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THE ELECTROLYTIC REFINING OF URANIUM

by

C. Marzano and R. A. Noland

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THE ELECTROLYTIC REFINING OF URANIUM

by

C. Marzano and R. A. Noland

ABSTRACT

This report describes work done on the electrolytic refining of natural uranium in fused salt baths composed of various eutectics of alkali metal chlorides into which were dissolved UF_4 or UCl_3 .

Near spectroscopic* purity was achieved with two electrolytes. One electrolyte was composed of 33 w/o UCl_3 , 20% KCl , 47% BaCl_2 , and was maintained molten at $600^\circ\text{--}625^\circ\text{C}$. The other electrolyte containing 33 w/o UCl_3 or UF_4 , 30% LiCl and 37% KCl melted at a lower temperature permitting operation at $390^\circ\text{--}425^\circ\text{C}$. The first electrolyte was shown to be more sensitive to impurities in the feed salts; the second was rather tolerant to impurities, permitting lower purity salts and metal to be used without lowering the high purity of the refined product. Other electrolytes melting at higher temperatures were also investigated.

The metal to be refined is made the anode, and the product, a woven mass of dendrites and small crystals, is collected on a Mo or Ta cathode. Argon or helium is required as a cover gas to protect the electrolyte and to protect the uranium crystals after removal from the bath.

Clear fused quartz or Vycor contain the electrolyte without contamination. Because these materials are fragile, tests were run on many other materials, including various stainless steels, Ta, Pt, Ni, certain Ni alloys, and several grades of graphite with no outstanding substitute having been found, except that Hastelloy C appeared promising.

Low voltage direct current required for electrolysis may be furnished by motor generator sets or rectifiers. Power requirements, including that necessary to keep the electrolyte molten, are small.

Current efficiencies of the order of 50-60% were obtained.

The product must be very carefully washed to remove all traces of electrolyte if high purity is to be achieved. Attempts to produce extremely coarse crystals or coherent cathode sheet by employing nucleating agents, periodic polarity reversals (PR), and superimposed alternating current on the plating current were unsuccessful.

Samples of the refined material were vacuum melted in UO_2 crucibles without significant change in purity. (See also ANL-5019.)⁽⁷⁾ The resultant metal was soft, ductile, and easily worked.

*No attempt is made to specify purity as a fraction of 100% because analyses were not made for many elements and the analytical precision of the optical spectrograph would compromise the accuracy of such terminology.

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I. INTRODUCTION

The work to be described in this report was originally undertaken to provide a supply of high purity uranium for fundamental studies in physical metallurgy. After a survey of the literature a decision was made to concentrate on electrolytic processes, which, in addition to producing high purity melting stock, could conceivably be used for the production of single crystals.

Three general types of electrolytes capable of dissolving uranium compounds were considered.

A. Aqueous Solutions

The strong tendency of uranium compounds to react with water to form uranyl compounds which are too stable to permit electrolytic reduction to free metal at the cathode indicated little chance of success from this type of bath.

B. Organic Baths

No information was available in the literature describing the electrolysis of organic baths containing uranium compounds, and exploratory work done by Babcock and Noland at Argonne using baths similar to the ethyl pyridinium bromide used by Wier and Hurley⁽¹⁾ in the deposition of aluminum were not encouraging.

C. Fused Salts

This approach appeared to be the most promising, largely because of the early success of the Westinghouse process originally developed by Liliendahl and Driggs, and which was used in the early days of the Manhattan Project to produce fairly large quantities of metal.⁽²⁾ Their original electrolyte was composed of a mixture of sodium chloride, calcium chloride, and potassium uranium fluoride, contained in a graphite cell which was maintained at a temperature of 800°C, with the cell acting as the anode, and the product being collected on a molybdenum cathode. The potassium uranium fluoride (KUF_5) was produced photochemically in accordance with the following reaction:⁽²⁾

Because of a general lack of sunshine, a dependable supply of KUF_5 (green salt) was not available, and it was replaced in the process by UF_4 , made by hydrofluorination of the oxide produced from ether-extraction purified uranyl nitrate. It was claimed that the material efficiency of the process was of the order of 80%, and that metal of 99.9% purity was produced.⁽²⁾

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C. A. Krause⁽³⁾ indicated that uranium halides formed complex salts with the halides of the alkaline metals and the halides of the alkaline earths. The salts formed were fusible and were known to be good conductors of electricity when molten.

It was felt, therefore, that the successful experience of Westinghouse, complemented by the encouraging data of Krause, justified a concentration of effort on fused salt processes, and work was begun in this direction.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. Initial Investigation

Work was begun using a fused electrolyte containing BaCl_2 , NaCl , KCl , UCl_3 , in the following proportions by weight:

BaCl_2	41.7%
NaCl	16.7%
KCl	25.0%
UCl_3	16.6%

This electrolyte, in a type 347 stainless steel cell, was maintained in a molten condition by heating in a resistance furnace in the range $650^\circ\text{--}700^\circ\text{C}$. No atmosphere was provided to protect the salts from oxidation. A strip of molybdenum was used as a cathode, and various anode materials such as graphite, tungsten, and uranium were employed. It soon became obvious that there existed a very serious problem involving chemical attack of the cell at or below the air line by the electrolyte. The following materials were tested as cells contain the electrolyte at 650°C and were found to be unsatisfactory:

1. Stainless steels

Types 304, 316, 347, 309, 310, and 430.

2. Nickel alloys

Monel, Type A Nickel, Inconel, 35-15 (35 Nickel - 15 Chrome), and Hastelloy alloys A and C.

3. Refractory Metals

Tantalum, Niobium, and Platinum. Platinum was found to be satisfactory unless rendered anodic or bipolar, conditions difficult to prevent during electrolysis.

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4. Graphite

Various grades of graphite were tried and were generally unsatisfactory, because all grades tested permitted seepage of electrolyte to points outside of the container.

5. Quartz

Unfused quartz of the gray variety was too porous to retain the electrolyte, and areas directly adjacent to the electrolyte had a strong tendency to spall.

The weakness apparent in the gray quartz did not exist in clear fused quartz, and it developed that the latter was completely satisfactory.

No deposits of metallic uranium were obtained from this electrolyte when operated without a protective inert atmosphere such as argon. A slight amount of work involving electrolysis under a protective atmosphere had led to encouraging results; at this time information became available which indicated that M. Kolodney, H. L. Slatin, and associates⁽⁴⁾ had perfected a process at Los Alamos for which all of the details had been worked out.

B. Performance and Development of Various Electrolytes

1. KCl-BaCl₂-UCl₃ Bath

Kolodney and Slatin, who had by this time become consultants to the AEC, were contacted. They suggested Argonne perform initial experiments with an electrolyte formed by pre-fusing an eutectic mixture of 46 weight % BaCl₂ and 54% KCl at 1000°C in a platinum dish, and adding to this eutectic approximately 30 weight % of UCl₃ to form a salt mixture of the following composition:

BaCl ₂	46.7 (w/o)
KCl	20.0
UCl ₃	33.3
U (Calculated as Metal)	23.3

The composition of the molten electrolyte is not homogeneous, the uranium content being considerably greater at the bottom than at the top of the melt. This bath was contained in a fused quartz cell and operated in the range 625°-650°C, using a molybdenum cathode to which was attached a tantalum collector disc. Soluble uranium or insoluble tungsten anodes were used. The cell design, similar to that shown in Figure 1, provided protection

