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PURIFICATION OF PLUTONIUM FUELS
BY MERCURY PROCESSING
(Experimental Survey)

LOS ALAMOS NATIONAL LABORATORY



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PURIFICATION OF PLUTONIUM FUELS
BY MERCURY PROCESSING
(Experimental Survey)

by

D. F. Bowersox and J. A. Leary

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ABSTRACT

The solubilities of selected fission product elements in mercury indicate that the purification of plutonium fuels by mercury processing is chemically feasible. Such a process was experimentally carried out on a ten gram plutonium scale with samples of two simulated fuels. If rare earth products were used as diluents in fuel, mercury processing resulted in satisfactory purification. If not, a combination with halide slagging was shown to be satisfactory. Yields of 80-96% of total plutonium were obtained in these small-scale experiments. Iron, cobalt, cerium, lanthanum, niobium, ruthenium, zirconium, and molybdenum were all removed to satisfactory levels. Plutonium was obtained as a metallic button by heating a mercury-plutonium solution to 750°C for two hours in a vacuum.

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INTRODUCTION

The study of mercury as a liquid metal solvent is one phase of the program being conducted to obtain data relative to the pyroprocessing of spent plutonium fuels.¹

Recrystallization from mercury has previously been proposed^{2,3} as a high temperature reprocessing method for spent uranium fuels. In such a process the fuel is dissolved in mercury at an elevated temperature and filtered. The rare gas fission products and insoluble fission products would be separated in this step. After the filtrate is cooled and filtered to remove soluble fission products, the residue of uranium tetramercuride would be decomposed to recover the uranium.

A similar process for plutonium fuels would appear to be feasible on the basis of the solubility of plutonium in mercury as a function of temperature.⁴ In this study the solubilities of selected fission product elements in mercury were measured to further establish such feasibility. Based on these solubility measurements, several processes for separating fission product elements from plutonium were evaluated experimentally.

SOLUBILITY OF SELECTED ELEMENTS IN MERCURY

The solubilities of iron, zirconium, niobium, molybdenum and tantalum in mercury were determined by immersing weighed coupons, each approximately 0.5 g., into 200 ml. of boiling mercury and periodically measuring the coupon weight. Thus the weight loss would correspond to the amount of element dissolved.

The solubilities of ruthenium, cerium, and lanthanum were determined individually by the method used for the plutonium-mercury solubility study.⁴ A weighed quantity of the desired element was equilibrated with 90 ml. of redistilled mercury in an inert atmosphere for 24 hours at 350°C. The mixture was adjusted to a selected temperature, and samples were drawn through a coarse Pyrex frit at intervals of 5 to 90 hours. Each sample was cooled, weighed, and analyzed for the appropriate element.^{5,6}

Results obtained in these experiments are summarized in Table 1. The solubilities of zirconium, iron, niobium, and molybdenum at 25°C were in agreement with those reported at 25°C.^{7,8} Plutonium, lanthanum, and cerium all appear to be temperature-dependent in solubility, and these solubilities are all of the same magnitude. Although ruthenium apparently dissolved in mercury at 350°C, it did not pass through a coarse Pyrex frit at either 350°C or 30°C. Therefore, since the "solubility" is considered here to be the quantity that passes through such a frit in mercury, ruthenium would be by definition insoluble.

Table 1

THE SOLUBILITIES OF SELECTED ELEMENTS IN MERCURY

<u>Element</u>	<u>Temperature, °C</u>	<u>Solubility, grams solute/liter mercury</u>
Zr	350	< 0.001
Nb	350	< 0.001
Mo	350	< 0.001
Fe	350	0.002
Ta	350	< 0.001
Pu	20	2.65
	150	20.0
	325	85.7
Ru	20	< 0.002
	250	< 0.002
La	20	2.87
	150	22.9
	250	37.0
Ce	20	1.31
	150	19.8
	250	74.5

These results indicated that good purification of plutonium fuel may be possible by mercury processing provided there are no insurmountable difficulties encountered in dissolution or in coprecipitation. Apparently the rare earths are sufficiently soluble at 20°C, while the other elements are relatively insoluble at 350°C.

