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SCALE-UP OF HIGH-PURITY URANIUM PRODUCTION

by

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ABSTRACT

Routine production techniques have been developed to supply high-purity uranium in sufficient quantities to meet the needs of diversified research programs. This report describes the equipment and operating procedures used in this work. Also, information is presented with regard to process efficiency, operational difficulties, and ingot production. Typical analyses are given for the cast ingots.

I. INTRODUCTION

The need for high-purity metal as a base material for studies of uranium and its alloys was recognized several years ago. Work in connection with developing equipment, bath compositions, and procedures for electrolytic refining of the metal in fused salt has been reported by Marzano and Noland.⁽¹⁾ Studies of the prior procedures for obtaining electrolytic crystals and their consolidation melting in high-vacuum furnaces were carried out by Blumenthal.⁽²⁾

It soon became evident that facilities used in the earlier works were insufficient to furnish the quantity of high-purity uranium needed to support the diversified research investigations at Argonne National Laboratory. A program was undertaken to develop equipment and procedures for producing an adequate supply of high-purity uranium on a routine basis. Since the metal was needed for alloy studies and for preparation of single crystals of alpha uranium to investigate such properties as elastic constants, deformation mechanisms, and self-diffusion, the purity of the product could not be sacrificed in any way. With this in mind, effort was continued throughout the program to increase the ultimate purity of the product.

This report describes the equipment and operating procedures employed in the production of high-purity uranium. Also given are operational experiences with regard to process efficiency, difficulties encountered, quantity of production, and product analyses.

II. EQUIPMENT

The primary operations in connection with preparation of high-purity uranium ingots are: 1) deposition of the electrolytic crystals in a fused salt bath, 2) preparing them for melting by cutting to a size suitable for use in the furnace feed mechanism, followed by washing to remove adherent and entrapped salts, plus cleaning by acid pickling, and 3) melting the crystals and casting the metal under high-vacuum conditions. The various pieces of equipment used in these operations and the main considerations in their design are given below.

A. Electrolytic Cells

Two types of cells have been used to electrolytically refine uranium on a semiproduction basis. The earlier work was done in Vycor cells; more recent production has been in a Hastelloy C cell.

1. Vycor cells: Figure 1 shows a schematic drawing of a Vycor cell. Its design was similar to the cell used by Marzano and Noland.⁽¹⁾ At peak production three of these units were in operation.

Fig. 1
Vycor Electrolytic Cell

Each cell consisted of a $\frac{1}{8}$ -in.-thick wall, 6-in. diameter, 26-in. long, rounded bottom Vycor tube. The tubes, encased in a stainless steel shell, were inserted into resistance-wound electric furnaces. The shells were provided with a top cover also made of stainless steel. A single unit employed one uranium anode and one molybdenum cathode. The anodes were in the form of round rods, 1.10 in. in diameter by 15 in. long, and made of commercial-grade fabricated or high-density cast stock. The cathodes were made from $\frac{1}{16}$ -in.-thick fabricated strips, $1\frac{3}{8}$ in. wide by $7\frac{3}{4}$ in. long. Stainless steel rods were used as electrical connectors to the anode and cathode. Since the electrodes must be insulated one from the other, low carbon steel bushings, flame coated on the outside with Al_2O_3 , were inserted in the top cover around the stainless steel connection rods.

Each cell contained approximately 25 lb of electrolyte of nominally 32% by weight LiCl , 38% KCl , and 30% UF_4 . The fused salts were maintained at approximately 440 to 450°C by automatic furnace controls. A dynamic flow of argon was maintained over the electrolyte as a protective atmosphere. For electrolysis, the three cells were connected in series to a 300-amp, direct-current rectifier.

2. Hastelloy C cell: A schematic drawing of the main production Hastelloy C cell, which measured 20 in. in diameter by 36 in. deep, is shown in Figure 2. In addition to increasing facilities for preparing electrolytically refined uranium, one of the main goals in designing this cell was to provide equipment capable of maintaining a positive pressure of argon over the fused salt bath. Operation in a completely closed atmosphere has three advantages over the conditions in the Vycor cells: the deposit was kept bright, the portions of the anodes inside the cell were protected from excessive oxidation, and, most importantly, contamination of the electrolyte by water was minimized.

The cell had six anodes surrounding the centrally located $\frac{1}{8}$ -in.-thick wall, 3-in. diameter by 36-in. long zirconium tube cathode. The anodes were of the same diameter as those used in the Vycor cells. They were 24 in. long with one end threaded and the other end tapped, so that the rods could be coupled together, thereby permitting continuous feeding of the anodes into the cell. A detailed sketch of the water-cooled assemblies for inserting the anodes through the type 347 stainless steel cell cover is shown in Figure 3. These ports contained ceramic-coated steel insulators much like those used on the Vycor cells. Silicon rubber "V" seals provided a gas-tight closure around the anode rods.

Two other gas-tight closures were necessary. Because of the high temperature, a metal "O" ring was used between the large cover and the Hastelloy C body. A rubber gasket was satisfactory for the smaller stainless steel cover plate that supported the cathode. This gasket also acted as an electrical insulator between the cathode and the cell body. The small cover was held in place with a removable clamp partially made of Micarta to prevent short circuiting the cell.

Fig. 2. Large Hastelloy C Electrolytic Cell

Fig. 3. Anode Bushing and Water Jacket Assembly for Hastelloy C Electrolytic Cell

The protective atmosphere of argon was admitted to the cell through four equally spaced stainless steel inlet tubes located in the large cover. The gas entered a circular manifold. Stainless steel wire screen on the inner surface of the manifold broke up the gas flow better to distribute it over the top of the electrolyte. The bottom of the manifold was located just over the top of the fused salts.

A charge of approximately 450 lb of electrolyte was kept at a temperature of from 440 to 450°C by a 50-kw resistance-wound furnace with automatic controls. The direct current for electrolysis was provided by a 300-amp selenium rectifier.

A stainless steel tube was employed as a protective cooling chamber during the removal of the electrolytically deposited crystals from the cell. The tube was designed to fit on top of the small cover flange, and its inside diameter was slightly larger than the diameter of the cover which supported

the cathode. The cover, cathode, and crystals were lifted into the chamber with a chain hoist, from whence they were moved over and lowered into a deep stainless steel tank filled with water. Figure 4 shows the cooling chamber in place on the Hastelloy C cell, and Figure 5 shows the chamber over the quenching tank.

Fig. 4. Hastelloy C Electrolytic Cell with Stainless Steel Cooling Chamber in Place

Fig. 5. Quenching of Electrolytic Uranium Crystals after Removal from Hastelloy C Electrolytic Cell

B. Crystal Cutting Equipment

To accommodate the feed mechanism of the vacuum melting furnace, it was necessary to cut the electrolytic crystals into smaller pieces. The best method developed made use of a Cincinnati-Model EA Plain Automatic Milling machine, shown in Figure 6. The crystals were cut between a uranium bar and a gang of 5 high-speed, side-mill cutters; three of these were 5 in. in diameter by $\frac{3}{4}$ in. wide, and the other two were $4\frac{1}{2}$ in. in diameter by $\frac{1}{2}$ in. wide. As indicated in the sketch of Figure 7, the cutters had a staggered arrangement with respect to their diameter, and they were placed with the teeth staggered from one cutter to the next. Rather slow cutting speeds, of the order of 20 to 30 rpm, were found to be the most satisfactory.

Fig. 6. Milling Machine Used to Cut Uranium Electrolytic Crystals

Fig. 7. Crystal Cutting Apparatus

The maximum crystal length obtained with this arrangement was approximately $\frac{5}{8}$ in.; however, the crystals were not cut into extremely fine pieces which would result in excessive ratios of surface area to volume and cause large losses in subsequent preparation for melting.

C. Crystal Washing and Pickling Equipment

Figure 8 is a sketch of the equipment used for washing the electrolytic crystals free of all electrolyte and for pickling them prior to melting. The cut crystals were contained in a stainless steel, fine mesh screen drum, 20 in. long by 12 in. in diameter. The drum was fitted with solid ends, one of which was removable for loading and unloading purposes.

