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INVESTIGATIONS FOR THE PRODUCTION OF THORIUM METAL

**Technical Progress Report - Sixth Quarter,
September 1 to November 30, 1953**

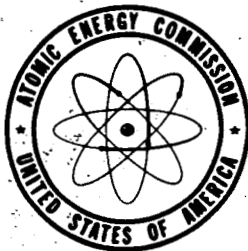
**By
Jason C. Bleiweiss**

AEC RESEARCH AND DEVELOPMENT REPORT

December 1, 1953

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INVESTIGATIONS FOR THE PRODUCTION OF THORIUM METAL. TECHNICAL PROGRESS REPORT [FOR] SIXTH QUARTER, SEPTEMBER 1 TO NOVEMBER 30, 1953

By Jason C. Bleiweiss

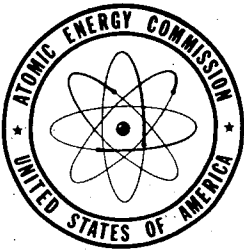
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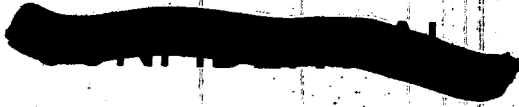
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Summary

The research program on electrolytic production of thorium metal from fused chloride baths has been continued. A large portion of the effort has been devoted to preparation of a chloride source electrolyte.

The method selected for preparation of NaCl-ThCl_4 as a cell feed material was the reaction of ThOCO_3 with concentrated HCl and addition of NH_4Cl . Several modifications in procedure were made to simplify the chemical engineering operations involved. These include saturation of the solution with anhydrous HCl , and cooling to about 10°C . Both steps decrease the solubility of the $(\text{NH}_4\text{Cl})_2\text{ThCl}_4 \cdot x \text{H}_2\text{O}$, precipitating it from solution. The ammonium thorium chloride crystals filter easily.

The intermediate complex $(\text{NH}_4\text{Cl})_2\text{ThCl}_4 \cdot x \text{H}_2\text{O}$, protects the thorium chloride from oxidizing while it is being dehydrated. In previous work the NH_4Cl was sublimed in the electrolytic cell atmosphere. On a small scale this did not cause any serious difficulties, but on a large scale the amount of NH_4Cl subliming from the cell feed material would seriously contaminate the cell, plug the exhaust opening with NH_4Cl , and in general be objectionable.

A method has been evolved in which the NH_4Cl can safely be removed from the salt at high temperatures outside the electrolytic cell without oxidizing the ThCl_4 cell feed material.

The determination of electrolysis conditions for maximum efficiency is being carried out in a cell capable of producing 150-300 grams of thorium metal per cathode. The results indicate that increasing the thorium ion concentration while maintaining the same current density, yields higher current efficiency. Lowering the current density while maintaining the thorium ion concentration

Summary (continued)

constant, indicates that the crystal size increases with a resulting decrease in hardness.

The best results to date have been accomplished with a thorium ion concentration of 15%, using an overall cell voltage of 3.0 volts DC, and a cathode current density of 185 amps/dm². Current efficiencies were in the order of 70%, and in one instance the thorium metal produced had an as-cast hardness of Vickers 70.

Results regarding the quality of metal produced in the small-scale cell, quality of cell feed material, and the current efficiencies and metal recoveries obtained, are very satisfactory. Electrolysis in the intermediate-sized cell capable of producing 5-10 lbs. of metal per cathode is now underway.

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INVESTIGATIONS FOR THE PRODUCTION OF THORIUM METAL

Technical Progress Report - Sixth Quarter, September 1 to November 30, 1953

By Jason C. Bleiweiss

I. INTRODUCTION

During the previous contract period, the electrolysis of NaCl-ThCl_4 , showed considerable promise as a commercially feasible means of thorium production.

