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INVESTIGATIONS FOR THE PRODUCTION OF THORIUM METAL

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INVESTIGATIONS FOR THE PRODUCTION OF THORIUM METAL

Contract No. AT(30-1)-1335

I. INTRODUCTION

The electrolysis of $ThCl_4$ in molten NaCl has been continued during this contract period; some electrolytic runs, performed in a small, bench scale cell as described in the Sixth Quarterly Report, are reported and runs made to date in a larger cell are summarized. This larger cell is described in detail in this report.

Several changes in the procedure for preparation of thorium chloride have been instituted and are reported here.

Current experimentation has been largely devoted to the determination of the proper operating conditions for this larger cell. While these conditions of current density, bath concentration and bath temperature have been established for the laboratory size cell, they are not completely defined as yet for this larger unit.

II. PREPARATION OF CELL FEED MATERIAL

Thorium chloride is being prepared from thorium carbonate generally by an aqueous procedure to provide cell feed material for the electrolytic operations. The overall reactions remain as previously reported and the chemistry is summarized by the following equations:

1. $ThOCO_3 + HCl \longrightarrow ThCl_4 \cdot xH_2O$

2. $ThCl_4 \cdot xH_2O + 2NH_4Cl \longrightarrow (NH_4Cl)_2\ ThCl_4 \cdot xH_2O$

3. $(NH_4Cl)_2\ ThCl_4 \cdot xH_2O \xrightarrow[500-600°C]{} ThCl_4 + \overline{xH_2O} + 2NH_4Cl$

or 4. $(NH_4Cl)_2\ ThCl_4 \cdot xH_2O \xrightarrow[500-600°C]{NaCl} ThCl_4 + NaCl + \overline{xH_2O} + 2NH_4Cl$

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Current preparation practice is as follows. Thorium carbonate is reacted with concentrated hydrochloric acid. Two mols of ammonium chloride are added and the reaction vessel is cooled to about 5° C in order to precipitate the hydrated ammonium thorium chloride. Further to improve this recovery, anhydrous HCl is bubbled into the solution until saturated.

The hydrated ammonium thorium chloride is filtered. The precipitate filters easily, but retains appreciable quantities of mother liquor. The wet filter cake is dehydrated at 150-200° C in an air oven. During this operation the salt goes through a fluid stage until most of the water has been eliminated. Further heating at 300° C removes the last traces of HCl and water. The ammonium thorium chloride is then pyrolized in the presence of sodium chloride at 650-800° C in an inert atmosphere furnace with the formation of thorium chloride in sodium chloride with possible formation of $NaCl$-$ThCl_4$ compounds.

Care must be taken to thoroughly dehydrate at 150-200° C, and at 300° C. Residual water remaining after these steps will result in the formation of thorium oxide at the higher decomposition temperatures. When this precaution is observed, no difficulty is encountered in producing an $NaCl$-$ThCl_4$ compound with only traces of insoluble matter (thorium oxide). This procedure is now used to produce batches of 20-25 pounds of contained-thorium cell feed material.

III. ELECTROLYTIC EXPERIMENTATION

A. Laboratory Size Cells

Experimentation was continued into this quarter on the laboratory cell used in the electrolytic work summarized in the preceding report. This

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electrolytic cell has a four inch diameter crucible and a cathode three-quarters of an inch in diameter, two inches long. The entire unit operates in an inert argon atmosphere.

The run summaries presented in Table I refer to electrolytic runs made in this laboratory unit. The runs were made at 800-850° C. Each bath, comprising a mixture of $ThCl_4$ and NaCl, was pre-electrolyzed at 7 volts DC at 100 amperes throughput for two and one-half minutes using a graphite rod cathode. Current densities on the initial cathode surface area (during electrolysis) were 225 amps/dm^2, when the electrolyses were carried out using 75 amperes current.

This work was done to complete the study of operating conditions in this cell and to study in a preliminary way the potentiality for continuous operation offered with this particular electrolytic system.

The runs summarized in Table I illustrate the practicability of continuous operation. The fused baths are capable of continuous operation if thorium ion concentration can be maintained without undue increase in bath weight. For example, if the thorium chloride cell feed is prepared with large amounts of sodium chloride present, more total salt must be recharged to reestablish the thorium ion concentration than is being removed in the previous electrolysis, more than the crucible can accommodate.

In run 196-1, thorium cell feed salts were added to the cell during electrolysis with excellent results in terms of process efficiency and product hardness, establishing this as a satisfactory procedure.