Fig. 8. Crystal Processing Apparatus

Six $1\frac{1}{2}$ -in.-high internal baffles caused tumbling of the crystals. A stainless steel tray, located under the drum, held either distilled water for washing and rinsing, or nitric acid solutions for pickling. Two rubber-stoppered drains were located in the bottom of the tray for quick removal of solutions. Another small stainless steel container was placed below the tray to collect the metal fines which passed through the screen. The drum was rotated by a $\frac{1}{4}$ -hp motor via a speed-regulating Zero-Max Torque

Converter and a gear mounted on the drum end. Rotation speeds from zero rpm to as many as needed were possible with this arrangement. A second Zero-Max control unit was provided for a spare processing drum.

The whole assembly fitted into a large stainless steel tank over an open pit drain serviced by an active waste treatment facility outside of the building. A slit-type exhaust hood around three sides of the tank top removed fumes and possible air-borne activity associated with the washing and pickling operations.

D. High Vacuum Melting Furnace

In the earlier work,⁽²⁾ the electrolytic crystals were consolidated by compacting the loose crystals, melting them in a high-vacuum resistance-heated furnace and allowing the melt to freeze in a urania crucible. This procedure had several disadvantages: 1) The crucible life was extremely short because of the low thermal shock resistance of urania, and many times only one melt was obtained per crucible. 2) Because the metal was solidified in the melting crucible, a skull was present on each primary ingot and a portion of the metal was lost upon its removal. Finally, 3) because of the low overall density of the crystal compacts, only small quantities could be melted at one time, and two or more primary ingots had to be remelted together to obtain a reasonable ingot size. The double melting process was objectionable both from the viewpoint of time consumption and the possibility of increased contamination. The outstanding advantage of melting in the resistance furnace was the fact that the lower density impurities, such as uranium carbides, nitrides, oxides and intermetallic compounds,⁽³⁾ tended to float out of the melt due to its "quiet" nature and the relatively long solidification time. The effect of holding time and melting temperature on the composition of liquation melted high-purity electrolytic uranium is shown in Table I. From these data it can be seen that only the average oxygen content is appreciably and consistently lowered in value over those reported later for induction-heated cast ingots. This value of 3-4 ppm for the average oxygen content is considered to be a more reliable one than the 8-9 ppm which had been reported during earlier work. The data on the earlier work were obtained by vacuum fusion analysis in an iron bath within a graphite crucible. The later data, which were consistent and could be duplicated, were done by the present technique based on the reaction of uranium oxide with carbon in platinum melt in a purified argon atmosphere.

In an attempt to overcome the above difficulties associated with liquation melting, Blumenthal and Cocubinsky ran some preliminary experiments wherein compacted crystals were melted in urania crucibles fitted with bottom-pour stopper rods. The charges were melted in a high-vacuum furnace by induction heating and cast into a water-cooled copper mold. This procedure had several advantages: 1) Larger quantities of metal were melted at one time. 2) Induction heating resulted in a shorter melting cycle and, consequently, less contamination. 3) The skull was separated from the ingot.

The primary disadvantage was that the uranium compound impurities had less chance to float out and some were carried along with the melt when it was cast. Chemical analyses (see Table I), however, showed the ingots to be comparable to those made in the resistance furnace with the exception that contents of carbon and oxygen were higher.

Table I
ANALYSES OF PRELIMINARY HIGH-PURITY URANIUM INGOTS

Ingot No.	Melting Condition	Sample Location	Composition, ppm								
			Chemical			Spectrochemical*					
			C	N	O	Al	Cr	Cu	Fe	Mg	Si
Resistance-Heated Liquation Melts											
B-337	5 min at 1350 ⁰ C	Top	27,26	12,10	2,4,4	<5	1	1	<2	<0.5	<10
		Bottom	29,34	<10	1,3,2	<5	1	1	<2	<0.5	<10
B-335	15 min at 1350 ⁰ C	Top	17,16	4	-	5	<1	2	2	<0.5	10
		Center	-	-	2,3	-	-	-	-	-	-
		Bottom	18,19	6,7	-	5	<1	1	2	0.5	10
B-353	3 hr at 1200 ⁰ C	Top	34,29	<10	-	7	<1	3	<2	<0.5	5
		Bottom	24	<10	5,4,5,4	5	<1	1	<2	<0.5	3
Induction-Heated and Cast Ingots											
369		Center	117**	<10	26,24	<5	<1	1	<2	0.5	<10
277		Top	47	<10	-	<5	<1	<1	<2	0.5	10
		Bottom	67	<10	43,35	<5	<1	<1	<2	0.5	12
416		Top	31	-	-	5	1	<1	<2	1.0	2
		Bottom	29	-	14,15	5	1	<1	<2	0.5	3

* Other elements below limits of spectrochemical detection: Ag - <1, As - <10, B - <0.1, Be - <0.5, Bi - <1, Ca - <20, Co - <5, Mo - <20, Na - <10, P - <50, Pb - <1, Sb - <1, Sn - <5, Ti - <50, Zn - <50

** Contaminated by oil

Based upon the preliminary work of Blumenthal and Cocubinsky, Macherey designed and constructed a furnace for melting high-purity uranium ingots up to 10 kg in weight. Two important new features were incorporated in its design. To avoid the time-consuming operation of compacting the crystals, a Syntron unit was incorporated to feed them into the hot crucible. This gave the added advantage of keeping the time between start of heating and melting of a crystal at very small values and further reduced associated contamination. In the past, the cleaned and compacted crystals were transported through air to the melting furnace. Because of the extreme chemical reactivity of clean uranium and the relatively large ratio of surface area to volume of the crystals, it was impossible to prevent some contamination of the surface during this operation. To minimize this problem, Macherey included equipment in the furnace to receive the freshly processed crystals, dry them, and then charge them into the Syntron feeder, all under vacuum conditions. The equipment, as originally designed and constructed, was first used by Macherey and Dunworth, with satisfactory results, and it has been used in the same condition for all subsequent ingots.

A block diagram of the furnace unit is shown in Figure 9, and a schematic drawing with some details of the more important parts is given in Figure 10. The unit was composed of two major parts: the drying section, or dry box, and associated vacuum equipment, and the high-pumping speed, high-vacuum, induction-heated melting section.

Fig. 9. Block Diagram of High Purity Uranium Melting Furnace

The dry box employed a cement-mixer-type drum with internal baffles to tumble the crystals. An external motor and speed reducer rotated the drum via a vacuum-sealed shaft mounted through the dry box wall. The tumbler could be turned through 180° from outside the box. This allowed the crystals to be charged from the top of the dry box and, after drying, to be discharged through the bottom. Dry, clean crystals were transferred into the Syntron Vibrating Feeder, located below the dry box, through the valve separating the drying section from the furnace section. A stainless steel funnel, which was remotely lowered by a worm gear assembly, guided the crystals through the valve. Two vacuum systems were employed in the dry box section of the furnace. System I consisted of a cold trap and a large 110-cfm capacity Kinney mechanical forepump. System II, which was used for the final stages of drying the crystals, had two parallel vacuum lines. One line consisted of a cold trap, a 6-in. oil diffusion booster pump, and a Welch Duo-Seal Vacuum Pump, and the second line was the same except that it had an added 6-in. fractionating oil diffusion pump in series with the booster and roughing pumps. The vacuum systems were connected to the dry box via valves to permit selection of the various systems as needed.

Fig. 10. Schematic Diagram of High-purity Uranium Melting Furnace

The Syntron Vibrating Feeder was used to regulate the flow of crystals into the melting crucible. A short length of flexible bellows tubing provided a vacuum connection from the feeder to the furnace chamber. A stainless steel funnel with a tantalum extension tube directed the crystals into the crucible.

The stainless steel melting chamber was of double-wall construction to provide for water cooling. Internal components of the melting chamber were as follows:

1. An induction heating coil, 6 in. in inside diameter and 8 in. high, was made from approximately seven turns of $\frac{1}{2}$ -in. copper tubing.
2. The insulator for the induction coil was an Al_2O_3 tube, 5 in. in inside diameter, $5\frac{3}{4}$ in. in outside diameter, and 8 in. high.
3. A tantalum susceptor tube, $4\frac{7}{8}$ in. in outside diameter, 8 in. high with about a 0.040-in.-thick wall, was located inside the insulator, and it served as a radiation heater for the crucible and metal charge.
4. The crucible, manufactured by Norton Company, was of slip-cast and fired high-purity thoria. Two shapes (see Figure 11) were used, the choice depending upon the size of the ingot to be cast. A tapered bottom crucible, which facilitated pouring and removing the skull after casting, was used for 1-in.-diameter ingots. Due to the larger volume of metal, it was necessary to use a flat-bottom crucible when casting 2-in.-diameter ingots.
5. A thoria stopper rod, also made by Norton Company, $\frac{5}{8}$ in. in diameter by 10 in. long, with a 60° included angle tip, was used to retain the metal in the crucible during melting and to permit bottom pouring into the ingot mold.
6. A graphite heater disk beneath the crucible helped to maintain uniform temperature in the crucible.
7. The insulator below the graphite was made of K-32 firebrick.
8. All of the aforementioned items, with the exception of the induction coil, were supported free of the mold by a water-cooled copper stand.

