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TITLE AMERICIUM METAL PREPARATION ON THE MULTIGRAM SCALE

AUTHOR(S) J. G. Reavis, MST-13
S. A. Appar, MST-13
L. J. Mullins, MST-13 (Consultant)

Los Alamos National Laboratory
Los Alamos, New Mexico 87545
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Los Alamos National Laboratory
Los Alamos, New Mexico 87545

AMERICIUM METAL PREPARATION ON THE MULTIGRAM SCALE

J. G. REAVIS, S. A. APGAR, III, and L. J. MULLINS

Materials Science and Technology Division, Los Alamos National Laboratory,
Los Alamos, NM 87545

Americium metal was apparently first prepared on the microgram scale by Westrum and Eyring (1) in 1946, although this work was not reported in the open literature until 1951. There are several reports (2, 3, 4, 5) of preparation and study of the metal on the microgram and milligram scales during the ensuing years up to 1962. Reduction of americium trifluoride at elevated temperatures by barium or lithium vapor in a vacuum system was the method most often used, but reduction of the dioxide by lanthanum was also used in these studies.

Preparation of americium metal on the multigram scale was first reported by Johnson and Leary (6) in 1964. Since that time, multigram batches of americium metal have been prepared at Los Alamos, Livermore (7), Karlsruhe (8), and Rocky Flats (9, 10). There have also been reports of metal preparation on the 1-g scale (11, 12). This is a report of the evolution of the preparative techniques used at Los Alamos.

Choice of the Metal Preparation Process

The commonly used quantities for prediction of the course of reactions at high temperatures between halides or oxides and active metals are the free energies of formation of the reactants and products of reactions. Free energies of formation of several oxides, chlorides, and fluorides that may be considered in the preparation of americium metal are listed in Table I. The values listed in Table I are in general based on the compilation by Glassner (13), although extrapolations were made for americium dioxide and tetrafluoride by comparison with other actinides. It would be predicted that the americium compounds listed here could be reduced by heating them with an excess of metals that would form compounds

TABLE I

FREE ENERGIES OF FORMATION OF SELECTED OXIDES,
CHLORIDES, AND FLUORIDES AT 1000 K

(Values stated in kcal per gram-atom of anion)

<u>Oxide</u>	<u>-ΔF</u>	<u>Chloride</u>	<u>-ΔF</u>	<u>Fluoride</u>	<u>-ΔF</u>
CaO	127	BaCl ₂	84	CaF ₂	125
ThO ₂	123	LiCl	79	BaF ₂	123
La ₂ O ₃	122	CaCl ₂	78	LiF	122
Am ₂ O ₃	120	NaCl	76	LaF ₃	121
BaO	111	LaCl ₃	67	NaF	112
UO ₂	109	AmCl ₃	66	MgF ₂	111
AmO ₂	95	PuCl ₃	59	AmF ₃	110
H ₂ O	46	HCl	24	HF	65

having more negative free energies of formation (these found higher in the listing of Table I) than the free energy of formation of the americium compound. Care must be used, however, in using this oversimplified method of predicting suitability of a reductant. This is illustrated by the experience with americium reduction. At first glance, one would predict successful reduction of americium trichloride by calcium, but this method failed (6). It should be pointed out, however, that this method might have been successful had it been known at that time that the melting point of americium is 1171°C instead of the much lower value (996°C) that had been reported (5). This reduction might have been successful had a different heating cycle been used. On the other hand, one would predict from Table I that hydrogen would not reduce americium compounds, but it has been

demonstrated that under certain conditions americium dioxide can be reduced by hydrogen (8, 12).

In addition to the thermochemistry of the reactions, one must also consider certain engineering details when selecting a method for preparation of active metals such as americium. These details include availability of pure reductants and suitable container materials, separability of the products of the reaction, and radiation exposure of personnel performing the operation. After consideration of the many factors involved, those who wished to prepare americium metal on the multigram scale selected the methods listed in Table II. As was mentioned in the preceding paragraph, all of the reactions are energetically favored, with the exception of reaction No. 3. A number of factors combine to make this reaction proceed. The system is operated with ultrapure flowing hydrogen containing concentrations of oxygen and water in the low parts-per-billion range (12). The free energy of formation of Pt_3Am helps to drive the reaction, but the free energies of formation of the actinide-noble metal intermetallic compounds is probably

