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# Production of Rarer Metals

by  
George Meister

Westinghouse Electric Corporation

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Technical Information Division, Oak Ridge Directed Operations  
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## PRODUCTION OF RARER METALS

By George Meister

The rarer or less familiar elements to be considered in this discussion are thorium, zirconium, and uranium. All these metals were prepared more or less pure in the early part of the nineteenth century. Since that time purer raw materials were produced, improvements were made in these earlier methods, and new methods were developed so that metals have been prepared in a purer state. High purity metals are desirable for industrial utilization and for the production of wire and sheet. The methods to produce these metals in the required purity will be treated later in detail but the general processes in use will now be considered.

### GENERAL METHODS OF PREPARING METALS

- a) Reduction of oxides with hydrogen.
- b) Reduction of oxides with carbon.
- c) Reduction of oxides with calcium, magnesium, or aluminum.
- d) Reduction of halides with alkalis or alkaline earths.
- e) Thermal dissociation of compounds.
- f) Electrolytic reduction of compound in fused salts.

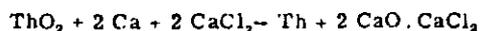
The hydrogen reduction method, although used successfully commercially in reducing tungsten and molybdenum oxides, fails completely in the case of thorium, zirconium, and uranium. When the oxides are reduced with carbon the resulting metal generally has a high carbon content and is brittle. Reduction of oxides with magnesium generally produces a low grade metal powder, but when calcium is used, especially in the presence of calcium chloride, a fairly good metal is obtained. Alumino-thermic reductions of the oxides generally are violent and produce some beads of metal, but usually the product is not satisfactory and often forms alloys with aluminum which are not easily decomposed.

The thermal dissociation of compounds, as the iodide, has been commercially used in the production of zirconium and produces a very high purity metal. The iodide is decomposed by a hot filament, usually tungsten, and the pure metal deposited thereon.

Deposition by fused salt electrolysis has been developed and it produces a good grade of powder especially in the case of thorium, uranium, and tantalum.

### THORIUM PRODUCTION

Thorium was discovered in 1829 by Berzelius who prepared the impure metal by heating a mixture of potassium thorium fluoride ( $KThF_6$ ) with potassium. In 1914 Lely and Hamburger prepared 99% pure thorium by distilling sodium and thorium chloride into an exhausted steel cylinder. In 1927 Marden and Rentschler prepared metallic thorium by reducing the oxide with calcium in the presence of calcium chloride.



This method was by far the simplest of all the methods developed and produced a good grade of powder which after heat-treatment in vacuo analyzed as high as 99.7% pure thorium metal. This metal powder could be sintered or melted and rolled or swaged into wire and sheet.

In 1930 Driggs and Lilliendahl prepared thorium by fused salt electrolysis. This method is simply an electrolysis in which the electrolyte is a fused salt instead of an aqueous solution.

Figure 1 shows the different cells used in fused salt electrolysis. In Type I the deposited metal is collected as a fused metal in which the temperature of the bath is hotter than the melting point of the metal. In Type II the molten metal is deposited on a cathode that is sufficiently chilled to collect the metal as a solid. In Type III melting point of the metal exceeds that of the bath and the metal is collected as a powder.

The method as applied to thorium involves the preparation of potassium thorium fluoride which is then electrolyzed to thorium powder in an electrolyte consisting of equal parts by weight of sodium and potassium chloride. The electrolysis is conducted in a graphite crucible which acts as the anode while a molybdenum strip centrally located and extending into the bath serves as the cathode. The salts are melted, potassium thorium fluoride added, and a d-c voltage applied. Thorium deposits on the cathode and collects as a mixture of a salt and metal. After completing the electrolysis the cathode is slowly raised from the bath, the solidified salts act as a protective coating on the metal powder preventing oxidation. The deposit is broken off the cathode, collected, and the soluble salts leached with water and dilute acid. The metal powder obtained is recovered by washing and final drying in vacuo. This powder can be pressed into metal compacts and sintered in vacuo or melted on a suitable refractory.