PURIFICATION OF PLUTONIUM FUEL ALLOYS

These survey experiments were conducted with plutonium-fissium alloy. This alloy was prepared by comelting zirconium, niobium, molybdenum, ruthenium, lanthanum, and cerium in a master fuel alloy (90 atom percent plutonium-10 atom percent iron), followed by quench-casting to prevent segregation.⁹ The master alloy was representative of the LAMPRE-I fuel. Typical fission product elements were added in amounts that correspond to 10 percent burnup of the plutonium. Only six fission product elements were added because of limitations in alloying and analyses for the other fission products. However, the elements that were added, together with easily removable volatile fission products, represent the majority of the impurities that will be present in irradiated liquid fuel.

Three processing methods were tried. Although solubility data obtained with individual elements had indicated that good purification could be achieved by simple recrystallization, experiments with fissium alloy showed that rare earth elements coprecipitated with plutonium. Therefore a second method using halide slagging combined with recrystallization from mercury was evaluated. The third method was used to process plutonium-cerium-cobalt alloy, since this liquid metal has been proposed as a fuel for future molten plutonium reactors.

Processing of Plutonium-Iron Alloy by Recrystallization

The flowsheet for these experiments is shown in Fig. 1. A 10 g. rod of fissium alloy was contacted with mercury at 325°C for 7 hours in