A distinction is being made in this report in remarks concerning process

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TABLE I

Run No.	Th Ion Conc.%	Bath Temp. °C	Cell Voltage DC	Cell Current DC	Amp Hrs.	Metal Wt. Gms	Process Efficiency %	Process Recovery %	Hardness R_B	Remarks
97-172	10	850	3.0	75	94	121	59.5	55	18	Salt 165-39. Salt made using evaporation method. NH_4Cl driven off in cell. 2 mols NH_4Cl per mol $ThCl_4$. Part of deposit fell off cathode and was recovered.
97-174*	15	850	3.0	75	140	215.5	71	65	31.5	Salt 165-39.
97-176	15	850	2.2-2.9	75	278	110.5	18.4	33.5	82	Salt 165-40. Salt made using same method as 165-39. 3 mols NH_4Cl per mol $ThCl_4$. Most of deposit fell into the bath.
97-178	20	840	2.8-3.0	75	208	276	69.5	61.5	46	Salt 164-121. Electrolyzed until deposit shorted out on crucible wall. Salt bath had 3.2% thorium remaining. Particles were very large and were rolled in the pulverizer.
97-180	15	845	2.7-3.0	75	63	--	--	--	--	Salt 165-39. Used salt bath from 97-178. The voltage dropped very fast. Stopped run with no deposit obtained.
97-182	10	845	2.8-3.0	50	106	158	69	72	36.5	Salt 164-121. Repeat of 97-166. Ceramic tube cracked during run Possibility of contamination.
97-184 (1)	14.1	850	2.8-3.0	75	170	267.5	72.5	86.5	13.5	Salt 164-128. Start of continuous run with salt bath reused.
97-186 (2)	14.1	845	2.8-3.0	75	175	269	71.0	86.8	23.5	Salt 164-128. Ceramic tube split. Removed bottom of fused salt bath as possible SiO_2 contamination.
97-188 (3)	9.5	830-850	2.9-3.0	75	175	184	48.7	88	28	Salt 164-128.

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TABLE I (continued)

[redacted]

Run No.	Th Ion Conc.%	Bath Temp. °C	Cell Voltage DC	Cell Current DC	Amp Hrs.	Metal Wt. Gms	Process Efficiency %	Process Recovery %	Hardness R_B	Remarks
97-190 (4)	9.5	845	2.9-3.0	75	131	175.5	58	84	A=57 B=43	Salt 164-128. Part of deposit fell into bath and was recovered. Washed separately. A on rod, B in bath.
97-192 (5)	10	850	2.9-3.0	75	140	213.5	70.5	96	A=37 B= 5	Salt 164-128. Same as 97-190.
97-194 (6)	15	820	2.8-3.0	75	175	278	73.5	89.2	A=27 B-62.5	Salt 164-128. Same as 97-190. Continuous run stopped!
97-196 (1)	15.6	830	2.8-3.0	75	181	317	81	92.4	21	Salt 164-128. First run of three run series.
97-200 (2)	15.6	835	2.7-2.9	75	165	266.5	75	87.5	26	Salt 164-128. Bath was not depleted. Used average process recovery for 97-200 and 196-1.
196-1 (3)	12	835	2.7-2.9	75	144	245.5	79	87.5	18	Salt 164-128. Used modified washing technique which lowered the hardness from R_B 53 to R_B 18. End of run.
196-8	10	840	3.0	75	112	152.5	63	67.5	53	Evaluation of salt 164-138.
196-9	12	800-820	3.2	75	117	169	66.5	64	38	Evaluation of Salt 164-140.

* Used graphite sleeve with no porcelain.

[redacted]

efficiency. In previous reports, this percentage has been called current efficiency. Since this data is calculated as the percentage of weight of metal recovered divided by the theoretically possible weight of metal (electrochemical equivalent), the resulting value of current efficiency actually incorporates losses encountered in metal recovery steps and in handling. These losses, on this scale, have been determined as approximations. The loss of thorium metal in cathode crushing and preparation for aqueous leaching is nil. There is about a three percent maximum loss in weight of thorium as fines in the aqueous leaching. There is about a 5% maximum loss of weight in the final acid recovery step. In general, therefore, process efficiencies in this report, and current efficiencies as reported in earlier reports, if reported as current efficiency, would be about 1.08 times the process efficiency. For example, in run 196-1, the current efficiency is about 85%, the process efficiency 79%.