#### PROPERTIES OF THORIUM

Thorium metal is very soft with a Vickers hardness of about 100 (Rockwell B10) which is comparable to annealed copper. A freshly prepared surface is bright. It subsequently becomes covered with a protective oxide film that prevents any further attack. The density of sintered thorium is approximately 11.3 and the melted metal 11.5. The X-ray density reported by Hull is 11.7. It may be cold-rolled into wire or sheet. It may also be cold-swaged but cannot readily be cold drawn because of its relatively low tensile strength.

#### ZIRCONIUM PRODUCTION

Zirconium was prepared by Berzelius in 1824 by the reduction of potassium zirconium fluoride with potassium. This method was the same one that he used in 1829 to prepare thorium. All attempts, however, to produce a pure cold-ductile zirconium by reduction of the oxide, chloride, and potassium zirconium fluorides with sodium, calcium, and magnesium at a reasonable cost have more or less failed. Even the fused salt electrolysis of zirconium compounds was futile. Some of these difficulties may be inherent in the metal itself, which absorbs gases such as oxygen and nitrogen readily at elevated temperatures, and consequently results in a brittle metal. The only ductile zirconium metal prepared commercially today is that obtained by the thermal decomposition of zirconium iodide. This method is the invention of De Boer and Fast who prepared and obtained the physical properties of ductile zirconium and is now utilized commercially by Foote Mineral Company.

Nevertheless, there has been some degree of success in the preparation of pure zirconium by Dr. Kroll and co-workers at the Bureau of Mines (Figure 2). His method is essentially the reduction of zirconium chloride with magnesium. Zircon sand is converted into a carbide by heating with carbon in an electric furnace. The resulting carbide is then chlorinated, yielding zirconium chloride which is then vaporized in a specially designed reduction furnace and reacted with molten magnesium metal in an atmosphere of helium. The mass of spongy zirconium, excess magnesium, and magnesium chloride is then purified by vacuum distillation and the residual zirconium melted in an arc furnace under purified helium. This process is ingenious but somewhat complicated. However,