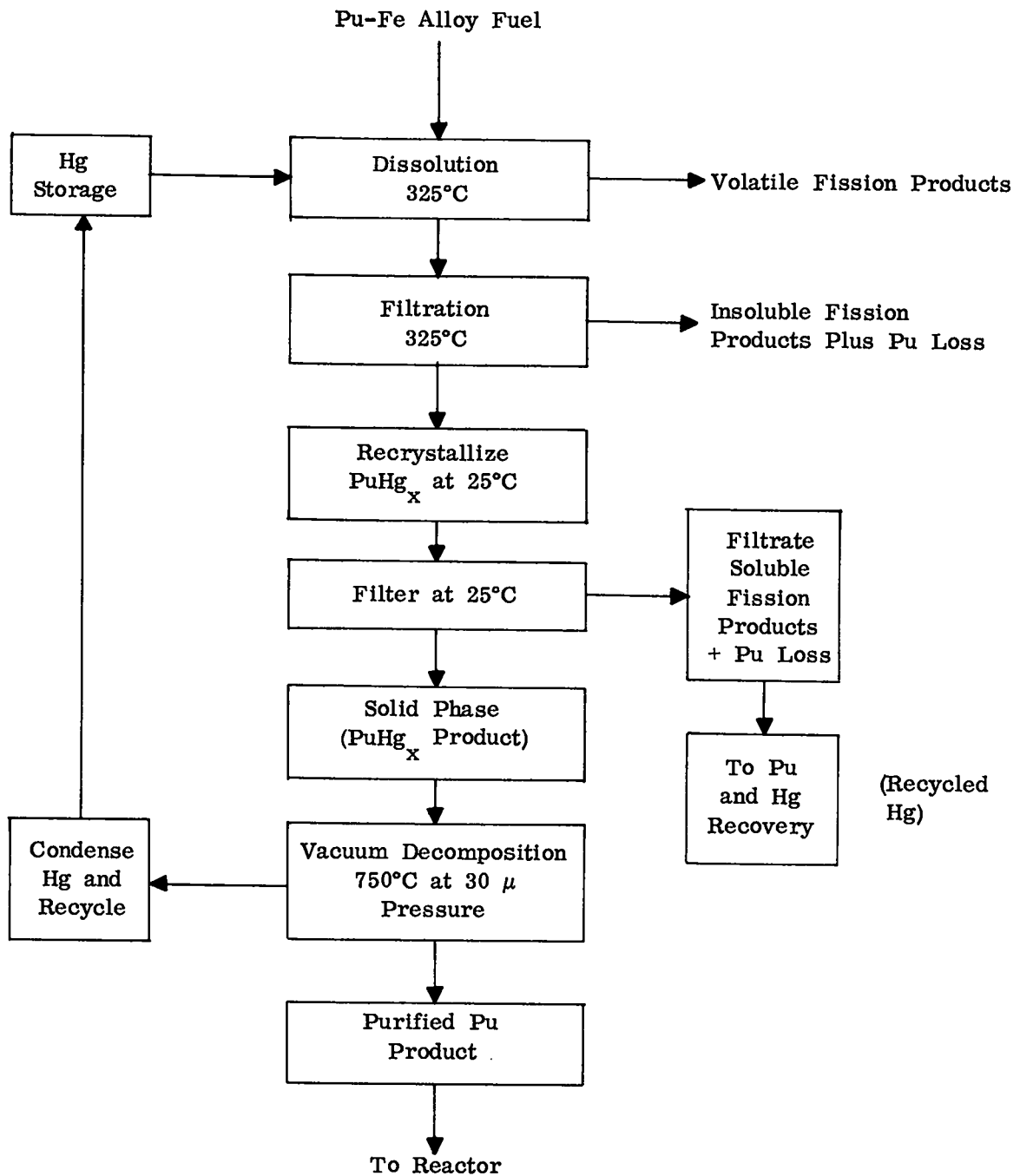


Fig. 1. Flowsheet for processing of plutonium-iron alloy fuel by recrystallization.

a Pyrex vessel filled with argon. After dissolution of the plutonium, the mercury solution was passed through a coarse Pyrex filter disk at 325°C to remove elements that were not soluble in hot mercury. The filtrate was then cooled to 25°C to recrystallize a plutonium-mercury intermetallic compound (probably PuHg₄), then filtered again through a coarse fritted disk. This solid phase was heated in vacuum to ~750°C in order to recover the metal product as a coalesced ingot.

Analyses of the fissium alloy and final product are shown in Table 2. Calculations based on individual solubilities shown in Table 1 had indicated that all impurities in the plutonium should have been below the limits of detectability, i.e., < 0.01 percent. A comparison of the lanthanum and cerium impurities actually present in the plutonium product with predicted values indicates that a large fraction of the rare earth fission products will coprecipitate with plutonium in the recrystallization step. Therefore a simple dissolution recrystallization process is inadequate for a high degree of purification from rare earths. Plutonium yields varied from 80-96% of the total Pu present. Higher yields should be attainable in larger scale processing.

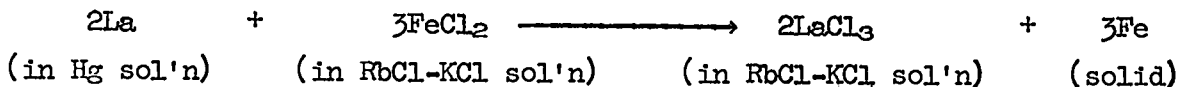
Table 2
PURIFICATION OF PLUTONIUM-IRON FISSIUM ALLOY BY
RECRYSTALLIZATION FROM MERCURY

Element	Concentration of Element, w/o	
	Fissium Alloy	Final Product
Pu	91.3	98.3
Fe	2.37	0.060
Zr	0.67	0.019
Nb	0.04	N.D.
Mo	0.75	0.0088
Ru	0.97	N.D.
La	1.59	1.06
Ce	0.74	0.53

Processing of Plutonium-Iron Alloy by Slagging and Recrystallization

Removal of rare earth elements from molten plutonium alloy by halide slagging at 600°C has been demonstrated previously.¹⁰ Therefore, a slagging step was incorporated into the dissolution step of the flow-sheet shown in Fig. 1 in an attempt to convert the rare earths in the mercury solution to insoluble rare earth chlorides. Although a solid reactive slag could be used, previous experience had indicated that a liquid slag phase was preferable. The slag selected was the 70 wt. percent rubidium chloride-30 wt. percent lithium chloride (solidus point 310°C) as the unreactive solvent system.