B. Intermediate Size Cell

A cell, designated in this laboratory as the Mark 20 cell, has been designed, constructed, and installed. This electrolytic unit is similar in principle and in over all operational characteristics to the smaller laboratory cell. An assembly drawing of this unit is shown in Figure 1. The cell consists of a nickel shell internally insulated with K-23 firebrick coated with Korundal cement. The unit has an internal, graphite resistor heating element, connections to which are made by vacuum-tight, electrically insulated power leads through the shell. The graphite resistor consists of

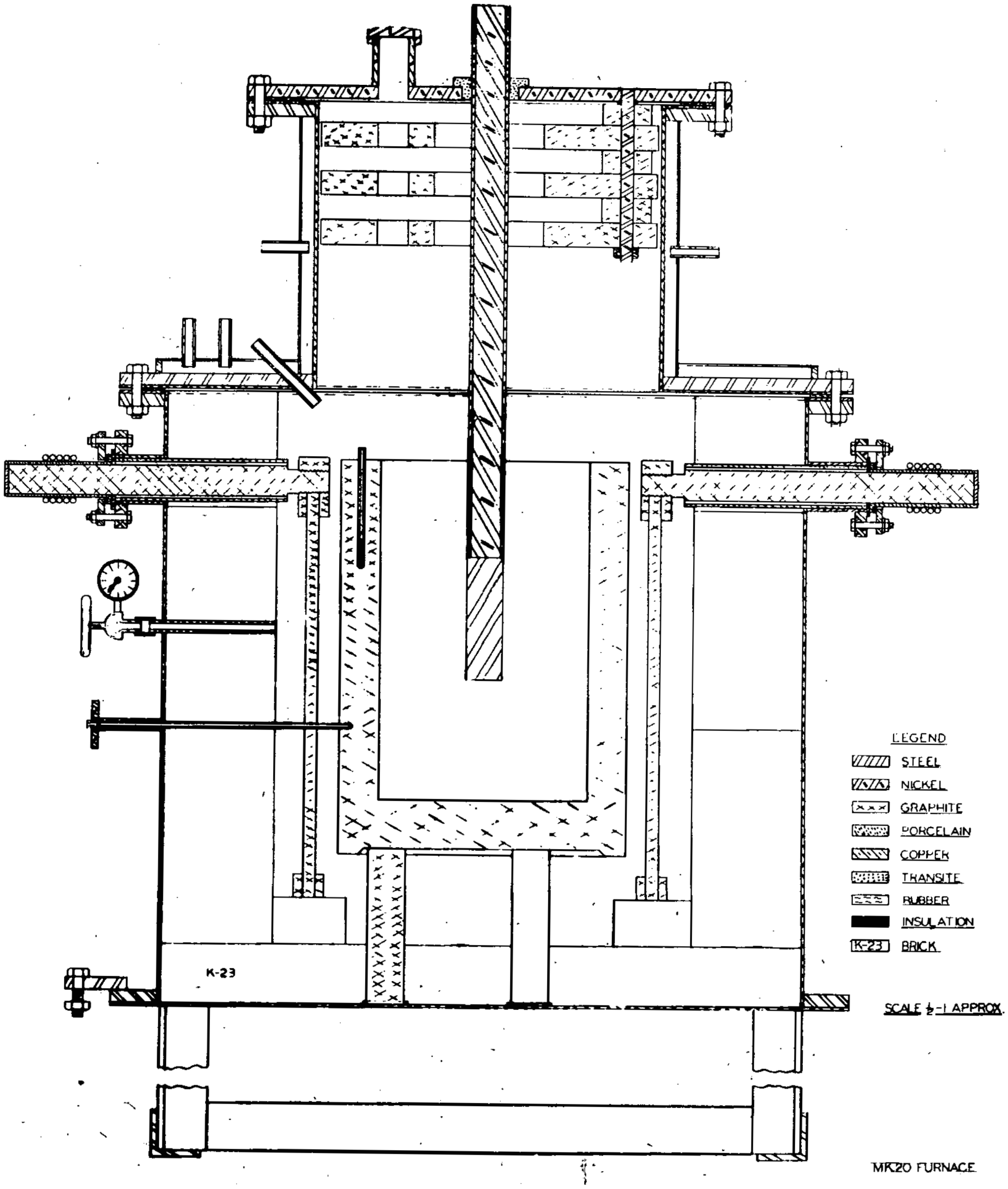

Figure 1. Assembly Drawing of March 20 Cell

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graphite rods linked together by graphite connector blocks in two parallel circuits. The over all resistor resistance at temperature (800° C) is about 0.12 ohms.