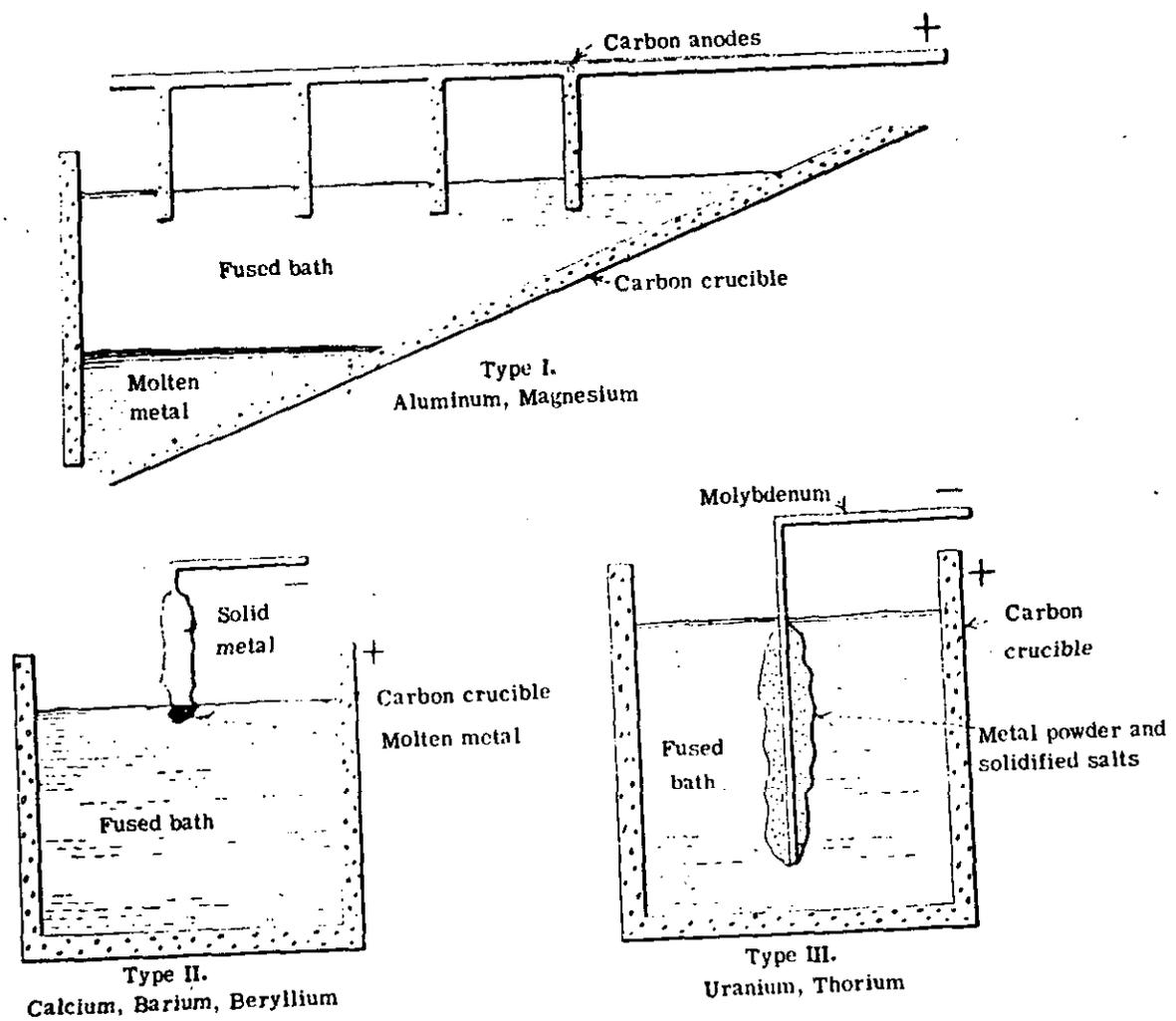


Figure 1. Three types of fused bath used in electrolysis.

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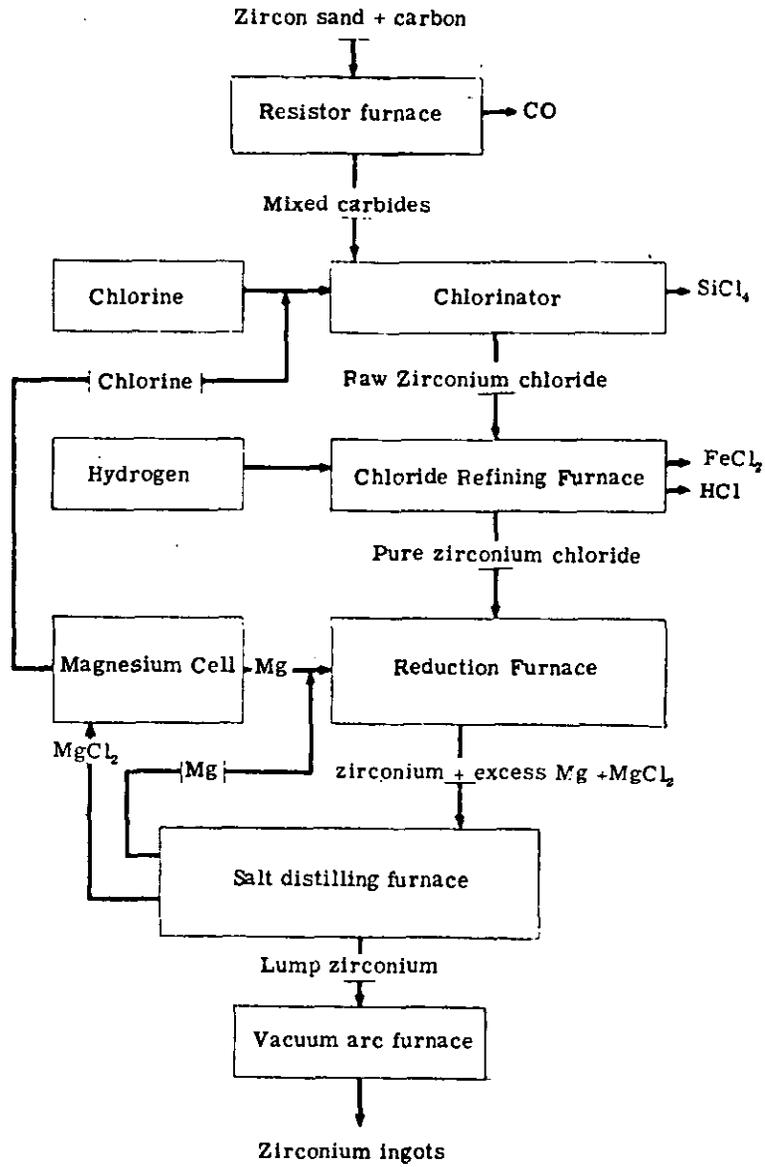


