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PREPARATION OF PLUTONIUM-238 METAL

Frank D. Lonadier

Joseph S. Griffo

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ABSTRACT

The chemical procedures and the processing equipment to prepare plutonium-238 metal for SNAP heat sources are described. Plutonium nitrate is precipitated as the oxalate, the oxalate is converted to the fluoride, and the fluoride is reduced to the metal. Techniques to store and cast the metal are also described.

INTRODUCTION

The chemical procedures and the processing equipment for the preparation of plutonium-238 metal for SNAP heat sources are described. The starting material is a concentrated solution of plutonium-238 nitrate. The overall procedure entails precipitation of plutonium-238 oxalate from the nitrate solution, conversion of the nitrate to the oxalate and then to the fluoride, and reduction of the fluoride to the metal.

Calcium metal is the reductant and iodine is the reaction initiator. The reduction procedure was described previously by Maraman and Baker, Los Alamos Scientific Laboratory.*

Because of the chemical reactivity and toxicity of plutonium-238, the process line consists of a completely enclosed, self-contained system (shown in Figure 1). Wet chemical procedures are conducted in Section A of the process line while reduction procedures are conducted in Section B. A vacuum air-lock chamber is the passbox to transfer material from the wet to the dry section.

An argon atmosphere is maintained throughout Section B and is continuously recirculated through a "Lectrodryer" system (Figure 2) which dries the gases over activated alumina beds to a dewpoint of -50°C. Analyses has shown that this atmosphere is composed of greater than 96 mole per cent argon and less than 0.04 mole per cent water.

The system is provided with appropriate shielding, gloves and pneumatically operated equipment. Mechanical manipulators are available for working with radioactive compounds which could not be handled directly.

*"Extractive and Physical Metallurgy of Plutonium and Its Alloys", edited by W. B. Wilkinson, Interscience Publishers, New York (1958) pages 43-59.

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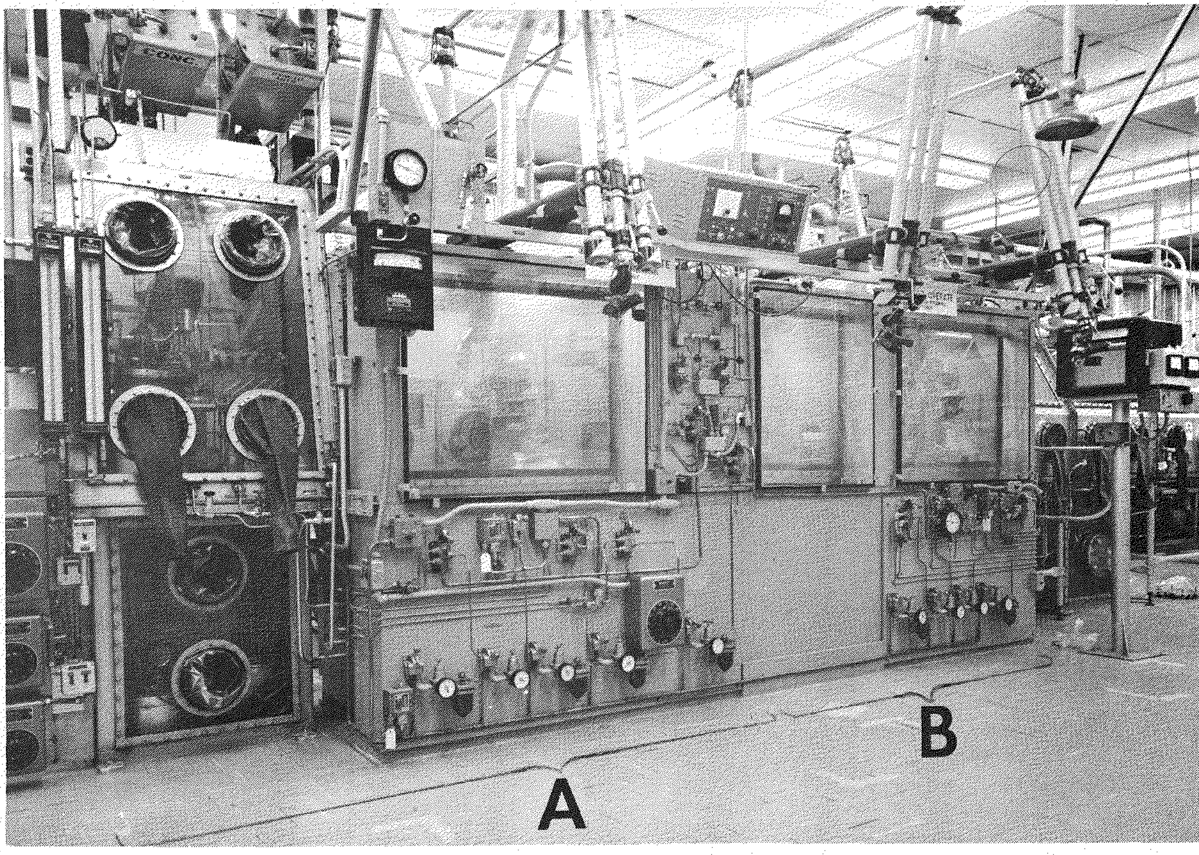