This cell employs a monolithic graphite crucible, eight and one-half inches in inside diameter, and fourteen inches in inside height. The crucible rests upon three graphite posts which in turn rest upon the bottom plate of the cell. A steel boss, welded to the bottom plate, is the anode connection to the bus bar. The anodic connection to the crucible is from the shell bottom through the graphite posts to the bottom of the crucible. A smaller nickel chamber between the main furnace shell and the operating head allows room for the cathode to be withdrawn from the bath and to remain in the inert cell atmosphere. The cathode consists of a steel cylinder one and one-half inches in diameter and five inches long welded to a one and one-quarter inch diameter nickel rod. A porcelain sleeve protects the nickel bar at the bath interface. A graphite sleeve protects the nickel bar against chlorine attack and extends through the operating head. The cathode connection from the bus bar is made directly to this nickel rod. A transite bushing insulates the cathode from the operating head.

The operating head is a solid piece of nickel to the bottom of which are attached three graphite heat reflector shields. This head is bolted to the smaller chamber described above. Besides the cathode port, a sight and charging hole is provided.

Argon is introduced through a port in the side of the main cell body and a thermocouple well extending into the crucible wall is also made through

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the shell. A second thermocouple well to the crucible wall is made through the large flange.

The cell is provided with a 32 KW single phase AC transformer for its AC power, and a selenium oxide rectifier and rectifier transformer rated at 1500 amps at 15 volts DC. The cell has a ventilating hood and other auxiliary equipment. A photograph of the Mark 20 cell is shown as Figure 2. This cell has been tested and is now in operation. Eleven runs have been made to date and are summarized in Table II.

Pre-electrolysis is carried out at 5 V, 220 amps on a steel rod for 2-5 minutes. Several pre-electrolysis deposits are obtained for each run.

The first run, 184-20, was made using a one inch diameter, six inch long cathode tip. After 550 ampere hours of electrolysis, the current rose sharply indicating that the cathode was shorting out against the bottom of the crucible. The cathode had been immersed to a depth of eight inches in a ten inch deep bath. Electrolysis was continued after the cathode was raised one inch, but the current rose sharply again after a total of 640 ampere hours. The deposit obtained was symmetrical in shape.

The second run, 184-22, was made using a one and one-half inch diameter cathode tip, four inches long. The electrolysis was started at 3.6 volts and 240 amperes (180 amps/dm^2). The current rose gradually to a value of 295 amperes after almost two hours. During this period there was continuous chlorine evolution. The current was then lowered to 250 amperes, and a cell voltage of 2.9 volts, at which time the chlorine evolution decreased markedly. When the cathode was raised there was a definite resistance at

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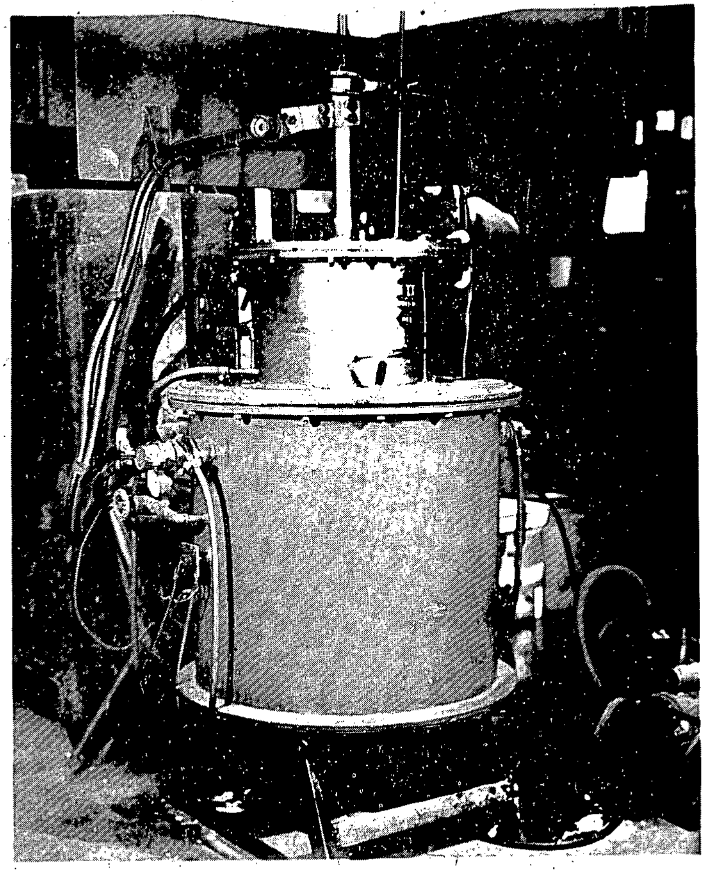