The process is particularly promising because of its potential as a low-cost, continuous process. Electrolysis of a melt of NaCl-ThCl_4 and NaCl produces thorium metal with NaCl , and chlorine as by-products. Thus, any given salt bath should have an infinite life requiring only make-up salt to account for that removed with the cathode deposit. Considerable advantage is also inherent in the simplicity of the salt system with respect to recovery of the metal produced. The only impurity noted in the deposits is a small amount of ThOCl_2 , which may be removed by a dilute acid wash.

Thorium chloride is easily prepared by simple chemical techniques starting with thorium oxycarbonate which can be purchased directly or made from the cheaper thorium nitrate. Processing involves solution with HCl , precipitation of an ammonium thorium chloride complex by saturation with anhydrous HCl and cooling, filtering, drying, and melting in NaCl under a chlorine atmosphere to prevent oxidation.

Conditions of electrolysis have been fairly well-defined with regard to temperature, voltage, current density, and concentration. Investigations are now being completed concerning electrolysis conditions for maximum efficiency. These indicate that slightly higher current density and higher concentration tend toward greater current efficiency. A minimum operating temperature of about 820°C is indicated, but may be further lowered by use of higher thorium ion concentrations.

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Voltage is a critical factor with respect to elimination of concurrent sodium production. An operating range of 2-4 volts DC across the cell seems to be desirable from this standpoint.

II. PREPARATION OF CELL FEED MATERIAL

In the reaction: $\text{ThOCO}_3 + \text{HCl} \rightarrow \text{ThCl}_4 \cdot x \text{H}_2\text{O}$, etc., the addition of at least two moles of NH_4Cl is necessary to form the intermediate complex $(\text{NH}_4\text{Cl})_2\text{ThCl}_4 \cdot x \text{H}_2\text{O}$. Heating to about 150°C eliminates the water of hydration leaving anhydrous $(\text{NH}_4\text{Cl})_2\text{ThCl}_4$. Further heating at about 500°C sublimes the NH_4Cl leaving anhydrous ThCl_4 . If the heating is carried out in the presence of NaCl , NaThCl_5 is presumably formed.

The elimination of NH_4Cl at elevated temperatures without oxidation was successfully accomplished in the small electrolytic cells in a bath of molten NaCl under an argon atmosphere prior to electrolysis. On such a small scale, the amount of NH_4Cl subliming from the salt and condensing on the operating head was only about 60 grams. The NH_4Cl was scraped from the thermocouple and cathode openings in the operating head to keep these openings from plugging solid.

In the large cell capable of producing about 75 pounds of thorium metal per cathode, more than ten pounds of NH_4Cl would have to be sublimed using the same technique. The difficulties inherent in such a scale-up due to sublimation and condensation of NH_4Cl are obvious. It was, therefore, considered imperative that the cell feed material, ThCl_4 or NaThCl_5 , should be free of NH_4Cl , or at least have the NH_4Cl present in such low concentration that the difficulties described above are reduced to a tolerable minimum.



A. Heating in Air

Several attempts were made (Table I) at heating the $(\text{NH}_4\text{Cl})_2\text{ThCl}_4$ to 500°C in air, with excessive amounts of oxidation taking place. From the analyses of these salts, (Table II) the amount of insoluble material was very high for three of the salts heated in air. The insoluble material is ThO_2 ; the oxychlorides which are also undesirable are soluble.

In the fourth run, No. 5, the ammonium thorium chloride fused to a solid mass, with highly oxidized, unfused material on the surface. The fused mass separated from the white oxide, had only 0.29% insolubles and contained 90.5% ThCl_4 . The remainder is presumed to be NH_4Cl (about 9.2%).

When this salt was electrolyzed, a very nice pre-electrolysis deposit was obtained, but the electrolysis deposit fell into the bath, and the metal was dispersed in the salt bath.

One attempt was made to remove the NH_4Cl near its sublimation temperature at 340°C (No. 6). The salt was kept at this temperature for 69 hours. Analysis showed no insolubles, 85% ThCl_4 and 15.1% NH_4Cl .