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FIGURE 1

QUARTZ ELECTROLYTIC CELL

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tubes around each electrode and permitted the use of an inert cover of argon to protect the melt during electrolysis. With this arrangement, electrolysis was continued for a period of time at approximately 5-10 volts and with a current of 10 amperes on the 2 in. diameter tantalum collector disc. At the end of the plating period, ordinarily from 5 to 10 days, the salts were allowed to freeze. Expansion of the salt mass occurred upon solidification and cracked the cell. It was broken away, and the residual salt remaining on the cluster of crystals deposited on the cathode was removed by washing in cold running water. Upon completion of washing, the crystals were found to be silvery bright and quite ductile. The crystals collected on the cathode in a dense interwoven cluster containing a mixture of coarse and fine dendrites. Figure 2 is a photograph of such a cluster, and Figure 3 includes pictures of crystal groups removed from a larger cathode cluster.

a. Runs Made Using Low Grade UCl_3

Further work done at Argonne was accomplished by electrolyzing the fused salt mixture mentioned above in clear fused quartz cells using soluble uranium anodes, which were usually fabricated rods made from standard reactor grade uranium, graphite melted and alpha rolled. The deposit was collected on a 2-1/2 in. diameter Ta disc which was fastened to a 1/2 in. round by 22 in. long Mo rod. Anodes were alpha rolled from billets vacuum cast at Argonne and were machined into 1/2 in. diameter rods, 12 in. long, threaded at both ends to permit several rods to be assembled into a single length. Figure 1 is a sketch of the completely assembled cell. The melt and the electrodes were covered at all times with argon which had an initial purity of 99.96% and was further purified by passing it over heated uranium and zirconium turnings and a drying train of towers of P_2O_5 and CaCl_2 . A copper coulometer was connected in series with the cathode so that the cathode current efficiency of each run might be calculated. Only a few of the early runs were made with the coulometer in the circuit, since consistent efficiencies ranging between 50 to 60% were obtained when electrolysis was conducted under the conditions outlined above.

Baker and Adamson Reagent Grade BaCl_2 and KCl were used to make up the first eutectic, as it was believed that their reagent purity would be sufficient to permit high electrolytic metal purity. The original UCl_3 , later found to be quite impure, was obtained from the Oak Ridge National Laboratory through the efforts of the Chicago Operations Office of the AEC.

The bath was made by first fusing the BaCl_2 and KCl at 1000°C in a platinum dish to form the eutectic and casting the fluid mixture into platinum molds. After solidification and cooling, the salt cake was ground by hand in a stoneware mortar with a chromium plated steel pestle. Before the salts were installed in the cell (Figures 1 and 4), it was flushed thoroughly with argon. A weighed amount of UCl_3 was placed into the cell

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Figure 2. Photograph of Typical Uranium Deposit on Cathode.

Macro 12419

1X

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Figure 3. Crystal Groups Removed from A Cathode Cluster of Electrolytic Uranium As Refined in a $\text{KCl-BaCl}_2\text{-UCl}_3$ Electrolyte.

Macro 14488

3X

Macro 14520

3X

Macro 14521

3X

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Figure 4. Small Scale Electrolytic Cell Showing
General Arrangement of Components

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first, and it was covered with a suitable amount of crushed eutectic, so that the eutectic upon melting would cover and flow around the solid UCl_3 which soon dissolved in the eutectic to form a molten ternary.

The first few runs were of short duration, varying in length from one to four days, with a current of 10 amperes on the collector disc; the voltage was varied to keep this current constant. It was observed that at the start of electrolysis an applied potential of 8 to 9 volts was necessary, but that after the first few hours of operation lower applied voltages, of the order of 2 to 3 volts, were sufficient. This was believed to be due to the removal of interfering materials, such as trace amounts of water and oxygen from the electrolyte during early electrolysis, because heating alone does not accomplish the same results.

Spectrographic analysis of the metal produced in the first three runs, listed in Table 1, indicated that of the principal impurities normally found in reactor grade material, namely, carbon, iron, silicon, nickel, and chromium, were present in the electrolytic product. The deposit was slightly higher in nickel, chromium and molybdenum, and contained considerably more silicon. Of the major impurities, carbon had been reduced by the greatest factor, namely, ten.

It was believed that the impurities observed in the deposit had come from the quartz cell SiO_2 , the molybdenum cathode (Mo), or the UCl_3 . A spectroanalysis was obtained of the latter (see Table 1, Item 5) indicating that this material was very impure, containing large amounts of the elements observed as contaminants in the metal crystals.

b. Preparation of Higher Grade UCl_3

Because there was no existing outside source of high purity UCl_3 , several small batches were made in the electroplating laboratory using the method reported in CC-G1974⁽⁵⁾ which utilizes the following reactions:

After the uranium turnings were charged into a pyrex reaction chamber, the process was carried to completion entirely within the system. Provision was made to permit easy removal of the reaction chamber from the furnace without admission of air, so that the charge could be broken up by periodical shaking during each of the reactions. It is imperative that each reaction be carried to completion. This is especially true of the second reaction, because even tiny patches of remaining UH_3 burn on contact with the air, and the fire will spread to the entire batch. A schematic diagram of the process equipment is included as Figure 5.

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Table 1

DATA OBTAINED FROM CHEMICAL ANALYSES OF ELECTROLYTIC URANIUM AND
VARIOUS MATERIALS USED IN ITS REFINING

Item	Elements	C(e)	Cu	Fe	Si	Ni	Mg	Mn	K	Li	N(e)	Al	B	Cr	Mo
	Limits of Detection, ppm (f)	5	1	1	10	5	0.5	0.2	10	1	10	20	0.1	1	50
1	Run #1	65-145	1	30	70	40	20	<5	200	100	-	<20	<.1	5	200
2	Run #2(a)	60-80	5	10	100	<5	<.5	8	200	100	-	<20	<.1	1	50
3	Run #3(a)	80-90	5	20	300	20	.5	<.5	200	100	48	<20	<.1	5	60
4	Runs 1-4(b)	60-80	3	30	150	20	.5	3	200	100	48	<20	<.1	5	60
5	Oak Ridge UCl ₃	-	15	500	600	200	8	<10	<1	-	-	<20	<.1	1000	<50
6	ANL UCl ₃ (c)	-	15	10	10	10	7	2	<10	<1	-	<20	<.1	<1	<50
7	ANL UCl ₃ (d)	-	15	10	5	5	10	2	<10	<1	-	<20	<.1	<1	<50
8	Run #5	27	3	5	5	<5	.5	1	100	100	14	<20	<.1	<1	<50
	Run #5 Melted	23	1	2	5	<5	<.5	<.2	<10	<1	17	<20	<.1	<1	<50
9	Run #6	<10	2	20	2	<5	1	.2	100	100	-	<20	<.1	<1	<50
10	Run #7	23	1	<1	<1	<5	<.5	<.2	100	100	18	<20	<.1	<1	<50
11	Run #8	22	2	10	5	<5	<.5	<.2	100	100	-	<20	<.1	<1	<50
12	Hanford Metal														
	As Received	300-500	2-10	15-50	10-40	2-10	2	1-5	<10	<1	50	<20	<.1	1	<50
	As Refined	12	2	2	3	<5	<.5	<.2	100	100	19	<20	<.1	<1	<50
13	Mallinckrodt Metal														
	As Received	80	5	15	20	10	10	1	<10	<1	18	<20	<.1	<1	<50
	As Refined	12	2	2	3	<5	<.5	<.2	100	100	14	<20	<.1	<1	<50
14	Foundry Casting														
	3D-505														
	As Received	585	20	1730	700	100	<1	40	<10	<1	-	<20	<.1	100	<50
	As Refined	5	<1	2	3	<5	<1	1	100	100	-	5	<.1	<1	<50
15	Mallinckrodt Uran. Commercial Grade														
	As Received	895	2	1000+	50	100	<1	60	<10	<1	-	5	4	100	<50
	As Refined	11	1	1	4	<5	<1	<.2	100	100	-	5	<.1	<1	<50
16	R-16-Stationary														
	Cathode	<2	1	1	1	<5	<.2	<.2	200	200	14	<20	<.1	<1	<50
17	R-17-Rotating														
	Cathode	8	1	1	1	<5	<.2	<.2	200	100	-	<20	<.1	<1	<50
18	1st Sample	-	1	1	3	<5	<.5	<.2	300	300	-	<20	<.1	<1	<50
	17th Sample	-	1	1	2	<5	<.5	<.2	200	200	-	<20	<.1	<1	<20
	33rd Sample	-	2	1	1	<5	<.5	<.2	100	100	16	<20	<.1	<1	<20
	44th Sample	12	1	1	2		1	1	200	200	-	<20	<.1	<1	<20
19	UCl ₃ Electrolyte														
	R-7 to R-23 (Average)	12	1	1	3	<5	<.5	<.2	200	200	18	<20	<.1	<1	<50
20	UF ₄ Electrolyte														
	F-1 to F-44 (Average)	10	1	1	2	<5	<.5	<.2	200	200	15	<20	<.1	<1	<20