Two different mold sizes were used, either 1 in. or 2 in. Figure 12 is a sketch of the 2-in. mold and its support assembly. Both copper molds were 12 in. long with rounded bottoms. Each was slightly tapered, larger in diameter at the top than at the bottom, to facilitate removing the ingot after casting.

Fig. 11. Thoria Crucibles

Fig. 12. Water Cooled Copper Mold and Mold Assembly

Their wall thicknesses were approximately $\frac{3}{16}$ in; however, the bottom of the larger mold was increased to $\frac{5}{16}$ in. for reasons discussed in a later section of the report. High-velocity cooling water was supplied to the outer mold surface by means of the thin annulus created by inserting the mold into its support assembly.

Power for induction melting was supplied by a 30-kw, 10,000-cps Tocco Motor-Generator set. The melting and casting section of the furnace was served by vacuum system III. Starting at the melting chamber, it consisted of a chevron-type cold trap, a Freon refrigerated baffle, a high-vacuum 10-in. fractionating oil diffusion pump, an oil ejector booster pump and a mechanical forepump of 115-cfm capacity. Overall views of the furnace unit are shown in Figures 13 and 14.

Fig. 13. High-purity Uranium
Melting Furnace -
View 1

Fig. 14. High-purity Uranium
Melting Furnace -
View 2

III. OPERATING PROCEDURE

During the time in which high-purity uranium ingots have been produced, rather definite procedures were developed for operating the various pieces of equipment and for preparing a casting. These procedures are given below:

A. Electrolytic Cell Operation

1. Vycor cell: Normally the cells were attended twice a week with only an occasional check at other times. Weights of individual "pulls" of electrodeposited metal ranged from 400 to 500 grams. A typical operating procedure for removing the deposited crystals and again starting a Vycor cell was as follows:

1. The plating current from the rectifier was shut off, and the leads to the cell were disconnected.
2. The argon gas flow was increased.
3. The cell cover with anode, cathode, and electrolytic deposit was removed and quenched in water.
4. A spare cover was placed on the cell.
5. The cathode and crystal deposit were detached from the cell cover and transferred to another container, which was filled with distilled water, where they were allowed to soak a short time to aid stripping.
6. A putty knife was used to strip the crystal deposit from the cathode.
7. The crystals were flushed with running water to remove most of the electrolyte, and they were stored in a large battery jar under distilled water.
8. The uranium anode was electropolished, washed, dried, and refastened to the cell cover.
9. Also, a clean cathode was fastened to the cover.
10. The cover with the attached anode and cathode was replaced on the cell.
11. The flow of argon was decreased.
12. The rectifier leads were reconnected to the anode and cathode extensions, and a short period of time was allowed to bring the cathode and anode up to bath temperature.

13. The rectifier was started and run at 50-60 amp for about 30 sec.
14. When plating started, as indicated by an increase in current, the rectifier was set to give 7 to 8 amp at from 0.4 to 0.5 volt.

A continuous supply of argon, to serve as an inert atmosphere, was maintained at all times over the fused-salt bath. The gas was supplied from a six-tank manifold. These tanks had to be replaced once a week.

The fused salt bath had to be replenished with 1 to $1\frac{1}{2}$ kg of the metal-bearing salt (UF_4) about once every six months. Eutectic LiCl-KCl was added in the amount of 2 to $2\frac{1}{2}$ lb every month to a month and a half. Sludge, containing impurities, was scooped from the bottom of the cell on the average of once every month.

2. Hastelloy C cell: Because of the larger size of the Hastelloy C cell, the weight of individual "pulls" of electrodeposited metal ranged from 3 to 4 kg. Operating procedure for the cell was similar to that for the Vycor cells with a few exceptions. Since the anodes were not attached to the same cover which supported the cathode, they were not removed each time with the electrolytic deposit. Because they were continuously fed, as needed, through the large permanent cell top, they were electropolished once, just before attachment to the cell. The anodes and the cathode were kept 3 in. from the bottom of the cell. Although the cathode distance was automatically maintained because of its fixed length, the anodes had to be set after each run. This was done by lowering each anode until it rested on the cell bottom, raising it 3 in., and clamping in place.

The electrolytic deposit was removed from the cell twice a week. Because of the larger mass, it could not be manipulated as readily as the Vycor cell deposits, and somewhat different procedures were developed. Upon completion of a deposition run, the rectifier was shut down, the lead to the cathode was disconnected, the argon glow was increased, and the small cover hold-down clamp was removed. The stainless steel cooling chamber was set in place on the small cover flange with a chain-hoist. The hook was lowered through the center of the chamber and attached to an "eye" provided on the small cover. The cover, cathode, and crystal deposit were then raised slowly with the chain-hoist into the cooling chamber. Care was taken to avoid dropping the deposited crystals back into the salt bath. The assembly was left in this position long enough for the salt "dragout" to solidify on the crystals and form a protective cover. An inert atmosphere was maintained in the cooling chamber during this time by the argon gas flowing up and out of the cell. The assembly was then lifted with

the chain-hoist, transferred over the water-quenching tank, and lowered into it. Subsequent handling of the product was similar to that for the Vycor cells. Figure 15 is a photograph of a typical deposit obtained in the Hastelloy C cell.

Fig. 15

Typical Electrolytic Uranium
Deposit Obtained from the
Hastelloy C Cell

To prepare the cell for the next run, a cathode, cleaned by pickling in 50 volume percent HNO_3 in water, was attached to the cover, located in place, and connected to the rectifier. Start of electrolysis was accomplished by applying a current of 250 amp to the cell. As deposition proceeded, the current was reduced to approximately 17 to 20 amp at 0.35 to 0.50 volt.

The argon atmosphere of the cell was provided from a six-tank manifold. It was necessary to replace these tanks once a week. Salt additions to the cell were required more frequently than for the Vycor cell; at least 1 to 2 kg UF_4 was added each 2 to 3 months, and 8 to 10 lb of eutectic were added per month. Sludge deposits were removed from the cell with a zirconium ladle on the average of once a month. Occasionally a heavy load of crystals fell or was knocked off the cathode; these were scooped from the bottom of the cell with the ladle.

B. Crystal Preparation

1. Crystal cutting: As part of the preparation procedure, crystals were cut with the milling machine on the day preceding a melt. The initial charges varied in weight depending upon the sizes of the crystals. If a batch of excessively fine crystals was to be cut, a larger initial amount was used to compensate for greater processing losses. It became a matter of operating experience to determine a given batch weight. In the case of a 1-in.-diameter by 12-in.-long ingot, where the finished casting weighed just under 3 kg the processing batches varied from 4.5 to as high as 7.5 kg. For a 2-in.-diameter by 12-in.-long ingot, which weighed close to 10 kg, the initial charges ranged from 15 to 18 kg.

Just prior to cutting, the crystal batch was thoroughly flushed with running water to wash away loose oxides and residual salt. They were then transferred to the milling machine, where they were cut between the uranium cutting bar and the milling cutters. During the operation, the crystals were kept wet with distilled water to prevent burning. Of necessity, the milling cutters were made of steel, and it was impossible to prevent minute particles from breaking off the cutter teeth. A strong magnet was moved over the cut crystals in an effort to remove contamination from this source.

Practically no maintenance was required for the milling machine set up other than keeping the cutters sharp, plus a strict adherence to machine cleanliness. After each use, the cutter assembly was cleaned with acetone and covered with a plastic sheet.

