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## PYROCHEMICAL PROCESSING OF FUEL MATERIALS AND SCRAP CONTAINING PLUTONIUM-238

by

P. A. Nelson, J. Fischer, J. F. Lenc,
J. R. Haley, and J. D. Schilb

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for Plutonium and Uranium

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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Chemical Engineering Division

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# PYROCHEMICAL PROCESSING OF FUEL MATERIALS AND SCRAP CONTAINING PLUTONIUM-238

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## ABSTRACT

The use of pyrochemical processing techniques was investigated as a means of recovering $^{238}Pu$ from various types of materials and purifying it. One promising process tested consisted of reducing $^{238}PuO_2$ powder or microspheres with liquid Zn-Mg alloys in the presence of a molten chloride salt. A metallic $^{238}Pu$ product was then recovered by vacuum distillation of the solvent metals. This process was effective in removing the light-element impurities that cause neutron emission by $(\alpha,n)$ reactions. In an experimental test of this process, in which about 12 g of $^{238}PuO_2$ with a neutron count of 42,500 n/(sec)(g $^{238}Pu$) was used as the starting material, the neutron count of the product was 2930 n/(sec)(g $^{238}Pu$) [2360 n/(sec)(g Pu)].

Processes were also considered for (1) removing corrosion-product impurities from $^{238}PuO_2$ and (2) recovering $^{238}Pu$ from $^{238}PuO_2$-Mo and $^{238}PuO_2$-$ZrO_2$ fuel materials. Experiments with $^{239}PuO_2$ indicated the general feasibility of pyrochemical processes for these applications, but the procedures have not been sufficiently developed for use in production.

The results of this work indicate that pyrochemical procedures that may have immediate production applications are (1) reduction of $^{238}PuO_2$ scrap material to produce impure $^{238}Pu$ metal for subsequent aqueous processing, (2) reduction of relatively pure $^{238}PuO_2$ to remove light-element impurities and produce $^{238}Pu$ metal, and (3) dissolution of $^{238}PuO_2$-Mo cermets in a $CuCl_2$-containing molten salt for aqueous processing.

# 1. INTRODUCTION

Plutonium-238, which has a half-life of 87.2 yr, decays by the emission of ~5.5-MeV alpha particles. Self-absorption of the alpha particles by the material results in a heat-generation rate of ~0.55 W/g $^{238}Pu$. Because of these characteristics, $^{238}Pu$ is valuable as an isotopic heat source and is used for various applications, including space missions. The isotope is produced at the Savannah River Laboratory by the irradiation of $^{237}Np$. The fuel itself, usually in the form of $^{238}PuO_2$ microspheres, is prepared at Mound Laboratory.

The initial objective of this program was the development of a pyrochemical process for preparing high-purity $^{238}Pu$ metal from impure oxide feed material. Such a process might be suitable for recovery and purification of $^{238}Pu$ in the oxide scrap that results from the production of $^{238}PuO_2$ microspheres. Scrap of this type contains light-element impurities and, in some cases, corrosion products, including iron, nickel, and chromium. The light elements (atomic number $<14$) are undesirable, because the presence of many of the light elements results in high neutron-generation rates through $(\alpha,n)$ reactions; the corrosion products are undesirable, because they lower the melting points of both metallic plutonium and $PuO_2$.

As the work on this program proceeded, it became apparent that there might be other applications of pyrochemical purification processes for $^{238}Pu$ fuel materials. Consequently, other applications have been investigated, including (1) preparation of $^{238}Pu$ metal having a low radiation level by removing the light elements and uranium, and (2) recovery of $^{238}Pu$ from $^{238}PuO_2$-molybdenum and $^{238}PuO_2$-$ZrO_2$ fuel materials.

# 2. CHEMISTRY OF PYROCHEMICAL PROCESSES FOR PLUTONIUM REDUCTION AND PURIFICATION

## 2.1 Background

The Chemical Engineering Division at Argonne has acquired considerable experience in pyrochemical operations as a result of development work on fuel reprocessing both for the Second Experimental Breeder Reactor (EBR-II)[1-10] and for oxide and carbide fuels proposed for future fast breeder reactors.[11-12] The first process developed for EBR-II was melt refining, a simple oxidative-slagging procedure for the purification of the enriched uranium alloy core fuel. Equipment for this process was installed in the Fuel Cycle Facility at the EBR-II Site in Idaho and was operated successfully for several years in processing 10-kg batches of irradiated fuel.

Plant-scale remotely operable equipment has been designed and tested[3-5,13-14] for the recovery of melt-refining residues by a process (the skull-reclamation process) employing liquid-metal and salt solvents. Although this equipment has not been used to process irradiated material, it has provided valuable practical experience in various operations at high temperature, such as agitation, transfer of liquid salts and metals, separation of liquid from solid phases, and the removal of liquid-metal solvents from product metals by retorting. Techniques have also been developed for salt purification, liquid-level detection, control of transfer rates, and the addition of reagents to molten salt and metal solvents. Numerous materials for the containment of liquid salts and metals have been tested and evaluated.

These chemical and technological developments are presently being extended to liquid metal-molten salt processes for uranium-plutonium oxide and carbide fuels. Much of the development work on the pyrochemical steps used in these processes is being conducted on a laboratory scale in a high-alpha glovebox facility. Since the recovery of $^{238}PuO_2$ scrap would involve similar experimental techniques, the experience with pyrochemical operations is most valuable.

The basic steps that would be used for the recovery of $^{238}PuO_2$ scrap include (1) reduction of $PuO_2$ to metal by a liquid magnesium alloy, (2) separation of impurities by removal of impurity-bearing phases, and (3) recovery of a metallic product by evaporation of the liquid-metal solvent. These steps are discussed below.

## 2.2 Reduction Procedures

Laboratory-scale experiments have shown that $PuO_2$, $U_3O_8$, $UO_2$, $ThO_2$, and $NpO_2$ can be reduced to the respective metals by liquid Zn-Mg or Cd-Mg alloys in the presence of a $MgCl_2$-based salt.[15,16] Chlorides and fluorides of the actinide elements are also reduced by this procedure. With the proper choice of operating conditions, reduction yields exceeding 99% can be achieved.

The reduction of $PuO_2$ with a Cd-Mg alloy involves the overall reaction

$$PuO_2(\text{salt}) + 2Mg(Cd) \rightarrow Pu(Cd\text{-}Mg) + 2MgO(\text{salt}). \qquad (1)$$

The $PuO_2$ is added to a molten $MgCl_2$-based salt, which is contacted with the Cd-Mg alloy by vigorous agitation at 700-750°C. The metallic plutonium product dissolves in the Cd-Mg alloy. The solid MgO formed as a by-product of the reduction reaction is collected in the salt phase, which is discarded as waste.

In the uranium oxide and thorium oxide reduction studies,[15,16] the major variables affecting the rate of reduction were salt composition, temperature, vigor of agitation, particle size of the oxide feed, and the MgO loading in the salt phase. These variables were not investigated extensively in the $PuO_2$ reduction studies, but it was found that $PuO_2$ is reduced much more readily than is $UO_2$ or $ThO_2$, and that the reduction rate of $PuO_2$ is much less dependent upon the composition of the salt phase.

Scouting studies have also shown that magnesium alloys other than Mg-Cd and Mg-Zn can be used as reductants of actinide metal oxides. For example, reductions have been performed using Cu-Mg or Al-Mg alloys as reductants.[16-19]

## 2.3 Separation Procedures

In pyrochemical processes, most other elements are separated from plutonium by either of two methods: (1) selective precipitation of certain constituents from a liquid-metal solution[20] or (2) selective extraction from a liquid-metal solvent into a molten salt.[21]

Fuel-reprocessing studies have yielded extensive information on the solubilities and coprecipitation behavior of plutonium and other pertinent elements in liquid-metal solutions. Data are also available on many phase diagrams of importance, and on the thermodynamics of liquid-metal solutions.

In liquid metal-molten salt extraction procedures, separations are effected through differences in the distribution behavior of solutes between immiscible liquid salt and metal phases. Separations of this type generally employ liquid magnesium alloys and a molten chloride salt containing $MgCl_2$. Plutonium, for example, distributes between a magnesium alloy and a molten salt containing $MgCl_2$ according to the reaction

$$Pu(Zn\text{-}Mg) + 3/2\ MgCl_2 \rightleftharpoons PuCl_3(salt) + 3/2\ Mg(Zn). \qquad (2)$$

The relative plutonium concentrations in the salt and metal phases at equilibrium are expressed by the distribution coefficient, i.e.,

$$K_d = \frac{\text{wt \% Pu in salt}}{\text{wt \% Pu in metal}}. \qquad (3)$$

The factors that determine the distribution coefficient are: (1) the standard free-energy change of the reaction, (2) the concentrations of $MgCl_2$ and magnesium in the salt and metal phases, respectively, and (3) the activity coefficients of the reactants and products in their respective phases.[22] The value of a distribution coefficient depends primarily upon the free-energy

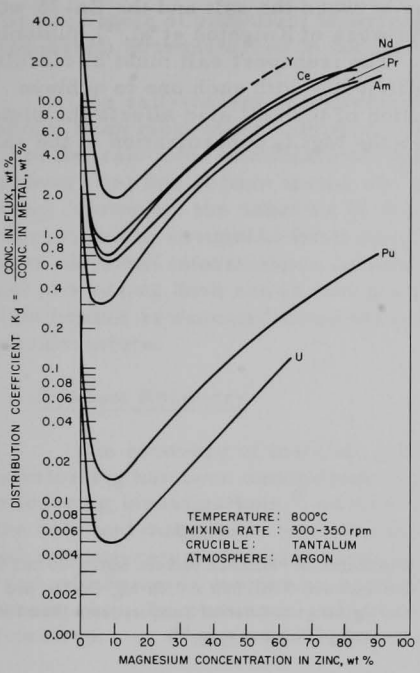



Fig. 1. Distribution of Selected Elements between Magnesium Chloride and Zinc-Magnesium Alloys

change, but it can be varied through several orders of magnitude by changes in the compositions of the salt and metal solvents. Some typical distribution data are shown in Fig. 1, where the distribution coefficients of various elements between Zn-Mg alloys and $MgCl_2$ are shown as a function of magnesium concentration in the liquid-metal phase.[21] In general, the alkali, alkaline earth, and rare-earth metals distribute more strongly to the salt phase than do plutonium and uranium, whereas the refractory and noble-metal elements distribute more strongly to the metal phase. The distribution coefficients of the alkali and alkaline-earth metals ($>\sim 10^4$) and those of the refractory and noble metals ($<\sim 10^{-4}$) are not shown in Fig. 1. Plutonium and uranium can be made to distribute to either phase by varying the relative quantities and compositions of the salt and metal solvents.

Many elements can be separated from plutonium by salt-metal extraction in a single-stage contact. For example, the reduction of $PuO_2$ by Zn-Mg alloy can be carried out under conditions such that >99% of alkali and alkaline-earth elements will remain in the salt phase.

A recently conceived separation procedure is the salt-transport technique,[17] which shows considerable promise for separations in salt-metal systems. The technique involves selective transfer of a solute between two liquid-metal solvents through an intervening molten-salt phase. This concept is illustrated schematically by the diagram in Fig. 2, in which a Mg-30 wt % Cd donor alloy containing plutonium and impurity elements and a Zn-25 wt % Mg acceptor alloy are in mutual contact with a molten-salt phase containing $MgCl_2$ (e.g., $MgCl_2$-42 wt % $CaCl_2$ eutectic). Since plutonium has a higher distribution coefficient between the salt

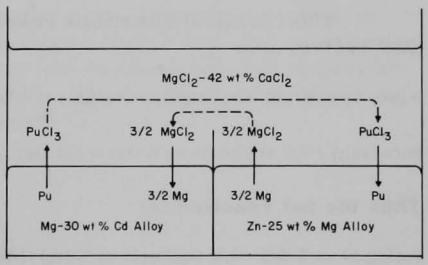



Fig. 2. Schematic Illustration of Salt-transport Step for Plutonium

and the Mg-30 wt % Cd alloy than it has between the salt and the Zn-25 wt % Mg alloy (see Fig. 3, prepared from the work of Knighton et al.[18]), plutonium is transferred to the Zn-25 wt % alloy. The transport salt must be circulated between the two alloys and contacted efficiently with each one to achieve practical transfer rates. The composition of the salt also affects the plutonium distribution coefficient; the higher the $MgCl_2$ concentration of the salt, the higher the distribution coefficient.

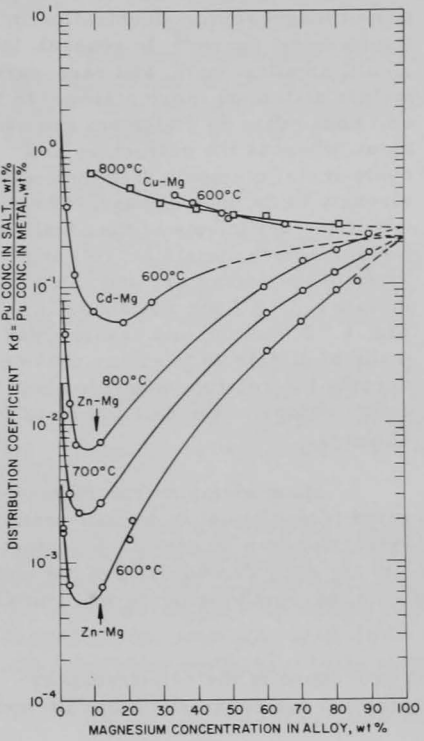



Fig. 3

Distribution of Plutonium between $MgCl_2$-30 mol % NaCl-20 mol % KCl Salt and Zn-Mg, Cd-Mg, and Cu-Mg Alloys at Selected Temperatures. (Based on the work of Knighton et al.[18])

The chemical reactions responsible for the transfer of plutonium in this system are:

$$Pu(Mg\text{-}30\ wt\ \%\ Cd) + 3/2\ MgCl_2 \rightarrow PuCl_3(salt) + 3/2\ Mg(Mg\text{-}30\ wt\ \%\ Cd); \quad (4)$$

$$PuCl_3(salt) + 3/2\ Mg(Zn\text{-}25\ wt\ \%\ Mg) \rightarrow 3/2\ MgCl_2 + Pu(Zn\text{-}25\ wt\ \%\ Mg). \quad (5)$$

Thus the net reaction is:

$$Pu(Mg\text{-}30\ wt\ \%\ Cd) + 3/2\ Mg(Zn\text{-}25\ wt\ \%\ Mg) \rightarrow Pu(Zn\text{-}25\ wt\ \%\ Mg) + 3/2\ Mg(Mg\text{-}30\ wt\ \%\ Cd). \quad (6)$$

For each mole of plutonium transferred to the Zn-Mg alloy, 1.5 moles of magnesium is transferred to the Mg-Cd alloy.