Figure 1

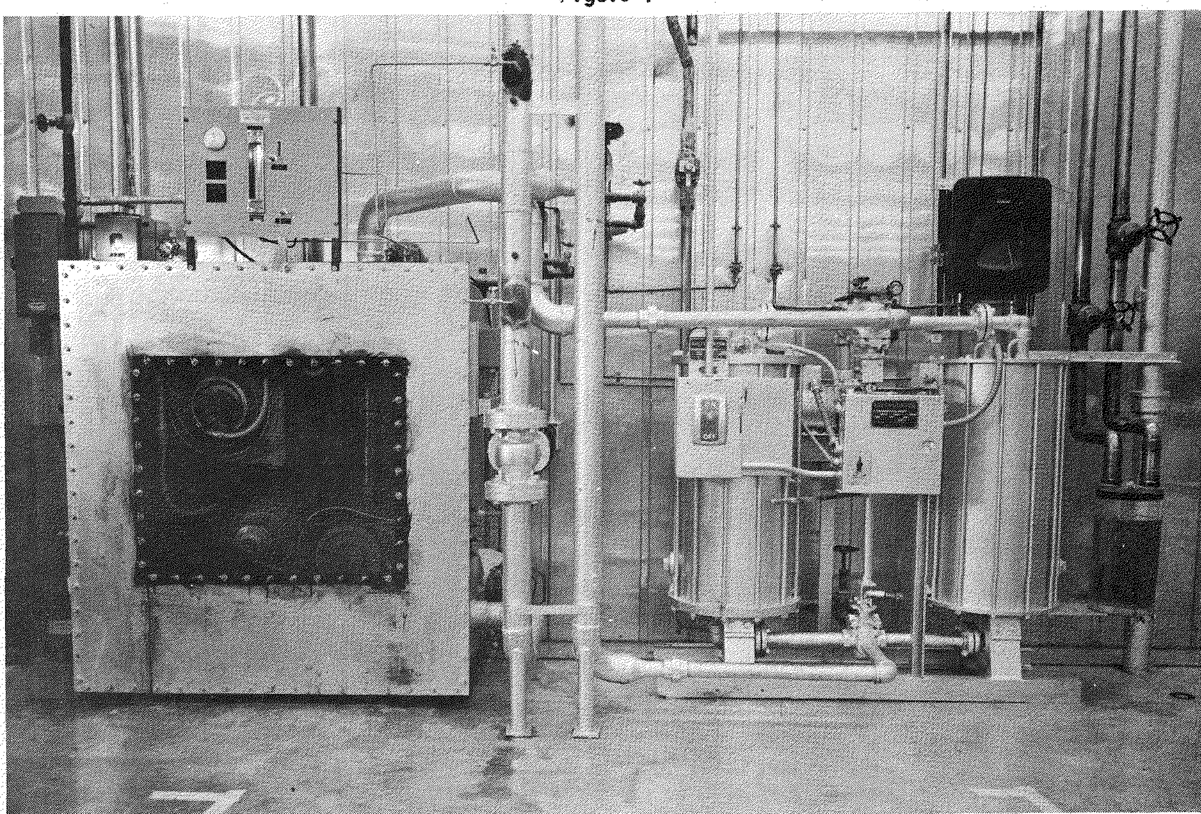

Figure 2

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PRECIPITATION OF PLUTONIUM-238 OXALATE

Plutonium oxalate is precipitated by the following reactions:

$$PuO_2^{++} + H_2O_2 + 2H^+ \longrightarrow Pu^{+4} + O_2 + 2H_2O$$

$$2Pu^{+3} + H_2O_2 + 2H^+ \longrightarrow 2Pu^{+4} + 2H_2O$$

$$Pu^{+4} + 2C_2O_4^{=} \longrightarrow Pu(C_2O_4)_2$$

One liter of plutonium nitrate (approximately 45 grams of plutonium-238 per liter) in 12 normal nitric acid solution was transferred by vacuum into a ten-liter stainless steel vessel, (Figure 3). The acidity of this solution was adjusted to between one and three normal by adding 0.35 normal nitric acid. Ten per cent hydrogen peroxide equivalent to one milliliter per gram of plutonium was added through an external funnel attached to the vessel (A).