2. Crystal washing: As soon as the batch of cut crystals was examined for oversize pieces, it was loaded into the washing and pickling drum. The drum and batch were rotated at a slow speed of 4 to 5 rpm under running water. During the first half hour or so of the washing time (2 to 3 hr), the water was kept lukewarm by means of a mixing valve; this aided removal of entrapped electrolyte. For the last hour of the washing time, the effluent water was completely clear. Finally, the crystals were kept under distilled water overnight.

3. Crystal pickling: The next day the crystals were cleaned by nitric acid pickling. Depending upon whether a 1-in.-diameter or a 2-in.-diameter ingot was to be cast, the time for starting this operation varied. For a large melt, the drying time was up to 7 hr and the pickling procedure was started around 9:30 AM. This permitted the batch to be charged into the drying section of the furnace no later than 11:00 AM, so that melting could be started at 6:00 PM. The drying periods for the smaller charges were up to 5 hr, and the pickling was begun around 11:00 AM in order to charge the batch into the dry box at about 1:00 PM. Crystal-processing techniques, however, were identical in either case; they were as follows:

1. The water in which the batch had been standing overnight was drained from the tray.
2. The batch was pickled in a solution of HNO_3 in distilled water (25-30 volume percent HNO_3). Because of the large surface area of the uranium crystals, the reaction was rapid. Excessive overheating and large metal losses were reduced by gradually diluting the solution with distilled water.
3. The pickling was followed by a thorough rinsing in distilled water until the effluent became clear; usually 4 to 5 rinses were required.
4. A second pickling was carried out in a more dilute solution of nitric acid (10-15 v/o HNO_3).
5. The batch was given a final rinse in distilled water until the effluent became clear; again 4 to 5 rinses were required.
6. The batch was removed from the drum and put into a clean stainless steel beaker which contained a predetermined quantity of distilled water. A small sample was removed at this point for spectrochemical analysis.
7. The weight of the batch was determined by measuring the gross weight of the filled beaker and subtracting the tare weight of the beaker plus water.
8. The batch was transferred to another building and placed in the dry box section of the melting furnace.

C. Melting and Casting

As early as possible on melting day, around 8:45 AM, vacuum system III and the induction-heating power supply were turned on. The various steps of the start-up included:

1. The Stokes roughing pump was turned on.
2. The vacuum valve between the pump and the furnace chamber was opened.
3. The oil diffusion and booster pumps were turned on.
4. The Freon refrigeration compressor was started.
5. The Tocco high-frequency motor-generator was turned on.
6. The high-frequency current supply was connected to the induction coil.
7. The chevron-type cold trap was filled with liquid nitrogen.

The thoria melting crucible had to be heated slowly to prevent its cracking from thermal shock; consequently, the power was raised at the rate of 1% of the total rated kilowatts every 25 to 30 min. This increased the temperature 125 to 150°C per hour.

When the crystal batch was ready for charging into the dry box section of the furnace, the following steps were taken:

1. The dry box, which had been kept under static vacuum while not in use, was brought up to atmospheric pressure by introducing argon.
2. The excess water was drained from the batch.
3. A stainless steel funnel was inserted through the small window on top of the dry box so that its neck extended down into the tumbler.
4. The batch was fed through the funnel into the tumbler.
5. The funnel was removed, and the small window was replaced on top of the dry box.
6. The Kinney roughing pump of vacuum system I was started, and the valve connecting it to the dry box was opened. The function of this system was to reduce the pressure to 50 to 100 microns and to trap the bulk of the water left on the crystals.
7. As soon as the argon had been pumped from the box, liquid nitrogen was added to the cold trap to freeze out the water vapor.
8. The drive motor of the tumbler was started, and the drum was rotated through 90° from its loading position so that the internal fins would tumble the crystals.
9. In the meantime, the two Welch pumps and the three oil diffusion pumps of vacuum system II were started, and liquid nitrogen was added to the cold traps.
10. Upon reaching approximately 75 microns pressure in the dry box, the vacuum valve to system I was closed, and the Kinney pump was shut off.
11. The valves to vacuum system II were opened. Whereas system II was at peak operation when it was connected to the dry box, the pressure was quickly reduced to the 20-micron level. As the remainder of the water was slowly pumped off and trapped, the pressure was gradually reduced to the ultimate 10^{-5} mm mercury.
12. Additional liquid nitrogen was added to the cold traps as needed.

By 6:00 or 6:30 PM the crystals were dry, as shown by a pressure of 1 micron or less in vacuum system II. Also, the crucible was at a temperature (1250 to 1300°C) sufficient to commence melting, and the crucible, refractory liner, and crucible stool were thoroughly outgassed. The following steps were then taken:

1. The valves of vacuum system II were closed.
2. The valve connecting the dry box to the Syntron Feeder was opened.
3. The funnel inside the dry box was remotely lowered through the valve into the Syntron Feeder.
4. The tumbler drum containing the batch was turned another 90° to put it in an upside-down position and to allow the crystals to pour through the funnel into the Syntron Feeder.
5. The funnel was raised back into the dry box, and the valve was closed.
6. The diffusion pumps of system II were shut off.
7. The crystals were then slowly fed into the crucible.

The feeding operation took from $1\frac{1}{2}$ to 2 hr for a 1-in.-diameter ingot and from $3\frac{1}{2}$ to 4 hr for a 2-in.-diameter ingot. Inasmuch as vacuum system III was at peak operating capacity when the dry crystals were poured into the Syntron Feeder, the crystals entered a vacuum at least as good as that of the dry box, and usually better, or about 10^{-6} mm mercury. Because the crystals had a very large ratio of surface area to volume, it was desirable to have the melting take place as quickly as possible. This was easily accomplished by keeping the crucible at a temperature more than 100°C higher than the melting point of uranium. Each crystal melted within 3 to 4 sec upon reaching the crucible, and the large vacuum system removed the small quantity of gas evolved. Also, the vacuum system readily removed elements with low vapor pressures, such as K, Li, Mg, and Na. These contaminants were contained in small quantities of electrolyte entrapped during crystal growth in the electrolytic process.

Upon completing the melting of the crystals, the following procedure was followed:

1. The induction-heating power supply was adjusted to hold the molten metal at a desired casting temperature, as determined by an optical pyrometer. Because these were chill-cast ingots, it was necessary to cast at a high temperature, 1390°C

for 1-in.-diameter ingots and 1375°C for 2-in.-diameter ingots. Slightly higher temperatures were required for the smaller ingots because of the greater chilling effect on the smaller volume.

2. The molten metal was cast in vacuum by lifting the stopper rod extension up through the Wilson seal on top of the furnace chamber.
3. After casting, the crucible temperature was gradually lowered by decreasing power from the Tocco motor-generator set at 5-min intervals. Power was lowered 3% of the total kilowatt capacity until the temperature reached about 1100°C, and then it was reduced 2% of the kilowattage until 0% was obtained. The critical temperature range for the crucible, from the viewpoint of sensitivity to thermal shock, seemed to be from room temperature to 1100°C. When 0% kilowatt capacity was reached, the crucible temperature was approximately 650°C. The power to the heating coil was shut off, and the crucible was allowed to cool by natural means to room temperature.
4. After the melt was cast, the diffusion pumps on vacuum system II were cool and the roughing pumps were shut off.
5. The cooling water to the mold was shut off.
6. An automatic timer was set so that the diffusion pumps of vacuum system III were shut down one hour after the induction heating power had been turned off.
7. Another automatic timer was set to shut off the Freon refrigeration unit about one hour following the diffusion pumps.
8. The cold trap was filled with sufficient liquid nitrogen to last until the furnace and diffusion pumps were at room temperature.

The following morning, the furnace was opened, the casting was removed from the mold, and the furnace was prepared for the next melt. A resume of the steps taken follows:

1. The vacuum valve which connected the roughing pump to the furnace chamber was shut off.
2. The panel controls for vacuum system III were switched from the automatic timers to manual control.
3. The main valve for the furnace-cooling water was closed.
4. Compressed air was blown through the water lines to clear them for disconnection.
5. Argon was admitted to bring the furnace chamber up to atmospheric pressure.