The reactive slag component, ferrous chloride, was added to the slag phase to a concentration of 110 percent of that calculated to oxidize all rare earth elements present. This excess is equivalent to < 0.7 w/o of the plutonium present. Rare earths were removed from the mercury solution according to the reaction



The flowsheet of Fig. 1 was further modified by conducting the high temperature filtration at 300°C to freeze the slag and prevent it from passing through the filter with the plutonium-mercury solution.

Results of the combined slagging-recrystallization methods are shown in Table 3. The decontamination factor (D.F.) is defined as the weight of an impurity, per gram of plutonium, in the fissium alloy

Table 3

PURIFICATION OF PLUTONIUM-IRON FISSIUM ALLOY BY
COMBINED SLAGGING-RECRYSTALLIZATION PROCESS

(38 g. salt phase, 9.3 g. fission alloy, 100 ml. Hg)

<u>Element</u>	<u>Concentration of Element, w/o</u>		<u>D. F.</u>
	<u>Fission Alloy</u>	<u>Plutonium Product</u>	
Pu	91.3	99.7	
Fe	2.54	N.D.	> 2540
Zr	0.77	N.D.	> 770
Mo	0.89	0.008	120
Ru	1.30	N.D.	> 1300
La	2.13	0.11	21
Ce	1.02	0.08	14

divided by the weight of the impurity per gram of plutonium in the final product. These results indicate that adequate removal of fission product elements, including rare earths, can be achieved by this combined slagging-recrystallization procedure.

Processing of Plutonium-Cerium-Cobalt Alloy by Recrystallization

The plutonium-cerium-cobalt ternary system has been proposed for liquid-fueled power reactors.¹¹ In this system the composition of cobalt can be fixed at approximately 12-25 atom percent, while the concentration of plutonium can be varied over a wide range without seriously altering the solidus point of the system.

Thus cerium is present in this type of fuel in gross amounts as an alloying constituent. For a power reactor fuel, the cerium concentration probably will exceed the plutonium concentration (on an atom basis). Employing a slagging step in the fuel reprocessing cycle probably would be undesirable, owing to the fact that essentially all of this cerium would be extracted into the slag phase. However, it seems likely that removal of soluble rare earth fission products is not necessary for such fuels. Because their atomic fractions will be low in comparison to the cerium already present, they should not seriously increase the liquidus point of the molten fuel. Moreover, in the proposed fast reactor application, substitution of rare earth fission product atoms for cerium in the molten fuel will not seriously alter the neutron economy or energy distribution.

Small scale experiments were conducted with 83 a/o plutonium-12 a/o cobalt-5 a/o cerium to determine the behavior of the fuel during dissolution and filtration. The alloy was prepared by comelting 100 g. of plutonium with 3.53 g. cerium at 900°C for 30 minutes in a tantalum crucible. This binary alloy was then cooled, 3.60 g. cobalt were added, and the system heated to 800°C for 15 minutes. A solidus point of ~420°C was observed by thermal analysis. The alloy was remelted and cast into 1/8 in. and 1/4 in. diameter rods by injection into quartz tubes. A 4 g. segment of these rods was then dissolved in 50 ml. of mercury at 325°C, followed by filtration and vacuum decomposition at 900°C. This decomposition product contained 90-95 percent of the plutonium initially

added to the dissolver. The chemical composition of the final product was 96.9 percent by wt. plutonium, 2.9 percent cerium, and 0.2 percent cobalt.

Experiments have not been conducted to determine the decontamination of fission product elements from this fuel because the actual fuel application is still in doubt. However, the information gained to date indicates that the simple flowsheet shown in Fig. 2 would provide adequate purification.