TABLE II
METHODS USED FOR PREPARATION OF AMERICIUM METAL
AND THE ATTENDANT FREE ENERGY CHANGES

No.	Reaction	ΔF , kcal per g-mole Am
1	$AmO_2 + 4/3 La \rightarrow 2/3 La_2O_3 + Am$	-40
2	$AmO_2 + Th \rightarrow ThO_2 + Am$	-55
3	$AmO_2(Pt) + 2H_2 \rightarrow H_2O + Pt_3Am$	+100 ^(a)
4	$AmF_4 + 2Ca \rightarrow 2CaF_2 + Am$	-140
5	Pu + Am distillation	

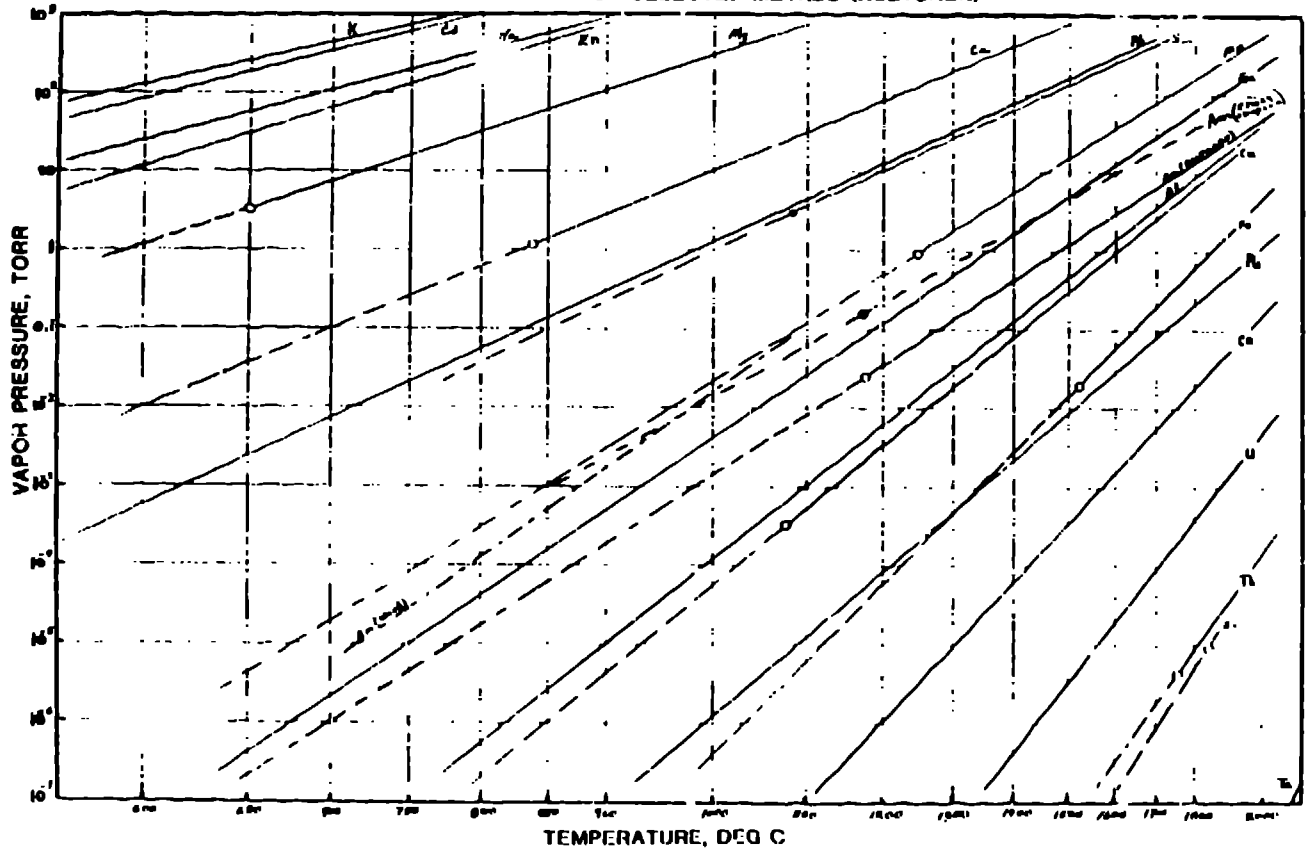
(a) This value of ΔF was calculated for the reaction in the absence of platinum.

only -10 kcal per mole (14). Another significant effect may be the introduction of a high activity coefficient of hydrogen in the presence of platinum. Americium is distilled away from the mixed products of reactions 1-3. The feasibility of this procedure can be seen by comparing vapor pressure curves as shown in Fig. 1. The vapor pressure of americium is greater than that of lanthanum by a factor of approximately 3×10^4 , while vapor pressures of platinum and thorium are much lower than that of lanthanum. Figure 1 also gives an indication of the feasibility of separation of americium from certain nonvolatile impurities as well as an indication of the difficulty of separation from certain more volatile impurities such as calcium, samarium, and manganese.