Figure 2. Photograph of March 20 Cell

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TABLE II

Run No.	Th Ion Conc.%	Bath Temp. °C	Cell Voltage DC	Cell Current DC	Amp Hrs.	Metal Wt. Gms	Process Efficiency %	Process Recovery %	Hardness R_B	Remarks
184-20	10	820-860	3.5	250	640	402	29	22	45	Salt 164-135. 40 lbs.salt bath. Deposit shorted against crucible bottom. 6 inch cathode is too long.
184-22	15	840	3.6	240-270	1500	--	--	--	--	Used fused salt bath from 184-20 plus 164-135. No deposit. Cathode badly corroded.
184-25	15	850-860	3.5-2.9	250	800	--	--	--	--	Used salt bath from 184-22. Cathode 1" diam. x 5" long. No deposit.
184-27	15	850	3.9	380	1200	A=105.5	--	--	46	Used salt bath from 184-25. Started electrolysis at 3.9 V and 380 amps and allowed current to rise gradually. Cathode 1" diam. x 5 " long.
184-29	10	835-850	3.6	230-300	755	457.5	28	25	93	Salt 164-138. Starting current density was 220 amps/dm². Uniform deposit. Cathode 1" diam.x 5" lg.
184-31	7	850	3.7	190-225	630	40	--	--	--	Salt bath from 184-29. Starting current density was 185 amps/dm². Most of deposit fell off. Metal on cathode would not melt. Cathode 1" diam. x 5" long.
184-33	10	850	3.5	240-300	1600	--	--	--	--	Salt 164-140. Cathode 1" diam. x 5" long. No deposit.
184-37	10	850	4.5	390-420	1500	--	--	--	--	Salt bath from 184-33. Cathode 1-1/2" diam. x 5" long. No deposit. Cathode was pitted slightly.
184-39	15	850	4.6	370-430	2270	--	--	--	--	Salt 164-140 and 164-142. Cathode 1-1/2" diam. x 5" long. Thorium alloyed with cathode and fell into bath. Cathode badly eaten away. Recovered thorium from salt bath loaded with iron.

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TABLE II (Continued) ~~CONFIDENTIAL~~

Run No.	Th Ion Conc.%	Bath Temp. °C	Cell Voltage DC	Cell Current DC	Amp. Hrs.	Metal Wt. Gms	Process Efficiency %	Process Recovery %	Hardness R_B	Remarks
184-42*	14.5	820	4 V	320-450	1100	--	--	--	--	Salt 164-145. Most of deposit slid off cathode. Four lbs. of thorium metal-plus-salt recovered from salt bath. Salt bath has 8.9% thorium remaining.
184-47*	13	800	4 V	320-380	705	--	--	--	--	Salt bath from 184-42 plus salt 164-149. 10 minute preheating of cathode at 1.3 V and 65 amps. Half of deposit slid off the cathode.

* Data not available to date.

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first, and then the cathode lifted easily out of the bath. The deposit fell off the cathode leaving it bare. In the chlorine atmosphere of the cell, the cathode became badly corroded.

The next two runs were made using the salt bath from 184-22. Because of the slackening of chlorine evolution at lower voltages, the electrolysis was started at the desired current density and then the current was allowed to rise gradually as the resistance of the bath decreased, the voltage remaining fairly constant. This is not in accordance with procedure in the laboratory size cell where the current source, from a DC motor generator, is constant and the voltage drops off gradually during electrolysis.

In run 184-29 a uniform deposit was obtained at low process efficiency. The metal had a high hardness of R_B 93, but part of this may be attributed to the thorium salt. A check run was made in the laboratory sized cell, and resulted in a hardness of R_B 53 (Run 196-8 in Table I).

Run No. 184-39 which was carried out at 850° C resulted in thorium metal alloying with the steel cathode. The resulting alloy dripped from the cathode until about 10% of the latter was consumed.

Alloying can only be attributed to too high a temperature of operation. Since it is well known that the cathode is at a higher temperature than the bath during electrolysis, this fact, in addition to the high temperature of the bath, can account for the alloying.

A second thermocouple was added to the unit. This, as shown in Figure 1, goes down into the crucible wall and should result in more accurate bath temperature control.

During the pre-electrolysis procedure for Run 184-42, the first deposition was carried out at 850° C and resulted in a good deposit. The second one was electrolyzed at 804° C. Although the bath was molten the salt froze to the rod, and the metal was electrolyzed over the salt. A third rod electrolyzed at 820° C was uniform and good. After electrolysis on a one and one-half inch diameter, five inch long cathode tip, most of the deposit slid off the rod, but was recovered from the crucible.

