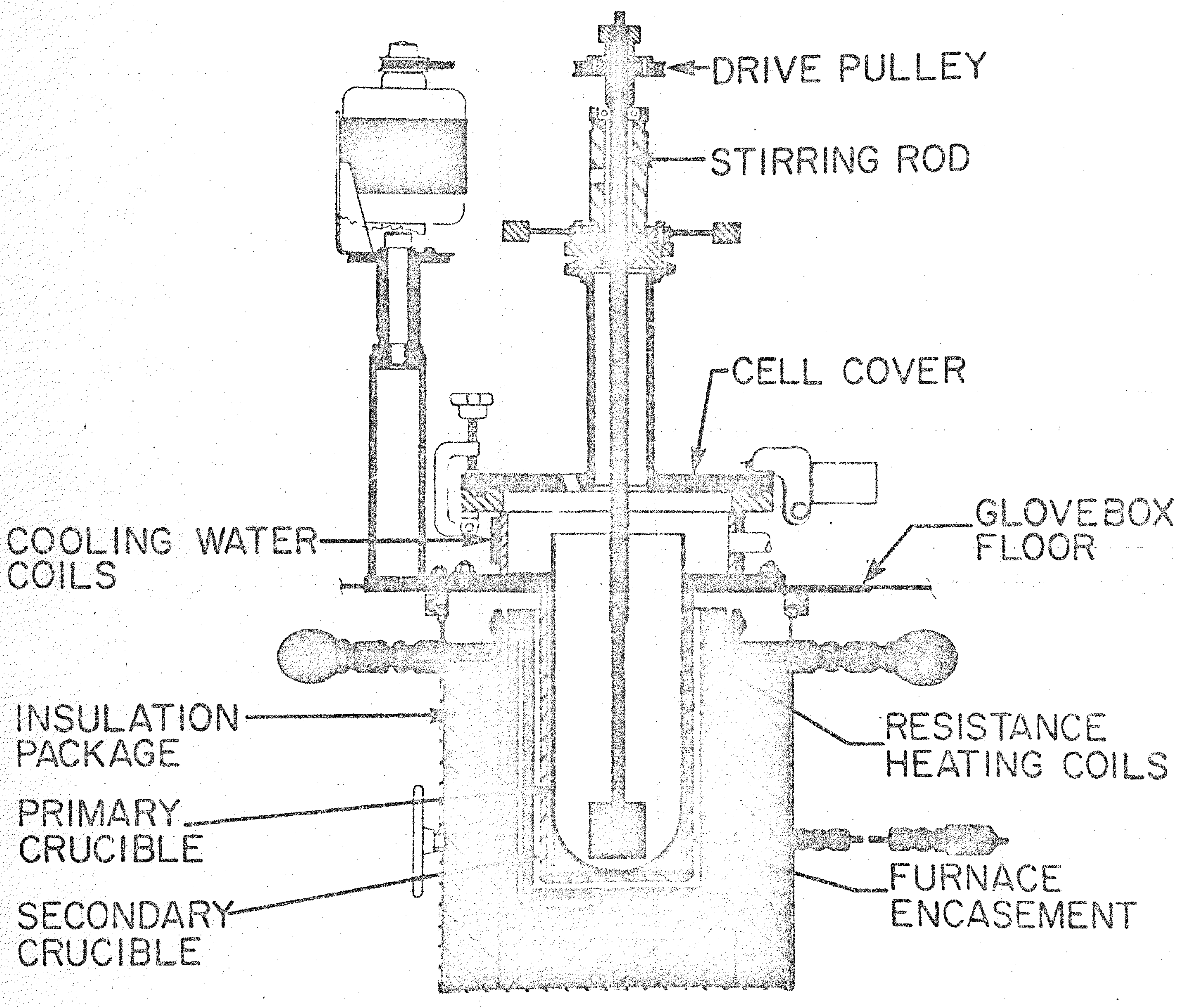
The reactions using molten salts and molten metals are carried out in either stationary furnaces or tilt-pour furnaces (Figures 1 and 2). These furnaces are either resistance heated or induction heated. The molten materials are contained in tungsten or tantalum crucibles, which are reusable, or in once-used, expendable, high-density magnesium oxide (MgO) refractory crucibles. The molten contents are stirred using a tantalum or ceramic stirring rod which is lowered into the melt for stirring, then raised out of the melt before the contents either freeze in the crucible or are poured into a mold.