(a) Acid Washed 10% HNO₃ (Volume)

(b) Figures are Approximate Mean Values

(c) Made from Mallinckrodt Metal

(d) Made from Ames Metal

(e) Carbon and Nitrogen not Determined by Spectrograph. See Appendix for Method of Analysis.

(f) See Appendix for Complete Table of Spectrographic Limits of Detection.

Note: Ag, As, Be, Bi, Ca, Co, Na, P, Pb, Sb, Sn, Ti, and Zn below Limit of Detection.

FIGURE 5

SCHEMATIC DIAGRAM OF APPARATUS FOR PRODUCING UCl_3

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Pyrex glassfittings connected with Tygon tubing or ground taper joints were used in constructing the system. This arrangement permitted the use of a vacuum, but limited the amount of positive pressure which could be used without opening the joints. Gas flow was estimated by observing the bubbles in a gas bubbler which exhausted into the hood in which the entire assembly was mounted. The bubbler arrangement also helped to limit the pressure in the system, but it did not completely prevent pressure build-up if excessive flows were used.

The operating procedure followed in making the UCl_3 began by loading 100 to 200 grams of uranium turnings, cleaned just before use by pickling in cold dilute HNO_3 followed by thorough water washing and acetone drying, into the reaction cell shown in Figure 6. After sealing, the cell was attached to the system and evacuated with a roughing pump to remove the air. At this stage, the gas purification tube containing uranium and the reaction cell were heated to 300°C . When the charge had reached the desired temperature, the vacuum pump was shut off, and hydrogen was passed through the reaction chamber. It was found advisable to carefully observe the bubbler flow for quite some time during the hydride-forming period, because a point is reached in the reaction where the uranium takes up hydrogen much faster than it is supplied, creating a negative pressure which will draw air into the system if arrangements, such as the check valve and water trap shown in the schematic diagram, Figure 5, are not provided. Periodically the charge is shaken to break up the hydride.

The total time required to completely react the charge varied directly with the size of the load, a 200 gram charge taking approximately 1-1/2 hours. When the charge has been completely reacted it is a fine gray black powder.

At this point the hydrogen was turned off and dry HCl gas was admitted to the reactor. A light, muddy green layer of UCl_3 soon appeared over the outside of the UH_3 mass. The UCl_3 exhibited a stronger tendency to agglomerate than did the UH_3 , and required more frequent shaking of the cell to break up the agglomerated charge and to replace the UCl_3 with UH_3 at the outer surfaces. Circulation of the HCl was continued until all of the gray hydride had been converted to the green chloride as confirmed by careful examination of the product through the glass cell. When all the hydride had reacted, the HCl was turned off, the excess pumped out, and the heaters turned off to permit the charge to cool. Because the total time involved was approximately 5 to 6 hours, and runs were begun in the morning, the system was allowed to cool overnight before the reaction vessel was opened. The hygroscopic UCl_3 was placed in dry screw top bottles. In order to introduce a minimum of impurities the trichloride was made from the most pure material then available, which were metal produced at Ames and biscuit material produced by Mallinckrodt, both grades made by bomb reduction.

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FIGURE 6

PRODUCTION CELL FOR UCl_3

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The salt produced from this feed was spectroanalyzed (Table 1), and it was found to be considerably better than that originally used.

c. Production and Preparation of High Purity Electrolytic Uranium

The first electrolytic run (Run # 5) using the higher purity metal salt was made with salt made from Ames high purity stock and high purity Mallinckrodt uranium anodes; all other conditions were identical with the previous runs. Uranium of exceptional purity was produced. Only trace amounts of Na, K, Si, Fe, Cu, and Mn remained, and it was felt that most of the Na, K, and Mn could be removed by vacuum melting. No analysis was obtained for nitrogen. At the time that this work was done there were no facilities available at Argonne for the accurate determination of carbon in uranium in amounts less than 50 ppm, but samples of Run 5 were submitted at a later date, and the results are included in Table 1, Item 8, together with the spectrographic results.

Some of this material (approximately 40 grams), was melted with the assistance of R. D. Dunworth and J. Haran of the Argonne Foundry and Fabrication Group, in a UO_2 crucible to determine the effect of melting upon purity. Spectrographic analysis (Table 1, Item 8) showed no increase in impurities and that the volatile elements such as manganese and potassium were appreciatively reduced. Melting conditions were as follows:

1. Crucible - UO_2 - high fired.
2. Furnace Pressures
 - a. Cold - 7×10^{-7} mm Hg
 - b. At start of melting - 1.4 to 1.8×10^{-6} mm Hg
 - c. At maximum temperature - (1325 - 1350°C)
- 1.5 to 2.0×10^{-6} mm Hg
3. Maximum power - 8 kw.
4. Crucible cooled in furnace.

Before loading into the crucible, the crystals were given an additional cleaning by immersing in dilute nitric acid, followed by drying with acetone. Immediately after drying, they were poured into the UO_2 crucible which was then placed inside of a Ta radiator in a high vacuum melting furnace equipped with an induction heater powered by a 30 kw., 10,000 cps Tocco motor generator set. The furnace was sealed and evacuated as quickly as possible, and, when evacuation was complete, the power was applied as rapidly as was believed feasible without destroying the ceramic crucible. Approximately 3-1/4 hours were required to bring the charge up to its melting point, and it was then raised to 1300°C in another 1/2 hour of heating.

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The molten metal was kept at temperature for one hour by keeping a small amount of power on the induction coil so that the melt would have ample time to react with the crucible if such was its tendency. The power was then turned off, and the uranium was allowed to freeze in the crucible and cool to room temperature in the furnace.

Upon removal from the crucible, the uranium was found to have solidified into a solid button, fairly smooth on the sides which had been in contact with the crucible, with some oxide mechanically attached to the button on these faces, although no reaction appeared to have occurred. The top of the button was rough and wrinkled. After pickling in dilute nitric acid the surfaces cleaned up quite well, and a few cold shuts were observed.

The button was sectioned, polished, and examined microscopically. Photomicrographs shown in Figures 7 and 8 indicate that the metal was exceptionally free of inclusions and eutectoid structure, appearing to be very clean throughout.

In order to precipitate materials which may have been held in solid solution, a portion of the button was reheated in vacuum to a temperature in the range 950° - 1000°C , slowly cooled in the furnace and examined. The microstructure of this specimen was essentially identical to that of the first specimen.

Small sections of the button were removed and hammered by hand on an anvil to approximately 75 % of their original thickness without cracking, indicating excellent ductility.