Figure 2. Flow sheet of process for preparing pure zirconium in Bureau of Mines.

Dr. Kroll has been successful in fabricating large pieces of zirconium up to one pound and has definitely shown that it can be rolled into sheet.

Lilliendahl and Rentschler of Westinghouse were also interested in producing pure zirconium. Formerly oxide reductions with the alkaline earth metals were accomplished in heavy-walled closed iron cylinders referred to as "bombs" and this method was fairly successful. However, there were difficulties in that the reaction products were confined in a closed system and could not be controlled especially as to gas impurities. Therefore, an improvement in this method was thought to be the logical solution. Raw materials, particularly calcium and magnesium, are now obtainable with a higher degree of purity than formerly, also improved techniques allowed the reactions to be controlled and effected in vacuo or an inert atmosphere (Figure 3). Thus, it was possible to prepare pure zirconium by reducing the oxide with calcium or magnesium contained in a molybdenum crucible in an atmosphere of argon. This assembly was surrounded with a special glass bulb that has the high temperature resistant qualities of quartz and the crucible heated by high frequency. Any excessive vaporization of calcium or magnesium at 1000 or 1200°C was suppressed by the inert gas filling. Thus, it was possible to reduce considerably the contamination with active gases as oxygen and nitrogen, which are exceedingly harmful in producing a pure workable zirconium. The metal was obtained in powder form and compressed in hardened steel dies into compacts in a hydraulic press at 40-50 psi. These compacts are strong and can readily be handled. (Figure 4). They may be sintered in high vacuo or (Figure 5) melted in high vacuo on a suitable refractory. The vacuum should be  $10^{-3}$  millimeters or better.

The analysis of this metal powder showed on the average

C	0.02%
SiO	0.02%
Fe	0.04%
Ca	0.10%
Ti	0.01%

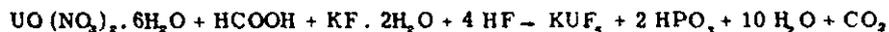
#### PROPERTIES OF ZIRCONIUM

The sintered zirconium had a Rockwell hardness of B90. Melted zirconium was harder, but both could readily be machined, tapped, and drilled. It is hoped eventually to produce cold ductile zirconium by this method with further refinements in the technique. This metal is stable in the air and does not tarnish as thorium and uranium.

#### PRODUCTION OF URANIUM

Uranium was first prepared in 1841 by Peligot who reduced uranium chloride ( $UCl_4$ ) with potassium. Since that time practically all the reduction methods had been tried with some degree of success. About 1920 Marden and Rentschler successfully applied their method of reduction in a closed metal bomb with calcium and calcium chloride. A better product was obtained by reducing uranium double fluoride with calcium.

About 1930 Driggs and Lilliendahl, who were successful in producing other pure rare metals by fused salt electrolysis, made high purity uranium metal by electrolyzing potassium uranium fluoride in a fused mixture of sodium chloride and calcium chloride. The potassium uranium fluoride was prepared by photochemical reduction of a solution of uranyl nitrate.



Thus, when the time came when quantity production was needed, Westinghouse had experience with two processes. Primary considerations now were purity of metal. The purity requirements of the metallic uranium required for atomic power experiments were very rigid.