Electrolysis with this salt resulted in a deposit which fell off the cathode. Conclusions regarding the quality of the salt as cell feed material are therefore difficult to draw, but it is fairly safe to assume that the 300°C - 350°C range is still below the critical temperature for oxidation. However, the amount of ammonium chloride remaining in the salt is too high for the salt to be used as a cell feed material in a large scale electrolytic cell.

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TABLE I

PREPARATION OF THORIUM SALTS

Notebook No.	Temp. °C	Time Hours	Starting Wgt. Thorium Carbonate	Code No.	Reaction	Atmosphere	Remarks
128-37	150 315	2 14	1232 grams	1	$\text{ThOCO}_3 \cdot \text{H}_2\text{O} + 10 \text{HCl} + 2\text{NH}_4\text{Cl} + 1.1 \text{NaCl} \rightarrow \text{NaThCl}_6 + 2\text{NH}_4\text{Cl} + 7\text{HCl} + 3\text{H}_2\text{O} + \text{CO}_2$	Air	HCl evaporated almost to dryness at 150°C prior to heating cycle in graphite crucibles. Gray colored salt.
164-77	150 450	2 18	616 grams	2	$\text{ThOCO}_3 \cdot \text{H}_2\text{O} + 10\text{HCl} + 3\text{NH}_4\text{Cl} + 2\text{NaCl} + \text{Anhydrous HCl to Saturation} \rightarrow \text{ThCl}_4 \text{ etc.}$	Air	Filtered $(\text{NH}_4\text{Cl})_2 \text{ThCl}_4 \cdot x\text{H}_2\text{O} - \text{NaCl} - \text{KSNH}_4\text{Cl}$ from cold, saturated HCl solution. Heated in graphite crucible. Much oxide. Small yield
164-80	150 475	2 18	616 grams	3	Same as 2 using the mother liquor from 2	Air	Much oxide. 250 grams yield.
164-83	150 300 500	17 6 16	616 grams	4	$\text{ThOCO}_3 \cdot \text{H}_2\text{O} + 10 \text{HCl} + 4\text{NH}_4\text{Cl} \rightarrow \text{ThCl}_4 \text{ etc.}$	Air	Most of the ThCl_4 remained behind in the mother liquor
164-85	150 500	2 20	616 grams	5	Same as 4 using mother liquor from 4	Air	Top layer was white and full of insolubles. Bottom was fused mass weighing 460 grams.
164-89	150 340	17 69	616 grams	6	Same as 4 using mother liquor from 5	Air	Top crust was separated. 45 grams. Remainder weighed 880 grams.
138-120	150 250 400 530 575	1.5 1 0.75 1.75 2.0		7	Same as 4. Used 100 grams wet filter cake from 6	Argon	There was probably some air in-leakage with the argon. Appeared promising.
164-94	150 350 550	37 100 50	25 lbs.	8	Same as 4	Argon-Air	Although an argon atmosphere was used, there was enough in-leakage of air to cause oxidation.

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Table I (Continued)

Notebook No.	Temp. °C	Time Hours	Starting Wgt. Thorium Carbonate	Code No.	Reaction	Atmosphere	Remarks
164-105	150 350 850	23 6 3		9	Same as 4. Used 5.5 lbs. wet filter cake from 8. After 350°C added 12 lbs. NaCl	Argon- Air Cl ₂	Melted in chlorine atmosphere at 850° C with NaCl.
164-112	150 310	20 23	25 lbs.	10	Same as 4. Used mother liquor from 8	Argon- Air	
164-121	310 310-700 up to 820	23 4 7		11	Used NH ₄ Cl-ThCl ₄ mixture from 10. Mixed with 19.5 lbs. NaCl	Argon- Air- Chlorine	Used chlorine atmosphere when heating with NaCl above 310°C. Furnace shorted out at 700°C. Completed heating after repair.