The results obtained from the metal produced in Run # 5 showed that it is possible to prepare ductile uranium of near spectrographic purity by electrolysis, and that this material can be vacuum melted without significant change in purity. It is noteworthy, however, that later attempts to melt high purity crystals and obtain microstructures having cleanliness of the same order have not met with the same degree of success as that achieved in Run # 5. The reasons for this have never been apparent, despite the application of a considerable amount of effort.(7)

The analyses for Runs 6, 7, and 8, included in Table 1, Items 9-11, compare favorably, with the exception of iron, which was later shown to have been unnecessarily high because of inadequate washing.

2. Development of LiCl-KCl-UCl_3 Electrolyte

a. Characteristics of Bath and Product

All the work described had been done with a $\text{BaCl}_2\text{-KCl-UCl}_3$ electrolyte operated at $600\text{-}650^{\circ}\text{C}$, contained in clear quartz. Only negligible attack of the quartz by the electrolyte occurred during electrolysis, but because

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Figure 7. Electrolytic Uranium - Melt R-5

- a. A Typical Area Showing an Extremely Small Number of Inclusions.

Micro #6979 Unetched 50X
Electropolish H_3PO_4 Polarized Light

- b. Another Area of Same Specimen Shown in Figure a.

Micro #6980 Unetched 50X
Electropolish H_3PO_4 Polarized Light

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Figure 8. Electrolytic Uranium - Melt R-5

- a. Bright Field Photomicrograph of Area in Melted Sample of R-5 Indicating General Cleanliness of Structure.

Micro #6976
Nitric-Citric Acid (Electrolytic)

Bright Field

50X
Etched

- b. Typical Inclusions Found on Surface Adjacent to UO_2 Crucible of Melted R-5.

Micro #6977
Electropolished H_3PO_4

500X
Bright Field

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a cell was destroyed with each run the problem of supply became serious. At that time quartz in the size desired was very difficult to obtain commercially, and our organization was not equipped to do the work. Since quartz appeared to be satisfactory from a chemical standpoint, it seemed logical to expect that other high silica materials like pyrex glass might be satisfactory if the electrolyte could be operated below 500°C. It was also believed that a lower temperature bath could make the process less sensitive to impurities in the electrolyte since they might be less soluble at lower temperatures.

A literature search revealed the existence of a eutectic of 41 mol % KCl and 59 mol % LiCl, melting at 352°C.⁽⁶⁾ UCl₃ was found to be quite soluble in this eutectic without appreciably raising the melting point. A thermal analysis was obtained on a mixture of the following proportions by weight:

KCl	36.7
LiCl	30.0
UCl ₃	33.3

indicating that freezing started at 360°C and was complete at 320°C. (Figure 9).

Several runs (Runs # 6, 7, 8) were made in pyrex using the above electrolyte with high purity Ames anodes containing 37 ppm of Fe, 89 ppm of Mn, and 44 ppm of carbon. The UCl₃ had been previously prepared at Argonne from feed of the same order of purity. A cover of purified argon was maintained over the bath and the electrodes at all times during the electrolysis which varied from 7 to 10 days. The temperature of the bath was controlled between 390° and 410°C. Current on the cathode disc was maintained at a constant value of 10 amperes throughout the entire plating period.

The metal deposited as coarse crystals which ranged from 3/8 in. to almost one in. in length, being much chunkier in appearance than those obtained from the higher temperature electrolyte (Figure 10).

The purity of the product, listed in Table 1, Items 9, 10, 11, was of the same order as the best metal produced from the earlier bath. One run, No. 7, was below spectrographic limits of detection except for 1 ppm Cu and 100 ppm of K and Li, the latter known to be easily removable by vacuum melting. Run 8 was slightly less pure than the other runs, probably due to the use of less care in cleaning the residual salts from the deposit.

The cleaning step is very important, because the anode impurities remain in the electrolyte and will seriously contaminate the uranium if not completely removed. The following procedure has been found to be satisfactory:

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Figure 10. Uranium Crystals Produced by Electrolysis
of LiCl-KCl-UCl_3 Electrolyte at $390-410^\circ\text{C}$.

M=4527

3X

M=4527

3X

M=4527

3X

Typical Cluster

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1. Immerse cathode, with deposit attached, in beaker of cold water. Cathode is allowed to soak in order to soften entrapped salts. This permits the crystals to fall off or to be easily removed with tweezers.
2. Rinse with continuously running water to remove sludge and any residual salts until supernatant liquid appears clear.
3. The rinsed crystals are placed in a fine-meshed stainless steel wire basket and swirled in a large beaker of water to remove crystal fines.
4. Aliquots of the crystal deposit are placed in beakers and treated with dilute nitric acid to remove any remaining salt layer and surface oxide.

The correct concentration of the nitric acid varies with the state of subdivision of the uranium crystals in each bath, and is arrived at by slowly adding acid to the water containing the crystals until the reaction produces a gas envelope around the crystals. Several such treatments may be required to give the crystals a shiny and bright surface appearance.
5. The clean crystals are then rinsed several times with distilled water and finally allowed to soak approximately a half hour or more to remove any residual acid. A murky supernatant after standing is indicative that the preliminary acid cleaning treatment was not complete; therefore a check on the acid treatment can be made here.
6. The supernatant is then decanted. The crystals are rinsed several times with acetone (C.P. Grade), swirling the crystals so that all the surfaces come into contact with the acetone. Then they are allowed to stand approximately an hour to assure removal of all residual water. Here again a murky supernatant liquid indicates incomplete crystal cleansing.
7. After acetone decantation, the beakers are laid on their sides and allowed to dry in a hood, occasionally swirling the crystals to expedite drying. Acetone washing is followed by a thorough rinsing in ethyl alcohol and drying if samples are being prepared for analysis or melting, because it was found that acetone, with or without stabilizers, remained trapped in the crystal clusters, resulting in analyses indicating abnormally high (up to 200 ppm) carbon.
8. The dry clean crystals are placed in clean glass containers, weighed, and stored for further use.

b. Effect of Feed Purity on Product Purity

The work described had demonstrated that uranium of near spectroscopic purity could be produced from the lower melting LiCl-KCl-UCl_3 electrolyte, providing the electrolyte and soluble anodes were of fairly high purity.

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It was thought feasible to use chemicals and anode feed materials of lower purity and to use the same electrolyte for long periods of time. A direct method to determine the effect of purity, or refining ratio, was to make UCl_3 and anodes from uranium of various purity grades. Grades readily available were Mallinckrodt biscuit, Hanford graphite melted, as well as a grade commercially available from Mallinckrodt which is heavily spiked with Fe, Si, B, and other elements. In addition to these, a casting, #3D-505, was made in the ANL foundry to which had been added large amounts of Fe, Si, Ni, Cr, and C. Photomicrographs which permit comparison between the microstructures of the familiar Hanford uranium and the heavily contaminated open market Mallinckrodt material are shown in Figure 11. Anodes and UCl_3 were made from each of the four grades, and electrolytic refining runs were made in separate cells containing electrolyte made with UCl_3 which had been made from the same metal used for the anodes.

Analysis of the chemical data obtained from as-received and as-refined samples of all four grades listed in Table 1, Items 12 through 15, reveals that all as-refined samples were of the same order of purity as metal produced from fairly high purity feed. This indicates that the low temperature process is capable of refining to near spectroscopic purity uranium containing greater than 1000 ppm of Fe, 50 ppm of Si, 4 ppm of B, 895 ppm of C, and 100 ppm of Cr. No work was done beyond this to determine the maximum concentration of each element permitting maximum refinement.