Reaction No. 4 of Table II is seen to be very energetic and is used only with the sealed pressure vessel or "bomb" technique (9). The products of reaction are mechanically separable and the americium appears in the attractive form of a regulus having almost the minimum possible surface area per gram of product. The use of the fluoride, however, has a serious drawback. The alpha particles emitted by americium react with fluorine atoms and generate an intense field of neutrons. It is much more difficult to shield personnel from these neutrons than from the alpha activity or the 60-keV gamma radiation of americium-241.

The fifth process listed in Table II is an attractive method of preparing americium metal, but it requires a special feed material that has a limited availability. Hundreds of kilograms of americium-241 are formed worldwide each year (15) by decay of plutonium-241, but the concentration is very low and direct separation by distillation of the americium is not feasible. One product of a process called "molten salt extraction" consists of a plutonium-amerccium alloy containing about 5% americium (10, 16). As can be seen from Fig. 1, the vapor pressure of americium is more than three orders of magnitude greater than

FIGURE 1. VAPOR PRESSURE OF SELECTED METALS (HULTGREN)



that of plutonium, allowing separation of the two by a double distillation process.

Consideration of the various factors discussed above led the authors to prefer lanthanum reduction of americium oxide over the other methods of metal production that are discussed. Factors that influenced this decision were availability of equipment, facilities, and feedstocks. Other investigators may select other methods because of their particular situations.

Equipment

Americium metal has been prepared in our laboratories in batches of 10-25 g in stainless steel gloveboxes routinely used for plutonium processing. The current design of these gloveboxes includes walls consisting of a sandwich of 0.25 in. of lead between an inner wall of 0.28 in. stainless steel and an outer skin of 0.0625 in. stainless steel. Leaded glass, 0.25 in. thick, was added to the standard 0.25-in.-thick safety glasses. The gloves were 0.030-in.-thick leaded neoprene with Hypalon coatings both inside and outside. The atmosphere inside the glovebox was argon containing less than 500 ppm oxygen and water. The pumping system consisted of a two-stage mechanical pump and an oil diffusion pump equipped with a water-cooled baffle. The vacuum envelope of the furnace was a 54-mm-o.d. quartz tube sealed to metal flanges at both ends by means of Viton O-rings. Heating of the reactants and products was by direct coupling of a 10 kHz induction field directly to the walls of the tantalum furnace. A thin (0.010-in.) split cylinder of tantalum in direct contact with the inside wall of the quartz vacuum envelope served as a heat reflector. The temperature of the tantalum crucible was determined by sighting an optical pyrometer through the 0.1-in.-wide vertical slit in the heat reflector. The general method of operation was heating lanthanum and americium dioxide in the bottom of the furnace

and distilling the product americium metal into a cooler condenser section. The americium was recovered by peeling it away from the condenser or by changing the position of the condenser, reheating, and allowing the metal to drip into a ceramic casting crucible.

Evolution of Furnace Design

The evolution of the design of the furnace for americium metal preparation at Los Alamos has been toward simplification. This evolution is illustrated in Fig. 2. Designs (a) and (b) were used in the earliest multigram preparations. Design (c), which was originated at Livermore (7), was used at a later date. There were two major problems with these designs. One of these was the high expense of fabrication of a device that had a low rate of reuse (usually 0 to 3 times). The second problem was retention of 25-35% of the product metal because of formation of a surface film that would not drain into the casting crucible. Later preparations were performed in design (d). In this design, the reactor/distillation pot and the distillate condenser are combined in the form of a single flat-bottom, welded construction tantalum crucible that is 1 in. in diameter by 8 in. deep with 0.020-in.-thick walls. A loose-fitting entrainment baffle consists of two thin tantalum discs penetrated by small random holes. The discs are held approximately 0.25 in. apart by tantalum wire and the assembly rests on the surface of the reacting mixture. The crucible is covered by a loose-fitting tantalum lid and the top section is cooled by a water-cooled collar.