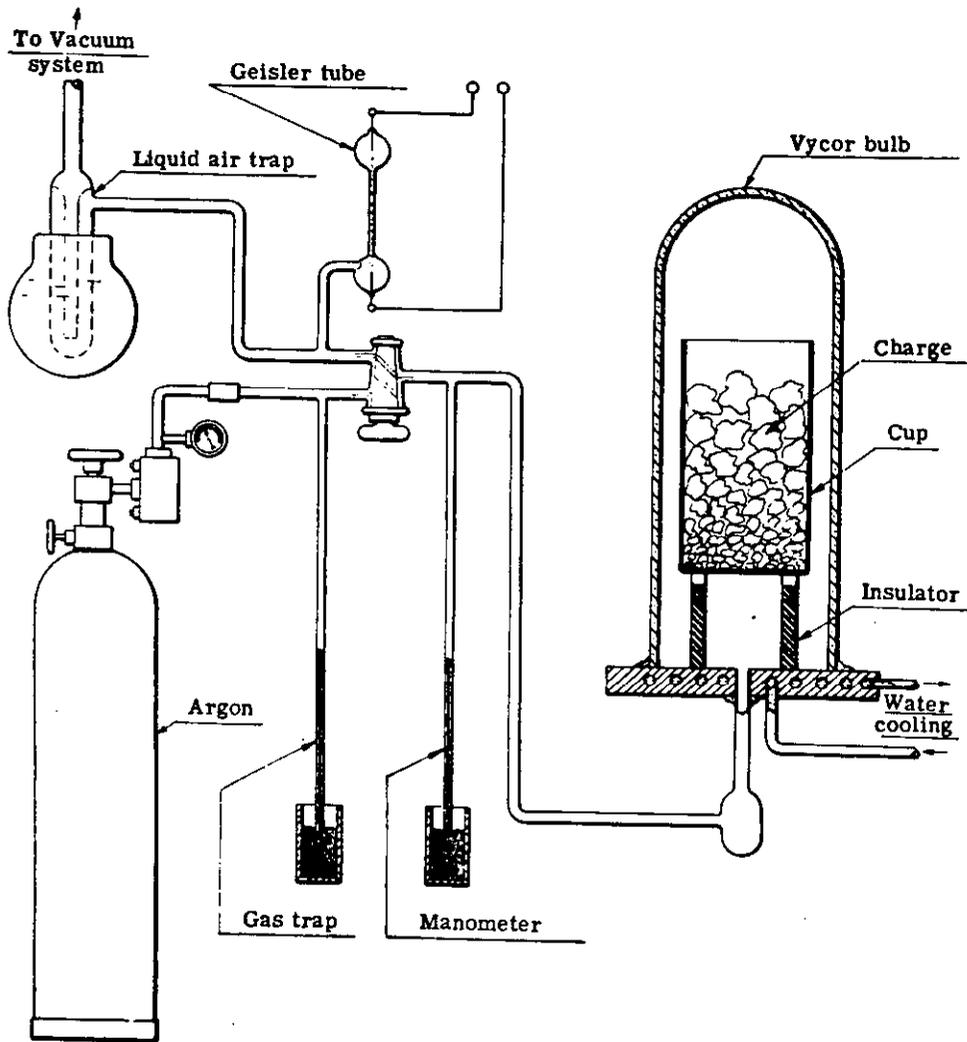


Figure 3. Apparatus used by Lilliendahl and Rentschler to produce pure zirconium.