To prevent electrolyzing on a frozen salt layer, as done in the pre-electrolysis for 184-42, the cathode during Run 184-47 was immersed for ten minutes at 1.2 volts and 60 amps DC. Some chlorine evolution was noted at this small voltage. Electrolysis was carried out at 4 volts and from 320 to 380 amps. After the electrolysis was stopped, the cathode deposit was allowed to cool to the bath temperature by lowering the DC current to 150 amps at 2.5 volts. A fairly large deposit was obtained, but about half of it slid off into the salt bath.

IV. METAL RECOVERY

Cathode deposits are a composite of about 50% thorium metal and about 50% salts. Of the salts, about 2% are soluble thorium salts, the remainder sodium chloride. The deposits are broken away from the cathode by hammer and chisel or by air hammer and are then jaw crushed. The jaw crushed segments are then lightly pulverized in a secondary crusher to -200 mesh.

The fine particles of thorium-salt agglomerate are then water leached. This leaching is done either by leaching and decantation in a beaker or as a

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fluidized mass in an adaptation of counter current leaching principles. (See Report No. 3) In this case the crushed deposit is loaded into a cone shaped washer in which water flows from the apex of the cone up through the fluidized deposit. When the soluble salts have been dissolved, the metal deposit is removed, drained free of excess water, and treated with 3.5% by weight hydrochloric acid at room temperature for five minutes. The metal is then washed free of acid and air-dried at 35° C.

V. PHYSICAL PROPERTIES AND COMPOSITION

Thorium metal produced by electrolysis of thorium chloride has exhibited hardnesses, as-cast, as low as Vickers 67. It is expected, from consideration of the many runs reported upon in this and the preceeding report that as-cast thorium metal of Vickers 70-80 can be considered the expected average hardness. As the run summaries indicate, thorium of higher hardness has been produced. In each case, however, the higher hardnesses are explained by variations in salt preparation, electrolytic procedure, etc. The production of low hardness thorium in several instances alone establishes the capabilities of the process.

Through the good offices of the Atomic Energy Commission, the New Brunswick Laboratory has analyzed thorium metal produced in several of the electrolytic runs reported. These analyses are shown in Table III.

This analysis can be compared to the results published * for Ames Thorium (Billet A-520) in 1952. This bar had a hardness of R_E 44. Horizons electrolytic

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*Compilation of Analytical Results for Ames Thorium Billet A-520 - Thorium Analytical Meeting, September 23-24, 1952, at Argonne National Laboratory

[redacted]

TABLE III

Horizons Run Number	97-162 Powder	97-170 Powder	97-174 Powder	97-174 Pellet	97-170 Rolled Strip
NBL No.	B-4748	B-4749	B-4750	B-4751	B-4752
R_B	(R_B 26)	(R_B 10.5)	(R_B 31.5)	R_B 31.5	---
Ag	a 1	a 2	a 2	a 1	a 1
Al	a 20	a 30	a 20	a 30	a 30
Au					
B	a 0.5	> 10	a 1	a 5	a 5
Ba					
Be	a 10	a 5	a 5	a 3	a 10
Ca	< 100	< 100	< 100	< 100	< 100
Cd	a 0.3	a 0.2	a 0.1	a 0.1	< 0.1
Co	--	--	--	--	--
Cr					
Cs					
Cu	a 80	a 80	a 20	a 100	a 80
Fe	600	550	110	210	350
Ge	--	--	--	--	--
In	--	--	--	--	--
K					
Li					
Mg	a 10	a 10	a 10	a 10	a 10
Mn	a 5	a 5	a 3	a 2	a 3
Mo	--	--	--	--	--
Na	a 150	a 150	a 300	< 150	< 150
Ni	a 300	a 300	25	19	a 200
P	--	--	--	--	--
Pb	15	15	5	2	5
Rb					
Sb	--	--	--	--	--
Si	a 50	a 50	a 100	a 50	a 30
Sn	5	10	5	6	10
U	--	--	--	--	--
Zn	< 10	--	--	--	--
As	< 5	< 5	< 5	< 5	< 5
HCl insol.	0.7%	0.2%	3.1%		
C	*410; 460 ppm	*310; 360 ppm	*290 ppm	--	**480 ppm
N	34 ppm	32 ppm	27 ppm	26 ppm	37 ppm

NOTE: a = approximate; -- = not detected

* Results of individual determinations.

** Probably somewhat low. Sample could not be prepared properly to burn completely.

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thorium is somewhat higher in aluminum, boron, and bismuth content; somewhat lower in silicon, zinc, and tin content; appreciably higher in calcium, copper, iron, nickel, and lead content. In nitrogen, carbon, and HCl insoluble contents, the metals appear to be equivalent.