6. The mold was lowered from the bottom of the furnace and the ingot was "shaken-out."
7. The top cover of the furnace was removed, and the feed funnel, stopper rod and crucible were taken out.
8. The skull was removed from the crucible, and if it was still intact, the crucible was cleaned for future use.
9. The stopper rod was cleaned for reuse if it was not broken.
10. The crystal feed funnel and the metal rod used to lift the stopper rod were sandblasted and then cleaned to remove any residual abrasive.
11. The inside surfaces of the furnace were wiped clean and dry of any condensate.
12. The furnace was reassembled for the next melt. This included careful alignment of the crucible pouring hole over the mold.
13. Both the dry box and furnace chamber were evacuated with the roughing pumps and then isolated via the appropriate vacuum valves.
14. The roughing pump was shut off and remained so until the next melt was to be made.

Figure 16 is a photograph of typical 1-in. and 2-in.-diameter ingots.

D. Preparation of Analytical Samples

Samples were submitted for chemical analyses from both the crystal batch and from the cast ingot. The preparation procedures were very similar to those given previously by Blumenthal⁽²⁾ with the exception of samples for oxygen analyses.

After processing the crystal batch, approximately 5 gm of the crystals were placed in a clean sample bottle. Since the sample was to be submitted for spectrochemical analysis, the only further treatment required was drying in a vacuum desiccator.

Various analytical samples were machined from the cast ingot under conditions of more than adequate cooling with distilled water by the following procedure. The ingot top was cut off with an abrasive wheel. To insure that samples were taken from clean metal, a skin cut was taken from the top face of the ingot and down the side for approximately $\frac{1}{4}$ in. Three samples of coarse turnings, each weighing approximately 3 gm, were machined from the top face of the ingot; these samples were used for carbon, nitrogen, and

spectrochemical analyses. If an isotopic analysis was desired, an additional sample was prepared. In the earlier work, turnings were also used for oxygen analyses; however, through cooperative effort of Blumenthal and Cocubinsky of the Metallurgy Division and Bain of the Chemistry Division, it was found that more reproducible results were obtained with solid samples. Consequently, samples for oxygen analysis were obtained with an abrasive cut-off wheel in the form of cubes approximately $\frac{1}{8}$ in. on an edge. Usually two cubes, each weighing 0.5 to 1 gm, were prepared for each requested oxygen analysis. Occasionally, samples were taken from the bottom of a suspect ingot and always from the 2-in.-diameter ingots. The sampling procedures for the bottom of the ingot was the same as that used for the top.

Fig. 16

One-inch and Two-inch-Diameter
High-purity Uranium Ingots

The samples of turnings were prepared for analysis by pickling in a dilute solution (30-40 v/o) of nitric acid, thoroughly rinsing in distilled water and drying in vacuum. To preclude any possibility of contamination, the treatments were carried out in the glass bottles which were used to transfer the samples to the Chemistry Division. The solid samples for oxygen analyses were not given a preparatory treatment. The spectrochemical and carbon samples were analyzed in the as-prepared condition, whereas the nitrogen and oxygen samples were given further treatment before analyses.

IV. OPERATING EXPERIENCE

The program for producing high-purity uranium on a semiproduction basis has been active for almost four years. Throughout this time considerable knowledge and experience has been accumulated with regard to various aspects of this work; some of the interesting points are discussed below.

A. Process Efficiency

The overall procedure certainly cannot be claimed as efficient. Electrolysis was the only portion with fair efficiency; upward to 70% of the input anode stock was recovered as deposited crystal. From this point on, rather drastic losses were incurred. Considerable metal was lost by reaction of the crystals with distilled water while they were stored in battery jars; no good estimate of the percentage loss was available. Depending upon the type of crystals for a particular melt, whether they were heavy or fine, the quantity of the original batch weight lost as fines during washing combined with chemical solution loss during pickling ranged anywhere from 30% up to 50% in extreme cases. Losses incurred during melting and casting, due to oxidation both in the drying cycle and during melting, were also heavy because of the large ratio of surface area to volume of the cut crystals; these ranged anywhere from 50% of the charge weight in very extreme cases to as little as 20%. Other metal losses occurred when, for one reason or another, unsuccessful castings were obtained. In addition, small quantities of cast metal were lost when the ingots were cropped and machined for chemical analyses samples. From an overall viewpoint, it was estimated that about 20% of the anode stock was recovered as useable high-purity uranium ingots.

B. Problems Encountered

Many difficulties arose during the course of this work; some of these had vital effects upon the ultimate product. The more outstanding problems are discussed below, and the steps taken to overcome these difficulties are given for those instances where it was possible to do so.

1. Electrodeposition: The continuous operation of the electrolytic cells was relatively trouble free. Occasionally, when attempting to remove a massive deposit from the large cell, some of the crystals were knocked loose because of the small opening in the cover. When this happened, the crystals had to be removed from the bottom of the cell by means of a zirconium scoop, and the equilibrium of the fused salt bath was disturbed. Likewise, salt additions or contamination by moisture unbalanced the salt-bath equilibrium. Upon such occasions, the crystals obtained in subsequent runs were of poorer quality. The only solution to the difficulty was to continue operating the cell until the crystals were again good; fortunately these incidents did not occur too frequently.

In the earlier runs with the large Hastelloy C cell, considerable difficulty was encountered because crystals burned before they could be quenched in water; this was especially true when the crystals were fine. The addition of the stainless steel protection tube successfully solved this problem by providing an inert-gas-filled cooling chamber for the crystals. At times, small lengths of anode stock were found when sludge or crystals were being scooped from the bottom of the large cell. This was due to the salt eating away the material at the reduced diameter where the anode rods were threaded together. To circumvent this condition, the machined joints were made as tight as possible. The loss of the anode pieces was not serious, except that complete utilization of the stock was not realized.

A change was made in the design of the copper block which served both to support the anode rods and to make an electrical contact to them. Formally this split block, through which the anode passed, was tightened to provide the connection between the copper and the electropolished surface of the anode. In service, however, as the oxide layer became thicker on the exposed surface of the anode, it became difficult both to feed the anode through the block and to get a good electrical connection. This was solved by opening up the hole in the block and by providing three pointed stainless steel set screws placed 120° apart. When the set screws were tightened, they penetrated the oxide film on the anodes and they provided an adequate electrical connection for the small currents required to operate the cell.

2. Crystal processing: Prior to the use of the milling machine, crystals were cut by hand operations. The original method was to cut the crystals with side-cutting pliers; this technique was much too slow and laborious. In an attempt to semiautomate the operation, an air-operated Whitney Slitting Shear was purchased, and a set of hardened uranium blades were substituted for the steel blades to minimize the possibility of contaminating the crystals. This technique speeded up the operation somewhat, but still necessitated feeding the crystals one at a time by hand. This technique was advantageous in that a precise length of the crystals could be cut and a uniform batch size with a minimum amount of surface area was obtained. The method, however, also was too slow and time consuming. The procedure for cutting the crystals in a milling machine, as described previously, was developed to overcome this problem.

A change in crystal-drying procedure was made over that reported by Noland and Blumenthal.⁽⁴⁾ It was felt that there was a strong possibility of carbon contamination through the use of ethyl alcohol as the drying agent to remove water from the processed crystals. The alcohol was eliminated and, instead, the crystals were transported under distilled water to the furnace, where the excess water was decanted and the remainder was pumped off in the vacuum dry box. Carbon contents of the ingots

were consistently lower with this procedure. The time for drying water from the crystals over that for alcohol was only slightly longer and not a serious consideration.

3. Melting and casting: One of the most serious problems encountered was that of crucible failure. Most of the melting crucibles were of high-purity, slip-cast thoria manufactured by Norton Company, Worcester, Massachusetts. The extremely high cost and slow delivery made it very desirable to obtain several melts from a crucible. Because of susceptibility to cracking by thermal shock, they required slow heating to prevent loss of a melt and slow cooling if they were to be saved for reuse. The crucibles available in the earlier part of the work were reasonably satisfactory and gave 4 to 5 melts before failure. Later, it got to the point where it was fortunate to successfully complete a melt without a major crucible failure, and almost always they were cracked. Fortunately, the cracked crucibles could and were used, as a matter of necessity, for additional melts without frequently encountering complete failures, but this was not considered good practice. Some other conditions found from time to time in as-received crucibles included out-of-roundness, poorly centered pouring holes, badly chipped areas adjacent to pouring holes, and thin wall. Although the problem of crucible failure has not been completely solved to date, cooperative effort on the part of Norton Company and the Ceramics Group of the Metallurgy Division has led to the conclusion that the difficulties were related to the particle size of the thoria used in the manufacture of the crucibles. Contrary to what one might expect, coarse-grained, less-dense crucibles seemed to be less susceptible to thermal shock. Stopper rods made from the same high-purity thoria as that used to make the crucibles which had extremely poor thermal shock resistance, for some reason, had adequate lives; normally they were used for 5 to 10 melts.