Hydrogen peroxide was added to maintain the plutonium as plutonium (IV) which insured complete precipitation of the plutonium as the oxalate.

The solution was heated at 60°C by an external steam line (B). Approximately one-fifth of the stoichiometric quantity of oxalic acid required for precipitation (500 milliliters of a 40-gram per liter solution) was added to initiate the precipitation of plutonium oxalate. The mixture was held at 60°C for 1.5 hours before sufficient oxalic acid to provide a stoichiometric amount plus enough excess to make the filtrate 0.04 molar with respect to the oxalate ion was added to the solution. The plutonium oxalate precipitate was digested at 60°C for an additional 1.5 hours and filtered by suction through a medium-fine platinum frit (Figure 4). The solution was stirred continuously during the entire operation with a mechanical stirrer (labeled C in Figure 3). The precipitate was washed with one liter of 0.04 molar oxalic acid, the wash solution was removed by suction, and the self-heating plutonium-238 oxalate was air-dried.

The stepwise addition of oxalic acid resulted in an easily filtered precipitate and enhanced the yield of plutonium oxalate. Plutonium oxalate has a negligible solubility in a solution one molar in nitric acid and 0.04 molar in oxalate ion.

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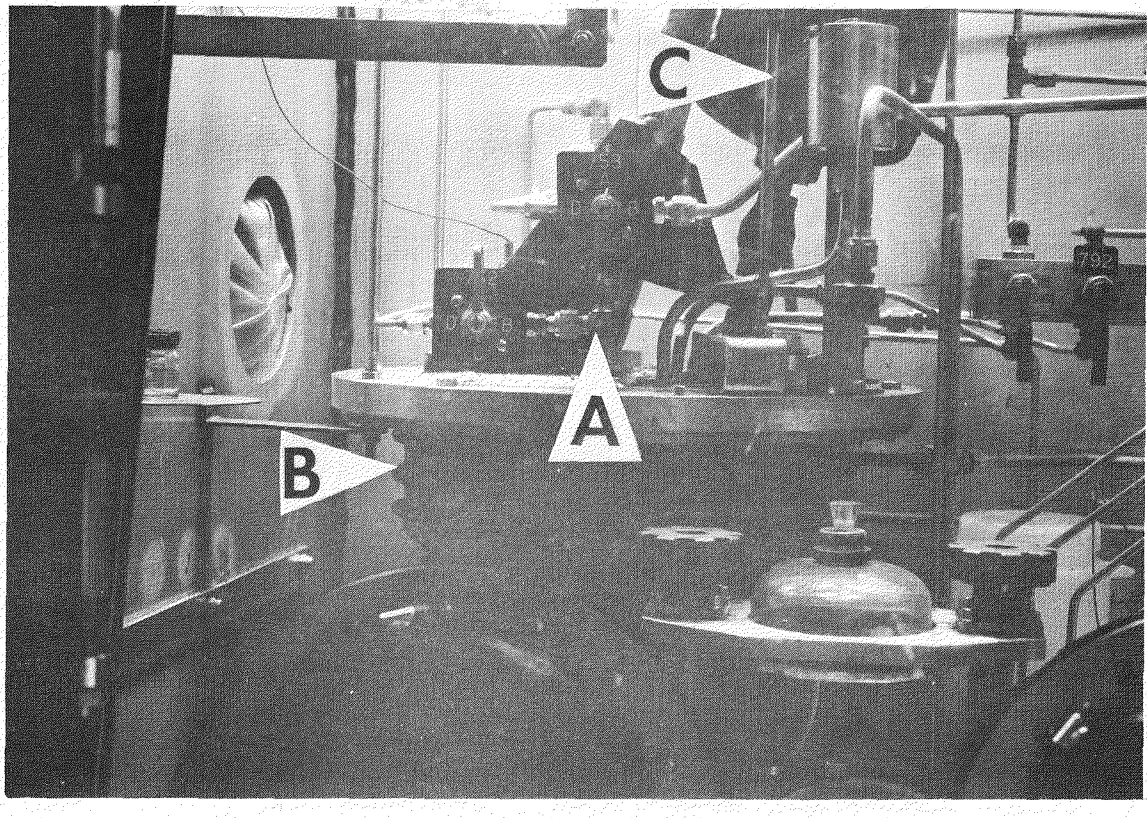