The refining mechanism is not completely understood at this time. Some feeling existed for quite some time that anode impurities such as Fe, Si, Cr, and Ni formed compounds which were not soluble in the electrolyte at its operating temperature. The growth of an insoluble viscous sludge at the bottom of the cell which continued to grow with electrolysis gave some support to this theory, because it was expected that the sludge was composed of the impurities. Analyses of the bath at various levels and of the sludge which was obtained from samples taken from molten baths indicate the sludge to be no higher in Fe than any other part of the bath. It is not known now whether the same is true of all impurity elements, with the exception of Al, Ag, and Cu which transfer readily to the cathode, but it is expected that this will be so.

Dilution of the impurity fraction which occurs when the anode is dissolved into the comparatively large volume of electrolyte probably contributes to the refining capacity of the process. High concentrations of impurities are not reached for considerable lengths of time because of the regular withdrawal of electrolyte which adheres to the dendrites and is later replaced with new, pure salts.

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Figure 11. Photomicrographs of Mallinckrodt Commercial Grade and Standard Hanford Reactor Grade Uranium

13509

Mallinckrodt

100X

13726

Hanford

100X

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c. Attempts to Alter Character of Deposit

The deposit, as mentioned previously, is an interlocked mass of crystals which vary in size from a fine powder to fairly coarse crystals. The ratio of coarse to fine crystals varies inversely with cathode current density and operating temperature. Comparative analysis between large and coarse crystals indicate that both are equally pure. This is a contradiction of what was expected, and the data may not be real because the larger crystals are known to contain small volumes of residual salt which are completely surrounded by metal making their removal by washing impossible. The metal surrounding these small salt pockets is, however, quite clean and free from ordinary inclusions as shown in the photomicrograph of a section of a large dendrite in Figure 12. The smaller crystals do not contain these inclusions, and although they are much more difficult to wash, they may be cleaned if enough care and patience are applied. In fact, it appears that once purity of a certain order became possible, most variations in purity were found to have come from small amounts of salt which had not been removed, or, in a few cases, by accidental contamination of the analytical sample. Probably the easiest shape to wash would be a coherent cathode sheet such as that obtained in conventional electrolytic nickel copper refining; however, such a deposit is seldom obtained from fused salt baths, dendrites being formed instead. A number of theories have been proposed to explain the dendrite phenomena. The explanation which has gained the most general acceptance postulates that crystal growth initially takes place in all directions; each crystal face continues to grow until interrupted by the growth of a film of unknown composition. It has been shown by L. T. Lloyd that the crystals grow toward the anode in the (310) direction. His work, done on a large bi-crystal, is included in Appendix C.

A run was made (Run #17) in which the cathode was rotated at 5 rpm to provide agitation which could possibly eliminate the concentration-gradient conducive to the plating out of the alkali metals, potassium and lithium. All other conditions were maintained as in previous runs. The experiment was discontinued after a day and a half because the deposit built up to such an extent that it scraped the sides of the cell. No coarse crystals were obtained, the deposit being made up entirely of very fine crystals. Metal purity compared quite well with that obtained in Run #16 (see Table 1, Items 16-17), a run made under comparable conditions except that the cathode remained stationary. Results, in general, did not indicate that any advantages were obtained by rotating the cathode, and such experiments were discontinued.

Various other techniques were used in attempts to produce cathode sheet or larger crystals, all with little effect. Among those tried were:

1. Periodic reversal of the current (PR) with a considerable number of variations in plating and deplating time.

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Figure 12. Photomicrograph of Electrolytic Uranium Polycrystal Showing Absence of Inclusions

10070

131X

Electropolished H_3PO_4 Polarized Light

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2. Operation of the bath near its freezing point (385°C).

3. Introduction of nucleating impurities, such as cesium and lead chlorides. In a 650 gram melt up to 5 grams of cesium chloride had no effect on dendrite size. Lead chloride in concentrations of 2.5 to 7.5 grams in a melt of the same size also had no effect.

4. Because evidence existed that ion travel between anode and cathode is almost direct, an internal alternating current field was imposed around the cathode by inserting two tungsten leads between the anode and cathode, so that all ionized particles from the anode would have to oscillate through the field, thus extending their path. No change in crystal pattern was observed.

Coherent deposits much greater than a few mils in thickness have never been produced in the baths studied, although a porous pseudomorphic continuation of the molybdenum base metal almost always is found next to the cathode. No attempts to extend this film have succeeded to date.

d. Modification of Cell to Extend Bath Life and to Simplify Operation of Process

For the first 17 runs, the uranium was protected from oxidation during cooling from the operating temperature by permitting the cell and its entire contents to cool completely to room temperature, a procedure which forced destruction of the cell and loss of the electrolyte. Evidence that the impurities were insoluble in the melt was indicated by the formation and continued growth of a viscous sludge at the bottom of the electrolyte.

The presence of the insoluble sludge indicated that a bath could be expected to produce high purity material for a period well in excess of the 7 to 10 day period, an interval which had been employed simply because the deposit at the end of this period had completely filled the cell, occasionally to the extent of penetrating thru the apertures of the anode protection tube, thereby short circuiting the cell.

Provision was made to permit periodic withdrawal of the cathode at will by a simple re-design of the cell to provide a long top extension above the molten salts which would permit the cathode to be raised into the chamber to allow the deposit to cool before removal into the room air. A drawing of a cell of this type is included as Figure 13. The cathodes were 22 in. long and 1/2 in. in diameter. The anodes were 12 in. long and about 1/2 in. in diameter. Nearly continuous electrolysis was believed possible with a cell of this type if spare cathodes were available, so that a fresh cathode would be ready for inspection as soon as a loaded cathode was cooled and removed.

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FIGURE 13

SMALL ELECTROLYTIC CELL WITH COOLING CHAMBER

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These cells were immediately successful. The cathode crystals were not as fully bright as they had formerly been, but they did clean completely by the regular cleaning procedure. Essentially the same design has been used for all cells which have been operated since the initial test run, with uniformly excellent results.

Cell life was automatically increased by a large factor by the addition of a cathode cooling extension, as it was no longer necessary to freeze the electrolyte and to break the cell to remove the product. A stress corrosion phenomena at the interface between the melt and the argon atmosphere causes the cells to fail after periods which may be as short as a few weeks, but ordinarily are of the order of 3 to 6 months if Vycor or fused quartz is used. Only a small amount of etching is observed, and this is generally at the site of failure, the rest of the inner surfaces remaining smooth. Pyrex was found to be very susceptible to this type of fault, failing quite often in periods of less than a week. Some Pyrex cells had somewhat better life, but despite attempts at annealing, stress relieving, etc., they were not dependable and their use was not continued.

Tests were run to determine the useful life of the electrolyte as a function of product purity by analyzing deposits removed from given baths at various intervals. As originally designed, the experiments required daily sampling of the product, but this was discontinued when it became apparent that no changes were observable over such short intervals. Actually, as indicated in Table 1, Item 18, there is no observable change in deposit purity even after baths have been in daily electrolysis for up to eight months, the latter period having been the longest interval which has elapsed before cell failure occurred. Slight variations in chemistry have been noted from time to time, but they have not been duplicated when additional samples were submitted for analysis. There does not appear to be a single reason for this type of phenomena, but rather a combination of variables, such as careless cleaning, improper sample containers, analytical precision, etc. To date all electrolyte life tests have been interrupted after eight months or less, and significant changes in the refining capacity of the electrolyte have not been observed. It would be interesting to determine the useful life of the bath, but this does not appear to be possible until a more durable cell material than quartz or Vycor is developed.

3. Development of LiCl-KCl-UF₄ Electrolyte

a. Description of the Bath and Product

Attempts to increase the size of the cathode crystals by the addition of UF₄ to the electrolyte terminated in the development of a new bath of the following composition:

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LiCl	31.7 (w/o)
KCl	38.6
UF ₄ (Calculated as Metal)	29.7
U	22.5

All operating conditions were identical to those used in the operation of the UCl_3 - LiCl - KCl process. Although no effect on crystal growth was obtained by adding fluoride, some simplification of operation was derived from its use principally because of its availability in suitable purity, as it is necessary for bomb reduction. In addition, UF_4 is less hygroscopic than UCl_3 , and thus is easier to store.