The salt-transport procedure should permit good separation of plutonium from most other elements. The procedure has not been tested for all of the salt-alloy combinations that might be considered for $^{238}$Pu scrap recovery nor has it been tested for all of the impurity elements in the scrap. However, the behavior of the systems and impurity elements of interest can be estimated from known distribution data, solubilities, and other chemical information. Laboratory-scale studies on fast reactor fuel processing have shown that plutonium, uranium, cerium, and zirconium behave as expected from estimates based upon these chemical considerations.

### 2.4 Product Recovery

The recovery of metallic plutonium buttons from Zn-Mg solutions by retorting has been demonstrated experimentally in fast reactor fuel processing investigations,[15] as well as in the experiments discussed below. The zinc and magnesium are evaporated at a pressure of about 0.1 Torr and at temperatures ranging from about 700 to 950°C. Under these conditions, plutonium is melted (m.p. ~640°C) and consolidated as a button. Presumably, the plutonium could be alloyed with other metals at this stage if desired.

## 3. NEUTRON-RADIATION CONSIDERATIONS

The available $^{238}$Pu consists of a mixture of isotopes: 81 wt % $^{238}$Pu, 15 wt % $^{239}$Pu, 2.9 wt % $^{240}$Pu, and 1.1 wt % other plutonium isotopes.[23] The rate of spontaneous neutron emission, which results almost entirely from $^{238}$Pu content, is approximately 2100 n/(g)(sec). Impurity atoms that are intimately mixed with the plutonium and have low atomic numbers are capable of producing additional neutrons by $(\alpha,n)$ reactions. Neutron production as a result of the presence of light-element impurities can be calculated from measured neutron yields and alpha shielding factors. Specific neutron-production rates for light elements are given in Table I. For elements having atomic numbers higher than that of silicon, the neutron yield is insignificant, because the coulomb barrier is greater than the alpha particle energy of 5.50 MeV. The neutron-production rate, Y, can be calculated from the relationship[23]

$$Y = \frac{\Sigma m_i s_i y_i}{\Sigma m_i s_i}, \qquad (7)$$

where

$m_i$ = atom fraction of the ith element,

$s_i$ = shielding factor = $Z/\sqrt{Z+7}$

and

$y_i$ = thick target yield.

TABLE I. Specific Neutron-production Rate from Light-element Impurities in $^{238}Pu$[a]

| Element | Calculated Neutron Production Rate,[b] n/(g $^{238}$Pu)(sec) | Element | Calculated Neutron Production Rate,[b] n/(g $^{238}$Pu)(sec) |
|---|---|---|---|
| Li | 4.6 | F | 18 |
| Be | 133 | Na | 2.2 |
| B | 41 | Mg | 2.1 |
| C | 0.2 | Al | 1.0 |
| N | 0.0 | Si | 0.2 |
| | ($\alpha$,n threshold too high) | P | $<0.03$ |
| O | 0.1 | S | $<0.03$ |

[a]From Ref. 23.
[b]Each indicated impurity element is assumed to be present at a concentration of 1 ppm.

A computer program was devised to calculate neutron-production rates from the above relationship for any mixture of elements. This program was checked and found to be correct by calculating the neutron-production rates for a variety of materials and comparing these with the rates given in Ref. 23. The method was then applied to processing materials of the type that would be encountered in pyrochemical processing of $^{238}Pu$ (see Table II). The plutonium concentrations assumed for these calculations were the maximum that could be expected to be present in the salts and metals used in a pyrochemical process for purifying $^{238}Pu$.

The highest neutron-emission rate encountered in a pyrochemical purification process would be from the donor alloy. The dose rate that would be received at a distance of 2 m from a donor alloy containing 10 g of $^{238}Pu$ (about the batch size for the experimental studies) would be 11.5 n/(sec)(cm$^2$) or 1.6 mRem per hour of exposure.

The neutron-production rate resulting from alpha radiation originating within the salt would be significant, but would not be a serious problem. The weight of the salt phase would be about twice that of the donor alloy. As a result, the neutron-production rate from the salt phase would be only a small fraction of the neutron-production rate from the donor alloy, even for 83 wt % $MgCl_2$-15 wt % $MgF_2$-2 wt % $^{238}PuCl_3$ salt. Interaction between plutonium in the metal phase and the light elements in

the salt phase in contact with the metal would be negligible. All alpha radiation originating in the metal, except that originating in a thin layer adjacent to the salt phase, would be absorbed by the metal matrix.

TABLE II. Calculated Neutron Production Rates for Various Materials Containing $^{238}Pu$[a]

| Material | Neutron Production Rate, n/sec | |
|---|---|---|
| | Per Gram of Mixture | Per Gram of $^{238}Pu$ |
| $^{238}Pu$ metal (no impurities) | 2,100 | 2,100 |
| $^{238}Pu$ metal containing 0.1 wt % B, 0.06 wt % Na, 0.01 wt % Mg, 0.01 wt % Al | 7,810 | 7,820 |
| $^{238}PuO_2$ | 10,100 | 11,400 |
| $^{238}PuF_4$ | 2,220,000 | 2,930,000 |
| 63 wt % Mg-27 wt % Cd-10 wt % $^{238}Pu$ (donor alloy) | 57,500 | 575,000 |
| 70 wt % Zn-23 wt % Mg-7 wt % $^{238}Pu$ (acceptor alloy) | 16,400 | 235,000 |
| 57 wt % $MgCl_2$-41 wt % $CaCl_2$-2 wt % $^{238}PuCl_3$ | 1,700 | 123,000 |
| 56 wt % $MgCl_2$-40 wt % $CaCl_2$-2 wt % $MgF_2$-2 wt % $^{238}PuCl_3$ | 2,950 | 242,000 |
| 55 wt % $MgCl_2$-39 wt % $CaCl_2$-4 wt % $MgF_2$-2 wt % $^{238}PuCl_3$ | 4,200 | 304,000 |
| 83 wt % $MgCl_2$-15 wt % $MgF_2$-2 wt % $^{238}PuCl_3$ | 11,700 | 846,000 |

[a]In this table, $^{238}Pu$ denotes plutonium of the following isotopic composition: 81 wt % $^{238}Pu$, 15 wt % $^{239}Pu$, 2.9 wt % $^{240}Pu$, and 1.1 wt % other plutonium isotopes.

Pyrochemical processes requiring the use of magnesium as a reducing agent or solvent metal would have to be performed inside a lightly shielded glovebox. If production-scale operations were undertaken at a level of 200 g of $^{238}Pu$ per batch, shielding would have to be adequate to reduce neutron transmission by a factor of 10. This amount of shielding could be provided by 7-8 in. of water or Plexiglas.[24]

Several hundred grams of $^{238}PuO_2$ could be stored in an unshielded glovebox without a serious hazard to those working in the area. This amount could be processed in a facility if fluorine, sodium, magnesium, or other light elements were not present.

## 4. PYROCHEMICAL PROCESSES FOR PLUTONIUM-238 FUELS

### 4.1 Types of Fuels To Be Processed

Pyrochemical purification processes were considered for four types of feed materials: (1) relatively pure $^{238}PuO_2$, requiring removal of only light elements, uranium, and thorium; (2) $^{238}PuO_2$ rejected for use in fabrication because of contamination by light elements, iron, nickel, carbon,

silicon, and uranium; (3) $^{238}PuO_2$-molybdenum cermets, requiring removal of molybdenum and light elements; and (4) solid solutions of $^{238}PuO_2$ with other oxides such as $ZrO_2$ or $ThO_2$. In all processes considered, the product would be unalloyed $^{238}Pu$ metal that could be either used in this form or dissolved in aqueous solutions and recycled to the standard fabrication processes.

## 4.2 Removal of Light Elements, Uranium, and Thorium from $PuO_2$

### 4.2.1 Processing Requirements

The allowable neutron-radiation level from $^{238}Pu$ may be severely limited for certain manned space missions. These limits also apply to $^{238}Pu$ for biomedical uses. The $^{238}PuO_2$ produced at Savannah River Laboratory normally has a neutron-emission rate of 40,000 to 60,000 n/(sec)(g), whereas the neutron-emission rate from high-purity $^{238}Pu$ metal is only about 2500 n/(sec)(g). The high neutron-emission rate of the as-produced oxide is due to $(\alpha,n)$ reactions with $^{18}O$ and with light-element impurities (atomic number $<14$). A product having a neutron emission rate no greater than 2500 n/(sec)(g) is desirable. Therefore, $^{18}O$ and the light-element impurities should be removed to obtain fuel of low neutron-emission rate. Oxygen-18 can be removed by exchange with isotopically pure $^{16}O$, which does not participate in $(\alpha,n)$ reactions.

The major radiation from the available $^{238}Pu$, other than neutrons, is gamma rays produced both by the decay of $^{238}Pu$ and by the decay of the daughter products of $^{236}Pu$ (present at a concentration of ~1.2 ppm in the material used in this work). The gamma radiation from $^{238}Pu$ decay is of sufficiently low energy so that it is absorbed by the usual containment materials. Higher-energy gamma rays are produced, however, by $^{212}Pb$, $^{212}Bi$, and $^{208}Tl$, which are daughter products of $^{232}U$ (half-life, 74 yr) and $^{228}Th$ (half-life, 1.9 yr). The $^{232}U$ and $^{228}Th$ are, in turn, daughter products of $^{236}Pu$ decay. Therefore, for a given $^{236}Pu$ content, the level of the more energetic gamma radiation can be minimized for the near term (5 yr) by removing the uranium and thorium. Removal of uranium and thorium from newly prepared $^{238}Pu$ would be less effective in reducing the radiation level.

The development of a process for removing the light-element impurities, $^{232}U$, and $^{228}Th$ would be required if $^{238}Pu$ were to be used for space and biomedical applications.

### 4.2.2 Flowsheet

Figure 4 shows a proposed pyrochemical process that will accept $PuO_2$ feed, remove light-element impurities, uranium, and thorium, and

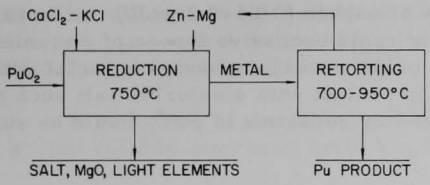



Fig. 4. Processing of $^{238}PuO_2$; Light-element Removal Only

produce a plutonium product. In the first step, $PuO_2$ containing light elements is reduced by Zn-25 wt % Mg alloy in contact with a $CaCl_2$-KCl salt at 750°C. The chemical reaction taking place is

$$PuO_2 + 2Mg \rightarrow Pu + 2MgO. \qquad (8)$$

The plutonium product dissolves in the Zn-Mg metallic phase, and the MgO byproduct is suspended in the salt phase. The metal phase is then drawn off from under the salt phase and is retorted to recover a metallic plutonium product. Most of the light-element impurities are removed during reduction by transfer to the salt phase. Some of these impurities, such as lithium and beryllium, form oxides that are suspended in the salt. Others, such as fluorine and sodium, form ions in the salt. Part of the carbon impurity reacts with uranium and thorium impurities to form UC and ThC, which are suspended in the salt. Thus, the undesirable isotopes, $^{232}U$, $^{234}U$, and $^{228}Th$ can be removed by this mechanism. Magnesium, zinc, and other volatile impurities are removed during retorting, leaving a product containing only a few parts per million of these elements.

To minimize neutron emission during processing and thus avoid the need for shielding, it would be necessary to eliminate light elements such as magnesium from the processing streams. To accomplish this, reduction might be carried out with Zn-Ca alloys in contact with $CaCl_2$-KCl salt.

## 4.3 Recovery of Plutonium-238 from $PuO_2$ Scrap Materials

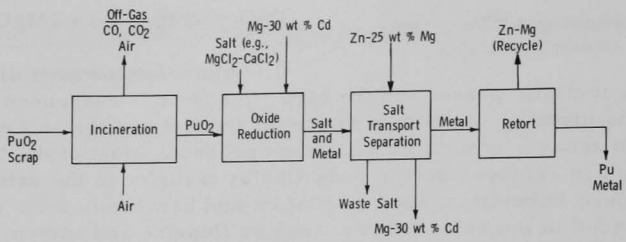
### 4.3.1 Processing Requirements

Development of a process to recover $^{238}Pu$ from the type of scrap generated at Mound Laboratory was the main objective of this program. The scrap-recovery process would have the objective of recovering $^{238}Pu$ from off-size $^{238}PuO_2$ microspheres and powder contaminated with elements of the alkali series, elements of the alkaline-earth series, silicon, chromium, iron, nickel, uranium, and various other impurities (including organic materials). The product would be metallic plutonium with low concentrations of the elements having atomic numbers below 14 and low concentrations of iron, nickel, and chromium.

### 4.3.2 Flowsheet

Figure 5 is a schematic diagram of a process that should successfully meet the above requirements, and shows the fates of various elements in the process (based on their expected chemical behavior). If the feed

material contains appreciable amounts of carbon (>0.1-0.2 wt %), incineration would be required as a first step to avoid excessive losses of plutonium in later steps. After incineration, the oxide would be reduced to metal with Mg-30 wt % Cd alloy (the donor alloy) in contact with a chloride salt such as MgCl-42 wt % $CaCl_2$. The MgO produced by reduction of $PuO_2$ would be suspended in the salt.