Figure 3

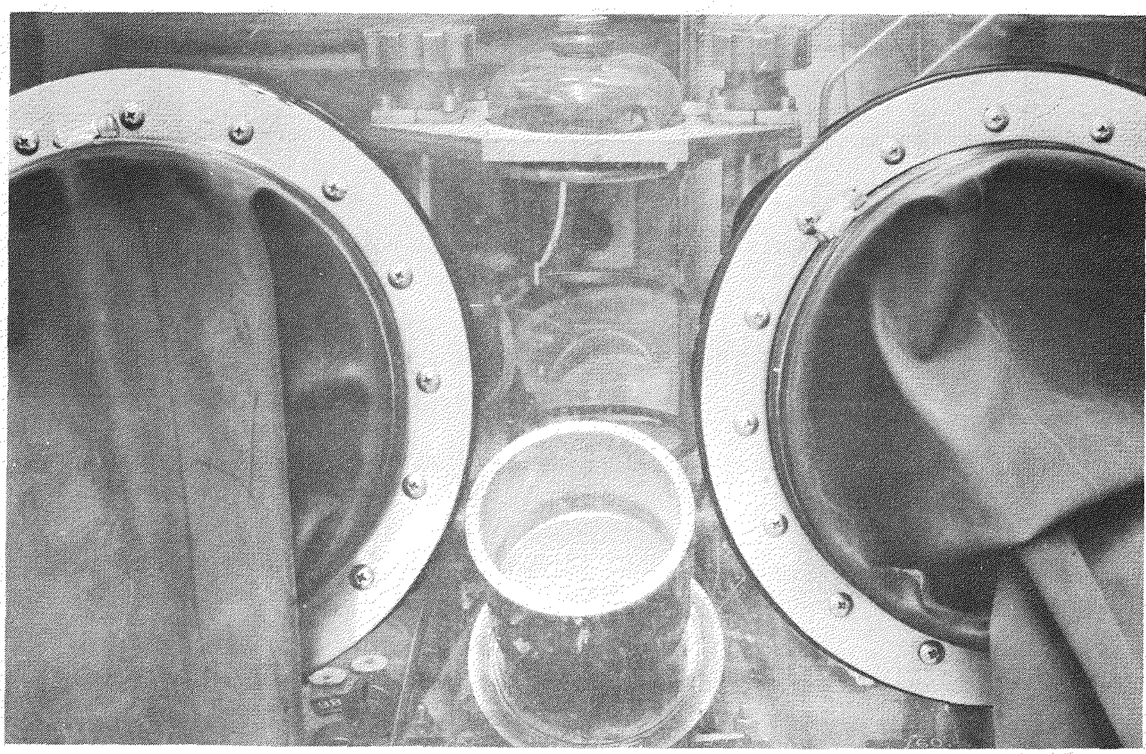

Figure 4

CONVERSION TO PLUTONIUM FLUORIDE

After partial drying, the caked plutonium oxalate precipitate was roughly ground in a mortar and pestle. The filter with its contents was transferred to a pneumatically operated Inconel furnace (Figure 5). The oxalate was completely dried by heating for one hour at 100°C in a stream of dry argon. After the argon flow was shut off, a dried mixture of hydrogen fluoride and oxygen was passed over the oxalate precipitate at 300 and 2.8 grams per hour, respectively. The hydrogen fluoride was preheated with a coaxial steam line to prevent condensation, and mixed with oxygen prior to introduction into the furnace. Simultaneously, the flow rates of the gases were adjusted and the temperature of the system was increased to 450°C over a 30 minute period. This temperature was maintained for an additional 30 minutes to complete the fluorination process.

The plutonium oxalate decomposed to the oxide at the elevated temperature, and hydrogen fluoride reacted with the plutonium oxide to form plutonium tetrafluoride. The presence of oxygen prevented the reduction of plutonium to the trifluoride. These reactions are described by the following equations:

$$Pu(C_2O_4)_2 \xrightarrow[O_2]{150^\circ C} PuO_2 + CO_2$$

$$PuO_2 + 4HF \xrightarrow[150\text{-}450^\circ C]{O_2} PuF_4 + 2H_2O$$

During the course of the fluorination, the neutron flux rapidly increased because of the alpha bombardment of the fluorine in the plutonium tetrafluoride. The neutron flux on the completely fluorinated batch was 1.4 x 10^4 neutrons per second per square centimeter at a distance of approximately 30 centimeters. The calculated total neutron flux of the batch was 9.7 x 10^7 neutrons per second. After the fluorination was completed, the furnace was allowed to cool. The hydrogen fluoride and oxygen flow was continued until the temperature dropped below 300°C. The flow of reactant gases was then replaced by a flow of dry argon which flushed the excess hydrogen fluoride from the system into a scrubber that contained potassium hydroxide (Figure 6). Here, the circulating caustic neutralized the excess hydrogen fluoride, and the inert gases were pumped to a vent for radioactive gases. When the temperature of the system dropped to 100°C, the flow of argon was stopped and the furnace was opened. The plutonium tetrafluoride was transferred to a tared fused-magnesia crucible by mechanical manipulators and a pneumatically operated powder transfer unit (Figure 7).