A considerable number of analyses were obtained over a period of several months on a large variety of samples, and no significant difference in purity was observed between metal which had been produced from either the UF_4 or the UCl_3 containing baths. This is clearly shown in Table 1, Items 19-20, which lists the results of a number of analyses made on material from both electrolytes.

As mentioned above, the problem of obtaining high purity metal bearing salt was eased considerably after the UF_4 was substituted for UCl_3 , but with this exception very little if anything is gained with its use. UF_4 dissolves extremely slowly in the LiCl - KCl electrolyte, and a heating period of three to five days, during which the fluoride dissolves, is ordinarily required when starting up a new bath. Considerably longer washing periods are required to remove the last traces of fluoride from the crystals. This is especially true in the first few days operation of a new bath, because an excessive amount of fluoride, which has not gone into solution in the electrolyte, becomes trapped in the woven mass of dendrites which surround the cathode.

The first work done with the fluoride-containing electrolyte was in pyrex cells as shown in Figure 13. As indicated previously, this material is not dependable, and Vycor was soon substituted for it. These cells were essentially large diameter, round-bottom test tubes, fitted at one end with a 71-60 ground tapered joint at the top to permit accommodation of the cooling chamber. The latter was left open at the top to permit the insertion of a rubber stopper which had holes drilled in it to position the anode and the cathode. Cells of this size produced 100 to 130 grams of metal per overnight run at currents of 10 to 15 amperes, these conditions listed being those normally employed.

One of the small Vycor cells was utilized as a production cell and yielded about 3 kilograms of high purity uranium. The cell eventually broke because of the freezing of the salt during a power failure on the

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32nd run of metal from the original melt mixture. During the operation of the cell over a three-month period the only additions made to the bath were small quantities of the LiCl-KCl eutectic to maintain the bath level which had dropped because of the drag out of fused salt incurred in each run. The cathode product had the following average analysis:

Fe	1 ppm
Cu	2 ppm
Si	2 ppm
C	8 ppm
K	200 ppm
Li	200 ppm

The remainder of the spectrographically detectable elements were below the limits of detection.

This experience is not isolated, in fact all similar runs have been found to be capable of identical results.

b. Testing of Various Materials as Cells to Contain Electrolyte

Demands for quantities of high purity material well in excess of the amounts which could be readily produced by the available manpower from small cells, forced restudy from time to time of crucible materials in an effort to find a material which could be fabricated into large cells and which would withstand attack by the electrolyte for very long periods of time without contaminating the product. More than a superficial look had been taken at this problem, as indicated previously, but the earlier tests were run under conditions slightly different than those which prevailed during the operation of the low melting point fluoride containing bath. The earlier work had been done in cells which contained a salt mixture which was maintained at a temperature above 600°C, and the cells and their contents were not protected by argon at any time. Obviously these conditions were no longer pertinent, and a review of the subject was in order.

Because it was believed that serious differences could develop from data obtained in static tests without the effects of electrolysis, it was decided that all crucible tests be run on materials incorporated into and an actual part of operating cells.

The first experiment, one which permitted a slight scaling up of the process, involved the making of a uranium crucible from reactor grade material, wherein the crucible would act as a container for the molten salt and as anode material. The crucible was vacuum cast in

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graphite by G. V. Bennett and R. E. Macherey of the Foundry and Fabrication group at Argonne. This crucible was machined all over after casting to 9 in. in length by 2-3/4 in. outside diameter leaving a 2 in. bottom and a 1/4 in. wall. The top of the crucible was tapped so that a 3/8 in. copper rod screwed into this hole could serve as an electrical connection. To protect the cell and its contacts from the air, it was inserted into a stainless steel jacket 17-1/2 in. long by 2-7/8 in. inside diameter, 1/32 in. wall thickness, with a small tube welded at the top to permit argon entry. A tight fitting transite plug with appropriate holes for the anode and the cathode was inserted into the top of the stainless steel container. Figure 14 is a drawing of this arrangement.

The cell was heated by a wire-wound pot furnace which was automatically controlled at a temperature of 400°-425°C. A molybdenum rod, 1/2 in. diameter and 20 in. long, served as the cathode. It was most convenient to begin a run in the late afternoon and continue it overnight until morning, maintaining a steady current at the cathode of the order of 10 amperes. The cathode was raised into the cooling chamber, the deposit cooled and removed for washing. High purity material of the same order of purity as that produced in Vycor cells was obtained.

On examining the uranium pot after the electrolysis was discontinued, it was found that corrosion was not uniform on the inside surfaces of the pot. Some areas were quite thin, and the bottom was apparently untouched. Because of the very uneven attack, it was difficult to estimate how long the pot might last when used as an anode.

This experiment was discontinued after 600 grams of metal had been produced, and it was decided to attempt the same type of arrangement, making the crucible from uranium but without deliberately connecting the cell in the electrolytic circuit.

Another large uranium casting was cast in vacuum at Argonne (see Appendix B), and it was machined into a pot 13 in. long having an inside diameter of 6-1/4 in., a 2 in. bottom and a 1/4 in. wall. This crucible, considerably larger than the one described above, was held in a stainless steel chamber, 7 in. in diameter by 22 in. long with a 1/8 in. wall, which was flanged at its top so that another stainless steel assembly with provisions to hold the uranium anodes and molybdenum cathode during operation. A small tube was welded at the top of the latter unit so that argon could be admitted into the cell. This cell assembly is shown in Figure 15.

Heating of the cell and its contents was effected by inserting the assembly into a wire-wound furnace which was automatically controlled at 425°-450°C.

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FIGURE 14

ELECTROLYTIC CELL WITH URANIUM POT AS ANODE

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FIGURE 15

ELECTROLYTIC CELL WITH URANIUM POT AS CELL

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A series of runs were made in this apparatus using currents which were permitted to vary between 75 and 150 amperes. An average yield for a three-hour run, the period ordinarily used, was around 650 grams.

No essential difference in the purity of this material could be noticed when a comparison was made between its purity and that of material produced in other cells, although it was observed that higher carbons were obtained. Carbon analyses averaged around 20 ppm. Carbon, in amounts of this order, had never been found in metal produced from the low temperature electrolyte, and no explanation was found for its presence in such quantities.

On the eleventh run the furnace elements were severely attacked by the fused chlorides, which by this time had corroded through the crucible at a point about two to three inches below the melt line and through the stainless steel protecting jacket. It is possible that acceleration of corrosion may have occurred by the action of stray currents near the anodes which could have rendered the pot locally anoded.

A third experiment was designed and run using a uranium pot in a setup identical to that for the experiment described above, but in which the uranium pot was connected into the plating circuit so that a low cathodic charge was allowed to remain on it at all times.

The application of a small potential to the uranium cell of the order of one-half to one volt during electrolysis to alleviate the corrosion of the uranium by the fused chlorides resulted in very poor yields, and after several runs the experiment was discontinued.

As a result of these experiments it appeared fruitless to further investigate the potential use of uranium as a cell material, because all tests clearly showed that enough corrosion occurred to perforate the cell wall.

Small cells employing aluminum (2S) were tested, and it was found that after a short period considerable amounts of aluminum appeared in the cathode deposit, a condition which was regarded as intolerable.

Other cells were made up of 2S aluminum which had been electrolytically anodized. The results were almost identical.

