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INVESTIGATIONS FOR THE PRODUCTION OF
THORIUM METAL

Technical Progress Report for Third Quarter,
November 1, 1952 to January 31, 1953

By
Merle E. Sibert

AEC RESEARCH AND DEVELOPMENT REPORT

March 9, 1953

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Summary

A further study has been made on the electrolytic ^{winning} ~~recovery~~ of thorium metal from double halide salts. Current work has dealt exclusively with the electrolysis of a fused sodium-thorium-chloride system. This procedure was described in the previous report. At that time difficulty was reported in obtaining an adherent cathode deposit.

This difficulty has been shown to be a function of purity of the starting material and operating voltage. Previously the double salt had been prepared from the hydrated chloride giving a product of high oxide content. Such materials give very fine loosely held deposits. Improved materials have yielded adherent coarsely crystalline thorium deposits.

The voltage factor is significant from the standpoint of simultaneous sodium production. When sodium is also produced, this diminishes the current efficiency as well as making recovery of the deposited thorium more difficult. With a proper operating voltage however, sodium production is not evident until the thorium content of the bath is substantially depleted.

Ductile thorium has been produced by this method. Rockwell B hardness values of 24-57 have been obtained, the variation being primarily dependent on starting materials and resultant particle size of the deposit.

Preparation of the double salts used is described, and complete operating data for the electrolysis is reviewed.

Some arc melted specimens have been processed into sheet thorium; data on this work is included along with hardness data for results reported.

Technical Progress Report
(Third Quarter, November 1, 1952 to January 31, 1953)

INVESTIGATIONS FOR THE PRODUCTION OF THORIUM METAL

A. Introduction

The current phase of this investigation has dealt almost exclusively with the electrolytic preparation of thorium from the double chloride of sodium-thorium. This procedure has been previously described (Report for Second Quarter), but, at that time, metal so produced was generally not satisfactory in quality.

The difficulty encountered previously in regard to recovery and current efficiency has been shown to be principally governed by the purity of the double chloride. As a result of this, considerable work has been done on the preparation of this salt. Crystal size, adherence of the deposit and purity of the metal have all been shown to be functions of purity of the starting material.

The double salt, NaThCl_5 , has been prepared under a variety of conditions and adapted to the preparation of metallic thorium by fused salt electrolysis. A sodium chloride bath has been exclusively employed in all of this work.

It has been shown that a normal yield and current efficiency can be obtained by use of chloride source materials. Considerable difficulty was formerly encountered due to excess carbide formation, but this is completely eliminated when an adherent deposit is formed, enabling the process to be operated on a continuous basis.

All of the current work has been accomplished in the cell previously described (Report for First Quarter). The decomposition

potential cell has been completely revised and data has been obtained on two of the source materials employed. A current voltage controller and recorder have been incorporated in the circuit for greater accuracy. A new AC heating source has also been installed for closer temperature control.

B. Preparation of NaThCl_5

All compounds utilized as source materials have been prepared from ThOCO_3 or $\text{ThCl}_4 \cdot x\text{H}_2\text{O}$. The principal problem involved is the elimination of hydrated water. Bifluorides such as KHF_2 and NH_4HF_2 have been used, but generally NH_4Cl has been used in a straight thermal reaction with NaCl and the appropriate thorium compound.

In most cases water and ammonium chloride remained in the mix. It is also probable that considerable ThOCl_2 is produced during the course of this type of reaction.

Recently ThOCO_3 has been dissolved in concentrated HCl , and NH_4Cl and NaCl subsequently added. The mixture is evaporated to dryness and then heated at 300°F to remove water, followed by heating at 600°F until NH_4Cl is no longer in evidence. Salts prepared in this manner have shown evidence of higher purity with respect to oxide or oxy-chloride content.

A tabulation of NaThCl_5 preparations employed is given in Table I.