Impurities Removed in Each Stream

Incinerator off-gas: Organic material.

Waste salt: Li, Na, K, Rb, Cs, Be, Ca, Sr, Ba, F, Cl, Br, U, Th, insoluble oxides, carbides, etc.

Mg-30 wt % Cd alloy: Cu, Ag, Au, Zn, Cd, Al, B, Si, Ge, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Tc, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt.

Decomposed and vaporized: Carbonates, nitrates, sulfates, all gases, Hg.

Zn-25 wt % Mg alloy: Pu, rare earths.

Fig. 5. Pyrochemical Scheme for Recovery of $^{238}Pu$ from $PuO_2$ Scrap

After reduction, a salt-transport step would be carried out to transfer plutonium into an acceptor alloy, such as Zn-25 wt % Mg, and thereby separate it from the nobler elements, such as iron, chromium, and nickel. The principles of this step are discussed in Section 2.3. If the feed material contains only a small percentage of foreign matter (< 5 wt %), the same salt may be used for reduction and for salt transport. In fact, if impurities in the feed material add little insoluble matter to the salt, the salt can be reused several times. The use of the same salt for both reduction and salt transport was investigated in the experimental studies described in Section 5.

If the feed contains a large percentage of foreign matter (~10-20 wt %), the reduction salt might be excessively viscous and unsuitable for the salt-transport step. In such cases, the salt would be discarded after reduction and a separate salt used for transport. To minimize loss of plutonium in the reduction salt, either a $KCl-CaCl_2$ or a $CaCl_2-CaF_2$ salt eutectic (instead of $MgCl_2-CaCl_2$) could be used for reduction, and a $MgCl_2$-containing salt for salt transport. Plutonium has a low distribution

coefficient between the reduction alloy and the $MgCl_2$-free salts suggested for reduction. Both suggested salts have been tested for the reduction of $UO_2$-$PuO_2$ in other programs.[25,26]

Retorting of the plutonium-bearing Zn-25 wt % Mg alloy removes all the volatile elements, including the metals used as process solvents.

## 4.4 Recovery of Plutonium-238 from $PuO_2$-Molybdenum Cermets

### 4.4.1 Processing Requirements

A cermet of $^{238}PuO_2$-molybdenum is an alternative fuel form being developed at Battelle Memorial Institute. This fuel, when compared with loose $PuO_2$ microspheres, has the advantages of greater plutonium density, greater thermal conductivity, and greater chemical stability. It is especially resistant to attack by oxidation and acid dissolution. These characteristics, although beneficial in practical applications of $^{238}Pu$ isotopic power sources, would increase the difficulty of recovering $^{238}Pu$ from rejected fuel forms and fuel to be recycled.

The main objectives in the processing of $^{238}PuO_2$-molybdenum cermets are separation of molybdenum and recovery of $^{238}Pu$. Only minor concentrations of other contaminants such as light-element impurities would be expected in this material.

### 4.4.2 Flowsheet

A schematic diagram of a process that should successfully meet the requirements given above is shown in Fig. 6. In the first step, the $PuO_2$-molybdenum cermet is chlorinated at 600°C with $CuCl_2$ dissolved in $MgCl_2$-NaCl-KCl. A reaction sequence would take place leading to dissolution of both major components of the cermet:

$$Mo + 4CuCl_2 = MoCl_4 + 4CuCl; \tag{9}$$

$$MoCl_4 + 2PuO_2 = 2PuOCl + MoO_2Cl_2. \tag{10}$$

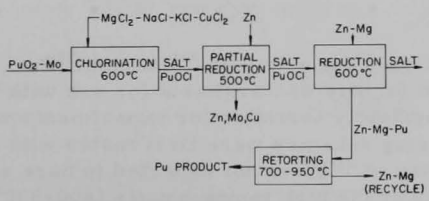



Fig. 6

Processing of $^{238}PuO_2$-Molybdenum Cermets

Recovery of the $^{238}Pu$ from the resulting salt mixture would be accomplished by the following four steps:

(1) Reduction to metal of the molybdenum and copper contained in the salt by contacting the salt phase with a zinc metal phase.

(2) Transfer of the $^{238}$Pu-bearing salt phase from the Zn-Mo-Cu metal phase to a Zn-Mg metal phase.

(3) Reduction of the $^{238}$Pu contained in the salt phase and its dissolution in the Zn-Mg metal phase.

(4) Retorting of the Zn-Mg-$^{238}$Pu metal phase to recover the $^{238}$Pu metal product.

Because of the high copper concentration expected in the zinc-rich phase in the partial-reduction step, the salt might have to be contacted with zinc twice to obtain a salt phase of low copper content.

### 4.5 Recovery of Plutonium-238 from $PuO_2$-$ZrO_2$ Solid Solution

Solid solutions of $^{238}PuO_2$ and $ZrO_2$ are of interest as isotopic fuel forms, because of their high thermal stability and because the reactivity of such solid solutions is less than that of $^{238}PuO_2$.[27]

Requirements in the pyrochemical processing of this fuel are to reduce the mixed oxide and to separate the zirconium from the plutonium. In the application of the salt-transport process to this separation, zirconium would be retained in the donor alloy, and plutonium would be transferred to the acceptor alloy via the transport salt. A donor metal-salt combination with a high distribution of plutonium to the salt phase is required. Thus, Cu-Mg or Cd-Mg alloys would be suitable donor alloys, and Zn-Mg alloys would not be suitable (see Fig. 3). The alloy used as the donor would also be the reducing agent. A small amount of calcium might be added to the donor alloy to improve its reducing capabilities.

## 5. EXPERIMENTAL STUDIES

### 5.1 Experimental Facilities

Experiments were carried out with both $^{238}$Pu and $^{239}$Pu. At the beginning of this program, no facility was available for use with $^{238}$Pu. Because facilities were immediately available for experiments with $^{239}$Pu, most of the proposed processing schemes were first tested with $^{239}$Pu. [The higher rate of alpha decay of $^{238}$Pu is not expected to have any effect on chemical-reaction kinetics at the high temperatures (600-900°C) associated with pyrochemical processes.] The facilities for these $^{239}$Pu experiments consisted of a nitrogen-atmosphere glovebox and appropriate furnaces and sampling facilities, which are discussed under the description of the individual experiments in Section 5.2.

During the period when the preliminary experiments with $^{239}Pu$ were being conducted, a small laboratory was constructed specifically for work with $^{238}Pu$ (see Fig. 7). The facilities in this laboratory included:

1. A glovebox (glovebox A) for pyrochemical work, $16\frac{1}{2}$ ft long by $3\frac{1}{2}$ ft deep by 7 ft high (exclusive of support), consisting of a 343-$ft^3$ helium-atmosphere section and an 86-$ft^3$ air-atmosphere section.

2. Helium-purification equipment for maintaining the impurity content of the glovebox atmosphere at less than 5 ppm each of oxygen and water vapor.

3. One induction furnace and two resistance furnaces located in the helium-atmosphere glovebox.

4. Equipment for high-temperature sampling of molten salt or metal solutions.

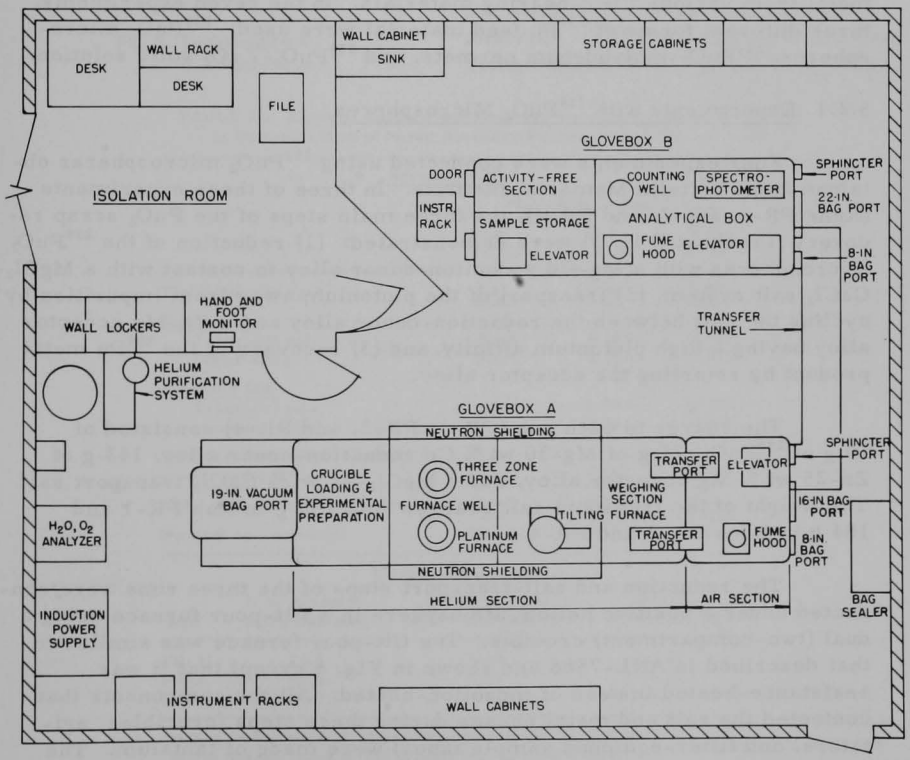



Fig. 7. Floor Plan of $^{238}Pu$ Laboratory. ANL Neg. No. 308-1772.

5. All necessary instruments for maintaining temperature and pressure control during experiments.

6. An air-atmosphere glovebox (glovebox B) for dissolution and analysis of samples and other aqueous work, connected to the pyrochemical glovebox by a transfer tunnel.

7. A multichannel analyzer with a lithium-drifted germanium detector for determining $^{238}Pu$ concentrations by gamma counting.

A detailed description of this facility and its equipment is presented in ANL-7568.[28]

## 5.2 Demonstration Experiments with Plutonium-239

Seven experiments were conducted with $^{239}Pu$-bearing materials to evaluate potential pyrochemical processes for recovery of high-purity $^{238}Pu$ metal from various $^{238}Pu$-bearing materials. In the seven experiments, three different forms of $^{239}Pu$ feed material were used: $^{239}PuO_2$ microspheres, $^{239}PuO_2$-molybdenum cermets, and $^{239}PuO_2$-$ZrO_2$ solid solution.

### 5.2.1 Experiments with $^{239}PuO_2$ Microspheres

Four experiments were conducted using $^{239}PuO_2$ microspheres obtained from Battelle Memorial Institute. In three of these experiments (Runs PR-1, PR-2, and PR-4), the three main steps of the $PuO_2$ scrap recovery flowsheet (Fig. 5) were demonstrated: (1) reduction of the $^{239}PuO_2$ microspheres with a Mg-Cd reduction-donor alloy in contact with a $MgCl_2$-$CaCl_2$ salt system, (2) transport of the plutonium away from impurities by cycling the salt between the reduction-donor alloy and a Zn-Mg acceptor alloy having a high plutonium affinity, and (3) recovery of the $^{239}Pu$ metal product by retorting the acceptor alloy.

The charge to each run (PR-1, PR-2, and PR-4) consisted of 10 g of $^{239}PuO_2$, 75 g of Mg-30 wt % Cd reduction-donor alloy, 143 g of Zn-25 wt % Mg acceptor alloy, and a $MgCl_2$-42 wt % $CaCl_2$ transport salt. The weight of the transport salt charged was 150 g in Run PR-1 and 184 g in Runs PR-2 and PR-4.

The reduction and salt-transport steps of the three runs were conducted under a positive helium atmosphere in a tilt-pour furnace using a dual (two-compartment) crucible. The tilt-pour furnace was similar to that described in ANL-7568 and shown in Fig. 8 except that it was resistance-heated instead of induction-heated. All the components that contacted the salt and metal phases during these steps (crucibles, agitators, and filter-equipped sample tubes) were made of tantalum. The left compartment of the crucible was used for the reduction step, which

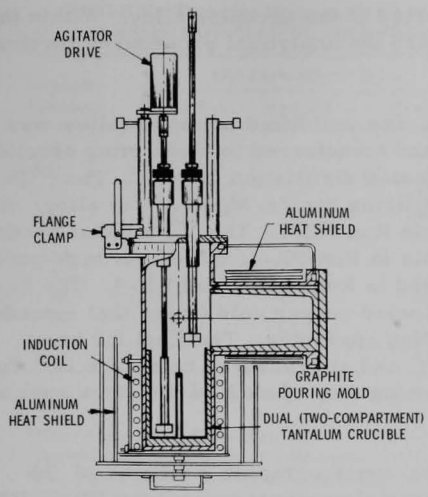



Fig. 8. Double-agitator Tilt-Pour Furnace

was conducted at 725°C for 3 hr with continuous agitation. After the reduction step, salt transport was achieved by tilting the furnace at intervals so that the salt phase could be poured back and forth between the reduction-donor alloy and the acceptor alloy contained in the right compartment of the crucible. Ten complete transport cycles were carried out. Samples of the salt and metal phases were taken after the reduction step, and samples of both phases in each compartment of the dual crucible were taken after the ten salt-transport cycles.