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TABLE II

SUMMARY OF ANALYSIS FOR THORIUM
SALT PREPARATIONS

Notebook No.	Code No.	Total Insolubles	Th	Chloride	NH ₃	Total	Remarks
128-37	1	0	29.8	35.2	5.2		
164-77	2	15.4					
164-80	3	35.1					
164-83	4	16.9+					
164-85	5	0.29	56.0				
164-89	6	0	52.8		5.1	100.1	
138-120	7	0	56.0	34.8	1.8	92.6	
164-94	8	---	58.9	29.0	3.44	91.4	After heating to 375°C
164-94	8-a	1.8	65.1	29.9	0.01	96.8	After heating to 535°C
164-105	9	0	7.6	62.1			After heating to 310°C
164-110	9-a	0	2.52	60.1	0		After melting in NaCl
164-112	10	0	19.3				Wet filter cake
164-116	10	0	38.2	46.6	13.5	98.3	After 300°C
164-121	11	0	27.5	53.05	0.006		Melted in NaCl

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B. Heating Under Protective Atmosphere

A furnace already ~~in existence~~ in this laboratory was used to drive off the NH_4Cl under an argon atmosphere. This was not an ideal set-up, but since it was an experimental effort, the expense of designing a more suitable large unit was not justified. The graphite crucible used in this furnace has a capacity of about 30 pounds of salt.

As the analysis shows, this thorium chloride heated to 530°C was not satisfactory. The total insolubles were 1.8% and the total of NH_3 , Th, Cl, and insolubles was only 96.8% indicating a possibility of oxygen present as oxychloride. Reporting of oxygen "by difference" does not seem reasonable when the total analysis is within several percent of 100, because of the possible errors in the several analytical determinations.

Heating in an argon atmosphere should theoretically produce oxygen-free ThCl_4 . However, the furnace atmosphere is not free of oxygen since air can enter by back diffusion as the exhaust gases leave.

C. Melting in NaCl Under Protective Atmosphere

When heating under the "argon-air" atmosphere proved unsatisfactory, the procedure was modified to provide more protection against oxidation at the critical temperatures above 350°C . After the $(\text{NH}_4\text{Cl})_2\text{ThCl}_4$ had been heated to $310\text{-}350^\circ\text{C}$ to remove water and HCl, it was removed from the graphite crucible, crushed, and mixed with NaCl to yield a suitable ThCl_4 concentration. A protective atmosphere of chlorine was maintained

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over the salt mixture while it was heated until molten.

Condensation of NH_4Cl in the vent hole in the head of the furnace caused some difficulty. In both runs, the supply of chlorine which was led in by a 1/2 inch graphite tube through the center of the 1-1/2 inch vent hole, had to be cut off at about 600°C when the annulus between the tube and the hole plugged solid with NH_4Cl . This difficulty can be easily eliminated in the design of a different unit to accommodate this sublimation.

Table II shows the analyses of the two salts made in this manner. According to the analysis for No. 9, most of the 5.5 pounds of wet filter cake used was NH_4Cl . This resulted in a low thorium ion concentration, 2.5%, but the experiment demonstrated that the method was satisfactory. Neither salt had any insolubles.

Electrolytic runs with No. 9 resulted in extremely hard metal. This may have been a function of the low thorium ion concentration.

No. 11 yielded metal of acceptable hardness, signifying that the method used in its production is satisfactory. (Hardness was as low as VHN 70.)

A flow diagram for the $\text{NaCl}-\text{ThCl}_4$ process is shown in Figure 1.

Mother liquor from the filtering operation contains about 130 grams/liter of ThCl_4 and is used with a small amount of "make-up" acid for the next batch. The HCl loss should be small.

It is quite possible that the crushing and blending operation which follows heating at 320°C can be eliminated by adding NaCl to the acid slurry before filtering, or to the $(\text{NH}_4\text{Cl})_2\text{ThCl}_4$ in the hot furnace.