Tamped high-purity urania crucibles, also made by Norton Company, have been used for melting high-purity uranium. In general, they were found to be even poorer in resistance to thermal shock than the thoria crucibles.

In the earlier work, an occasional long crystal would escape attention and be processed in a batch. When this crystal would reach the funnel and lie across the tube entrance, it would soon stop the flow of crystals into the melting crucible. At this point there was nothing that could be done but cast what metal was in the crucible and shut down the induction-heating unit. Attempts to recover the unmelted, clean, dry crystals without their ignition were not always successful. This problem was eliminated once the milling machine was used for cutting the crystal.

A difficult problem arose with melt-throughs at the bottom of the water-cooled copper molds during casting. When a mold failed in this manner, it not only resulted in a complete loss of the ingot but also

measurable damage was done to the furnace. As might be expected, molten metal was blown over the inside of the evacuated chamber, and many internal parts of the furnace, such as the ceramic insulator and tantalum susceptor, had to be replaced. A melt-through resealed itself in a matter of seconds when enough heat had been dissipated to cool the low-melting eutectic between copper and uranium (950°C) back to freezing; however, before resealing, enough water would enter the furnace chamber to require changing the oil in the various diffusion pumps and drying out other furnace parts. Needless to say, such an incident was unfortunate, and it resulted in considerable extra work and much loss in time.

Burn-throughs only arose in the case of 2-in.-diameter molds because of the greater volume of molten metal. Two factors were of vital importance in obtaining sufficient heat transfer from the uranium to the copper molds. First, an adequate supply of high-velocity cooling water was required at the outside surface of the mold, especially at the bottom where initial chilling took place. This was accomplished by providing a narrow annulus, approximately $\frac{3}{32}$ in., at the bottom radius of the mold. The annulus opened up at the side of the mold to about $\frac{3}{16}$ in. to facilitate faster discharge of the cooling water at the top of the mold-support assembly. The second, and more important, factor appeared to be the thickness of the mold wall. From experience, the safe minimum wall thicknesses were $\frac{1}{8}$ in. and $\frac{1}{4}$ in. for the 1-in. and 2-in.-diameter molds, respectively. The heavy wall was desirable in that it provided a better initial quench for the molten uranium, principally because of the high specific heat of copper plus its good thermal conductivity. As a final precaution against melt-throughs in the later runs, a short slice was taken from the bottom of the previous ingot and placed in the bottom of the mold to act as a thermal barrier. No mold failures have occurred since this practice was initiated.

An important point of consideration with regard to the design of the copper molds was the shape of the bottom. When casting the molten uranium, it was desirable to keep splashing at a minimum; thus, a hemispherical contour was the ideal shape for the mold bottom. Although there are probably more desirable shapes from the viewpoint of water-flow patterns on the outside of the mold, this contour has proved satisfactory.

C. Production to Date

Until recently, three Vycor electrodeposition cells were kept in continuous operation. Two of these were producing uranium containing 0.4 w/o U^{235} , and the third was used for a short time to produce uranium with 0.03 w/o U^{235} . The Hastelloy C cell has continually produced 0.4 w/o U^{235} crystals.

From the onset of the program, the operating schedule called for casting one high-purity uranium ingot per week with a total monthly production of approximately 10 kg; it took some time before these goals were

achieved. The work to improve techniques and, at the same time, to increase production rates was started late in July 1955. During the remainder of the year, six melts were attempted; all were successful. A total of 16.63 kg of uranium were cast in the form of ingots. In 1956, thirteen melts were attempted and eleven were successful, with a total production of 29.31 kg. During the year 1957 a total of 91.67 kg of uranium, 30 good ingots out of 36 attempts, was produced. In 1958, when most of the mold "burn-throughs" were experienced, a total of 33 ingots weighing 124 kg were obtained from 45 melts. A total of 51 melts were made during 1959, and 47 ingots were obtained; total weight of the ingots was 117 kg. In 1960, 28 melts were attempted; all but one were successful. A total of 74 kg of uranium were cast as ingots. The last ingot of the present series was cast on July 21, 1960.

The procurement of a sound casting, of course, did not insure that it was of good high-purity quality. In some cases, ingots contained certain concentrations of impurities in excess of the acceptable average content. Fortunately, the number of ingots with chance contamination have been small, and many have found use in special applications. Disbursements of high-purity uranium to date are given in Appendix I.

D. Product Analyses

The various pieces of equipment and procedures used in preparing the high-purity uranium did not cause any major problems with regard to increasing impurity content of the cast ingots. The one exception was contamination with carbon through use of alcohol for transferring the crystals from the washing and pickling operations to the furnace dry box. As was indicated above, this problem was alleviated early in the production work by substituting water for the transfer media.

Once the cells were "broken-in" and barring equilibrium disturbances by stirring, salt additions, etc., the electrolytic process quite satisfactorily reduced the heavy atom impurity contents. Lower weight atoms, such as K and Li, however, were present in the entrapped salt within the deposited crystals, but these were markedly reduced by the melting operation.

Throughout the production work, the major contaminants were carbon, nitrogen, oxygen, and silicon. Again, the residual entrapped electrolyte was considered to be the most probable source of carbon and silicon contaminations. These elements were present in appreciable quantities in the anode stock, and they seem to be easily carried along with the electrolyte. Unfortunately, they do not have high vapor pressures at the melting temperature and, consequently, they end up in the melted metal. Contamination by nitrogen and oxygen, on the other hand, was believed to be associated with the washing, pickling, drying and melting operations. The only satisfactory way to reduce considerably the content of these two elements and chance

contamination with other elements was to take exacting precautions towards cleanliness of the equipment, care during the operations and protection of the cells, stored crystals, stored salts, etc., from foreign matter.

Based on the early melts made by Macherey and Dunworth in the revised melting furnace, there was no apparent reaction between the high-purity thoria crucibles and the molten uranium. To substantiate this, several analyses were made on random cast ingots for thorium content. Following are the results of these checks: Ingots HPX - 38, 94, and 166 were sampled and in each case the thorium content was reported to be less than 0.2 ppm.

Table II gives chemical analyses for every 10th crystal batch and ingot. In cases where the ingot was unsound for one reason or another, the data are given for the next successful ingot. As indicated above, the primary contaminants, with the exception of a few cases (for example, the copper content of ingot HPX-160), were carbon, nitrogen, oxygen, and silicon. Some systematic variations of Al, Fe, Mg, and Mn are evident; these probably bear some relationship to the various batches of anode stock which have been used over the past years.