Small cells made up of Monel, "A" nickel, types 304, 347, and 316 stainless steel were all corroded by the electrolyte, and the purity of the product produced in these cells was detrimentally affected by the presence of the foreign elements of which the cells were composed. It should be borne in mind that these tests were run over periods of time of not less than

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three to seven days, and that it is conceivable that some of the materials tested might have been satisfactory if they had been tested for shorter periods.

Cells fabricated of Hastelloy-C and Stellite #6 are being tested at the present time, and although the results are not conclusive, a Hastelloy-C cell which has been in operation for several months is continuing to produce material of consistently high purity. No information is yet available on the performance of the Stellite #6.

Semi-production size cells, of the type illustrated in Figures 16 and 17, which contain 2000 g of UF_4 and 5000 g of LiCl-KCl eutectic, have been in operation for long periods of time, up to eight months. These cells consist essentially of large Vycor or quartz round-bottom cylinders which are contained in stainless steel shells equipped with inlet arrangements to permit the use of inert gas protection. Heating of the assembly is accomplished by inserting the stainless steel can and its contents into a large resistance-heating furnace which is maintained at a constant temperature through the use of conventional automatic controls. Cells of this type are capable of producing approximately 100 grams per hour of high purity crystals. Negligible maintenance of the cell or the furnace is required.

Although the purity of the product produced in these cells is uniformly high, and the cells themselves require very little maintenance, the physical dimensions of these units are limited to a fairly small size by the lack of availability of larger quartz or Vycor containers. For this reason it is intended that the search be continued for an equally satisfactory material which will permit the fabrication of larger cells. Some consideration had been given to the use of alternating current electrode heating, such as is used in conventional salt heat treating furnaces, which might make it possible to use silicon carbide crucibles and electrodes, or possibly a water-cooled container which would carry on its surfaces a layer of frozen salt which would protect the water-cooled container from corrosion. No cells have been constructed utilizing this type of heating, but it is still under consideration.

Any potential that the described process might have as a means of producing production amounts of uranium is closely associated with the development of a satisfactory material for large crucibles and improvements in the electrolyte and operating procedure which would result in the deposition of extremely coarse dendrites or coherent cathode plate.

c. Electrical Measurements

1. Determination of Current Efficiency Versus Voltage

Several attempts were made to compare cathode efficiency as a function of cathode current density, but the results were not reproducible because it was not possible to obtain accurate values for the

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FIGURE 16

SEMI PRODUCTION ELECTROLYTIC CELL

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Figure 17. Photograph of Semi-Production Cell Including Gas Purification Train

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cathode area which continued to increase by an unknown rate as deposition continued. However, under the conditions present during electrolysis, cathode current density remains essentially constant at constant voltage; therefore the measurements were taken under conditions wherein the voltage was maintained constant at a selected value. Measurements were made with the electrolyte operating at 425°C, using a large copper coulometer connected in series with the cathode (Figure 18). Six liters of copper sulfate solution was prepared in a large pyrex jar. This large volume of solution was used so that the entire plating current could be easily handled without the use of additional resistors which introduce inaccuracies generally tending to give cathode efficiencies considerably higher than the real values.

Figure 19 and Table 2 list the conditions under which the measurements were made, the data, and the curve which was drawn from the data. The cathode efficiency curve, Figure 19, indicates a peak efficiency of slightly over 60 % at a voltage of 2 volts, with the efficiency dropping at voltages below and above this value.

All measurements were reproducible to approximately ± 5 %. It should be noted that the values given are somewhat lower than the real values because of the loss of finely divided metal during the cleaning and washing of the cathode deposit prior to weighing. Additional losses are very likely incurred during electrolysis by the dropping off of some of the crystals into the electrolyte. It is quite likely that these losses were greater at the higher voltages because the cathode deposits at these voltages were composed of a much greater percentage of extremely fine crystals which have a far greater tendency to separate from the mass and be lost. The fact that the measurements were reproducible within the deviation mentioned is probably an indication of the uniformity used in processing the deposits, otherwise the reproducibility would be difficult to explain.

2. Measurement of Decomposition Voltage

Voltage-current measurements were made to determine the decomposition potential of the LiCl-KCl eutectic and the UF_4 -LiCl-KCl system. Current was measured as a function of cell voltage in the range 0 to 2 volts in a small cell similar to that shown in Figure 1. Successive measurements were made in the same cell under the following conditions:

- a. LiCl-KCl eutectic at 425°C using carbon rod as the anode and a molybdenum rod as the cathode.
- b. Conditions identical to the above with the exception that the measurement was made with UF_4 added to the eutectic in the same amount ordinarily used in the electrolyte.

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FIGURE 18

SCHEMATIC DIAGRAM OF ARRANGEMENT TO MEASURE
CATHODE EFFICIENCY VS. VOLTAGE

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Table 2

DATA FOR CURRENT EFFICIENCY CURVE

Run No.	Volts	Wt. of Copper Deposit	Wt. of Uranium Deposit	Theoretical Yield [U ⁺⁺⁺]	Current Efficiency
1	0.5	4.1261 gms.	6.0 gms.	10.6 gms.	53 %
2	1.0	4.8513 gms.	7.0 gms.	12.0 gms.	58 %
3	2.0	6.872 gms.	10.5 gms.	17.18 gms.	60.5 %
4	3.0	12.750 gms.	16.2 gms.	32.36 gms.	50 %
5	4.0	24.381 gms.	28.0 gms.	60.9 gms.	46.3 %
6	6.0	18.706 gms.	16.0 gms.	35.6 gms.	45 %

Potential was applied in steps of 0.05 to 0.1 volts. Current measurements were made within several seconds after closing the circuit. If longer periods of current flow were used, it was observed that a gradual drop in current occurred attributable to concentration polarization. An interval was allowed to expire between the taking of measurements at the various voltages, so that the back e.m.f. would have time to drop to a minimum. All readings were reproducible within several millivolts. Curves produced by plotting data obtained by increasing the voltage step by step, and decreasing the voltage in the same fashion, were identical.

Curve No. 1 in Figure 20 is a graphical representation of the data obtained from measurements made on the LiCl-KCl eutectic; it shows a slight plateau and a sharp rise at a value of 1.6 volt. This indicates that the primary anodic and cathodic reactions are the evolution of chlorine and the deposition of alkali metals, respectively. Curve No. 2, which was obtained from measurements made on the eutectic plus UF₄, indicates an earlier rise at 0.7 volts with a leveling off at about 0.15 amperes. The shape of this curve is indicative of a diffusion controlled reaction which would be expected to vary with the concentration of UF₄. If it is assumed that the decomposition potential is governed by the cathodic reaction, then the break at 0.7 volts would represent the deposition of uranium and the break at 1.6 volt the deposition of alkali metal. The alternative explanation would require an unlikely anodic oxidation of the uranium cation at the carbon cathode. Therefore the current rise at 0.7 volts is considered to represent the simultaneous evolution of chlorine at the anode and deposition of uranium at the cathode.

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These measurements are further indication of the suitability of the electrolyte for the work which it was selected to perform. The desired product, uranium, is readily obtained at the cathode at voltages sufficiently lower than those required to deposit the metals which make up the remainder of the electrolyte.

III. CONCLUSIONS

It has been shown that uranium metal containing various amounts of metallic contaminants may be electrolytically refined to near-spectrographic purity by making the metal to be refined the anode in a cell containing a fused salt mixture of 20-30 w/o UF_4 or UCl_3 dissolved in the eutectic which forms between LiCl and KCl . The refined product is collected on a molybdenum or tantalum cathode and deposits as a cluster of loosely woven crystals.

The crystals, if properly washed, may be vacuum melted and cast into ingots without significant loss of purity. It is, in fact, true that vacuum melting actually reduces certain impurities such as Li and K which are volatile.