C. Electrolysis of $\text{NaThCl}_5\text{-NaCl}$

The electrolytic procedure for preparation of thorium from an $\text{NaThCl}_5\text{-NaCl}$ mixture has been previously described (Report for Second Quarter). Work has been continued along these lines toward evolution

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TABLE I
Preparation of NaThCl₅

Run No.	Type Code No.	Temp. °F	Time Hrs.	Reaction	Remarks
69-109	1	600	4	$\text{ThCl}_4 \cdot 3\text{H}_2\text{O} + \text{NaCl} + 3 \text{NH}_4\text{Cl} \rightarrow \text{NaThCl}_5 + 3\text{NH}_4\text{OH} + 3\text{HCl}$	ThCl ₄ dried prior to reaction
69-124	2	600	16	Like 69-109	Possible SiO ₂ in product from pyrex container
69-126A	3	200	To dry- ness	Like 69-109	Yellow tinted product, heated in C crucibles
69-128	4	600	16	$\text{ThOCO}_3 + 4\text{NH}_4\text{Cl} + \text{NaCl} \rightarrow \text{NaThCl}_5 + 4\text{NH}_3 + 2\text{H}_2\text{O} + \text{CO}_2$	
69-126B	5	600	16	Like 69-126A	Contents white
69-127A	6	200	To dry- ness	Like 69-109	Product contains NH ₄ Cl
120-36	7	600	4	$\text{ThOCO}_3 + \text{NaCl} + 6\text{NH}_4\text{Cl} \rightarrow \text{NaThCl}_5 + \text{CO}_2 + 6\text{NH}_3 + 2\text{H}_2\text{O} + 2\text{HCl}$	Heated in graphite; pre-micro- pulverized
128-37	8	600	4	Same as 120-36	Micropulverized; contains NH ₄ Cl, heated in graphite.
128-38	9	300 600	2 14	$\text{ThOCO}_3 + 3\text{HCl} + \text{NaCl} + \text{NH}_4\text{Cl} \rightarrow \text{NaThCl}_5 + \text{CO}_2 + \text{NH}_3 + 2\text{H}_2\text{O}$	HCl solution evaporated to dryness prior to heating; gray color.

of a continuous process.

Up to this time, materials of a dubious oxide content have been employed producing a loosely packed fine particle size deposit. Such material was generally made from $\text{ThCl}_4 \cdot x\text{H}_2\text{O}$. Even though the chloride was previously dried at 200°F and later heated with excess NH_4Cl , the oxygen content was appreciable. Within practical limits, this can be overcome through a low voltage pre-electrolysis serving to break down oxygen bearing materials in preference to the chlorides.

Recently materials more carefully prepared and derived from the oxycarbonate, have shown more consistent uniformity, yielding ostensibly better results. Methods of producing the double chloride in situ through chlorination of the oxide are currently being investigated.

A secondary but important change in procedure has been the reduction in operating voltage. Formerly voltages of 5-6 were employed. This left a layer of sodium over the deposit exterior as well as patches throughout the deposit. This produced a deposit difficult to recover and made removal of thorium hydrates produced in the washing quite difficult. These are insoluble in basic media, and strong acid necessary to counter-act random sodium action with the solvent, also attacks the metal. The optimum operating voltage has been found to be just under the decomposition voltage of sodium chloride, approximately 3 volts. No evidence of sodium metal has been found in deposits so produced, unless they are deliberately run to exhaustion.

Presumably sodium so produced is derived directly from the NaThCl_5 . Probably the voltage values for deposition of sodium and thorium are quite close. The mechanism of the cell has not been definitively

ascertained, but probably is a simple oxidation-reduction. The most elementary mechanism would entail the following reaction types.

Table II lists a number of runs using different raw materials. Materials prepared from the ThOCO_3 have given more consistent results than those from the tetrachloride. Of some 20 runs on the tetrachloride produced, only run No. 97-57 showed the expected results.

Table III lists six runs made at different voltages. The effect of the lower voltage on recovery of the deposit and resultant yields and efficiency is clearly evident.