The fluoride was handled with mechanical manipulators from behind a Lucite barrier. The neutron flux behind the barrier was below maximum limits set by the AEC

The fluoride was transferred to the dry section of the system through a vacuum pass box (Figure 8). The pass box was equipped with pneumatically operated doors and transfer equipment for the crucible. All equipment was readily operated from behind the barrier. The pass box was evacuated and flushed three times with dry argon. The crucible and contents were then weighed to the nearest gram on a platform balance (Figure 9).

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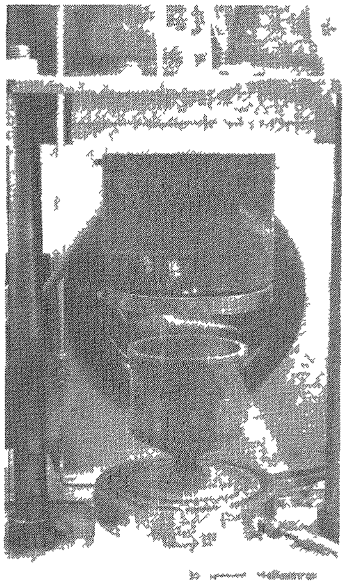

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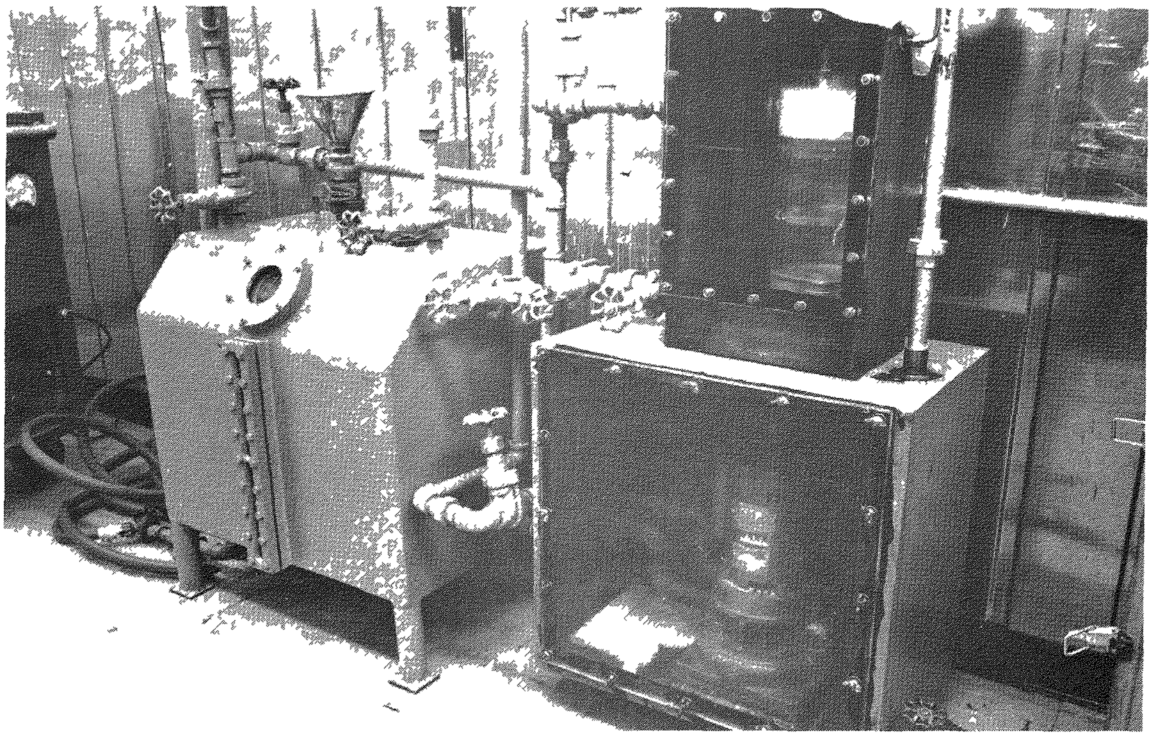

Figure 6

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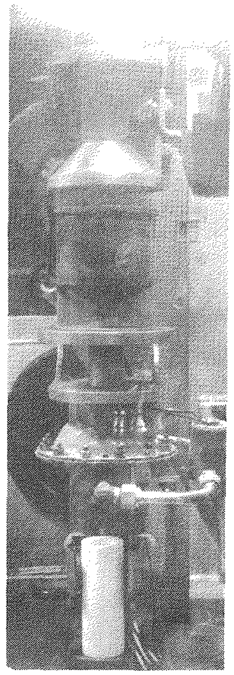