DESCRIPTION OF PYROCHEMICAL PROCESSES

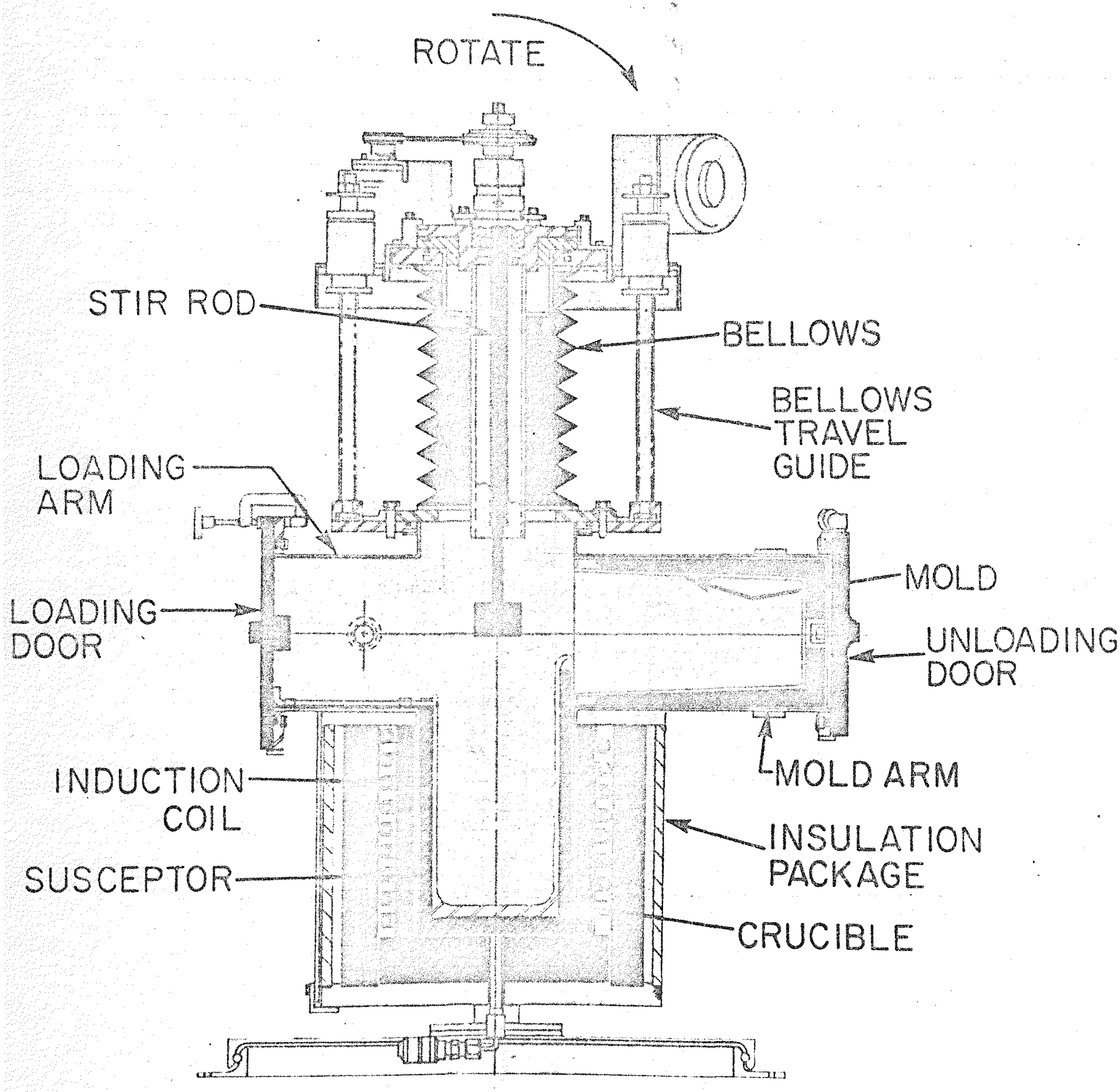
Molten Salt Extraction (MSE)

Weapons-grade plutonium, the plutonium used at Rocky Flats, typically contains about 0.4 percent of the isotope, plutonium 241. This radioactive isotope decays by beta decay (half-life = 14.4 years) to form americium 241. The result of this nuclear reaction is that americium "grows" in the plutonium at the rate of about 15 parts per million (ppm) per month. After a time, the americium must be removed. Its presence is undesirable. It has different nuclear properties and chemical properties from plutonium, and it presents a gamma radiation hazard to personnel.