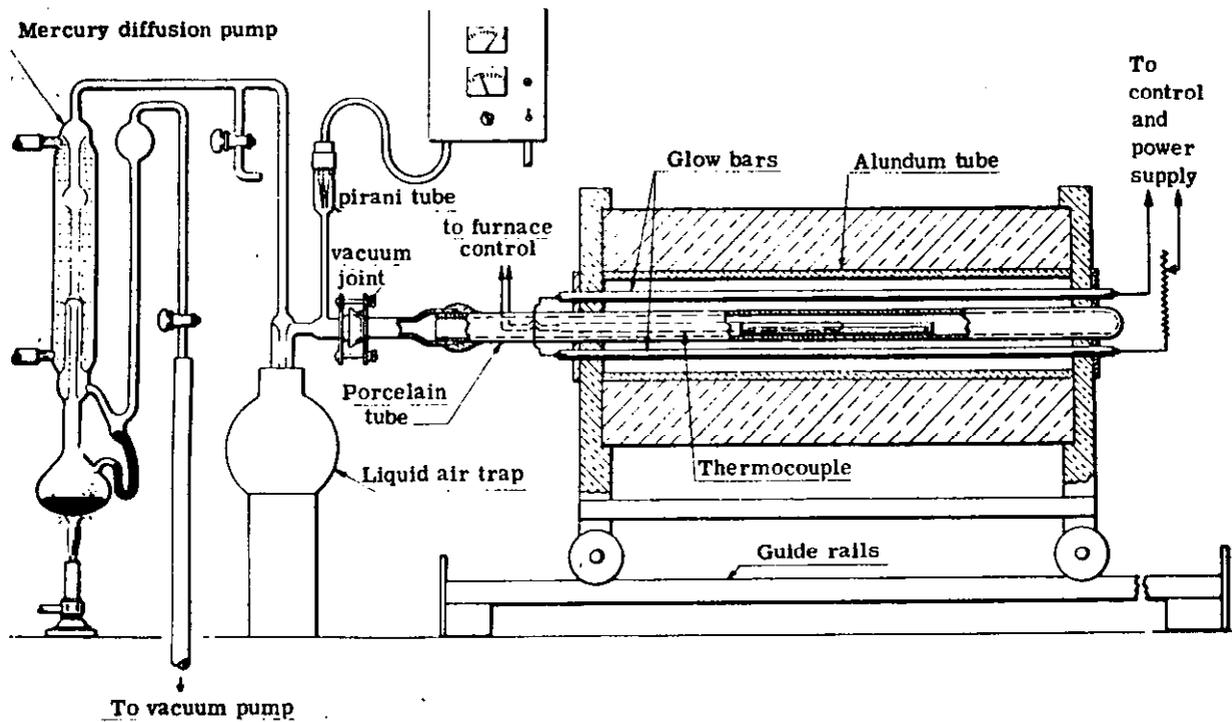


Figure 4. Vacuum sintering furnace for zirconium.

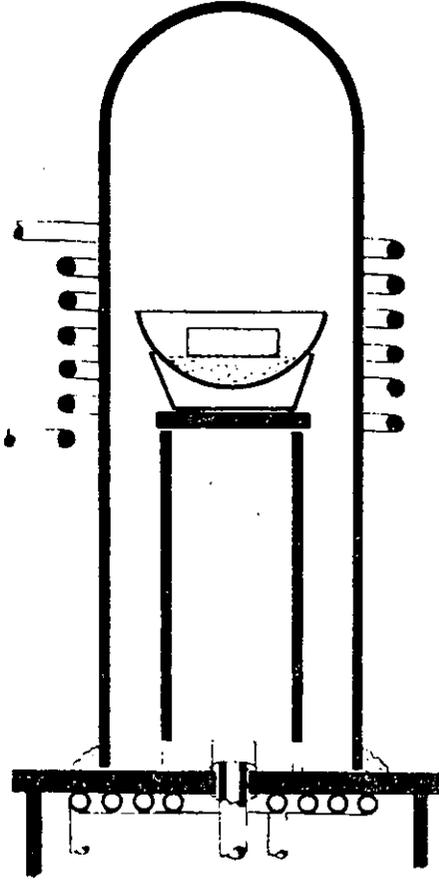


Figure 5. Vacuum melting furnace for uranium.

In the calcium bomb reduction process either uranium oxide or fluoride could be used in addition to the flux calcium chloride.