Plutonium material balances for each of the three runs, based on analyses of filtered samples, are presented in Table III. In all three runs,

TABLE III. Material Balance and Recovery Data for Plutonium in Demonstration of Scrap Recovery Process with $^{239}Pu$

Accountability

| | Plutonium Content,[a] g | | |
|---|---|---|---|
| | Run PR-1 | Run PR-2 | Run PR-3 |
| Plutonium Charged | 8.82 | 8.82 | 8.82 |
| Donor Side | | | |
| Transport salt | 0.405 | 0.253 | 0.199 |
| Donor alloy | 0.815 | 0.311 | 0.187 |
| Acceptor Side | | | |
| Transport salt | 0.025 | 0.081 | 0.050 |
| Acceptor alloy | 7.32 | 8.24 | 7.827 |
| Samples taken after reduction (metal and salt) | 0.087 | 0.211 | 0.355 |
| Total plutonium accounted for | 8.652 | 9.096 | 8.618 |
| Percent accounted for | 98.1 | 103.1 | 97.7 |

Product Recovery

| Run | % of Acceptor Alloy Retorted | Weight of Pu in Alloy Retorted, g[a] | Weight of Pu Product, g[b] |
|---|---|---|---|
| PR-1 | 73.5 | 5.38 | 4.22 |
| PR-2 | 85.4 | 7.04 | 6.89 |
| PR-4 | 84.0 | 6.58 | 6.05 |

[a]Based on analyses of filtered samples of the molten salt and metal phases taken at 725°C after the salt-transport step.
[b]The acceptor alloy was not all charged to the retorting step. The discrepancy between the calculated weight of plutonium in the alloy retorted and the weight of the product may indicate a high plutonium content in material not retorted.

the bulk of the plutonium was transported to the acceptor alloy. Within the accuracy of the sampling techniques and the analytical procedures involved, plutonium accountability was 100%.

After the salt-transport step, the solidified acceptor alloy was chipped out of the tantalum crucible and transferred to a retorting crucible, which was enclosed in a resistance-heated distillation furnace. The $^{239}Pu$ metal product was recovered by volatilizing the Zn-Mg acceptor alloy. A tantalum retorting crucible was used in Run PR-1. The $^{239}Pu$ metal product stuck to the tantalum retorting crucible in Run PR-1; therefore, high-purity magnesia retorting crucibles were used in Runs PR-2 and PR-4. The Zn-Mg distillate was condensed on a water-cooled copper cold finger that extended down from the top flange of the retorting apparatus. The final 2.5 hr of retorting was conducted at about 950°C and at pressures below $5 \times 10^{-6}$ Torr. Plutonium-recovery data for the retorting step of each of the three runs are shown at the bottom of Table III.

Results of spark-source mass-spectrographic analyses of the $^{239}PuO_2$ feed material and of the $^{239}Pu$ metal products from Runs PR-1, PR-2, and PR-4 are shown in Table IV. Removal of the light elements and uranium was fairly successful in all runs. This fact is especially encouraging, since removal of these elements is important in minimizing the radiation hazard for $^{238}Pu$ metal. Table V shows the calculated $(\alpha,n)$ contribution to the total neutron-production rate for $^{238}Pu$ metal having the same average purity as the $^{239}Pu$ metal products from Runs PR-1, PR-2, and PR-4 reported in Table IV. Although the overall $(\alpha,n)$ contribution would be satisfactory for many purposes, a great improvement could be obtained by reducing the beryllium and aluminum concentrations. These sources of contamination are

TABLE IV. Spark-source Mass-spectrographic Analyses[a] of Impurities in Runs PR-1, PR-2, and PR-4

| Element | $^{239}PuO_2$ Microspheres,[b] ppm | $^{239}Pu$ Metal Product, ppm | | | Element | $^{239}PuO_2$ Microspheres,[b] ppm | $^{239}Pu$ Metal Product, ppm | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Run PR-1[c] | Run PR-2[c] | Run PR-4[c,d] | | | Run PR-1[c] | Run PR-2[c] | Run PR-4[c,d] |
| Al | 39-130 | 110-190 | 400-500 | 46-51 | Mn | 8-14 | 120-150 | 120-150 | 8.2-9.2 |
| As | | 0.2-0.3 | 0.8-1.5 | 0.2-0.3 | Mo | 27-27 | 6.5-12 | 12-12 | |
| B | 0.7-2.0 | 1.2-2.3 | 0.3-0.5 | 0.1-0.3 | N | 1.4-2.4 | 4.8-4.8 | 0.7-0.9 | 11-19 |
| Be | 0.02-0.02 | 0.6-1.5 | 3.6-5.2 | 1.9-3.4 | Na | 200-200 | 1.5-3.0 | 1.5-2.0 | 15-15 |
| Bi | 9-48 | 0.8-1.4 | | 3.8-3.8 | Nb | | 0.06-0.4 | | 1.3-1.3 |
| C | 500-1100 | 9.7-11 | 12-24 | 35-56 | Ni | 33-48 | 130-180 | 30-55 | 18-18 |
| Ca | 70-130 | 2.6-13 | 7-18 | 39-194 | O | Matrix | 74-100 | 82-94 | 100-100 |
| Cd | 3.9-3.9 | | 0.6-1.1 | | P | 5.3-9.5 | 0.7-0.8 | 2.6-2.6 | 0.9-1.1 |
| Cl | 29-45 | 29-64 | 22-35 | 15-18 | Pb | 1.5-2.5 | 68-77 | 36-36 | 38-41 |
| Co | 0.5-0.5 | 1.3-1.4 | 1.3-2.0 | 0.7-1.3 | S | 24-43 | e | 0.7-1.2 | 1.5-2.5 |
| Cr | 170-220 | 240-400 | 82-130 | 58-65 | Sc | | 0.05-0.09 | 0.05-0.09 | 0.20-0.34 |
| Cu | 34-45 | 200-320 | 200-320 | 20-27 | Si | 51-139 | 120-220 | 195-220 | 57-57 |
| F | 1.6-1.6 | | 0.1-0.2 | 2.2-2.2 | Th | 160-160 | 8.4-15 | 12-12 | 39-39 |
| Fe | 820-1100 | 800-1100 | 430-780 | 225-245 | Ti | 3.1-5.4 | 0.8-2.4 | 0.3-0.4 | 4-14 |
| Ga | 0.4-0.7 | 4.6-5.7 | 2.2-2.2 | 0.3-0.3 | U | 1500-2600 | 6.3-7.1 | 5-8 | 230-230 |
| In | 0.8-1.4 | 0.2-0.3 | 0.2-0.4 | 19-19 | V | 0.3-0.5 | 0.1-0.1 | 0.1-0.1 | 43-43 |
| K | 4.2-13 | 3.2-3.6 | 0.9-3 | 5.0-6.7 | W | | | 7-9 | 10-10 |
| Li | 0.06-0.11 | | 0.03-0.05 | | Zn | 120-160 | 24,000-24,000 | 1.0-2.8 | 5.5-55 |
| Mg | 16-32 | 2.3-3.3 | 4.7-8.8 | 8-18 | Zr | 180-300 | 1.1-4.9 | 0.7-1.1 | 4.4-4.4 |

[a]Performed by the Dow Chemical Company, Rocky Flats Division, Rocky Flats, Colorado. The absence of a value indicates that element concentration was below the detectable limit.
[b]Lowest and highest values of four determinations.
[c]Values of two determinations.
[d]Run PR-4 used a Zn-Mg acceptor alloy of very high purity: zinc, nominally 99.9999 wt %; magnesium, nominally 99.995 wt %.
[e]Zinc interference.

TABLE V. Expected Neutron Yields for (α,n) Reactions in $^{238}Pu$ Metal with Same Average Purity as $^{239}Pu$ Metal Products from Runs PR-1, PR-2, and PR-4

| Impurity Element | Concentration,[a] ppm | | | n/(g Pu)(sec)[b] | | |
|---|---|---|---|---|---|---|
| | Run PR-1 | Run PR-2 | Run PR-4 | Run PR-1 | Run PR-2 | Run PR-4 |
| Be | 1.05 | 4.4 | 2.65 | 140 | 585 | 352 |
| B | 1.75 | 0.4 | 0.2 | 72 | 16 | 8 |
| C | 10.35 | 18 | 45.5 | 2 | 4 | 9 |
| O | 87 | 86 | 100 | 9 | 9 | 10 |
| F | c | 0.15 | 2.2 | - | 3 | 40 |
| Na | 2.25 | 1.75 | 15 | 5 | 4 | 33 |
| Mg | 2.8 | 6.75 | 13 | 6 | 14 | 27 |
| Al | 150 | 450 | 48.5 | 150 | 450 | 48[d] |
| Si | 170 | 207.5 | 57 | 34 | 41 | 11[d] |
| | 425 | 775 | 284 | 418 | 1126 | 538 |

[a]Based on arithmetic average of two determinations for $^{239}Pu$ metal product from each run.
[b]Based on values from Ref. 23.
[c]Below detectable limit of 0.02 ppm.
[d]Run PR-4 used a Zn-Mg acceptor alloy of very high purity: zinc, nominally 99.9999 wt %; magnesium, nominally 99.995 wt %.

avoidable. Any beryllium present in the $^{239}PuO_2$ microspheres charged to the process should be retained in the reduction salt as BeO, and any aluminum should be retained in the donor alloy.

Runs PR-2 and PR-4 were conducted under identical conditions, except that special high-purity zinc (nominally 99.9999 wt % Zn) and magnesium (nominally, 99.995 wt % Mg) were used for the acceptor alloy in Run PR-4. The effect of the high-purity Zn-Mg acceptor alloy used in Run PR-4 on the purity of the $^{239}Pu$ product is evident from the analytical data presented in Table IV. The aluminum, copper, iron, manganese, and silicon contents of the product from Run PR-4 were significantly lower than those of the products from Runs PR-1 and PR-2.

In the fourth experiment (Run PR-3) conducted with the $^{239}PuO_2$ microspheres, a reduction-oxidation-reduction procedure was tested. This process consisted of the following four steps: (1) reduction of the $^{239}PuO_2$ with a Zn-Ca reduction alloy in contact with a $CaCl_2$-KCl salt system, (2) oxidation of the $^{239}Pu$ and excess calcium in the reduction alloy to $^{239}PuCl_3$ and $CaCl_2$ in the salt phase by the addition of $ZnCl_2$, (3) transfer of the $^{239}PuCl_3$-bearing salt phase away from the impurity-containing reduction alloy to a Zn-Ca acceptor alloy, and reduction of the $^{239}PuCl_3$ in the salt to $^{239}Pu$ metal in the acceptor alloy, and (4) recovery of the purified $^{239}Pu$ metal by retorting the acceptor alloy. The use of this process in lieu of the salt-transport process shown in Fig. 5 offers three potential advantages: (1) Elimination of the light element magnesium from the processing solutions would result in low neutron emission rates during processing of $^{238}Pu$, (2) the stainless steel impurities associated with scrap $^{238}PuO_2$ microspheres

would be soluble in the reduction alloy, and their transfer to waste would be facilitated, and (3) the process is simpler in that only one transfer cycle of the salt phase would be required, instead of multiple transfer cycles.

The charge to Run PR-3 consisted of 15.25 g of $^{239}PuO_2$ microspheres, 0.307 g of Type 304 stainless steel tubing (to simulate the stainless steel impurity associated with $^{238}PuO_2$ scrap material), 276.41 g of Zn-3.13 wt % Ca reduction alloy, 127.45 g of $CaCl_2$-19.9 wt % KCl salt, and 276.45 g of Zn-4.48 wt % Ca acceptor alloy. The $^{239}PuO_2$, stainless steel, reduction alloy, and salt were charged to the left compartment of a dual (two-compartment) tantalum crucible, and the acceptor alloy was charged to the right compartment.

The first three steps of the process (reduction-oxidation-reduction) were conducted under a positive helium atmosphere in the same tilt-pour furnace used for Runs PR-1, PR-2, and PR-4 (see Fig. 8). All the components that contacted the salt and metal phases during the run (crucible, agitators, and filter-equipped sample tubes) were made of tantalum. The $^{239}PuO_2$ reduction (Step 1) was carried out in the left compartment of the dual crucible by agitating the molten charge for 5.5 hr at 750°C. The system was cooled to room temperature, and 38.39 g of $ZnCl_2$ was added to the left compartment of the crucible. Next, the $^{239}Pu$ metal was oxidized (Step 2) by agitating at 710°C for 1 hr. The resulting $^{239}PuCl_3$-bearing salt phase was transferred by tilting the furnace so that only the salt phase was poured from the left to the right compartment of the crucible, which contained the acceptor alloy. The $^{239}PuCl_3$ in the salt was reduced to $^{239}Pu$ metal (Step 3) in the acceptor alloy by agitating the two phases at 800°C for 3 hr.

The solidified acceptor alloy was chipped out of the right compartment of the dual crucible and transferred to a high-purity magnesia crucible enclosed in the same retorting furnace used in Runs PR-1, PR-2, and PR-4. The $^{239}Pu$ metal (Step 4) was recovered by volatilizing the acceptor alloy. The Zn-Ca distillate condensed on a water-cooled copper cold finger that extended down from the top flange of the retorting apparatus. The final 2.5 hr of the retorting step were performed at about 950°C and at pressures below $5 \times 10^{-6}$ Torr.

Spark-source mass-spectrographic analyses of the $^{239}Pu$ metal product from Run PR-3 indicated that the bulk of the iron and nickel constituents of the stainless steel impurity were removed from the plutonium. (The analysis showed 625 ppm iron and 235 ppm nickel in the product.) The analyses also indicated that the $^{239}Pu$ product may have had a high calcium content. Since calcium is not soluble in plutonium, the reliability of a spectrographic analysis for calcium in plutonium is questionable. However, some calcium could be associated with the product as a result of either incomplete evaporation of the calcium metal in the acceptor alloy or partial reduction of the magnesia retorting crucible by the calcium to form nonvolatile CaO.

The chromium concentration in the $^{239}Pu$ metal product from Run PR-3 was determined by colorimetric analysis and was found to be higher than desired (~1000 ppm). The $^{239}Pu$ product from Run PR-3 also contained a large amount of tantalum due to corrosion of the tantalum components of the experimental equipment by $ZnCl_2$. In a production process, this corrosion could be avoided by using tungsten and Mo-30 wt % W components, which are resistant to $ZnCl_2$ attack.