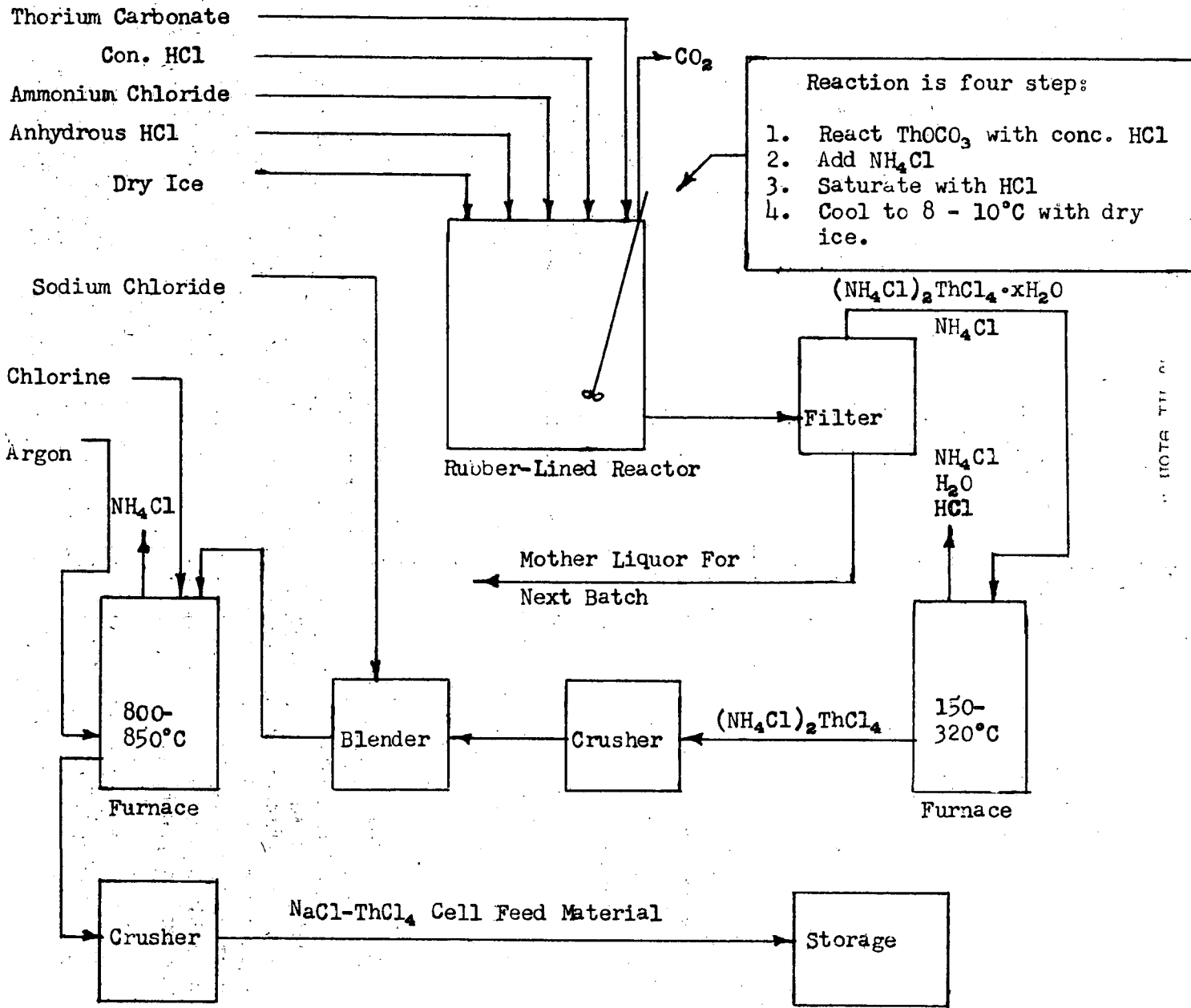


Figure 1. Flow Diagram for Wet Preparation of NaCl-ThCl₄ Cell Feed.

This would greatly simplify the process physically, and allow less exposure to air during processing.

D. Equipment for Large Scale NaCl-ThCl₄ Production

The furnace used in the production of salt No. 11 can be used to prepare about 20 pounds of ThCl₄ per batch. With some minor modifications, it will continue to be used to prepare enough cell feed material to maintain the electrolytic work in the 10 pound per cathode cell.