Operation of the System

The empty apparatus was degassed before use by heating to approximately 1500°C. in vacuo until the pressure indication had fallen to the background of about 10^{-5} torr. An excess (about 75%) of finely divided lanthanum chips was mixed with AmO_2 powder by tumbling in a lead-shielded steel container, transferred to the tantalum crucible by use of a long-stem stainless steel funnel

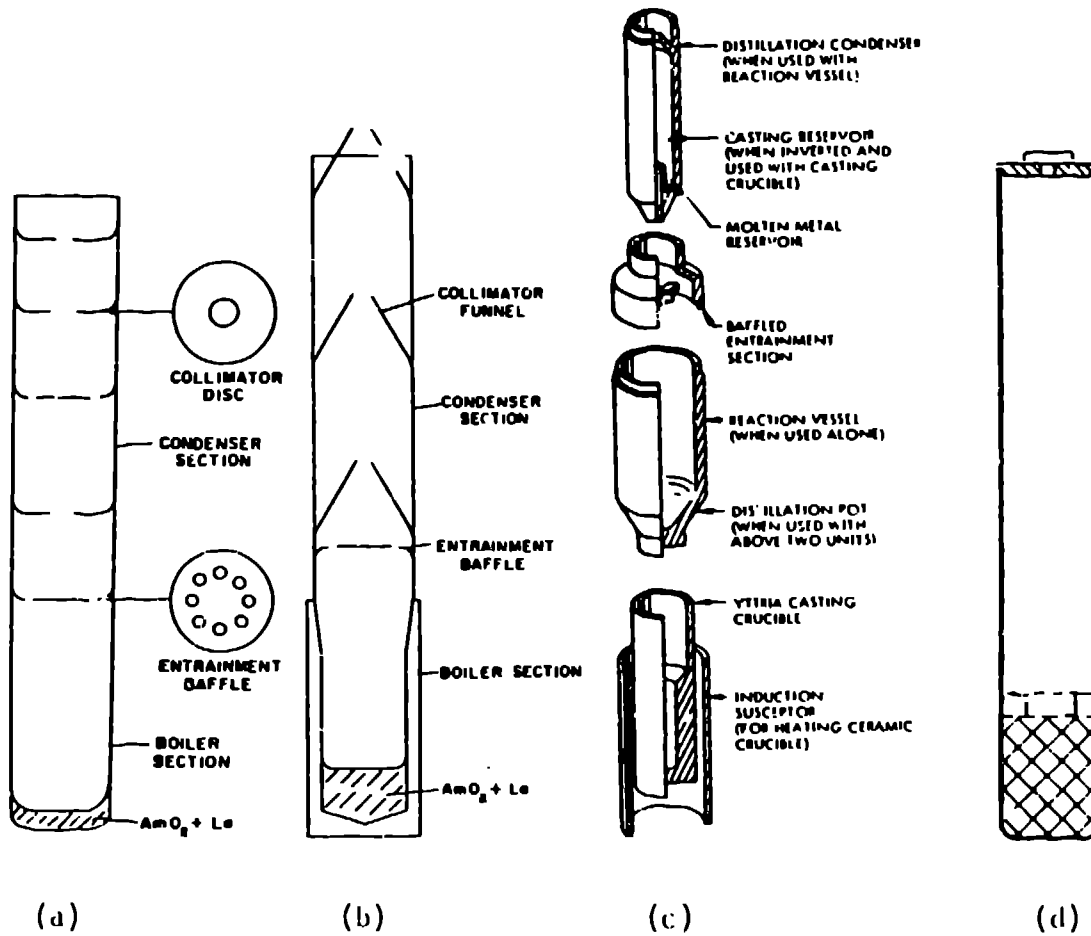


Figure 2. Evolutionary stages of the furnace used for americium preparation.

(to avoid dust transfer to the walls) and tamped to give intimate contact. These operations were performed in the argon atmosphere containing less than 500 ppm oxygen and water. The loaded crucible was placed in the vacuum system and alternately evacuated slowly to the background pressure and backfilled with high-purity argon three times. The last filling of argon was left in the furnace and the system was slowly heated. A temperature spike of about 350°C was usually observed when the reaction started at about 800°C. Heating was continued approximately one minute, then discontinued. The system was then evacuated and heated at a rate slow enough to maintain observed pressures only slightly above the background pressure. The temperature was held at about 1400°C for times sufficient for distillation of all the americium, assuring a distillation rate of 3 g/h. The system was cooled, disassembled, and inspected by gamma scanning to verify that the americium had indeed been transferred from the reaction zone to the condenser zone. Figure 3 shows the spatial relationship between the induction coil and the furnace, the temperature profile during distillation, and the gamma activity profile at the end of distillation.

The reactor and condenser sections of the apparatus were then separated and the condenser section was heated in an argon atmosphere to melt the americium and cast it into a yttria crucible. To lessen thermal shock of the crucible by the molten metal, a surrounding tantalum susceptor was used to heat the crucible simultaneously. In the use of furnace designs (b) and (c) (Fig. 2), the condenser sections were inverted for the casting operation. In the use of design (d), the bottom 2 in. of the crucible containing the lanthanum oxide, excess lanthanum, and the entrainment baffle was cut off by use of tubing cutters. This bottom section was discarded and the condenser section was inverted and heated to 1200°C for 1.5 min to cast the americium product.