The uranium content of the $^{239}Pu$ metal product from Run PR-3 was about the same as that of the $^{239}PuO_2$ feed material (~2000 ppm), indicating that essentially all the uranium was transferred with the plutonium. In contrast, excellent uranium removals were achieved in Runs PR-1, PR-2, and PR-4, which were conducted with a magnesium reductant. In Runs PR-1, PR-2, and PR-4, uranium probably reacted with small amounts of impurities in the system: e.g., carbon, sulfur, phosphorus. The reaction products of the impurities in these runs would be suspended in the salt phase and thereby separated from the plutonium. In Run PR-3, the calcium in the metal phase probably reacted with the impurities in the system to form compounds more stable than those of uranium. As a result, the uranium remained in the metal phase and was recovered with the plutonium. Consequently, it may be preferable to use magnesium rather than calcium as the reducing agent in processes requiring high uranium removals.

### 5.2.2 Experiments with $^{239}PuO_2$-Molybdenum Cermet Fuel Compacts

The need for a method of reprocessing scrap $^{238}PuO_2$-molybdenum cermet fuel led to an investigation of means for extending the plutonium salt-transport process to handle this fuel form. The $^{238}PuO_2$-molybdenum could be accommodated by the pyrochemical reprocessing scheme proposed for $^{238}PuO_2$ microspheres, provided that the material could be dissolved in a liquid metal or a molten salt before being charged to the purification process. If complete dissolution of both constituents of the cermet were not possible, sufficient disintegration may occur to allow the salt to react with the $PuO_2$. Various methods for accomplishing this head-end step were considered.

Two experiments (Runs PR-5 and PR-6) were conducted with $^{239}PuO_2$-17.8 wt % molybdenum cermet material to evaluate a process that would be applicable for recovery of high-purity $^{238}Pu$ metal from the cermets. The $^{239}PuO_2$-molybdenum cermet feed material consisted of quarter sections of a compacted disk (1-in. diameter by 1/2 in. thick) obtained from Battelle Memorial Institute.

The process used in Runs PR-5 and PR-6 consisted of the following five steps: (1) dissolution or disintegration of the $^{239}PuO_2$-molybdenum cermet feed material in a chloride salt system containing $CuCl_2$ as a chlorinating agent, (2) reduction of the molybdenum and copper compounds in the

salt by contacting the salt phase with a zinc metal phase, (3) transfer of the $^{239}$Pu-bearing salt phase away from the Zn-Mo-Cu metal phase to a Zn-Mg or a Zn-Ca metal phase, (4) reduction of the $^{239}$Pu compounds present in the salt phase to $^{239}$Pu metal in the Zn-Mg or Zn-Ca metal phase, and (5) recovery of the $^{239}$Pu product by retorting the Zn-Mg or Zn-Ca metal phase. The flowsheet for this process is shown in Fig. 6.

In Run PR-5, the charge to Step 1 consisted of 14.40 g of $^{239}PuO_2$-molybdenum cermet (10.44 g of $^{239}$Pu), 125 g of $MgCl_2$-21.90 wt % NaCl-18.62 wt % KCl, and 40 g of $CuCl_2$. The charge was contained under a positive helium atmosphere within a high-purity alumina crucible in a resistance-heated furnace. The cermet was dissolved by heating the charge to 590°C and agitating the melt with a fused silica stirrer for 6 hr. During this period, filtered samples were taken every 2 hr using fused silica sample tubes equipped with sintered quartz filters.

Steps 2-4 of Run PR-5 were conducted in a dual tantalum crucible. The charge to these three steps of the run consisted of 145 g of the $^{239}$Pu-bearing salt phase from Step 1, 257 g of zinc, and 143 g of Zn-25 wt % Mg. The $^{239}$Pu-bearing salt phase and the zinc phase were charged to the left compartment of the dual crucible, and the Zn-Mg metal phase was charged to the right compartment. These three steps of the run were carried out under a positive helium atmosphere in a resistance-heated, tilt-pour furnace similar to the one shown in Fig. 8. All the components that contacted the salt and the metal phases during these steps of the run (crucible, agitators, and filter-equipped sample tubes) were made of tantalum. Step 2 (reduction of the molybdenum and copper compounds in the salt phase to molybdenum and copper in the zinc phase) was conducted in the left compartment of the dual crucible by agitating the system for 0.5 hr at 500°C. Then the $^{239}$Pu-bearing salt phase was transferred (Step 3) at 500°C from the left to the right compartment, which contained Zn-Mg metal phase. The $^{239}$Pu compounds in the salt phase were next reduced (Step 4) to $^{239}$Pu metal in the Zn-Mg metal phase by agitating the system for 0.5 hr at 600°C. Following Step 4, the furnace was cooled to room temperature.

The solidified Zn-Mg-$^{239}$Pu alloy was chipped out of the right compartment of the dual crucible and charged to a high-purity magnesia crucible enclosed in a resistance-heated retorting furnace. The $^{239}$Pu metal product was recovered (Step 5) by volatilizing the Zn-Mg. The last traces of the Zn-Mg were vaporized by retorting for 2.25 hr at about 950°C and at pressures below $3 \times 10^{-5}$ Torr.

Plutonium analyses of the salt samples taken during Step 1 showed that the amount of plutonium in the molten-salt solution was essentially constant at about 85% of the total plutonium charged after 2, 4, and 6 hr of reaction time. Of the $^{239}$Pu in the salt phase charged to the molybdenum and copper reduction (Step 2), 95.5% was accounted for. Similarly, of the $^{239}$Pu transferred to the plutonium reduction step (Step 4), 82.5% was accounted for.

Chemical analyses of the $^{239}Pu$ metal product from PR-5 showed that the product contained less than 100 ppm molybdenum (the limit of sensitivity of the analysis) and 3720 ppm copper. The recovery process proved to be effective in removing the molybdenum associated with the $^{239}Pu$ metal in the feed material, but additional process modifications were deemed necessary to achieve satisfactory removal of the copper. There are two possible explanations for the presence of copper in the $^{239}Pu$ metal product: (1) Copper may have been entrained in (and transferred with) the $^{239}Pu$-bearing salt phase as metal, or (2) copper may have been dissolved in the salt phase and reduced by the Zn-Mg alloy. In either case, the copper would be present in the Zn-Mg metal phase that was charged to the retorting step.

On the basis of the results of Run PR-5, a second experiment (Run PR-6) was conducted incorporating certain modifications designed primarily to reduce the level of copper contamination in the final $^{239}Pu$ metal product. The same process steps were used, except that molybdenum and copper reduction (Step 2) was performed twice, using a new charge of zinc each time.

The first four steps of Run PR-6 were conducted under a positive helium atmosphere in high-purity alumina crucibles within a resistance-heated furnace. The other components that contacted the salt and the metal phases during these four steps of the run were made of fused silica in Steps 1-3, and of tantalum in Step 4. (The fused silica sample tubes were equipped with sintered quartz filters.) At the completion of each step, the salt and metal phases were allowed to solidify and the alumina crucible was broken away from the resulting salt and metal ingots, which were then separated mechanically. Alumina crucibles were used because they are relatively inexpensive and are compatible with the process solvents.

In Step 1 of Run PR-6, the charge consisted of 14.43 g of $^{239}PuO_2$-molybdenum (10.46 g of $^{239}Pu$), 135 g of $CaCl_2$-33.33 wt % NaCl, and 40 g of $CuCl_2$. The compacted cermet was disintegrated by heating to 600°C and agitating for 3 hr. Disintegration was nearly complete after 30 min, as indicated by analyses of samples taken during the run.

In Step 2a of the run, 157.5 g of the $^{239}Pu$-bearing salt ingot was charged to a new high-purity alumina crucible along with 360 g of special high-purity zinc (nominally 99.9999 wt % Zn). The molybdenum and copper compounds in the salt phase were reduced to molybdenum and copper in the zinc phase by heating to 550°C with agitation for 0.5 hr.

In Step 2b, 168.7 g of the $^{239}Pu$-bearing salt phase was charged to a new high-purity alumina crucible along with 390 g of the special, high-purity zinc. Additional molybdenum and copper were removed from the salt phase by heating to 600°C with agitation for 0.5 hr. Analyses of metal

phase samples taken during Step 2b indicated that 37% of the copper charged to the run was contained in the zinc-rich phase. Since the copper should have been removed in Step 2a, it was concluded that disengagement of the salt and metal was poor.

After Step 2b, the $^{239}Pu$-bearing salt phase was separated from the metal phase (Step 3). In Step 4, 135.7 g of the salt phase from Step 3 was charged to a new high-purity alumina crucible, together with 405.3 g of high-purity Zn-3.07 wt % Ca metal. The $^{239}Pu$ present in the salt phase was reduced to $^{239}Pu$ metal in the Zn-Ca metal phase with agitation at 750°C for 2 hr.

In Step 5 of the run, 379.6 g of the Zn-Ca-$^{239}Pu$ metal phase from Step 4 was charged to a high-purity magnesia crucible and loaded into a resistance-heated retorting furnace. The $^{239}Pu$ metal product was recovered by volatilizing the zinc and calcium present in the charge. The last traces of zinc and calcium were vaporized by retorting for 2 hr at about 950°C and at pressures below $5 \times 10^{-6}$ Torr.

Overall $^{239}Pu$ accountability for Run PR-6 was less than 50%. The $^{239}Pu$ not accounted for appeared to be insoluble inclusions in the zinc-metal phases from Steps 2a and 2b, and in the salt phase from Step 4. On the basis of Runs PR-5 and PR-6, it was concluded that the success of a pyrochemical process for recovery of high-purity $^{238}Pu$ metal from $^{238}PuO_2$-molybdenum cermet scrap depends on using high-purity molten salt and liquid-metal processing media. The low plutonium accountability and poor phase disengagements in Run PR-6 were ascribed to impurities in the salts. Purer salts used in PR-5 gave better results. Even with high-purity materials, however, for removal of molybdenum and copper, two steps would be required as in Run PR-6.

### 5.2.3 Experiment with $^{239}PuO_2$-$ZrO_2$ Solid Solution

Scrap $^{238}PuO_2$-$ZrO_2$ could be purified by the plutonium salt-transport process (see Fig. 5) for $^{238}PuO_2$ if the $^{238}PuO_2$-$ZrO_2$ could be reduced to $^{238}Pu$ metal and zirconium metal in a suitable reduction-donor alloy.

In three experiments (Runs PR-1, PR-2, and PR-4) conducted with $^{239}PuO_2$ microspheres, excellent separation of the zirconium present in the feed material from the final $^{239}Pu$ metal product was achieved. (See the description of the three experiments in Section 5.2.1 and the analytical results presented in Table IV.) On the basis of the favorable zirconium removals achieved in these three experiments, two experiments (designated Runs PR-7-I and PR-7-II) were conducted with $^{239}PuO_2$-39 wt % $ZrO_2$ solid solution to demonstrate the reduction step of the pyrochemical plutonium salt-transport process. The $^{239}PuO_2$-$ZrO_2$ feed material used in these experiments was a coarse powder obtained from Los Alamos Scientific Laboratory.

In Run PR-7-I, the charge consisted of 20.16 g of $^{239}PuO_2$-$ZrO_2$ (10.88 g of $^{239}Pu$), 150 g of Mg-28 wt % Cd-6.66 wt % Ca reduction alloy, and 210 g of $CaCl_2$-18.6 wt % KCl salt. The charge was in a baffled tantalum crucible inside a resistance-heated furnace having a positive helium atmosphere. All the components that contacted the salt phase and the metal phase during the run were made of tantalum.

The charge was heated to 725°C and agitated at 500 and 600 rpm for a total of 3.75 hr. Filtered samples of the Mg-Cd-Ca metal phase were obtained after 1, 2, and 3.75 hr of agitation. In addition, a filtered sample of the $CaCl_2$-KCl salt phase was obtained after 3.75 hr.

Plutonium analyses of the filtered samples of the metal phase showed that only 0.78% of the $^{239}PuO_2$-$ZrO_2$ had been reduced after 1 hr of reaction time, 0.85% after 2 hr, and 1.60% after 3.75 hr. Although these figures indicate an increase of the amount of $^{239}PuO_2$-$ZrO_2$ reduced with time, the rate of reduction was considered too low for an acceptable process.

Plutonium analysis of the filtered salt sample obtained after 3.75 hr of reduction at 725°C indicated that only 0.015% of the $^{239}Pu$ in the feed material was present as a soluble $^{239}Pu$ compound in the salt phase. To determine whether the remainder of the $^{239}Pu$ was present as insoluble $^{239}PuO_2$-$ZrO_2$ in the salt phase, samples were taken from various portions of the solidified salt phase after the run. Analyses of the samples showed that only 0.017% of the $^{239}Pu$ in the feed material was present in the salt phase, essentially the same amount as was detected in the filtered liquid sample. It was concluded that the bulk of the $^{239}PuO_2$-$ZrO_2$ had not been reduced, and that this insoluble material remained in the metal phase.

The poor reduction in Run PR-7-I may have resulted from any one, or a combination, of the following conditions: (1) inadequate reduction temperature, (2) insufficient agitation, and (3) unfavorable reduction salt. The choice of reduction salts in these various experiments was somewhat arbitrary, since very little information is available on the effect of salt composition on the reduction of $ZrO_2$.

After Run PR-7-I, the solidified $CaCl_2$-KCl salt phase was removed from above the Mg-Cd-Ca metal phase, and the metal phase was left intact in the baffled tantalum crucible. In Run PR-7-II, 215.2 g of $CaCl_2$-~15 wt % $CaF_2$ salt was charged on top of the metal phase. The charge was heated under a positive helium atmosphere in the same furnace as was used for Run PR-7-I. Reduction of the $^{239}PuO_2$-$ZrO_2$ was attempted in Run PR-7-II by increasing the temperature from 725 to 790°C and agitating at 520 rpm for 3 hr. Filtered samples were obtained after this period from two locations in the melt: (1) 1/2 in. above the crucible bottom and (2) $1\frac{3}{4}$ in. above the crucible bottom. The first was expected to be a sample of the metal phase, and the second a sample of the salt phase. However, inspection

of the samples revealed that they were both samples of the salt phase. Sectioning the crucible after Run PR-7-II showed that the bulk of the metal phase was on top of the salt phase. Reversal of the phases may have resulted from partial vaporization of the cadmium (b.p., 767°C) at the reduction temperature of 790°C; a loss of cadmium would lower the density of the magnesium-rich metal phase to a value below that of the salt phase.