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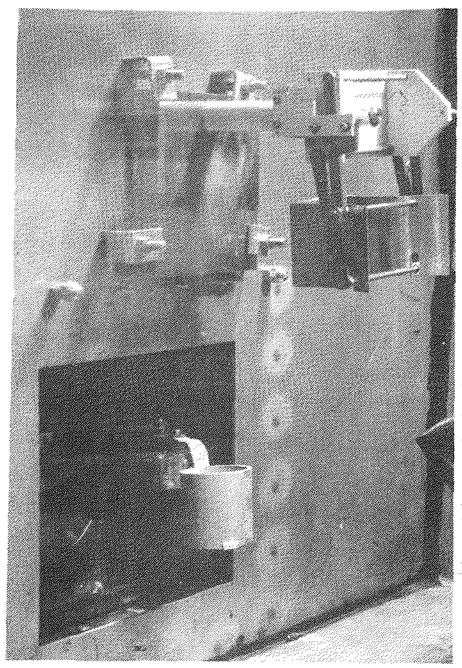

Figure 8

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Figure 9

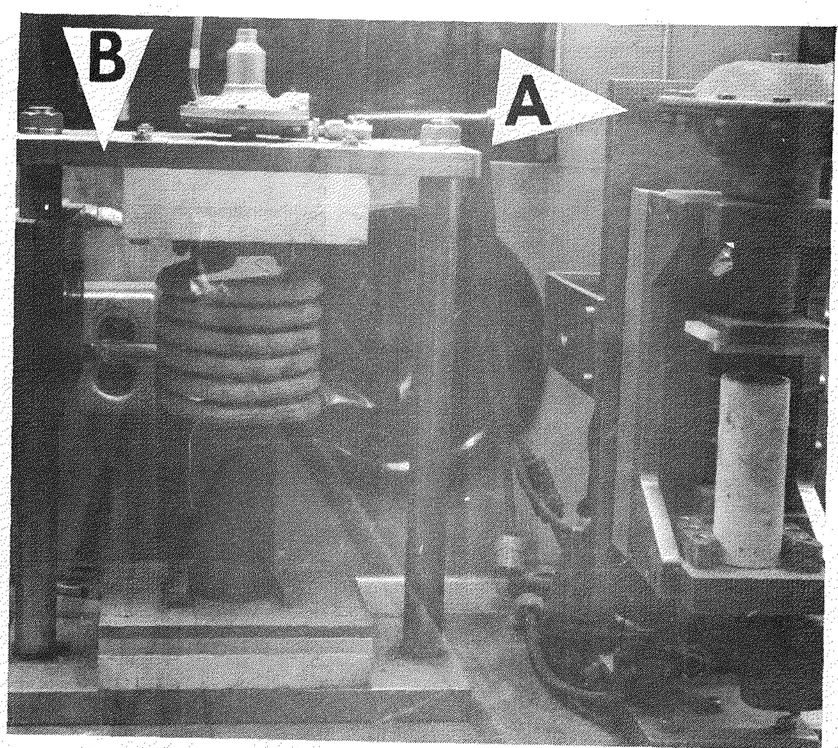

Figure 10

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REDUCTION OF PLUTONIUM TETRAFLUORIDE

High purity calcium metal (20-40 mesh, 2.5 moles of calcium per mole of plutonium tetrafluoride) was added to the crucible that contained the plutonium tetrafluoride. The crucible with contents was placed in a pneumatically operated blender (Figure 10 A) and the contents were thoroughly mixed. The crucible was placed into a 304 stainless steel reduction bomb. A perforated, fused magnesia disc was placed on the upper part of the crucible to support the iodine (Figure 11). A calculated quantity of iodine (0.25 moles I_2 per mole PuF_4) was placed on the disc to initiate the reaction.

Because of the high specific activity of plutonium-238, iodine could not be added directly to the charge and was, therefore, placed on the crucible disc. On heating, iodine vapors entered the crucible through the holes in the disc.

The charged stainless steel bomb was sealed in a pneumatically operated R. F. induction heating assembly, (Figure 10 B) and heated at such a rate to bring the internal temperature of the bomb to 720°C in six to seven minutes. The seal between the bomb and the furnace assembly was a copper ring gasket. At the elevated temperature, the exothermic reaction between the calcium and iodine started, causing the internal temperature to rise several hundred degrees. At this temperature the plutonium fluoride was completely reduced by the calcium metal. The reaction was accompanied by a rapid decrease in neutron flux which designated the exact time of reduction. The dense plutonium metal was collected in a cylindrically shaped mold at the bottom of the crucible. The external heat supply was turned off and the bomb was allowed to cool below 100°C. The bomb was opened and the crucible removed. The crucible was broken apart with a hammer and the metal transferred to an aluminum container provided with a side arm (Figure 12) through which argon flowed continuously. In this aluminum container, the metal was separated from attached slag.