At Rocky Flats, plutonium metal from which americium is to be removed is melted with an inert NaCl-KCl eutectic salt mixture containing magnesium chloride. The magnesium chloride selectively oxidizes americium from plutonium metal. The mixture is heated to melting by



STATIONARY FURNACE



TILT POUR FURNACE

resistance or induction heating, in a tantalum or tungsten vessel. Upon stirring, some of the plutonium and most of the americium are extracted into the salt phase. A much greater percentage of americium than plutonium is oxidized. After stirring for 1/2 to 2 hours, "equilibrium partitioning" of the americium and the plutonium between the molten salt and molten metal phases is attained. At varying ion concentrations, the values of the distribution coefficients, i.e.,

$$\frac{\text{concentration of an element in salt phase}}{\text{concentration of the element in metal phase}}$$

are much higher for americium than for plutonium. This behavior is predictable thermodynamically because the negative free energy of formation of americium chloride is higher than that for plutonium chloride or for magnesium chloride. With the proper extraction conditions, over 90 percent of the americium metal in the liquid-metal phase is oxidized to Am^{+3} as americium chloride and is dissolved in the salt phase. Similarly, about 4 percent of the plutonium is oxidized and taken up by the salt phase. The thermodynamically possible chemical reactions for americium extraction are as follows:

$$Am^\circ + {}^3/_2\, MgCl_2 \leftrightarrow AmCl_3 + {}^3/_2\, Mg^\circ \qquad \Delta G = -7.05 \text{ kcal at } 1000 \text{ K} \quad (1)$$
(magnesium metal is formed)

$$Pu^\circ + {}^3/_2\, MgCl_2 \leftrightarrow PuCl_3 + {}^3/_2\, Mg^\circ \qquad \Delta G = -2.7 \text{ kcal at } 1000 \text{ K} \quad (2)$$
(magnesium metal is formed)

$$Am^\circ + PuCl_3 \leftrightarrow AmCl_3 + Pu^\circ \qquad \Delta G = -4.35 \text{ kcal at } 1000 \text{ K} \quad (3)$$
(plutonium metal is formed)

As shown in Equation 3, plutonium chloride can also oxidize americium to americium chloride.

The materials of construction compatible with both the molten chloride salts and molten metal are very limited. As mentioned in the Equipment subheading, materials in use include tantalum, tungsten, and high-density magnesium oxide ceramics. Materials which might be evaluated include alloys of tungsten, tantalum and molybdenum, and refractories such as rare earth oxides.

When the metal (about 2 kg) and salt (about 250 g) are molten, a tantalum stirrer is lowered into the melt and reverse-motion mixing (washing machine action) is employed to mix the phases until the system approaches equilibrium. This mixing over a period of time is called "equilibration." As the above reaction occurs, some of the magnesium which is formed is vaporized from the molten phases and collects in the cooler regions of the equipment.

In practice, to effectively lower americium levels in plutonium, from a range of 1,000 to 4,000 ppm in the feed to less than 200 ppm in the product, crosscurrent or countercurrent extraction methods are employed (Figures 3 and 4). In two-stage crosscurrent extraction, the metal charge is contacted twice with new salt charges. In two-stage countercurrent extraction, a once-used salt charge from Stage 2 is used to contact a fresh metal charge in Stage 1 and a once-contacted metal charge from Stage 1 is contacted with a new salt charge in Stage 2. Countercurrent extraction requires less salt and removes less plutonium via Equation 2 than crosscurrent extraction. After two-stage countercurrent equilibrations, the plutonium metal typically contains 100 to 200 ppm americium and some of the magnesium metal formed. The spent chloride salt contains about 80 g plutonium and 4 g americium as the chlorides. The salt and metal, after cooling, are removed from round bottom tantalum crucibles or molds. The salt is separated from the top of the plutonium button, weighed, counted for plutonium content, and placed in drum storage for future processing for plutonium and americium recovery. The metal surfaces are brushed clean, and the metal is sampled for americium and impurities. The metal is used either by the Foundry or held for metal purification, depending upon analytical results.