Plutonium analysis of the filtered salt sample taken 1/2 in. above the crucible bottom showed that the salt phase contained 0.99% of the $^{239}Pu$ present in the $^{239}PuO_2$-$ZrO_2$ feed material. Similar analysis of a sample of the solidified metal phase indicated that 40.90% of the $^{239}Pu$ in the charge was in the metal phase. Inspection of the tantalum crucible after Run PR-7-II revealed that the balance of the $^{239}Pu$ in the $^{239}PuO_2$-$ZrO_2$ was probably present in a layer of the dark material located on the crucible bottom.

To carry out a complete pyrochemical process would require a metal reducing agent that has a high plutonium distribution coefficient (see Fig. 3) so that the plutonium can be transported away from the zirconium. To obtain a high-purity product, it would also be desirable to avoid the use of nonvolatile metals. For these reasons, a Cd-Mg reduction alloy was chosen. However, it is known from work on reduction of $UO_2$ pellets [29] that Cu-Mg alloy containing calcium as the reductant is a better reducing medium than Cd-Mg alloys. Therefore, if a process employing pyrochemical reduction and aqueous separation steps were being considered, Cu-Mg-Cd alloy would probably be the most satisfactory reducing medium.

## 5.3 Experiments with Plutonium-238

In a further evaluation of the pyrochemical processes under consideration for the production of high-purity $^{238}Pu$ metal, two experiments were performed with $^{238}Pu$-bearing materials. The feed materials for the two experiments were (1) relatively pure $^{238}PuO_2$ powder and (2) impure $^{238}PuO_2$ scrap material.

The experiments were conducted in the specially designed $^{238}Pu$ facility (see Fig. 7); the facility and its equipment are described elsewhere.[28] An additional equipment item used in these experiments was a tantalum pipetting apparatus (shown in Fig. 9) for transferring small amounts (10-100 g) of molten salt and metal from one process vessel to another. The body of the pipette was 6 in. long and 1 in. in diameter; the tip was 2 in. long and had a 3/32-in. opening. To locate the top surface of a melt, the pipette was lowered by increments and gas was drawn from the pipette with the syringe until the tip of the pipette contacted the melt; at this time, a deflection was observed on the compound gauge. The position of the pipette tip relative to the top surface of the melt was determined with a height gauge above the furnace. The position of a salt-metal interface could then be determined from the geometry of the vessel and the densities and weights of the salt and metal phases.

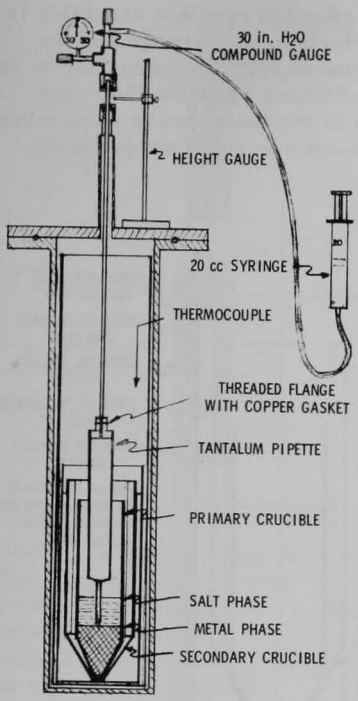



Fig. 9. Pipetting Apparatus

Throughout the experiments, $^{238}Pu$ concentrations in feed materials, products, and waste streams were determined by dissolution of representative samples and analysis by gamma counting of the $^{238}Pu$ peaks at 99 and 152 keV. The counting equipment, located beneath the analytical glovebox (see Fig. 7), consisted of a multichannel analyzer system having a lithium-drifted germanium diode detector.

The neutron activities of the feed materials and the final products were determined in a water-moderated neutron counter having four $^{3}He$ detectors. The counter, which had an efficiency of ~15%, was calibrated with a $^{238}PuO_2$ standard obtained from Mound Laboratory.

### 5.3.1 Recovery of $^{238}Pu$ Metal from $^{238}PuO_2$

The main purpose of the first experiment (Experiment 11-22) was to demonstrate a capability for handling $^{238}Pu$ by recovering $^{238}Pu$ metal from $^{238}PuO_2$. The procedure, which followed the flowsheet shown in Fig. 4, involved the reduction of $^{238}PuO_2$ with a Zn-25 wt % Mg alloy in the presence of a $MgCl_2$-50 wt % $CaCl_2$ salt phase, separation of the two phases, and recovery of the plutonium metal by vacuum distillation of the solvent metals.

The plutonium feed material for this experiment was relatively pure $PuO_2$ powder (designated ORNL No. 14) obtained from Mound Laboratory, Miamisburg, Ohio. The chemical and isotopic composition of the powder is shown in Table VI. The oxide, a granular powder, was prepared at Savannah River Laboratory by oxalate precipitation, followed by calcination at 700°C for 2 hr.

5.3.1.1 Reduction. The materials charged to the reduction step consisted of 12.388 g $^{238}PuO_2$, 100 g Zn-25 wt % Mg alloy, and 31.8 g $MgCl_2$-50 wt % $CaCl_2$. The magnesium was single-sublimed metal of 99.994% purity, obtained from Dow Metal Products; the zinc was of 99.9999% purity and was obtained from Cominco American Co. The $CaCl_2$ and $MgCl_2$ were reagent grade salts that had been pretreated with HCl at 800°C for 2 hr.

The reduction of $^{238}PuO_2$ to $^{238}Pu$ metal was conducted under a helium atmosphere ($<$2 ppm $H_2O$, 6 ppm $O_2$) in a stationary furnace described elsewhere.[28] All the components that contacted the salt and metal phases during

the reduction were made of tantalum. The reduction crucible assembly is shown in Fig. 10. Before the start of the reduction, the furnace and the charge materials were degassed under vacuum at 300°C. The reduction step was conducted at 700-790°C for 2 hr with continuous agitation (500 rpm). At the end of the reduction period, two samples of the metal phase were taken at 700°C, and the furnace was subsequently cooled to room temperature.

TABLE VI. Composition of Powdered $PuO_2$ Feed Material (ORNL No. 14) for Experiment 11-22

| Plutonium Isotope | wt % |
|---|---|
| 238 | 80.41 |
| 239 | 15.54 |
| 240 | 2.82 |
| 241 | 0.879 |
| 242 | 0.349 |

Total plutonium content: 87.29 wt %
Plutonium-238 content: 70.19 wt %
Neutron emission rate: $4.25 \times 10^4$ n/(sec)(g $^{238}$Pu)

| Impurity Element | ppm | Impurity Element | ppm |
|---|---|---|---|
| Np | 3000 | Cu | 2 |
| U | <100 | Fe | 60 |
| Th | 600 | Mg | <10 |
| $^{241}$Am | 200 | Mn | 5 |
| Al | 15 | Ni | 50 |
| B | <1 | Pb | 40 |
| Be | <0.5 | Si | 40 |
| Ca | 100 | Sn | 10 |
| Cd | 10 | Zn | 50 |
| Cr | 25 | | |

Total impurities = 8000 ppm (0.8 wt %)

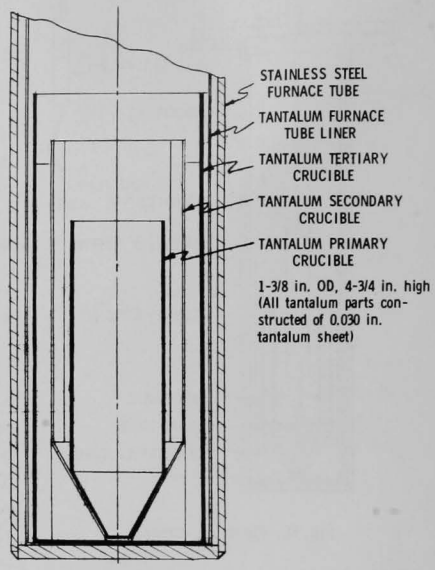



Fig. 10. Reduction Crucible Assembly

Examination of the primary and secondary tantalum crucibles after the reduction revealed that a small amount of metal had leaked from the primary crucible, apparently through a small crack that had developed at a weld joint during the latter part of the reduction. The metal phase was recovered by drilling a hole in the bottom of the primary crucible, heating the furnace to 715°C, and allowing the metal phase to drain into the secondary crucible. Subsequent examination showed that all the metal phase had been transferred to the secondary crucible and that all the salt had remained in the primary crucible.

5.3.1.2 Distillation. Most of the metal in the secondary vessel was transferred to the distillation apparatus by means of the tantalum pipette described previously. The metal was solidified within the pipette before the transfer between vessels and was subsequently remelted to allow transfer from the pipette to the tantalum distillation vessel. Approximately 87% of the reduction alloy was transferred to the distillation apparatus by this procedure.

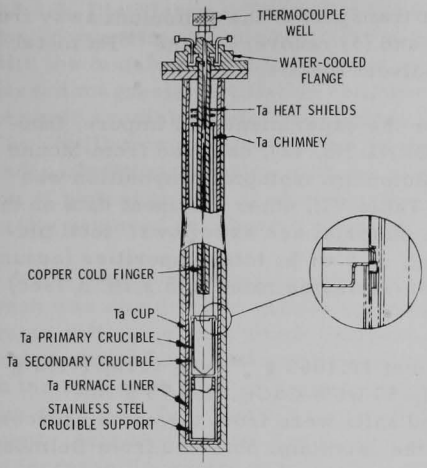



Fig. 11. Distillation Apparatus

The $^{238}Pu$ metal product was recovered by vacuum distillation of the Zn-Mg solvent and collection of the distillate on a cold finger (condenser). The distillation apparatus (see Fig. 11) and the platinum-wound resistance furnace are described in detail elsewhere.[28] The initial stages of the distillation were carried out at 770-790°C and ~1 x $10^{-5}$ Torr pressure; the temperature of the cold finger was 350°C. Final removal of the Zn-Mg was achieved by heating to 860-900°C at 4 x $10^{-5}$ Torr for ~1 hr. The cold-finger temperature during the last stages of distillation was 270°C.

The weight of the plutonium metal residue after distillation was 10.08 g, 2% higher than the amount calculated to be in the metal charged to the distillation apparatus. Most of the product was in the form of a large metal drop attached to the tantalum vessel; a small amount of the product was distributed as a thin film and as small droplets on the side wall of the vessel. The plutonium metal was clean and bright as was the inner surface of the tantalum vessel.

5.3.1.3 Salt-waste Treatment. A Zn-Mg wash step was used to reduce the amount of plutonium (estimated from distribution data to be ~0.4% of the plutonium charged remaining in the reduction salt) which would eventually be discarded as waste. The reduction salt in the primary crucible (35.6 g) was melted, and 97% was transferred by pouring to the secondary crucible, which still contained 12.2 g of the residual reduction alloy. Approximately 100 g of fresh Zn-25 wt % Mg alloy was then added, and the salt-metal system was heated at 710°C with 500-rpm agitation for 2 hr. After cooling, the entire salt phase was removed mechanically from the crucible for plutonium analysis of the bulk sample. The amount of plutonium dissolved in the salt after the wash step was estimated from distribution data to be 0.04% of the plutonium charged.

### 5.3.2 Recovery of $^{238}Pu$ Metal from $^{238}PuO_2$ Scrap Material

The second experiment with $^{238}Pu$ (Experiment 1-14) was designed to demonstrate the recovery of $^{238}Pu$ metal from impure $^{238}PuO_2$ scrap material, following the flowsheet shown in Fig. 5. The main steps of the process are (1) reduction of $^{238}PuO_2$ with a Mg-Cd reduction-donor alloy in contact

with a $MgCl_2$-$CaCl_2$ salt phase, (2) salt transport of the plutonium away from impurities to a Mg-Zn acceptor alloy, and (3) recovery of the $^{238}Pu$ metal product by vacuum distillation of the solvent metals.

The plutonium feed material for the experiment was impure, inhomogeneous $^{238}PuO_2$ scrap (designated ORNL No. 12), obtained from Mound Laboratory, Miamisburg, Ohio. The plutonium isotopic composition was the same as that of ORNL No. 14 (see Table VI); other pertinent data on the characteristics and composition of the material are as follows: total plutonium content, 69.0 wt %; $^{238}Pu$ content, 55.5 wt %; total impurities (assuming O/Pu = 2.00), 21.7 wt %; and neutron-emission rate, $8.93 \times 10^4$ n/(sec) (g $^{238}Pu$).

The charge to the run consisted of 10.1063 g $^{238}PuO_2$ scrap (7.92 g $PuO_2$), 60 g Mg-30 wt % Cd, 45 g $MgCl_2$-50 wt % $CaCl_2$, and 75 g Zn-25 wt % Mg. The magnesium, zinc, and salts were from the same sources as in Experiment 11-22; the purity of the cadmium, obtained from Belmont Refining Works, was 99.95%.

5.3.2.1 Reduction. The reduction was carried out under a helium atmosphere in a tilt-pour furnace equipped with a dual-compartment tantalum crucible (see Fig. 8). The $^{238}PuO_2$, Mg-30 wt % Cd, and $MgCl_2$-$CaCl_2$ were charged to one compartment of the dual-compartment crucible, and the Zn-25 wt % Mg alloy to the other compartment. As in the preceding experiment, the materials and equipment were degassed under vacuum at 300°C before the reduction. The $^{238}PuO_2$ was reduced at 700°C for 2 hr with 500 rpm agitation.

5.3.2.2 Salt-transport Step. Salt transport of plutonium from the donor alloy to the acceptor alloy was accomplished by cycling a molten salt between the two metal phases. In the equipment used for this experiment (shown in Fig. 8), the salt is transferred by tilting the furnace so that the salt flows from one compartment of the dual crucible to the other. However, when the planned 10-cycle salt-transport operation was attempted in Experiment 1-14, transfer of the salt from the donor alloy to the acceptor alloy was unsuccessful. Attempts to facilitate transfer by increasing the amounts of salt and metal alloys and by increasing the pouring angle were also unsuccessful. Examination of the crucible after cooling showed that some of the acceptor alloy had been transferred to the donor alloy; the salt-transport operation was therefore discontinued.