A conversion curve for R_B and R_E hardness determinations for electrolytic thorium metal as produced and melted at Horizons, versus Vickers Hardness Number has been prepared and is presented as Figure 3.

Some physical evaluation of the thorium metal produced under this contract has been begun at Horizons and at other laboratories through the cooperation of the Commission. This work is in the preliminary stages and is not ready for presentation in this report. The final report covering this product will contain this information upon the fabrication properties of electrolytic thorium metal powder.

Photomicrograms of typical thorium as-cast ingots are shown in Figure 4.

VI. CONCLUSIONS

The electrolytic process for producing thorium metal, including the preparation of anhydrous thorium chloride, the electrolysis of this salt in molten sodium chloride, and the recovery of the thorium powder, has been proven in laboratory sized equipment.

The development of this process at the next larger scale, a factor of about ten, has begun. As was expected, certain operating conditions must be established on this larger equipment. A number of factors which were inconsequential in the small scale have proven to be of extreme importance in the larger cell. One of

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Conversion Chart
R_B vs. R_E
R_B vs. VHN

For Horizons Incorporated Thorium

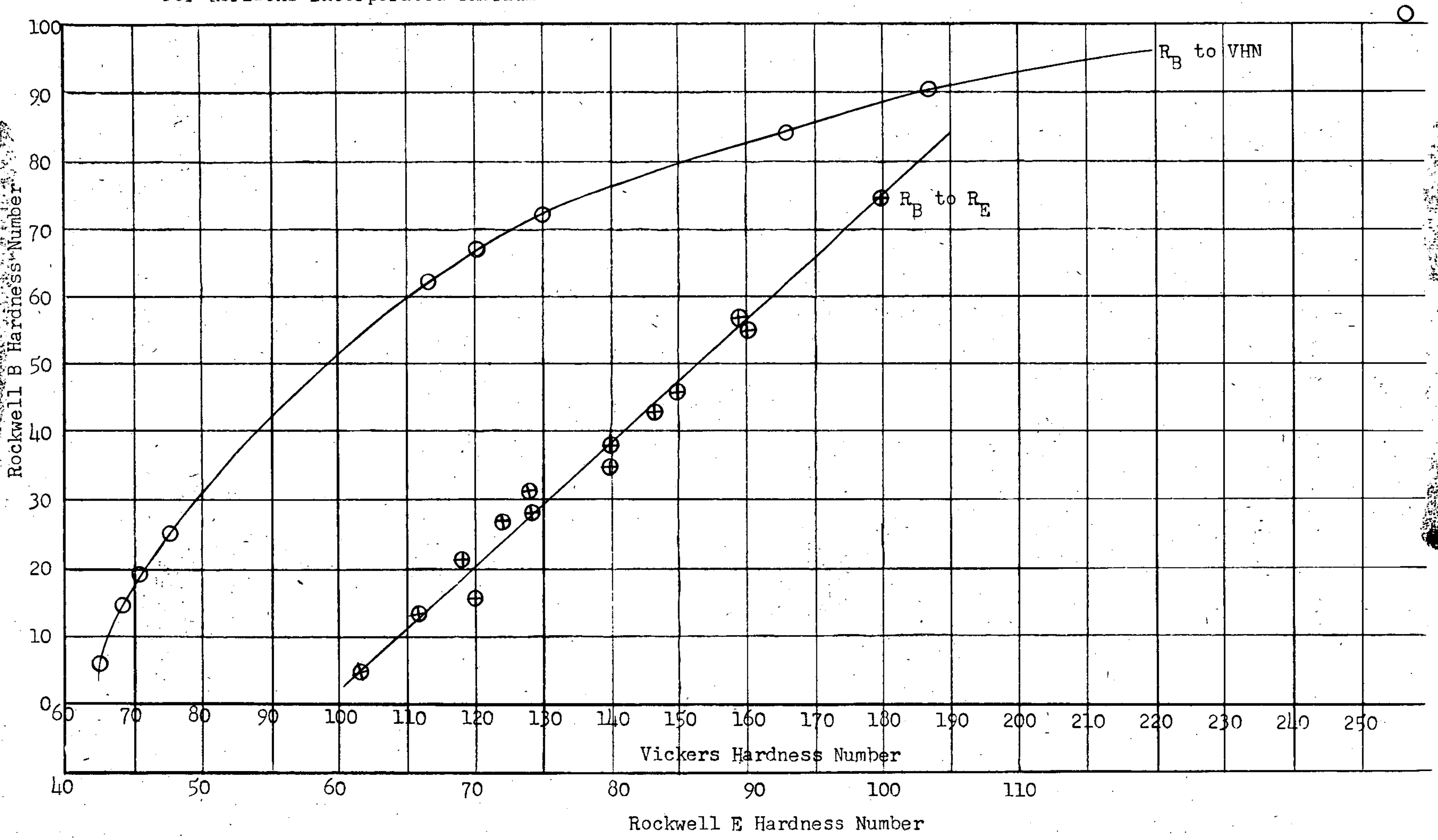

Figure 3

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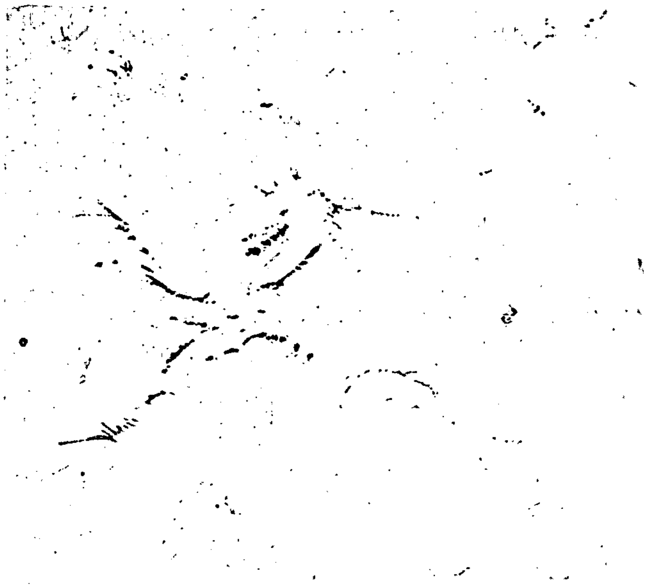
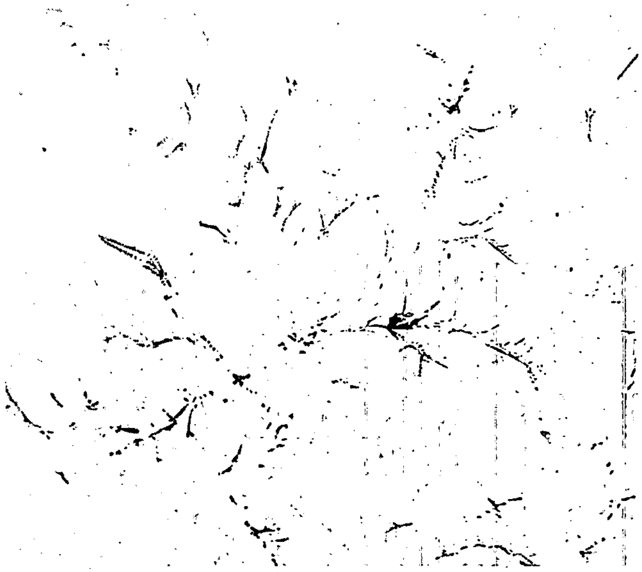


As Cast Thorium Ingot R_B 5 - Run No. 97-192. Magnification 250 X



As Cast Thorium Ingot R_B 20 - Run 97-151. Magnification 250 X

As Cast Thorium Ingot R_B 36. Magnification 250 X

Figure 4