Salt Cleanup (SCU)

The spent salt from MSE, containing plutonium chloride and americium chloride, must be processed to recover the plutonium and americium. This can be done via aqueous or pyrochemical processing. In pyrochemical processing, spent MSE salt is processed in 1,500- to 2,000-g batches. The salt is equilibrated with a metal or alloy which will reduce the plutonium, americium, and in some cases, the magnesium to metals. The product is a metal alloy. Typical reactions follow:

$$PuCl_3 + {}^3/_2\,Ca^\circ \rightarrow Pu^\circ + {}^3/_2\,CaCl_2 \tag{4}$$

(An alloy of Pu-Am-Mg results)

$$AmCl_3 + {}^3/_2\,Ca^\circ \rightarrow Am^\circ + {}^3/_2\,CaCl_2 \tag{5}$$

$$MgCl_2 + Ca^\circ \rightarrow Mg^\circ + CaCl_2 \tag{6}$$

$$PuCl_3 + {}^3/_2\,Mg^\circ \rightarrow Pu^\circ + {}^3/_2\,MgCl_2 \tag{7}$$

(Pu is collected in a Mg-Zn or Al-Mg alloy)

$$AmCl_3 + {}^3/_2\,Mg^\circ \rightarrow Am^\circ + {}^3/_2\,MgCl_2 \tag{8}$$

(Am is collected in a Mg-Zn or Al-Mg alloy)

Figure 3

Flow Diagram--Two-Stage Crosscurrent Extraction

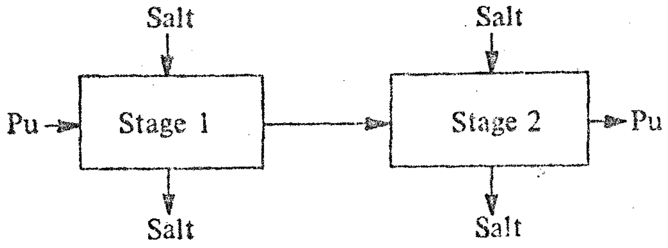
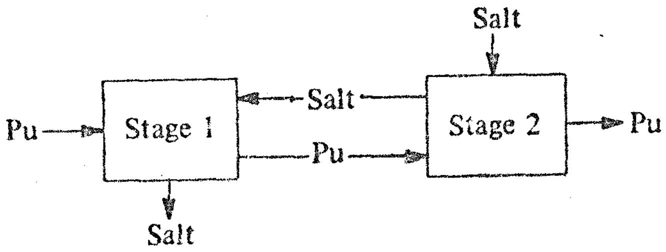


Figure 4

Flow Diagram--Two-Stage Countercurrent Extraction



If the spent salt is relatively free of contaminants, such as lead (from lead tape and shielding), carbon (from brush bristles, plastics, tape, and wood), iron, nickel, and chromium (from steel bristles), a discardable salt and an alloy button result.

The alloy product resulting from SCU may contain significant quantities of calcium, magnesium, and zinc. These metals possess high vapor pressures, so they may be separated from the plutonium and americium by volatilization. The calcium, magnesium, and zinc vapors are condensed in a cool collector. This process, called "Vacuum Melting," has been performed at Rocky Flats by melting the alloy in a vacuum of 10^{-3} torr. The resulting plutonium-americium alloy can be purified by pyrochemical or aqueous means. Americium may then be separated from the plutonium by multistage MSE, aqueous processing, or by high temperature, low pressure distillation of americium metal from plutonium metal.