The large amounts of impurities (~22 wt %) in the $^{238}PuO_2$ feed material probably were the source of the mechanical difficulties encountered in pouring the salt; insoluble compounds would cause the salt phase to have a high effective viscosity and thus would have an adverse effect on the pouring operation. To avoid this difficulty, the reduction salt could be discarded and clean salt of a different composition be used for salt transfer. A reduction salt would be used that would favor distribution of plutonium to the metal phase.

5.3.2.3 Distillation. The solidified salt was mechanically removed from the dual-compartment crucible; all the metal was then melted and transferred with the tantalum pipetting apparatus (shown in Fig. 9) into a previously degassed magnesia distillation crucible. The small capacity (35 cc) of the ceramic crucible made it necessary to distill the metal in three batches. The distillation was carried out in the platinum-wound resistance furnace under conditions similar to those of Experiment 11-22. A consolidated button of plutonium was produced in the round bottom of the crucible and was easily removed for neutron counting and $^{238}Pu$ assay.

5.3.2.4 Waste-salt Treatment. As in the preceding experiment, a Zn-Mg wash was employed to reduce the amount of plutonium remaining in the waste salt. The salt, which had been mechanically removed from the dual-compartment crucible, was placed in the tantalum secondary crucible used in the salt-wash step of Experiment 11-22. This crucible contained a residue of 15 g of Zn-25 wt % Mg plus 0.09 g of $^{238}Pu$ from the previous experiment. An additional 50 g of fresh Zn-25 wt % Mg was charged to the crucible to increase the extent of plutonium removal from the salt. The crucible was heated at 700°C for 2 hr under a helium atmosphere at glovebox pressure. The furnace was then cooled, and the salt phase was mechanically removed from the crucible for plutonium analysis of the bulk sample.

### 5.3.3 Results of Plutonium-238 Experiments

5.3.3.1 Plutonium Balance. The experimental runs reported here were much more complex than a production run, in which only the cumulative plutonium accountability would be of concern. In these experiments, each of the many side streams and residues was processed (rather than being recycled as in a production operation) to determine the mechanisms of plutonium losses. In Experiment 11-22, the total amount of plutonium accounted for was slightly greater than 100% (see Table VII); this value is considered within the limits of experimental error, in view of the complexity of the procedures and the many samples that were analyzed.

TABLE VII. Total Plutonium Balance for Experiment 11-22

| | Weight of Pu, g | % of Charge |
|---|---|---|
| Plutonium in $PuO_2$ feed material[a] | 10.813 | 100.0 |
| Plutonium in distillate residue[b] | 10.03 | 93.2 |
| Plutonium in metal residue in pipette[c] | 0.18 | 1.7 |
| Plutonium in Mg-Zn wash in secondary vessel[d] | 0.89 | 8.2 |
| Plutonium in salt waste[e] | 0.05 | 0.5 |
| Total | 11.20 | 103.6 |

[a]Calculated from weight of starting oxide and Savannah River Laboratory data.
[b]Weighed product.
[c]Based on assay of alloy after reduction.
[d]Based on assay of wash metal.
[e]Based on assay of bulk sample.

The starting oxide for Experiment 1-14 was not homogeneous and contained a high concentration of impurities (~22%). The characteristics of the starting material and the complexity of the experiment prevented an accurate plutonium balance. However, slightly more than 100% of the plutonium was accounted for in this experiment also, although this result is less meaningful than for Experiment 11-22.

The percentage of the $^{238}Pu$ charge that was lost in the salt wastes in these experiments is a better indication of the potential plutonium losses in a production process that is the overall plutonium balance. In a process for recovery of plutonium metal from the oxide, the only waste stream would be the salt; the metal would be recycled (see Fig. 4). Table VIII shows the plutonium concentration in the salt waste and in the Zn-Mg wash alloy with which the salt was contacted. Analysis of the bulk salt samples at the end of the experiment showed that about 90% of the $^{238}Pu$ in the salt was insoluble; only 10% of the $^{238}Pu$ in the salt could be accounted for in the analyses of filtered samples. The insoluble plutonium was probably in the form of suspended compounds such as PuC or PuS formed by reaction with impurities. In a production process, the total amount of plutonium lost by discarding salts of the compositions obtained in these experiments would be acceptable.

TABLE VIII. Plutonium-238 Content of Salt and Zn-Mg Alloy Wash Products

| | | % of Plutonium Charged | |
|---|---|---|---|
| Experiment | Phase | Filtered Sample | Bulk Sample |
| 11-22 | Salt | 0.049 | 0.49 |
| | Zn-Mg wash alloy | 8.3[a] | - |
| 1-14 | Salt | 0.11[b] | 1.07 |
| | Zn-Mg wash alloy | 4.5[a] | - |

[a]The plutonium in the wash alloys would be recovered in an actual process by recycling the alloys.

[b]Calculated using the distribution coefficient of 0.019 (wt % soluble Pu in salt/wt % Pu in metal) obtained in Experiment 11-22.

5.3.3.2 Removal of Impurities. In Experiment 1-14, the impurity content of the metal product was considerably lower than that of the starting material (see Table IX), even though the salt-transport step was unsuccessful. The incorporation of a salt-transport step in which clean salt is substituted for the reduction salt should result in a metallic product of acceptable purity.

The removal of light-element impurities in both experiments was effective, as indicated by the reduced neutron activity of the products

(see Table X). These results are consistent with the low concentrations of light-element impurities in the products from the experiments with $^{239}Pu$ (see Table IV).

TABLE IX. Plutonium and Impurity Contents of Starting $^{238}PuO_2$ and Metallic Product of Experiment 1-14

| Material | $^{238}Pu$,[a] wt % | Total Pu,[b] wt % | Impurity Content, wt % |
|---|---|---|---|
| Starting $^{238}PuO_2$[c] | 55.5 | 69.0 | 21.7[d] |
| Metallic product | 76.4 | 95.0 | 5.0 |

[a]By gamma-ray assay.
[b]Total wt % Pu = $^{238}Pu/80.41$.
[c]Mixture designated ORNL No. 12.
[d]Assuming oxygen atoms/plutonium atom = 2.0.

TABLE X. Neutron Activity of Feed and Product Materials

| | Neutron Activity[a] | |
|---|---|---|
| | n/(sec)(g $^{238}Pu$) | n/(sec)(g Pu) |
| Experiment 11-22 | | |
| Oxide feed | $4.25 \times 10^4$ | $3.42 \times 10^4$ |
| Metal product | $2.93 \times 10^3$ | $2.36 \times 10^3$ |
| Experiment 1-14[b] | | |
| Oxide feed | $8.93 \times 10^4$ | $7.18 \times 10^4$ |
| Metal product | $3.98 \times 10^3$ | $3.20 \times 10^3$ |

[a]Based on an isotopic composition of 80.41 wt % $^{238}Pu$.
[b]Based on analyses in Table IX.

Although the work with $^{238}Pu$ was terminated when only a few experiments had been performed, these experiments demonstrated that the chemical behavior of $^{238}Pu$ and $^{239}Pu$ is the same at the high temperatures at which pyrochemical processes are carried out.

## 6. FULL-SCALE EQUIPMENT CONCEPTS

The experimental work was carried out in equipment of simple design requiring manual manipulations. These equipment concepts would be unsuitable for full-scale processes. Components suitable for full-scale isotope-recovery processes, developed at Argonne in the course of work on

pyrochemical fuel reprocessing, are described below. Equipment items may be used for reduction and salt-transport steps and as components of an integrated processing unit for the scrap-recovery process (see Fig. 5).

## 6.1 Reduction

Oxide reduction is a process operation common to all flowsheets considered in Section 4. In the processing of high-fired oxides, vigorous agitation, the proper metal-salt combination, an inert-atmosphere cover gas, and a temperature of 700-900°C are required.

To provide the proper conditions in developmental experiments, tilt-pour furnaces (see Fig. 12) were used. Heating elements are outside the furnace vessel. Molten samples of the salt and metal phases can be removed from the furnace crucible through the sampling ports. A gas lock is usually provided above the sample ports to prevent contamination of the furnace gas with atmospheric gases. The samples are usually taken by pressurizing the metal or salt into a 1/4-in. tantalum sample tube fitted with a tantalum filter.[30] After completion of the reduction, the salt and metal are poured into the mold in the side-arm of the furnace by tilting the entire apparatus. Equipment of this type has been used at Argonne for reduction of $UO_2$ and $PuO_2$ on a scale of up to 200 g of oxide. The expected scale of operations for $PuO_2$ scrap-recovery operations is between 150 and 200 g.

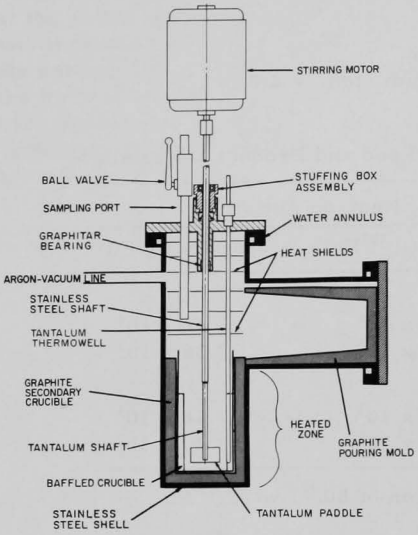



Fig. 12. Tilt-Pour Furnace. ANL Neg. No. 108-8528 Rev. 2.

For larger-scale operations or processes where reduction is to be followed by salt-metal extraction steps such as salt transport, reduction would be carried out in a stationary furnace. The heating elements can either be located outside the furnace vessel as in the tilt-pour furnace or inside the vessel, if a bell-jar type furnace enclosure is used. Either the metal or the salt phase could be removed independently from a stationary furnace through a heated metal transfer line, thereby providing a means of separating the phases. A schematic diagram of a heated transfer line is shown in Fig. 13. The use of such lines for pyrochemical operations is discussed in Ref. 31.

The most satisfactory crucible material for long-term use with molten zinc solutions containing plutonium or uranium is tungsten.[32]

Pressed-and-sintered tungsten crucibles up to 12 in. in diameter and 26 in. high have been used in reduction experiments with zinc alloys and molten salts.[33] The most satisfactory material for agitators and transfer lines, based on current data, is Mo-30 wt % W.[33]

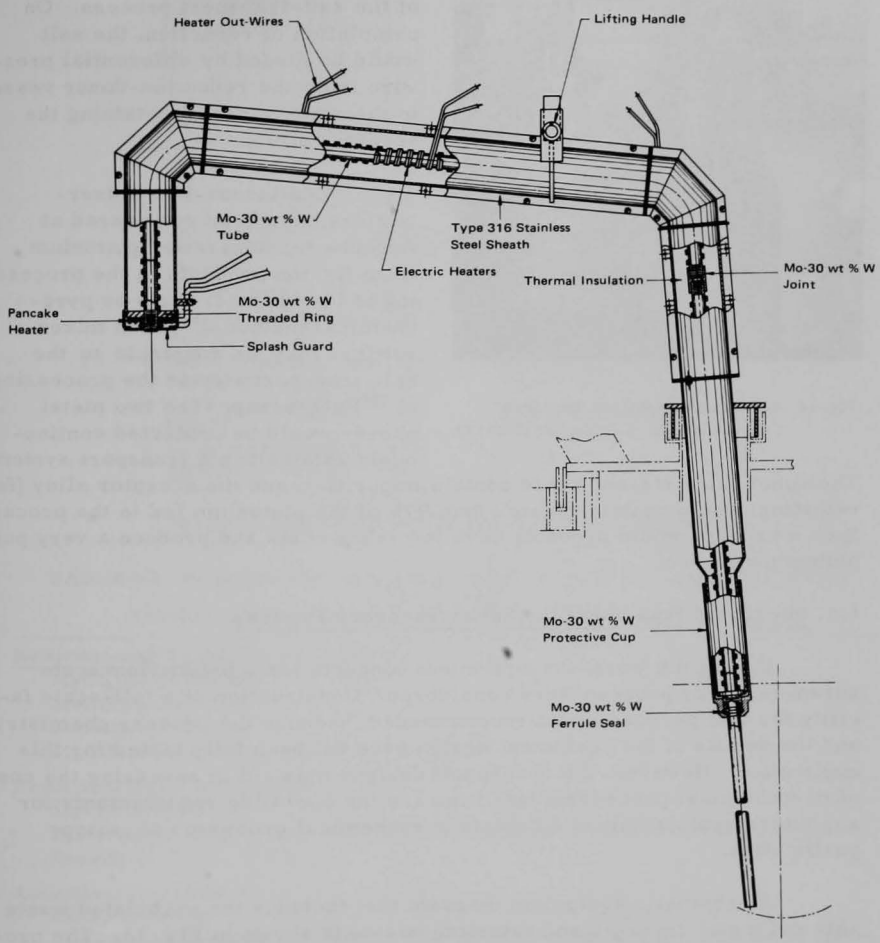



Fig. 13. Heated Transfer Line. ANL Neg. No. 308-1017 Rev. 2.

## 6.2 Salt Transport

The salt-transport operation can be carried out in two stationary vessels (of the type used for reduction) connected by a transfer line. This type of apparatus (shown in Fig. 14) has been used for transporting

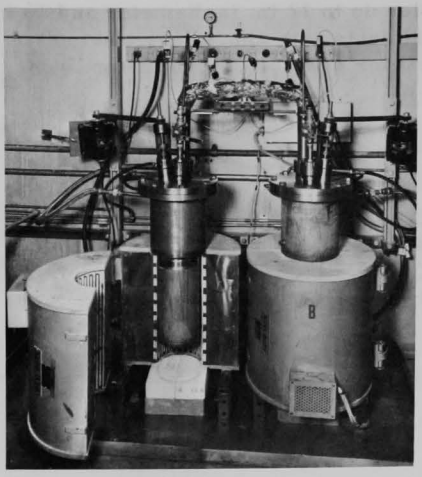


Fig. 14. Salt-transport Apparatus Employing 6-in.-ID Vessels. ANL Neg. No. 308-139.

plutonium-bearing salt on a scale of 200 g of plutonium per batch. One of the vessels can be used both for the reduction step and for the donor side of the salt-transport process. On completion of reduction, the salt would be forced by differential pressure from the reduction-donor vessel to the other vessel (containing the acceptor alloy).