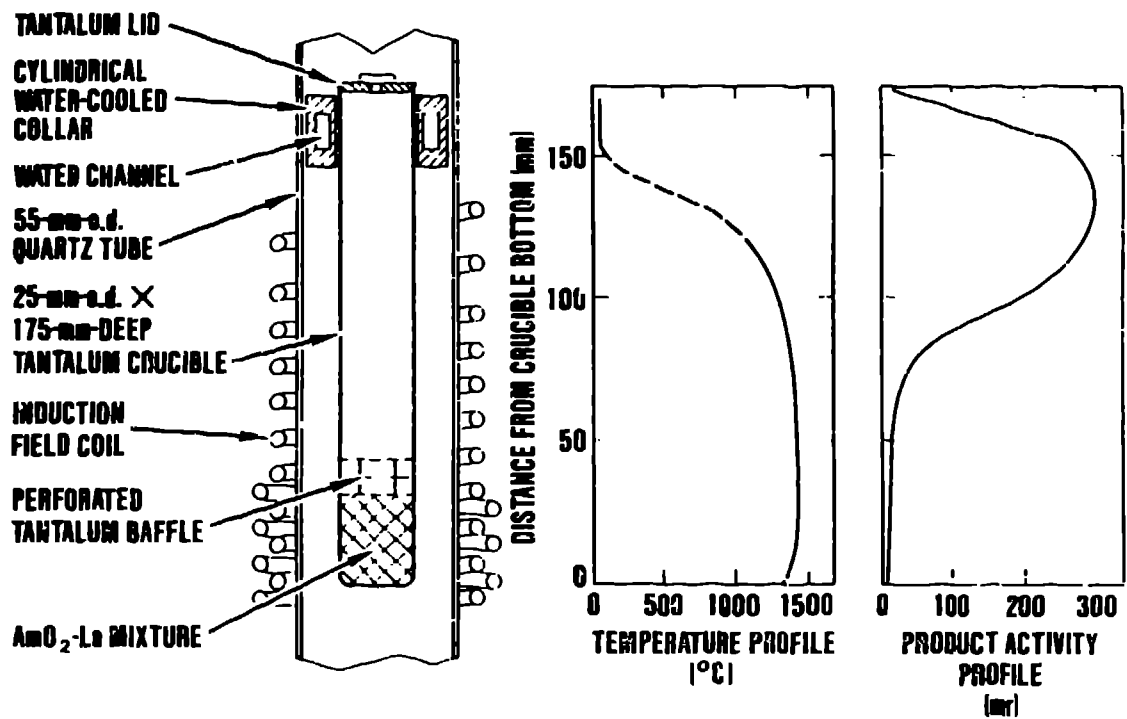


Figure 3. Americium preparation furnace with temperature profile and product gamma activity profile shown on the same vertical scale.

The yield of the casting operation was increased by using coatings to reduce the degree of wetting of the tantalum. Best results were obtained by use of yttria applied as a slurry to the inside and outside of the upper section of the crucible after it had been heated briefly to dull red heat in air. This heating seems to produce a surface that can be more evenly painted with the yttria slurry. The slurry was applied at a crucible temperature slightly less than 100°C. The coated crucible was first baked at a low temperature in air and outgassed in vacuo at 1500°C just before use.

Product Yield and Purity

The overall yields of americium in the early work (6) using designs (a) and (b) (Fig. 2) averaged about 75% per batch. The average yield using design (d) on the 25-g scale was 89%. It was feared that the simplified design (d) would allow greater contamination of the product by lanthanum, but the change was hardly significant. Americium product from design (b) contained 2500 ppm lanthanum, whereas that from design (d) contained 4000 ppm. The only other impurities in the latter product that could be detected by spectroscopic analysis were 20 ppm magnesium and 20 ppm calcium. The yttrium concentration was reported as less than 200 ppm. No analyses for oxygen or other anionic impurities were made.

Summary

It was demonstrated that americium metal of approximately 99.5% purity can be produced on the 20- to 25-g scale by lanthanum reduction of the oxide in a very simple apparatus. As was predicted from relative vapor pressures, volatile metal impurities such as calcium and magnesium accompany the americium during distillation. The major impurity detected was lanthanum at a concentration that would be predicted for the equilibrium vapor composition above lanthanum metal containing 1% americium. It is speculated that higher purity americium might be

produced if distillation were to be discontinued earlier, with no attempt at quantitative recovery of the metal.

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