Compatible Salt Study

This study involves selecting a salt system for MSE such that the plutonium and americium contained in the spent salt can be recovered pyrochemically, using calcium metal as a reductant (Equations 4, 5, and 6). The products would be discardable salt and an alloy button containing 85 to 90 percent plutonium and americium but no zinc or aluminum alloying material. Such a capability would allow streamlining MSE and SCU so SCU could be performed immediately after MSE, precluding storage of MSE spent salt. In order to employ calcium metal reductant in SCU, a $CaCl_2$-KCl-$MgCl_2$ salt system has been proposed rather than the NaCl-KCl-$MgCl_2$ salt system presently used. Calcium metal is not recommended to clean spent salt containing NaCl-KCl because sodium metal may be formed. Also, in past experiments, the reduced plutonium and americium metal did not consolidate to form a metal button.

In order for a different salt system to be implemented, it must be demonstrated that (1) the candidate salt will perform as well for MSE as the NaCl-KCl-$MgCl_2$ salt, (2) calcium metal will reduce plutonium and americium in the spent salt to obtain a discardable salt and a plutonium-americium-magnesium button, and (3) the plutonium-americium-magnesium alloy can be further processed to recover the plutonium and americium.

Direct Oxide Reduction (DOR)

Plutonium in the oxide form, plutonium dioxide (PuO_2), is a good, safe way to store plutonium because the oxide is noncombustible and nonreactive. ~~There are large quantities of PuO_2 produced and stored at Rocky Flats.~~ However, for fabrication, the plutonium must be converted from the oxide to the metal. Pyrochemical processes for plutonium purification (electrorefining and pyroredox) also require that the feed material be plutonium metal. DOR is a one-step process for converting plutonium oxide to plutonium metal. Calcium metal, a strong reducing agent, reacts with the plutonium dioxide as follows:

$$PuO_2 + 2\ Ca^\circ \rightarrow Pu^\circ + 2\ CaO \qquad (9)$$

The calcium oxide formed dissolves in molten calcium chloride salt.

To perform the reaction, about 1/2 kg of PuO_2, 2 kg of $CaCl_2$ salt, and 185 g of calcium metal are placed in a high-density MgO ceramic crucible. A tantalum crucible is unacceptable for stationary furnace operation because calcium metal also reacts with the passivating coating on the tantalum, causing the plutonium metal product to bond to the tantalum crucible. Either a tungsten or a tantalum crucible would be acceptable in a tilt-pour furnace.

The contents of the crucible are melted and then stirred in such a way that low-density calcium metal and high-density plutonium oxide are brought into contact, whereby they react within the molten salt. Breakout of the cooled contents yields a plutonium metal button and a discardable salt.

Plutonium Purification Processes

Two processes are available for purifying plutonium metal: (1) electrorefining (ER), which requires an electric current, and (2) pyroredox, which utilizes an oxidizing agent and a reducing agent.

Electrorefining (ER)

Impure plutonium metal, cast into a cylindrical shape or as metal pieces, is placed in a MgO ceramic cup called the anode cup. The loaded cup is lowered into a NaCl-KCl molten salt very slowly so as not to break the ceramic cup via thermal shock. The metal melts and the cup is filled with molten salt. A direct current is applied through an insulated tantalum rod immersed in the impure molten plutonium anode. The current then flows from the molten anode metal through the molten salt to a tungsten cathode. Either the molten salt is stirred using an electrically isolated tantalum stirrer, or the salt and anode metal phases are both stirred using a ceramic stirrer. The molten salt also contains a small quantity of $MgCl_2$, which reacts with a portion of the plutonium feed metal to form $PuCl_3$ (Equation 3). The Pu^{+3} ions are necessary in the salt phase at the beginning of electrolysis so that when the electric current is applied, proper anode and cathode reactions occur with the plutonium. Without a population of Pu^{+3} ions in the salt phase, the current can decompose sodium chloride to form sodium metal. This is an undesirable reaction.