In the meantime, design of a furnace more suitable for NaCl-ThCl₄ production is being prepared.

III. DETERMINATION OF CONDITIONS OF ELECTROLYSIS FOR MAXIMUM CELL EFFICIENCY

The determination of electrolysis conditions in a small cell capable of producing about 150-300 grams of thorium per cathode is now in progress.

Enough NaCl-ThCl₄ salt, No. 11, is on hand to be used for this entire study, thus eliminating the effect of variation of cell feed material.

As shown in Table III, excellent metal of hardness lower than R_B 50 has been produced from salt baths containing 7-15% thorium ion concentration at suitable current densities. At higher current densities difficulty was encountered due to failure of the cathode deposit to adhere to the cathode.

Two runs were very outstanding with regard to hardness, current efficiency, and per cent recovery of metal. Both runs, 97-162 and 97-170, were made at 75 amps, or about 185 amps/dm², and contained 10% and 15% thorium ion concentration respectively. With 10% thorium ion concentration, the hardness was R_B 26 (R_E-73), current efficiency was 62%, and the metal recovery was 78%.

TABLE III

SUMMARY OF ELECTROLYTIC THORIUM RUNS

Run No.	Thorium Salt No.	Bath Composition	Temp. °C	Volts	Amps	Amps Hrs.	Metal Recovery Wt. %	Hardness	% Current Efficiency	Remarks	
97-143	6	350 gm + 4 lbs. NaCl (8.7% Th)	850	2.0 2.9	2.0 50	120	Cathode 43.5 Crucible 65.5 59	Cathode R _B 67 Crucible R _B 47.5	22.8	Bottom portion of deposit fell into the bath. Metal in the bath was softer than metal on cathode	
97-145	5	330 gm + 4 lbs. NaCl (8.7% Th)	840 880	5.4 2.8	100 50	4 100				Excellent pre-electrolysis deposit. Deposit fell into bath and dispersed in it.	
97-146	5	270 gm + 4 lbs. NaCl (7.0% Th)	875 850	6.4 3.5-3.8	100 100	2.5 75	10.5 7.5	R _B 74	4.6		
97-147	120-36	350 gm. + 4 lbs. NaCl	850	6.2 3	100 50	4 130	55	--	R _B 76	19.5	This run was made to check cell conditions and procedures. The results were the same as previous runs made with the same salt.
97-148	8	135 gm + 4 lbs. NaCl (4.2% Th)	830	6.0 2.6-3.0	100 17-20	4 40				No deposit on pre-electrolysis. No deposit. Sludge on top of bath during run.	
97-149	9-a	4 lbs. 164-110 (2.5% Th)	840	9.0 2.6-3.0	100 11-32	2.5 47	12.7	28	R _B 104	12.5	A good-shaped deposit was obtained, but the metal was extremely hard. 0.28% Th left in salt bath.

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TABLE III (Continued)

Run No.	Thorium Salt No.	Bath Composition	Temp. °C	Volts	Amps	Amps Hrs.	Metal Recovery		Hardness	% Current Efficiency	Remarks
							Wt. %	%			
97-151	9-a	4 lbs. 64-110 (2.5% Th)	850	3.0 3.0	10-13 25	12 45	8	31	R _A 66 R _A 70	15	Heavy deposit from pre-electrolysis
97 152	11	2 lbs. 164-121 2 lbs. NaCl (13.9% Th)	840	2 at 5.0 2 at 3.3 4.0-5.0	100 50 200-250	-12 6 80	86	34	R _B 78.5	49.7	Metal deposit fell into bath. 4 pre-electrolysis deposits. Last two had fairly good deposits.
97-154	11	365 grams + 4 lbs. NaCl (4.6% Th)	850	7.0 3.4	100 50	4 96	52	51	R _B 93	24.6	Deposit was large in size but showed indications of carbiding.
97 156	11	600 gms + 4 lbs. NaCl (6.8% Th)	850	2 at 6.8 3.1-3.6	100 75	2 at 4 124	106	63.5	R _B 36	39.6	1st pre-electrolysis had no deposit. 2nd pre-electrolysis had good deposit. Large deposit.
97 158	11	800 gms + 11.00 gms NaCl (10% Th)	850	2 at 7.0 3.6	100 110	2 at 4 110	67.3	30	R _A 63	28.4	1st pre-electrolysis had fair deposit. 2nd pre-electrolysis had good deposit. Deposit fell into the salt bath. Dispersed salt bath.
97 160	11*	550 gms + 1650 gms NaCl (7.0% Th)	850	6.5 3.5	100 75	4 176	42	27.5	R _B 45	11	Pre-electrolysis had fair deposit. Used a ceramic sleeve on cathode instead of graphite one. Very good deposit. Bath very clear during electrolysis.