However, early in 1942 when these materials were needed it was found that there was no quantity of high purity calcium metal available. The best uranium compound procurable in quantity was recrystallized uranyl nitrate. This salt could be ignited to oxide or photoreduced and precipitated as pure potassium uranium fluoride. It was these factors that made the electrolytic process the preferred method over the calcium reduction method.

The electrolytic process as originally described by Driggs and Lilliendahl (Figure 6) consisted in fusing a mixture of calcium chloride and sodium chloride plus a small percentage of potassium uranium fluoride in a graphite crucible at 800°C. The crucible was the anode of the cell and a molybdenum strip suspended in the bath was the cathode. The uranium was deposited as a loosely adhering mass consisting of metal powder admixed with bath salts. The salts prevented oxidation as the electrode was withdrawn from the bath and cooled. The deposit was chipped off, crushed, washed with water, ground wet, and worked again. About 10 grams of metal powder was produced for each run of 30 minutes. The metal powder was filtered, dried in vacuo, pressed into pellets, and fused in vacuo. Also, the metal powder could be sintered below its melting point, but because many volatile impurities were removed and the oxide separated during vacuum fusion it was essential to fuse the metal for highest purity. The separation of the oxide as slag from the uranium was a decided advantage and is different in this respect from thorium or zirconium oxide. The vacuum-fused uranium pieces as prepared by Driggs and Lilliendahl weighed about 20-30 grams and were about the size and shape of a "cashew nut" and analyzed to 99.9% metallic uranium.

#### PROPERTIES OF URANIUM

Uranium, like thorium, has a steel-like metallic color. It slowly oxidizes in air and becomes brown in a few days. Fused uranium has a hardness of Rockwell B92-94 and can be cold-worked into wire and sheet. The density of the fused metal is 18.9.

#### INCREASED PRODUCTION

In December 1941 the first order for uranium was for 10 kilograms which seemed like a large quantity at the time. This order was filled by operating two small laboratory furnaces, a few wooden tubs on the roof utilizing the sunlight for the photochemical reduction to produce "green salt" ( $\text{KUF}_3$ ), and a somewhat larger vacuum melting apparatus. This material was supplied in various shapes and sizes for the use of physicists who were making measurements and calculations for the plutonium pile. Articles varied from cast spheres with pipes through the center, to spirals of square wire and many others which taxed the ingenuity of the man and the facilities of the laboratory.

Increased production was accomplished by merely enlarging the laboratory set-up. There was no time for extensive development of cells, photochemical reduction apparatus, and vacuum furnaces. All units were increased in size to a reasonable extent and then more units added to meet the increased demand.

However, some improvements were made. The material efficiency of the cells was increased from 40% to 80%, and  $\text{KUF}_3$  was replaced by  $\text{UF}_4$  which was made by hydrofluorination of the oxide which in turn was produced from uranyl nitrate purified by ether extraction. This uranous fluoride was of a purity seldom achieved even on a laboratory scale, thus the dependence of the process upon the weather disappeared.

The success in producing uranium for the Manhattan Project can best be quoted from the Smyth official report - Atomic Energy -