Table II
TYPICAL COMPOSITIONS OF ELECTROLYTIC URANIUM CRYSTALS AND HIGH PURITY URANIUM INGOTS

Batch No	Ingot No	Description	Analyses (ppm by weight)												
			Chemical				Spectrochemical*								
			C	N	O	Al	Cr	Cu	Fe	K	Li	Mg	Mn	Ni	Si
B20	HPX 10T	Early Production	23 25	40	ND**	7	2	1	4	<20	<1	1	1	<5	30
	HPX 10B		22 23	72	ND	5	1	1	2	<20	<1	1	<1	<5	20
			18	14	ND	10	<1	1	3	200	50	1	<1	<5	10
	HPX 20		30	15	12 16	7	2	1	3	<50	<1	1	<1	<5	10
			198 239	14 20	ND	7	<1	1	2	200	70	2	<1	<5	10
B30	HPX 30		116 117	<10	22 30	5	<1	1	2	<20	<1	1	<1	<5	20
B40			19 20	ND	ND	10	1	1	2	300	100	3	1	5	10
	HPX 40		12 15	<10	26	7	1	2	20	<50	<1	1	<1	<5	40
B50			ND	ND	ND	7	1	1	2	100	100	1	<1	5	10
	HPX 50		6 10	13	21 22	5	<1	1	10	<50	<1	1	<1	<5	15
B60	HPX 60T	Later Production	ND	ND	ND	5	<1	<1	<2	150	50	<1	<1	<5	10
B71	HPX 60B		7	15	33 34	<5	<1	<1	2	<50	<1	<1	<1	<5	15
			4	16	26 29	<5	<1	<1	<2	<50	<1	<1	<1	<5	10
	HPX 71T		ND	ND	ND	10	<1	1	<2	300	100	1	<1	5	15
	HPX 71B		6 7	10	31-31	7	<1	1	<2	<50	<1	1	<1	<5	15
B81			6 7	18	ND	5	<1	1	<2	<50	<1	1	<1	<5	10
	HPX 81		ND	ND	ND	10	<1	<1	<2	300	100	2	<1	<5	20
B90			18 28	<10	36 43	5	<1	<1	<2	<50	<1	1	<1	<5	15
	HPX 90T		ND	ND	ND	5	<1	2	<2	300	150	2	1	<5	100
B100	HPX 90B		27 28	<10	15	10	1	1	2	<50	<1	1	1	<5	30
	HPX 100		12-16	<10	19	5	1	<1	2	<50	<1	3	1	<5	20
			ND	ND	ND	15	1	<1	<2	150	200	<1	3	<5	10
			6 9	<10	9 17	5	<1	<1	<2	<20	<1	<1	2	<5	15
B110	HPX 110	Recent Production	ND	ND	ND	5	<1	<1	<2	200	150	2	2	<5	<10
B122			6 7	35	31-35	<5	<1	<1	<2	<50	<1	1	1	<5	<10
	HPX 122		ND	ND	ND	<5	1	<1	<2	50	40	<1	8	<5	<10
B131			12 15	15	26 126	<5	<1	<1	<2	<50	<1	<1	3	<5	<10
	HPX 131		17-19	ND	ND	<5	<1	1	<2	100	40	2	<1	<5	10
B140			10 14	18	43 45	<5	<1	<1	<2	<50	<1	<1	<1	<5	10
	HPX 140		ND	ND	ND	<5	<1	<1	<2	90	50	3	<1	<5	<10
B150			17 21	19	24 26	<5	<1	1	<2	<50	<1	2	<1	<5	20
	HPX 150		ND	ND	ND	<5	<1	<1	<2	100	100	2	<1	<5	<10
B160			32 40	15	36	<5	<1	<1	<2	<50	1	1	<1	<5	20
	HPX 160		ND	ND	ND	5	<1	1	<2	75	50	2	2	<5	15
B170			29-31	<10	21	<5	<1	40	<2	<50	<1	1	1	<5	10
	HPX 170		ND	ND	ND	8	<1	<1	<2	75	75	2	1	<5	15
B181			17 18	<10	72 89	<5	30	<1	<2	<50	<1	1	2	<5	10
	HPX 181T		ND	ND	ND	5	<1	<1	<2	150	100	5	1	<5	15
B189	HPX 181B		21 23	11	32	<5	<1	<1	<2	<50	<1	2	<1	<5	15
	HPX 189		35 39	<10	32	<5	<1	<1	<2	<50	<1	4	<1	<5	15
			ND	ND	ND	10	<1	1	<2	<50	<1	1	1	<5	20
			12-14	<10	13 14	<5	<1	1	<2	<50	<1	1	2	<5	10

*Other elements below limits of spectrochemical detection

**ND = not determined

V. SUMMARY

Sufficient quantities of high-purity uranium have been made on a semiproduction basis to supply a basic material for metallurgy research programs. Equipment and operating procedures have been developed for electrorefining uranium in a fused salt bath, for preparing the deposited crystals prior to melting, and for consolidating the material into cast ingots under high-vacuum conditions.

During the course of the work, several problems arose with regard to equipment design, materials, and operating procedures. For the most part, satisfactory solutions were arrived at for these difficulties. Although the overall efficiency of the process was low (approximately 20%), the ultimate product was of good quality and reasonably uniform in composition. The main contaminants were carbon, nitrogen, oxygen, and silicon. Most of the later ingots contained less than 70 ppm of weight of total analyzed impurities; however, occasionally a chance contamination of an ingot raised the total analyzed impurities up to 100 ppm or greater.

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APPENDIX I. DISBURSEMENTS OF HIGH-PURITY URANIUM

The primary objective of the high-purity uranium production work has been to furnish material for various research purposes. To this aim the product has been made available to persons engaged in work wherein the use of good-quality uranium was important. Table III records the high-purity uranium ingots which have been disbursed to various members of the staff at Argonne National Laboratory. In addition, some workers at ANL have required uranium in forms other than cast ingots; dispositions of this type of material are given in Table IV. High-purity uranium also has been made available to workers located outside. Appreciable quantities of ingots and special shapes have been furnished to other laboratories in the United States of America and in foreign countries as well. These disbursements are tabulated in Table V.

Table III

DISPOSITION OF HIGH-PURITY URANIUM INGOTS WITHIN ARGONNE NATIONAL LABORATORY

Date	Material ⁽¹⁾ Identification	Amount, gm	Disposition	Date	Material ⁽¹⁾ Identification	Amount, gm	Disposition
5-19-52	B185 ⁽²⁾	25.5	P. Fields CHM.	1-58	HPX-61 ⁽⁴⁾	175	S. Rothman MET.
8-1-55	HPX-10	2,720	E. Fisher MET.	1-58	HPX-69 ⁽⁵⁾	10,030	A. Fischer MET.
8-16-55	HPX-11	3,140	B. Blumenthal MET.	2-58	HPX-58	2,400	S. Zeyler MET.
9-30-55	HPX-12	2,840	W. Yario MET.	4-58	HPX-71	6,980	B. Loomis MET.
12-28-55	HPX-14	2,270	H. Kittel MET.	5-58	HPX-60, 64-67	620	C. Renken MET.
1-56	HPX-15	2,250	E. Fisher MET.	6-58	HPX-61 ⁽⁴⁾	501	S. Rothman MET.
1-24-56	HPX-16	2,020	B. Blumenthal MET.	6-58	HPX-80	1,440	B. Loomis MET.
6-56	HPX-13	800	Beederman CHM.	6-58	HPX-81	1,390	L. Lloyd MET.
6-56	HPX-18	2,590	E. Fisher MET.	7-58	HPX-76	4,630	K. Myles MET.
6-56	HPX-21	2,715	E. Fisher MET.	8-58	HPX-84	2,050	B. Loomis MET.
8-56	HPX-22	1,680	B. Blumenthal MET.	9-58	HPX-59	333	J. Goleb CHM.
8-56	HPX-23	2,740	L. Lloyd MET.	9-58	HPX-60	8,430	L. Lloyd MET.
9-56	HPX-24	2,730	A. Dwight MET.	9-58	HPX-67	6,500	E. Fisher MET.
10-56	HPX-25	2,750	B. Blumenthal MET.	9-58	HPX-88	2,120	A. Dwight MET.
2-57	HPX-28	278	J. Schnitzlein CEN.	10-58	HPX-77 ⁽⁴⁾	2,640	S. Rothman MET.
2-57	HPX-30	1,263	B. Blumenthal MET.	11-58	HPX-59	2,170	F. Yaggee MET.
3-57	HPX-26	503	B. Blumenthal MET.	11-58	HPX-89	5,010	K. Myles MET.
4-57	HPX-29	520	L. Kelman MET.	1-59	HPX-103 ⁽³⁾	1,660	F. Tomkins CHM.
6-57	HPX-32	1,140	D. Flikkema CEN.	1-59	HPX-66, 77, 8700 ⁽⁴⁾	140	K. Myles MET.
6-57	HPX-35	420	D. Flikkema CEN.	5-59	HPX-99	2,420	K. Myles MET.
7-57	HPX-39	2,330	B. Blumenthal MET.	6-59	HPX-98	2,520	J. Darby MET.
7-57	HPX-42	1,900	E. Fisher MET.	7-59	HPX-100	2,820	L. Lloyd MET.
7-57	HPX-43	6,680	L. Lloyd MET.	7-59	HPX-104	2,850	E. Fisher MET.
9-57	B700 ⁽⁴⁾	228	S. Rothman MET.	2-60	HPX-159	2,840	M. Nevitt MET.
9-57	HPX-29	933	B. Blumenthal MET.	4-60	HPX-115	667	S. Rothman MET.
9-57	HPX-33	2,420	A. Dwight MET.	4-60	HPX-143	1,420	L. Kelman MET.
9-57	HPX-34	862	B. Blumenthal MET.	4-60	HPX-172	2,770	A. Berndt MET.
10-57	HPX-51	960	B. Blumenthal MET.	5-60	HPX-137	1,280	L. Kelman MET.
11-57	HPX-51	1,400	B. Blumenthal MET.	6-60	HPX-183 ⁽⁶⁾	3,530	B. Loomis MET.
12-57	HPX-46	7,320	W. Yario MET.				