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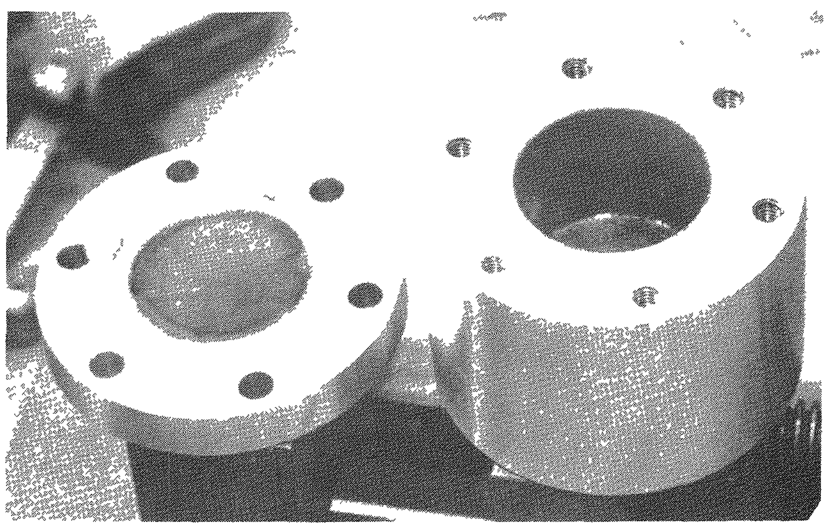

Figure 13

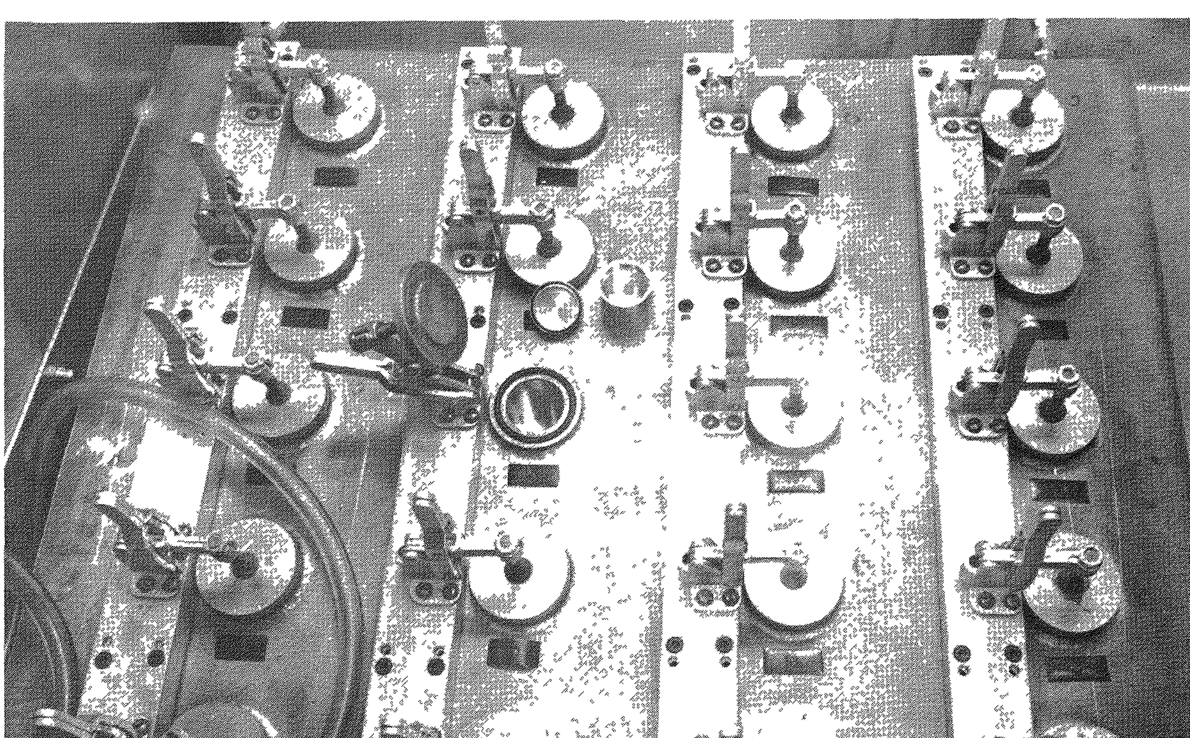

Figure 14

PURITY OF THE METAL

Representative samples of the plutonium metal were submitted for complete analysis. The analytical results of a typical sample are shown in Table 1 as determined by emission spectroscopy, mass spectroscopy, colorimetry, alpha counting and wet chemical analyses.