Cells to contain the salt mixture, which is kept molten at a temperature of the order of 400° to 425°C , may be fabricated of quartz (clear fused) or Vycor, both of which satisfactorily resist the combined effects of the potentially corrosive salt mixture and the elevated temperature.

Precautions must be taken to ensure that the salts are maintained in a dry state before and during use. Protection of the melt and the anodes with an inert gas such as argon or helium is essential at all times.

Voltages of the order of 2 to 4 volts are required for the operation of the process. This may be supplied readily by D.C. motor generator sets, rectified A.C., or storage batteries.

Power requirements are slight. After the salts are melted, some current is required to maintain the electrolyte in the molten condition, but this is not large if furnaces are adequately insulated, because some power is supplied to the melt by the direct current required for electrolysis. Cathode efficiency at an optimum voltage of 2 volts is approximately 60%, a value which puts this process in a range of the same order of relative cathodic efficiency as other electrolytic fused salt processes.

Close chemical control of the electrolyte is not required. Periodic additions of the LiCl-KCl eutectic and occasional additions of UF_4 , which are lost by drag-out, are necessary to maintain the bath level and the bath in operating balance.

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V. APPENDIX A

Determination of Carbon in Uranium*

The method of direct combustion of the uranium in oxygen is used. The carbon dioxide obtained is passed over hot copper oxide, dried with magnesium perchlorate and absorbed in a weighed absorber bulb of Ascarite (soda asbestos). The procedure is as follows:

1. The weighed sample (2-4 grams) is placed in a boat, and
2. Transferred to a quartz combustion tube, and then heated from
3. 800-900°C with a current of oxygen passing through absorber at all stages of the combustion.
4. The absorber bulb is then weighed on a micro-balance. Increase in weight represents carbon dioxide.

Determination of Nitrogen in Uranium

The usual micro Kjeldahl method for determining nitrogen in small quantities is used. The procedure is as follows:

1. The weighed sample (1-2 grams) is treated with 5 ml 1-1 HCl in a 100 ml test tube.
2. 30 %H₂O₂ is added, dropwise, to form a clear yellow solution.
3. Transferred to a micro Kjeldahl and 20 ml of 30 %NaOH is added.
4. The ammonia is distilled into a 2 % boric acid solution, and then
5. Titrated with 0.01 N HCl using a mixture of methyl red and brom cresol green as indicator.

*See ANL-5019 for additional résumé of chemical procedure.

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TABLE OF SPECTROGRAPHIC LIMITS (ppm)							
20	10	5	2	1	0.5	0.2	0.1
Ca	As	Al ⁽¹⁾	Bi	Ag	Be	Mn	B
Mo ⁽²⁾	K	Co	Pb	Cr	Mg		
P	Si	Ni	Sb	Cu			
Ti		Sn		Fe			
Zm				Li			
				Na			

(1) Al changed from 20 during course of work.

(2) Mo changed from 50 during course of work.

VI. APPENDIX B

Casting of an Uranium Pot for Electrolytic Cell Liner - R. E. Macherey and G. V. Bennett

An uranium container was needed to hold the fused salts used in the study of the electrolytic refining of uranium. This container or "pot" was cast in the foundry in the steel-shell furnace, a good casting being obtained in the first attempt.

The casting was made in the following manner: the uranium, weighing 96.80 kilograms, was charged in a graphite crucible, equipped for bottom pouring through a 3/4 in. hole and a graphite stopper-rod. The metal was raised to 1405°C, at a maximum pressure of 5.2×10^{-5} mm Hg, and cast into the graphite mold shown in Figure 21. The graphite core worked satisfactorily and was not crushed when the metal shrank on cooling. The mold proved to be satisfactory, although it had to be destroyed to remove the casting, due to the unexpected "burn in" of the uranium. The top of the mold was slightly up into the coil. Apparently the mold was too hot, causing reaction between the uranium and graphite,

Figures 22, 23, and 24 show, respectively, the top, bottom, and side of the casting. In these photographs, the "top" and "bottom" are to be taken as the position in which the casting was made. Actually, the casting was made in an inverted position, open end down. Figure 22 shows very clearly the "hot top," and the fact that there was no evidence of piping. This figure also shows the graphite clinging to the surface of the casting. A small portion of the graphite has been removed (bottom left) to show the thickness of the graphite. This graphite-uranium reaction resulted in a carbon analysis

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LOOSE FIT ALUNDUM TUBE
DIMENSIONS ROUGH: MACHINE
HOLE TO FIT ALUNDUM

$3\frac{1}{4}D$ GRAPHITE PINS
 $1\frac{3}{4}$ LONG SPACED 120" APART
(SLIDING FIT)

ALL PARTS OF FINE-GRAINED GRAPHITE EXCEPT
FOR ONE ALUNDUM PIECE NOTED.

Figure 21 Pot Mold for Casting Uranium.

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Figure 22 Uranium "Pot" Casting, Top View.

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Figure 23 Uranium "Pot" Casting, Bottom View.

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Figure 24 Uranium "Pot" Casting, Side View.

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of 0.135 % carbon, which is considerably higher than the ordinary. Figures 22, 23, and 24 show the casting in the as-cast condition, and no attempt was made to clean the surfaces of the casting before the pictures were taken, other than removing the graphite core.

VII. APPENDIX C

Direction of Growth of Uranium Electrolytic Crystals - Lowell T. Lloyd

For a more complete picture of the deposition of high purity uranium from fused salt baths by electrolysis, it is desired to know the direction of growth of the deposited uranium crystals. This information has been obtained from a large uranium bi-crystal produced by this method.

Three Laue back reflection photograms were taken, using copper anode white radiation, from the bi-crystal shown in Figure 25. The patterns were taken from the left side, front, and right side, using the top and one edge of the crystal as reference marks. Reproductions of these photograms are shown in Figures 26, 27, and 28.

Figures 26 and 28 (left and right sides of the bi-crystal) show the pole of the (130) plane at the center of the photogram. The zone that passes horizontally through this pole is the one connecting the (130) pole with that of the (001) pole (90° to the right or left in either case). The zone that passes vertically through this pole is the one connecting the (130) pole with that of the (100) pole (55.5° towards the top) and the (010) pole (34.5° away from the top). Figure 27 shows a pattern typical of uranium containing twins of the (130) type. The (001) plane pole of both halves is located at the center of the film. The horizontal zone is the one connecting the (001) pole and the (130) pole (90° to the right or left for either half of the bi-crystal).

The geometry of deposition of the bi-crystal was such that it grew from the cathode with an almost square cross section in the direction of the long axis (toward the top). The "chevron" shaped markings on the front surface have their point towards the direction of growth.

These data are sufficient to establish the crystallographic direction of growth of the uranium bi-crystal in the fused salt bath. The plane separating the two halves is a (130) type plane. The two portions are oriented with respect to each other according to the (130) type twin orientation relationship. The direction of growth of the bi-crystal is that crystallographic direction common to both the (001) and (130) planes, which is the [310] direction. The "chevron" markings make an acute angle of approximately 69° with the trace of the (130) plane that divides the two halves of the bi-crystal. This is where the trace of the other (130) plane should appear on the front surface.

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Macro #14365

5X

Figure 25. Macro Photograph of Bi-Crystal.

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Macro #14362

5X

Figure 26. Laue-back-reflection Photogram taken from left side of the bi-crystal. The pole at the center of the film is the pole of the (130) plane.

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Micro #14363

Figure 27. Laue-back-reflection Photogram taken from front surface of the bi-crystal. The pole at the center of the film is the pole of the (001) planes of the two halves of the bi-crystal.

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Macro #14364

Figure 28. Laue back-reflection Photogram taken from right side of the bi-crystal. The pole at the center of the film is the pole of the (130) plane.

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