⁽¹⁾ Ingots identified with B were prepared by melting and directionally solidifying in UO₂ crucibles using resistance heating. Ingots identified with HPX were prepared by melting in ThO₂ crucibles, using induction heating, and cast into water-cooled copper molds.

⁽²⁾ Transmittal document No. ANL-FF-262k

⁽³⁾ Transmittal document No. ANL-FF-262ar

⁽⁴⁾ Ingots B700, HPX-61, 66 and 77 had nominal isotopic analyses of 0.03 w/o U²³⁵.

⁽⁵⁾ HPX-69 had isotopic analysis of ~2 w/o U²³⁵.

⁽⁶⁾ HPX-183 had isotopic analysis of ~1.6 w/o U²³⁵.

Table IV

DISPOSITION OF OTHER FORMS OF HIGH-PURITY URANIUM WITHIN ARGONNE NATIONAL LABORATORY

Date	Material Identification	Description	Transmittal Document No.	Amount, gm	Disposition	
Electrolytic Crystals						
2-25-52	Lot B-289/VI Large Cell		ANL-FF-262h	101	H. Flotow	CHM.
9-16-59				150	J. Handwerk	MET.
Fabricated Shapes						
8-23-51	B-211	Sheet and Foil	ANL-FF-262j	125	C. Muehlhouse	PHY.
6-2-53	Ingot B-335	Small Cylinders	ANL-FF-262t	25	R. Vogel	CEN.
1-25-54	Ingot B-451	Small Cylinders	ANL-FF-262ab		R. Vogel	CEN.
1-57	Ingot H-209	1/8-in. dia Rod		130	H. Flotow	CHM.
1-57	Ingot B-716	1/8-in. dia Rod		124	H. Flotow	CHM.
3-58	HPX-68	3/16-in. dia Rod		1,550	L. Kelman	MET.
4-20-59	HPX-115	0.120-in. dia x 1 in.	ANL-FF-262ay	6.9	L. Kelman	MET.
4-59	HPX-115	3 Pcs. 0.125-in. dia x 21 in.	ANL-FF-262ax	270	M. Ader	CEN.
Miscellaneous-Non High Purity						
8-23-51	Hanford Stock	Sheet and Foil	ANL-FF-262j	121	C. Muehlhouse	PHY.

Table V

DISPOSITION OF HIGH-PURITY URANIUM OUTSIDE ARGONNE NATIONAL LABORATORY

Date	Material Identification	Description	Transmittal Document No.	Amount, gm	Disposition
Ingots					
9-22-52	B-282		ANL-FF-262p	300	Dr. H. Cleaves - B.S.
8-24-53	H-212		ANL-FF-262u	600	Dr. T. Magel - M.I.T.
1-4-54	B-335		ANL-FF-262aa	43	Dr. W. Leaders - M.C.W.
6-56	HPX-13	1-in. dia		800	R. Teeg - M.I.T.
6-56	HPX-20	1-in. dia		1,170	Westinghouse Elec. Co.
6-56	HPX-20	1-in. dia		550	Sylvania Elec. Co.
6-56	HPX-20	1-in. dia		530	Dr. D. Ragone - U.M.
1-57	HPX-28	1-in. dia		2,010	United Kingdom
2-57	B-716			67	C. Phillips - Ford Motor Co.
2-57	HPX-28	1-in. dia		371	C. Tipton - B.M.I.
3-57	HPX-26	1-in. dia		1,955	France
6-57	HPX-29	1-in. dia		222	Atomics International
6-57	HPX-35	1-in. dia		1,890	United Kingdom
12-57	HPX-44	1-in. dia		1,950	United Kingdom
12-57	HPX-55	1-in. dia		1,096	R. Resnick - Sylvania Elec. Co.
1-58	HPX-50	1-in. dia		2,740	F. Rough - B.M.I.
2-58	HPX-65	1-in. dia		2,150	United Kingdom
3-58	HPX-68	1-in. dia		892	Dr. C. Rodden - A.E.C.
4-58	HPX-67	2-in. dia		2,240	United Kingdom
6-58	HPX-67	2-in. dia		432	Lincoln Lab. - M.I.T.
7-58	HPX-84	1-in. dia		122	P. Stelson - O.R.N.L.
10-58	HPX-93	1-in. dia	ANL-FF-262am	914	E. Westrum, Jr. - Univ. of Mich.
1-59	HPX-107	1-in. dia		2,020	J. Savage - Atomics Int.
3-59	HPX-40	1-in. dia	ANL-FF-262av	1,620	J. Cadwell - H.A.P.D.
3-59	HPX-57	1-in. dia	ANL-FF-262av	2,340	J. Cadwell - H.A.P.D.
3-59	HPX-93	1-in. dia	ANL-FF-262av	1,900	J. Cadwell - H.A.P.D.
4-59	HPX-94	1-in. dia	ANL-FF-262az	464	P. Lacombe - France
12-59	HPX-126	1-in. dia	ANL-FF-262bi	1,210	United Kingdom
12-59	HPX-131	1-in. dia	ANL-FF-262bi	1,560	United Kingdom
12-59	HPX-140	1-in. dia	ANL-FF-262bi	2,310	United Kingdom
4-60	HPX-125	1-in. dia	ANL-FF-262br	29	A. Boltax - N.M.I.
7-60	HPX-163	1-in. dia	ANL-FF-262bv	2,040	Argentina
Electrolytic and Single Crystals					
2-8-52	Lot B-286/Y31	Electrolytic		106	J. Woodhouse - DuPont
9-12-52		Single Crystal	ANL-FF-262m		J. Waber - L.A.S.L.
12-23-52		Single Crystal	ANL-FF-262s		D. White - K.A.P.L.
8-21-53	Lot B-457	Electrolytic		150	Dr. W. Johnson - W.A.P.D.
9-15-53	Lot B-462	Electrolytic		200	R. Fisher - Iowa St. Coll.
3-17-54		(3) Single Crystals			J. Howe - N.A.A.
8-15-55	Lot B-636	Electrolytic	ANL-FF-262ai	23	Dr. C. Mathews - L.A.S.L.
10-22-57		(2) Single Crystals			Dr. R. Smallman - U.K.
1-58		Coarse Grain Specimens		100	E. Sturcken - S.R.P.
Fabricated Shapes					
6-5-51	B-194	Strip 0.040" x 2-1/8" x 4-3/16"	ANL-FF-262c	110.5	U.C.R.L.
6-5-51	B-195	Strip 0.040" x 2-1/8" x 10-3/16"	ANL-FF-262c	287.5	U.C.R.L.
7-3-51		Rod 1/4" d x 2-3/4"	ANL-FF-262e	36.5	J. Taub - L.A.S.L.
7-16-51	B-195	Sheet	ANL-FF-262f	0.9	P. Duwez - U.C.R.L.
11-8-51	B-211	0.020" Sheet	ANL-FF-262g	107.3	Dr. Coffinberry - L.A.S.L.
10-13-52	B-272-B	Rod 5 CML x 0.5 CMD	ANL-FF-262q	18.9	Vatican Observatory
2-5-53	I-363	Rod 0.337" d x 24-3/4" l		668	R. Ward - H.A.P.D.
2-9-54	H-217 TC and TA	1/2" Rod	ANL-FF-262ac	1,400	Dr. T. Nagel - M.I.T.
1-58	HPX-63	Plate and Rod		1,557	R. Ogilvie - M.I.T.
Miscellaneous-Non High Purity					
5-6-54	B-518	Biscuit Metal	ANL-FF-262ah		K. Goldman - W.E.C.
8-15-55	B-632	Re-Melted Dingot	ANL-FF-262ai	14.6	Dr. C. Mathews - L.A.S.L.
1-58		U-Zr Alloys		246	E. Sturcken - S.R.P.
5-6-58		U-Zr Alloys		87.7	E. Sturcken - S.R.P.
6-59		Dingot Slab	ANL-FF-262bc	1,180	J. Kearns - W.E.C.