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TABLE III (continued)

Run No	Thorium Salt No.	Bath Composition	Temp. °C	Volts	Amps	Amps Hrs.	Metal Recovery Wt.	Recovery %	Hardness	Current Efficiency %	Remarks
97-162	11*	800 gms + 1400 gms NaCl (10% Th)	850	6.0 7.4 3.5	100 100 75	4 4 129	173.5	78	R _B 26 R _E 73	62	Pre-electrolysis had nice deposit. Deposit was large.
97-166	11*	800 gms + 1400 gms NaCl (10% Th)	850	2 at 6.5 2.8-3.2	100 50	8 120	159.5	71.5	R _B 54	61	Very large deposit. Lower part of deposit fell into bath and was recovered intact. Washed entire deposit. Coarse crystals.
97-168	11*	550 gms + 1650 gms NaCl (7.0 Th)	850	7.0 2.6	100 50	4 105	--	--	--	--	Deposit fell into bath and dispersed.
97-170	11*	1200 gms + 1000 gms NaCl (15.0% Th)	850	7.0 2.8-3.0	100 75	4 210	326	99	R _B 10.5 R _E 67	72	Deposit was very large and very coarse.

* Porcelain protection sleeve used over cathode rod.

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With 15% thorium ion concentration, the hardness was R_B 10 (VHN 70), current efficiency was 72%, and the metal recovery was 99%.

The phenomenal 99% recovery will be checked by duplicating the run. It is quite possible that salt No. 11 is not homogeneous, and the salt added to the bath had more thorium than the analysis indicates. Thorium concentration of the spent salt bath was less than 0.05%. At any rate, the hardness of VHN 70 and current efficiency of 72% are quite satisfactory.

Figure 2 is a photograph of the cathode deposit of run 97-170.

In run 97-166 the lower part of the deposit fell into the bath and was recovered intact, indicating that it fell off while raising the cathode out of the bath. The appearance of the metal, gray, large crystals, was very good. The part of the deposit which fell into the bath was washed with the remainder of the deposit. This may account for the hardness of R_B 54, which was higher than expected. The effect which the lower current density, 125 amps/dm², had upon the hardness will be checked by duplicating the run.

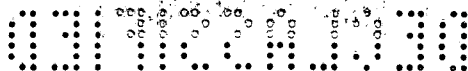
Concentration of thorium ion will be increased to a limit conclusive to maximum current efficiency and yield. From these data a correlation of current density vs. thorium ion concentration, particle size, and metal hardness will be made.

A. Cold Rolling

A 15-gram pellet of thorium metal with a hardness of VHN 70 (run 97-170) was cold rolled from 0.206 inches to 0.035 inches before appearance of edge cracking. Cold rolling was continued to a thickness of 0.006 inches without further edge cracking, an overall 97% reduction by cold rolling, being obtained.