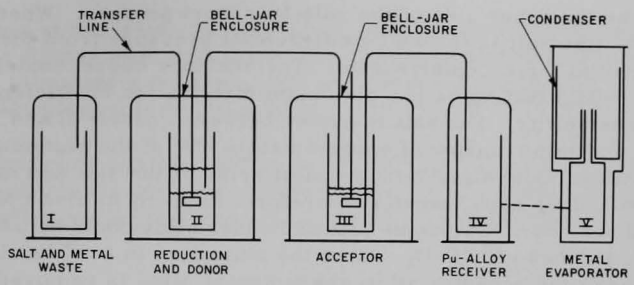
Continuous-flow mixer-settlers have been considered at Argonne for separating plutonium from fission products in the processing of fast-reactor fuels by pyrochemical methods.[34] Such mixer-settlers may be adaptable to the salt-transport step in the processing of $^{238}PuO_2$ scrap. The two metal phases would be contacted continuously with salt in a transport system. The donor alloy stream would contain impurities, and the acceptor alloy (for retorting) would contain greater than 99% of the plutonium fed to the process. Such a process would probably have low labor costs and produce a very pure plutonium product.

## 6.3 Integrated Equipment for Scrap-recovery Process

During the work, the equipment concepts for a production-scale scrap-recovery process were considered. Construction of a full-scale facility for that purpose is not recommended, because the process chemistry and the details of the equipment design have not been fully tested for this application. However, the conceptual designs may aid in assessing the cost of pyrochemical processing facilities and the operating requirements for any future applications of complete pyrochemical processes to isotope purification.

A schematic equipment diagram that includes the associated waste salt and metal receiver and retorting vessel is shown in Fig. 15. The process steps for a $^{238}PuO_2$ scrap recovery process also are described in Fig. 15. Reuse of the salt for several batches of $PuO_2$ is possible if only a moderate level of impurities (1-2 wt %) is present in the feed material.

The quantities and properties of materials for processing 200 g of scrap $^{238}PuO_2$ are given in Table XI. In this process, the $^{238}PuO_2$ is reduced by a two-phase system of molten alloy (Mg-30 wt % Cd) and salt ($MgCl_2$-42 wt % $CaCl_2$). The salt and the reduction alloy are also used for the salt-transport separation. The vessel (vessel II in Fig. 15) used for reduction is




Operating Sequence for Four Batches (800 g $^{238}Pu$)

1. Load $^{238}PuO_2$ scrap, reduction salt, and donor metal in II and load acceptor metal alloy in III.
2. Carry out reduction at 725°C in II.
3. Transfer back and forth between II and III at 725°C.
4. Lower temperature in III to 600°C, and freeze the salt.
5. Transfer acceptor alloy to receiver crucible in IV.
6. Transfer receiver crucible from IV to V, and evaporate solvent metal to recover $^{238}Pu$.
7. Load another batch of $PuO_2$ in II and acceptor alloy in III.
8. Repeat Steps 2-7 twice. Then repeat Steps 2-6.
9. Load the cleanup alloy (low-Mg alloy) in III.
10. Repeat Steps 3-6, Step 9, and then Steps 3-6 again.
11. Transfer the reduction salt and donor alloy to I.

Fig. 15. Schematic Diagram of Plutonium Scrap-recovery Equipment

TABLE XI. Properties of Processing Materials for Scrap-recovery Process

(Amounts required for 200 g of $^{238}PuO_2$ shown in parentheses)

Reduction and Transport Salt (3000 g)
- $MgCl_2$-42 wt % $CaCl_2$
- Melting point: 615°C
- Density: ~1.7 g/cc
- MgO loading after four batches: 7.4 wt %

Reduction-Donor Alloy (1500 g)
- Mg-30 wt % Cd
- Distribution coefficient at 725°C: 0.2 wt % Pu in salt per 1.0 wt % Pu in metal
- Density at 725°C: 2.1 g/cc

Acceptor Alloy (2500 g)
- Zn-25 wt % Mg
- Distribution coefficient at 725°C: 0.01 wt % Pu in salt per 1.0 wt % Pu in metal
- Density at 725°C: 4.0 g/cc
- Pu solubility at 600°C (transfer temp): ~10 wt %
- Pu loading: ~6 wt %

Clean-up Alloy (3000 g)
- Zn-10 wt % Mg
- Distribution coefficient at 725°C: 0.004 wt % Pu in salt per 1.0 wt % Pu in metal
- Density at 725°C: 5.2 g/cc
- Pu solubility at 600°C (transfer temp): ~3 wt %

also used as the donor side of the salt-transport process. When reduction is complete, the salt is forced by differential pressure from the reduction-donor vessel to the acceptor vessel. The acceptor vessel contains an alloy (Zn-25 wt % Mg) that has a low plutonium distribution coefficient and a high plutonium solubility. The salt is cycled between vessels II and III for 10 cycles to attain transfer of approximately 85% of the plutonium to the acceptor alloy. Only a few minutes of stirring of the salt and metal phases is required before each transfer; therefore, as many as five cycles can be completed per hour. The same salt and donor alloy could be used to process four 200-g batches of $^{238}PuO_2$. After the plutonium in each batch of $PuO_2$ is transferred to the acceptor alloy, the acceptor alloy is removed for distillation. Before the salt and the donor metal (which contain most of the impurities) are discharged, one or two additional salt-transport steps are carried out to transfer residual plutonium from these streams to a cleanup alloy. A fresh Zn-10 wt % Mg alloy would be the cleanup alloy, and no $^{238}PuO_2$ would be added to the donor alloy in the cleanup steps.

A conceptual design was prepared for a facility to contain the processing equipment for processing 0.2 to 1.0 kg $^{238}Pu$ per week by the procedure described above. A computer calculation of the neutron-production rates for the process solutions and alloys to be used in the scrap-recovery process indicated that shielding equivalent to approximately 10-15 in. of water would be needed. The equipment, therefore, would be remotely operated, and manipulators would be needed. The arrangement of the conceptual enclosure, associated glovebox, and process equipment is shown in Fig. 16.

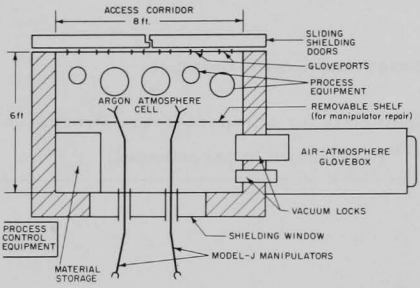



Fig. 16. Conceptual $^{238}PuO_2$ Scrap-recovery Facility

The enclosure would contain a high-purity argon atmosphere. It would be permanently shielded at the front and at the ends (probably by water tanks); sliding shielding doors would be provided in a maintenance corridor behind the facility. The process equipment, consisting of the five units (as shown in Fig. 15), can be repaired or maintained by operators using the gloveports when the shielding doors are open. Mound Laboratory is now using such maintenance corridors and sliding doors in their new $^{238}PuO_2$ production facility. The process equipment would be operated by remote-control equipment located outside the enclosure and by Model-J manipulators. Model-J manipulators have an unusually long reach and could cover the entire 6- by 8-ft floor area in the proposed facility. For repair of a manipulator, a shelf lowered over the top of the process equipment would provide space for repairs that could be performed through the gloveports at the back of the enclosure.

The Model-J manipulators can be sealed to the enclosure with gas-tight O-ring seals. In contrast, standard manipulators must depend on

plastic boots at the lower portion of the slave arms to maintain gas-tight seals. The tighter seal obtainable with the Model-J manipulator is believed necessary to maintain the high-purity atmosphere required for handling metallic plutonium without oxidation.

A traveling crane would be provided for the installation and removal of equipment and for removal of manipulators. Similar manipulator and crane installations in inert-atmosphere caves have been demonstrated at Argonne.

Two vacuum locks would be provided between the air-atmosphere glovebox and the argon-atmosphere shielded enclosure. A large lock would accommodate the largest equipment items to be installed in the cave. This lock would be provided with a sliding platform and motor-driven doors to accommodate loading and unloading. Drawings of vacuum locks of the desired types were prepared in designing another facility and are available.

The gas-purification system for the enclosure would probably consist of a catalytic reactor (using slow hydrogen addition) to convert oxygen to water, a Molecular Sieve bed to absorb water, and a blower to circulate the gas. It has been demonstrated in facilities at Argonne that this type of purification system can maintain the oxygen and water-vapor contents of the glovebox atmosphere at less than 5 ppm each. Pressure control and impurity-monitoring equipment would also be provided. The purification and recirculation equipment could be located outside the facility.

In the material-storage section, sufficient water cooling would be provided to allow storage of a total of 2 kg of $^{238}PuO_2$ scrap and recovered $^{238}Pu$ metal.

## 7. RECOMMENDATIONS

The work on pyrochemical processing of $^{238}Pu$ at Argonne was terminated before the purification processes were sufficiently developed for use in production. However, an evaluation of the results obtained in this work has indicated that some of the processes or parts of the processes may be ready for use. Other pyrochemical techniques may require refinements that could be developed during production operations.

### 7.1 Preparation of Metallic Plutonium-238

If the need arises to prepare several kilograms of $^{238}Pu$ metal from $PuO_2$, consideration should be given to the relatively simple process shown in Fig. 4. If a Ca-Zn reduction alloy is used, only minimal shielding (e.g., 4 in. of Plexiglas) would be required for processing batches of several hundred grams. After experience is gained, it should be possible to produce a

product of low neutron count from feed material of only moderate purity [1-2% total impurities, 20,000 to 60,000 n/(sec)(g)]. A final neutron count of 2930 n/(sec)(g $^{238}$Pu) [2360 n/(sec)(g Pu)] was obtained in an experiment (Experiment 11-22, Table X) with about 12 g of $^{238}PuO_2$ feed material that had an initial neutron count of $4.25 \times 10^4$ n/(sec)(g $^{238}$Pu).

The major equipment items required for this process are a tilt-pour furnace and distillation apparatus.

## 7.2 Reprocessing of $PuO_2$-Molybdenum Cermets

Although the pyrochemical process for $PuO_2$-molybdenum cermets (as shown in Fig. 6) is not yet well enough developed for production work, the initial dissolution step may be a desirable head-end step for an aqueous process. In experiments at Argonne (discussed in Section 5.2.2), quarter sections of a 1-in.-diam, 1/2-in.-thick compact of $^{239}PuO_2$-molybdenum cermet (10.44 g $^{239}$Pu) were dissolved or disintegrated in less than 30 min by a salt consisting typically of 125 g of $MgCl_2$-21.9 wt % NaCl-18.6 wt % KCl and 40 g of $CuCl_2$.

The chloride salt resulting from this process could be dissolved directly in an aqueous solution for further processing. An alternative that would avoid the corrosion problem associated with aqueous chloride solutions would be to reduce the plutonium (contained in the anhydrous salt) with a Zn-5 wt % Mg alloy. Essentially all the plutonium would be reduced and transferred to the metal phase. The salt could be separated and discarded and the metal dissolved in acid for further processing.

Whether or not the plutonium is reduced to metal after dissolution of the $PuO_2$ compact in the salt, this head-end step would require only a tilt-pour furnace such as that suggested above for reduction of $PuO_2$.

## 7.3 Dissolution of High-fired Oxides Containing Plutonium-238

High-fired $PuO_2$ or mixed oxides such as $PuO_2$-$ZrO_2$, which may be difficult to dissolve in aqueous solutions, could be reduced by molten salt-liquid metal media. Although there is no difficulty in reducing $PuO_2$ in Zn-Mg or Zn-Ca alloys in contact with a salt such as the $MgCl_2$-$CaCl_2$ eutectic, $PuO_2$-$ZrO_2$ is more difficult to reduce than $PuO_2$ microspheres (see Section 5.2.3). However, vigorously stirring a Cu-20 wt % Mg-5 wt % Ca alloy with a $CaCl_2$-18 wt % $CaF_2$ salt at 900°C might accomplish the reduction. In another program, these conditions were sufficient for reducing sintered $UO_2$, which is also difficult to reduce.

The metal solutions produced in reduction processes such as the one described above could be dissolved directly in acid solutions for further processing.

## 7.4 Equipment Recommendations

Most of the above operations can be carried out with a simple tilt-pour furnace of the type shown in Fig. 12. This type of furnace is equipped with an agitator and a means of taking samples of the salt and metal phases. After the completion of a run, the molten salt and metal are poured into a mold in the side-arm of the furnace. The crucible is then essentially emptied and ready for the next batch. Furnaces of this type, which are capable of handling 100-200 g of plutonium in the type of processes discussed above, have been operated routinely.

Because many of the salts required for pyrochemical processing are hygroscopic, it is necessary to carry out the work in a dry-atmosphere glovebox. In experimentation at Argonne, the work with $^{239}$Pu was carried out in a glovebox with a nitrogen atmosphere ("once-through" flow). The $^{238}$Pu experiments were carried out in a helium-atmosphere glovebox in which the atmosphere was recirculated at about 20 cfm through a purification system. However, a nitrogen atmosphere glovebox with "once-through" gas flow may be suitable for production-scale pyrochemical operations.

## ACKNOWLEDGMENTS

Irving Johnson and James B. Knighton made significant contributions in the initial evaluation of this project and in devising flowsheets for the various processes considered. Donald A. Wenz and Allen L. Chandler carried out some of the experiments involving $^{239}$Pu. Robert K. Steunenberg gave helpful advice and counseling throughout the project.

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