MATERIALS OF CONSTRUCTION

Pyrex was used as the container material for most of the experiments in the temperature range of 25-325°C. During vacuum decomposition, the mercurides were contained in either tantalum or magnesia crucibles located within a stainless steel tube. In all experiments an inert atmosphere (argon or helium) was used to prevent oxidation of the plutonium. The plutonium-cerium-cobalt alloy dissolution and filtration experiments were conducted in Type 304 stainless steel equipment, including stainless steel filter disks. A 7 hour corrosion test indicated no weight loss by 5-g. coupons of Type 304 stainless steel and tantalum after immersion at 340°C in boiling mercury containing 85 g. plutonium per liter, 0.7 g. cerium per liter, and 1.4 g. lanthanum per liter. This corresponds to a corrosion rate of less than 0.010 in. per year for the stainless steel and less than 0.005 in. per year for tantalum.

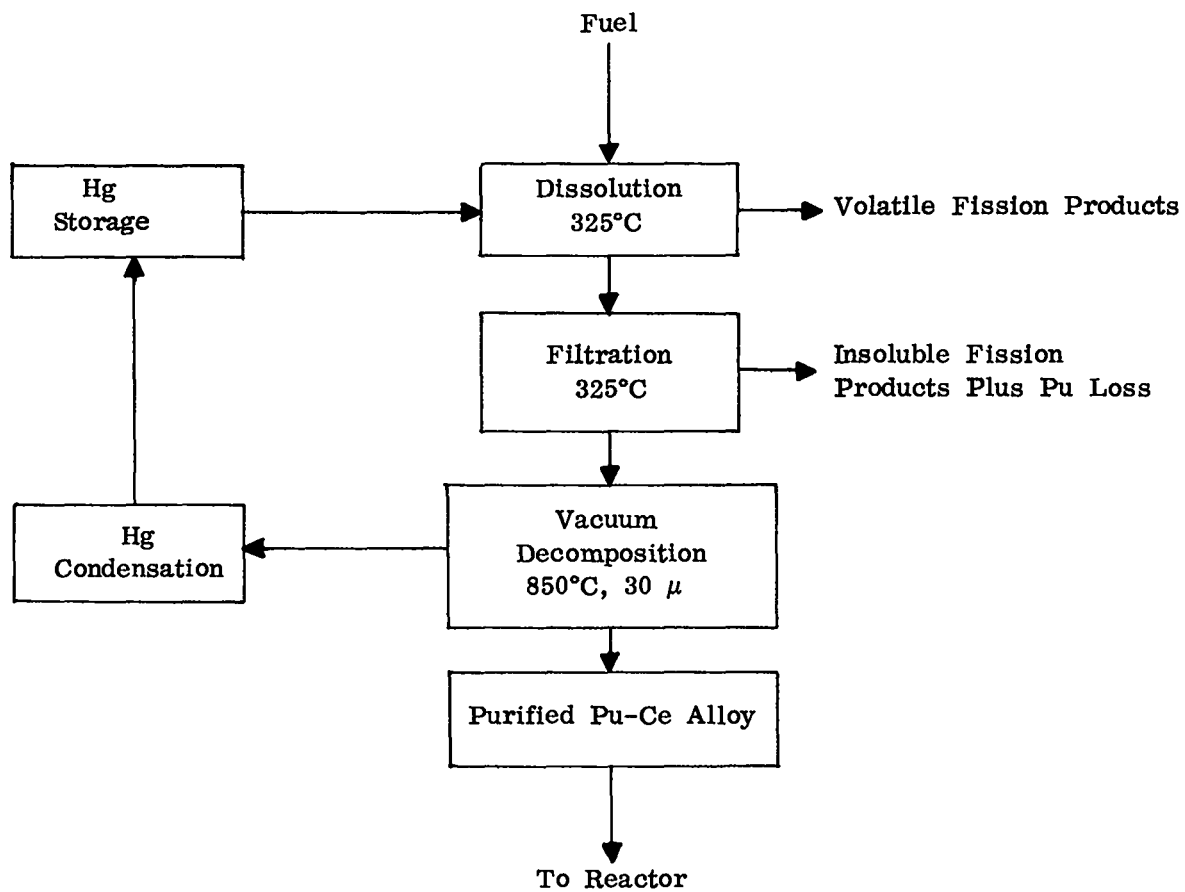


Fig. 2. Flowsheet for processing plutonium-cerium-cobalt fuel.

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