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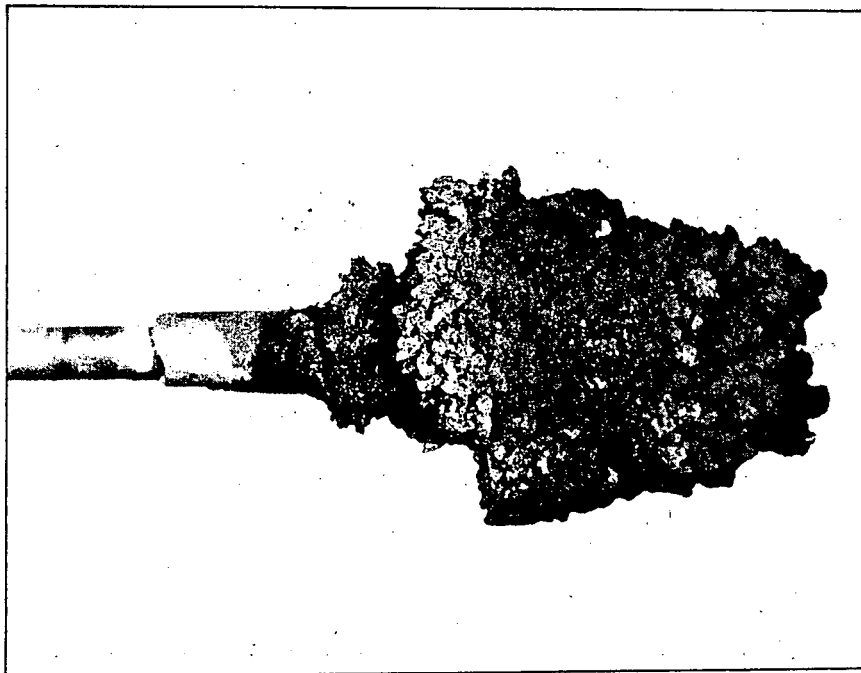


Figure 2

Cell II 97-170 Thorium - Reduced to half size

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B. Use of Porcelain Cathode Protection Sleeve

The cathode rod is made of 1/2 inch diameter nickel rod threaded into a steel cathode tip upon which the deposit is made. The cathode tip is a cylinder of 3/4 inch diameter, 2 inches in length. During electrolysis about 1/2 inch of the protection sleeve is immersed in the bath.

One change in the electrolysis procedure has been the substitution of an unglazed porcelain protection sleeve on the nickel cathode rod for the previously used graphite sleeve. This was done to eliminate carbide formation on the cathode deposit from the sleeve. In the runs which were made using the porcelain sleeve, there was no acetylene odor. This is a definite improvement over the graphite sleeve which previously had always carbided and contaminated the thorium metal product.

The service life of these porcelain sleeves under actual electrolysis conditions will be determined.

IV. DESIGN AND CONSTRUCTION OF A CELL CAPABLE OF PRODUCING TEN POUNDS OF METAL PER CATHODE

An intermediate-sized cell has been designed and constructed which is similar in principle to the smaller cells used in previous work.

The cell was tested in the operating temperature range to uncover weak points of design and construction. Several corrective changes have been made and the cell is now ready for electrolytic study.

Complete details regarding this cell will be included in the next Quarterly Report.

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V. CONCLUSIONS

The process for producing NaCl-ThCl_4 as a cell feed material by melting $(\text{NH}_4\text{Cl})_2\text{ThCl}_4$ with NaCl under a chlorine atmosphere has proved to be satisfactory. The chemical engineering problems involved are not complicated, and the metal produced from the cell feed material is very acceptable with regard to hardness and cold ductility.

The determination of electrolysis conditions for maximum efficiency carried out in a cell capable of producing 150-300 grams of thorium metal per cathode is reaching a satisfactory conclusion. Increasing the thorium ion concentration while maintaining a cathode current density of about 185 amps/dm^2 resulted in increased current efficiency, increased metal recovery, and lower hardness thorium product.

Electrolysis in the intermediate-sized cell capable of producing 5-10 lbs. of metal per cathode can commence shortly in view of the satisfactory results thus far obtained in the determination of electrolysis conditions in the smaller cell.

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