When the direct current is applied, the following reaction occurs at the molten metal-molten salt interface in the anode cup:

$$Pu^\circ - 3e^- \rightarrow Pu^{+3} \qquad (10)$$

The Pu^{+3} ions formed at the anode interface migrate through the molten salt to the negatively charged tungsten cathode, where the plutonium is reduced to metal. Droplets of plutonium metal collect on the tungsten cathode surfaces, run down and form a pool of purified metal, which is protected by the molten salt cover.

$$Pu^{+3} + 3e^{-} \rightarrow Pu^{\circ} \tag{11}$$

At the selected operating voltage and amperage, only plutonium and americium are oxidized. The impurities remain in the anode cup as long as there is plutonium metal available in sufficient quantity at the anode-salt interface. As plutonium is depleted at the anode, the concentration of the impurities in the feed metal increases. The passage of electric current must be terminated at the proper time to maximize yields but prevent the transfer of impurities. The time of termination can be calculated in terms of total amp hours. Theoretically, plutonium transfers at the rate of 2.97 g/amp hour. In practice, electrical efficiency is less than theoretical. About 2.4 g/amp hour are transferred. Termination can also be determined by monitoring the back electromotive force of the cell and terminating upon evidence of a significant increase in the back electromotive force. The increase in back electromotive force is correlated to a decrease in plutonium metal available at the anode.

Americium tends to remain in the molten salt rather than be reduced at the cathode. When the process is performed in a stationary furnace, the product metal forms a doughnut around the outside of the ceramic anode cup. Upon termination of electrolysis in a tilt-pour furnace, the anode cup containing the impurities is lifted from the molten salt by raising the bellows. After the contents of the anode cup have cooled and frozen, the furnace is tilted. Molten salt and the purified product metal are poured from the tungsten crucible into a tantalum mold.

Pyroredox

Pyroredox is also a process for purifying impure plutonium metal. The impure feed metal is placed in a ceramic or tungsten crucible with a solvent salt, such as a calcium chloride-potassium chloride eutectic, and an oxidizing salt, usually zinc chloride. Upon melting the contents and stirring, the zinc chloride reacts with the plutonium metal to form plutonium chloride and zinc metal.

$$Pu^{\circ} + {}^{3}/_{2}\, ZnCl_2 \rightarrow PuCl_3 + {}^{3}/_{2}\, Zn^{\circ} \tag{12}$$

Most of the impurities associated with the plutonium are less reactive than plutonium. These impurities do not react with zinc chloride but remain in the metal phase and alloy with the zinc metal which is formed. Impurities more reactive than plutonium will react with zinc chloride. Cations whose chlorides possess a higher negative free energy of formation than zinc chloride will be oxidized with the plutonium. Elements which follow the plutonium include calcium, americium, magnesium, uranium, and aluminum. Elements whose chlorides possess a lower negative free energy of formation than zinc chloride do not react with zinc chloride. The elements which do not oxidize with the plutonium but alloy with the zinc metal include iron, nickel, chromium, copper, lead, gallium, and silicon.

After the reaction of plutonium with zinc chloride is complete, the contents are poured (if a tilt-pour furnace is used), cooled, and broken out. The ceramic, if a stationary furnace is used, is separated from the salt and metal products. The salt is separated from the metal. The metal phase is composed of zinc and the nonoxidized impurities. The salt phase is composed of plutonium chloride, calcium chloride, potassium chloride, and the chlorides of americium, magnesium, uranium, and aluminum oxidized by the zinc chloride. The impure zinc metal phase is discarded and the plutonium-rich salt phase is reloaded into a crucible, this time with calcium metal. The contents are again melted and stirred, and a reduction reaction occurs:

$$PuCl_3 + {}^3/_2\ Ca^\circ \rightarrow Pu^\circ + {}^3/_2\ CaCl_2 \qquad (13)$$

After cooling, the metal phase and salt phase are again separated. The salt phase might be reused if it can be kept dry and if the eutectic composition is restored by the addition of potassium chloride, to compensate for the calcium chloride formed from the reduction reaction (Equation 13). The metal phase contains the purified plutonium, but also usually contains zinc and calcium metals.

The zinc and calcium may be removed from the plutonium product by the vacuum melting process, described under Salt Cleanup. After the zinc and magnesium are distilled away, the plutonium metal may be acceptable for Foundry feed.

CONCLUSION

As of FY 1983, processes which are in production or are nearing production status include MSE, DOR, and ER. The other processes, SCU, compatible salt study, and pyroredox, require additional development. The major advantages of pyrochemical processes over other conventional processes include a minimum number of processing steps, rapid turnaround time, decreased radiation exposure to personnel, and fewer residues generated. These advantages can result in lower costs and decreased manpower requirements.