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these factors is the bath temperature. At 850° C, no difficulty was encountered in the small cell. However, in the larger cell, the added factors of higher DC currents, and a larger cathode resulted in temperatures high enough to alloy thorium with the steel cathode and melt this alloy off into the salt bath. Another factor is the size of the cathode. The small cathode quickly reaches bath temperature, but the larger one which has approximately ten times the mass of the smaller one remains cold long enough to chill a layer of salt upon it. It has definitely been shown that the initial electrolysis takes place on this layer of chilled salt.

As soon as the operating conditions have been established on this larger scale, the unit will be operated on a continuous basis. Maintenance of a good cell atmosphere between runs by evacuation and flushing with argon should improve upon the continuous runs in the laboratory sized scale.

The thorium metal produced to date has been of excellent quality and purity. Fabrication properties will be investigated and reported upon in the next quarter.

In the laboratory sized scale, increasing the thorium ion concentration has resulted in increased process efficiency. At the limiting concentration of approximately 20%, the cathode grew until it shorted out against the crucible wall. There was still about 3% thorium in the salt bath at this time. Consequently, the limiting concentration was set by the size and shape of the crucible rather than by any electrolytic characteristics of the system. Investigation of concentration limit conducive to maximum efficiency will have to be determined in the next larger scale where the distance between cathode and crucible wall will not be a limiting factor.