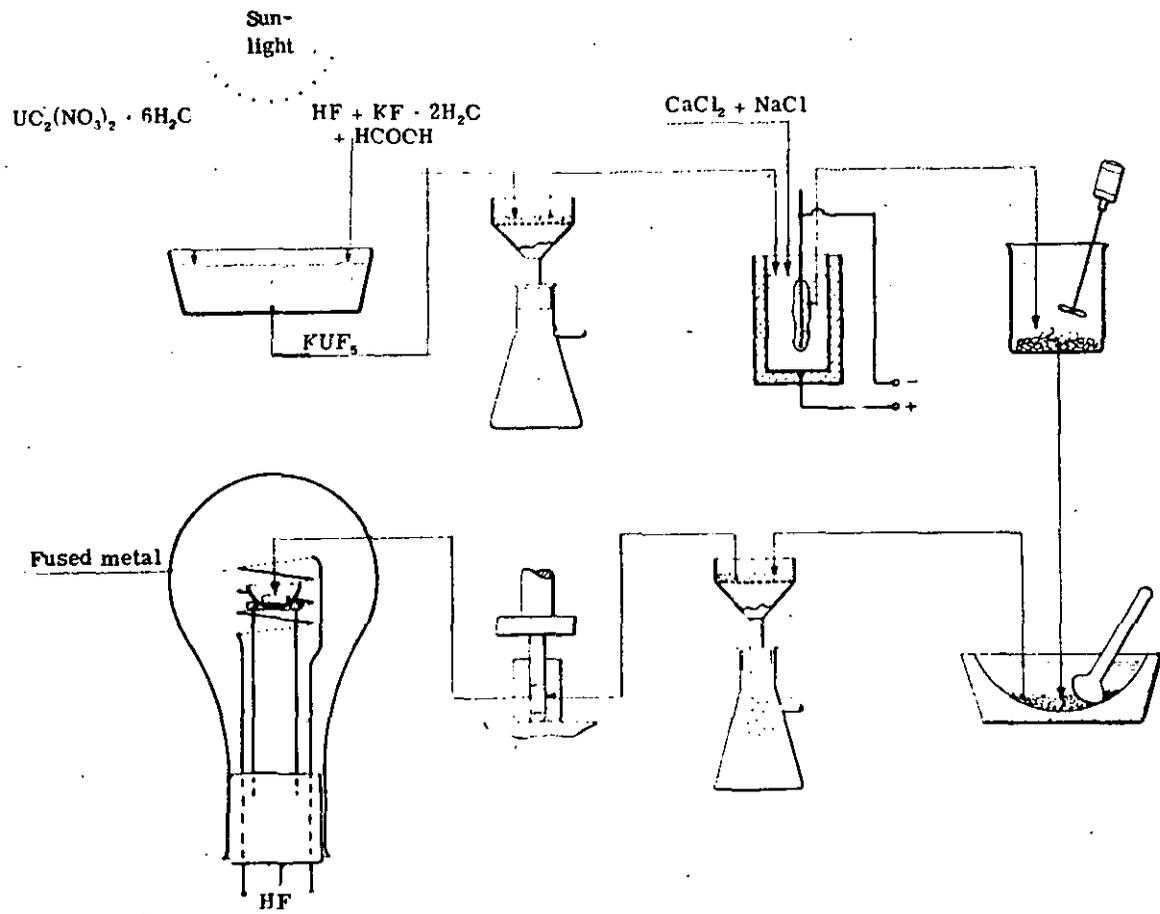


Figure 6. Apparatus used in electrolytic process for producing pure uranium.

"At the end of 1941 the only uranium metal in existence was a few grams of good material made on an experimental basis by the Westinghouse Electric and Manufacturing Company and others and a few pounds of highly impure pyrophoric powder made by another company."

Dr. Smyth noted that the production of  $KUF_3$  was a potential bottleneck and that steps were taken to make  $UF_4$  available.

"As the result of this supply of raw material to Westinghouse, and as a result of plant expansion, deliveries from Westinghouse had accumulated to a total of more than 6000 pounds by November 1942.....The purity of the metal was good and the cost had dropped to \$22 per pound."

Production reached an average of 500 pounds per day by January 1943 and totaled about 65 tons before this manufacture was discontinued in the fall of 1943. Costs, of course, decreased still further. The important contribution of Westinghouse was not the tons of metal produced, but the fact that small quantities of exceedingly pure metal were supplied for the very first experiments on atomic energy and thereby saved months of precious time.

Table 1. Physical properties of thorium, zirconium, uranium, and tungsten.

Metal	Atomic number	Type of structure	Hardness Rockwell	Melting point °C	Density (g/cc)	X-ray efficiency	$K_{\alpha 1}$ A°	Photoelectric threshold Å
Thorium	90	F.c.c.	B10	1842	11.5	120	0.134	3700
Zirconium	40	H.c.p.	B90	1857	6.53	-	0.784	3150
Uranium	92	Ortho-rhombic	B92	Ca 1150	18.9	125	0.126	3400
Tungsten	74	B.c.c.	C45	3382	19.2	91	0.208	2690