Table 1

Analysis of Plutonium Metal

Elements	Analytical Method	Analysis in Weight Per Cent
Pu (Total)	Chemical	99.13
Cd	Emission spec.	> 0.15
Al	Emission spec.	0.15
Na	Emission spec.	trace
Ca	Emission spec.	trace
Zn	Emission spec.	N.D.
Fe	Colorimetric	0.15
Mg	Emission spec.	trace
Pb	Emission spec.	trace
B	Emission spec.	0.09
Ni	Emission spec.	0.05
Bi	Emission spec.	N.D.
Cr	Emission spec.	0.05
Mn	Emission spec.	0.03
Cu	Emission spec.	0.03
Ti	Emission spec.	trace
Pu^{238}	Chemical	78.43 of Total Pu
	Mass spec.	78.62 of Total Pu
	Alpha Counting	77.76 of Total Sample

VACUUM CASTING THE PLUTONIUM

The self-contained reduction line for production of plutonium was also equipped for casting of the metal under high vacuum This assembly consisted of two quartz tubes (approximately 40 mm I.D., Figure 15), each fitted into the asbestos-insulated copper-coil heating element of a R F induction furnace. One unit was mounted vertically, the other horizontally to enable greater flexibility in application. Each quartz section was connected to a high vacuum system by a ground-glass ball joint

The vacuum casting system was employed for many purposes including (1) recasting of the metal into a different shape, (2) alloying the plutonium metal with suitable stabilizing agents to the more stable delta phase, and (3) purifying the metal by zone melting. In this process low atomic weight impurities that were more volatile than plutonium were vaporized from the melt.

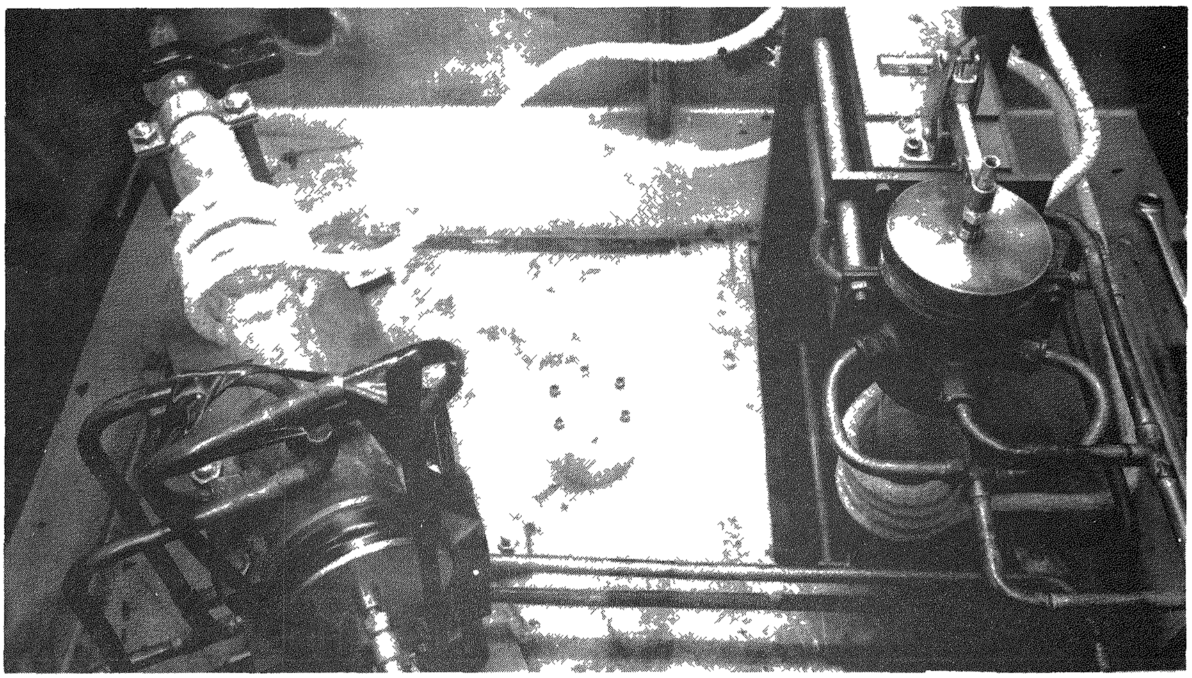

Figure 15

ACKNOWLEDGEMENTS

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