D. Recovery of Electrolytic Thorium

Thorium deposits as removed from the cell differ greatly in appearance dependent upon the electrolyte and the operating conditions. An impure bath produces a loosely held soft porous deposit consisting of a network of fine thorium particles in a heavy mass of salts. A pure bath yields a compact adherent deposit containing a network of coarse thorium particles in an essentially sodium chloride matrix. The latter has a uniform rough surfaced appearance while an impure deposit is smooth and striated.

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TABLE II
Electrolysis of NaThCl₅

Run No.	NaThCl ₅		T °C	E Volts	I Amps	t mins.	Amp. Hrs.	Yield %	Current Efficiency %	Remarks
	%	Type								
97-57	22	3	868	2.6-3.5	10-23	165	20	60	40	
			851	6.3	150	75	187			
97-67	18	4	865	2.6	10	45	7	54	37	
			855	3.8-4.2	50	180	150			
97-73	18	5	860	2.8	10	45	7	46	33	Porous deposit, carbide odor
			859	3.8-4.2	50	170	140			
97-75	18	6	860	2.8	10	30	5	60	48	2.9 V across cell
			850	4.0	50	150	125			
97-93	18	7	870	2.0	3-2.2	330	14	25	21	Some deposit lost on withdrawal
			856	4.5	50	150	120			
97-95	18	8	862	2.0	2	325	10	71	56	Coarse deposit 2.8 V across cell
			859	3.8	50	150	125			
97-97	18	9	860	2.0	2	555	18	63	57	Adherent very coarse deposit
			855	3.9-4.2	50	132	110			

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TABLE III

Voltage Effect-Electrolysis of NaThCl₅

Run No.	E Volts	A.Hrs.	Yield %	Current Efficiency %	Remarks
97-51	6.3-5.9	200	26	13	Very fine deposit - Na present
97-55	6.0-6.3	250	25	15	Heavy Na in deposit; very fine
97-65	7.2-6.4	187	9	5	Na entrapped in deposit - fine
97-75	4.0-3.9	125	60	48	
97-95	3.8	125	71	56	Light Na evolution-end run
97-97	3.9-4.2	110	63	57	Very coherent coarse deposit

A coarse deposit is obviously much easier to recover. Salts are washed away with a minimum of hydrate precipitate formation. An impure deposit however produces copious quantities of thorium hydrates due to hydrolysis of occluded ThCl_4 and hydrolysis of the very fine metal itself. This is further aggravated by inclusions of sodium metal. It is also suspected that ThO_2 is included in deposits from baths with high oxide or oxychloride contents.

Cathode deposits are first crushed in a jaw crusher to +10 -20 mesh. This material is then placed in a 1000 ml separatory funnel. A continuous flow of cold water is fed through the bottom with an overflow at the top. A fractionating three-compartment catch basin collects any fines which overflow. Such a device effectively removes all salts together with most of the fines and oxide particles. The residual metal is then treated with 10-15% HCl , thoroughly water washed and dried at 50°C . A photograph of the washing unit is shown in Figure 1.

Various other recovery procedures have been tried, but with lesser degrees of success. These have included HNO_3 , $\text{HNO}_3 + \text{Na}_2\text{SiF}_6$, HCl , etc. The fluosilicate methods successfully etch off oxide coatings or hydrate deposits, but produce violent reactions even in minute concentrations. The nitric acid treatments were not particularly successful at any concentration.

A tabulation of some washing procedures tried and their effects on hardness of arc melted specimens is given in Table IV.

A typical chloride cathode deposit is pictured in Figure 2.

E. Evaluation of Electrolytic Thorium

All runs have been evaluated by arc melting a 30-50 gram pressed

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Fig. 1 Thorium Metal Recovery Bench

Fig. 2 Typical Electrolytic Thorium Deposit
Produced from NaThCl_5

TABLE IV
Thorium Recovery

<u>Run No.</u>	<u>Procedure</u>	<u>R_H</u>
97-79	Cold H ₂ O 10% HCl	B-72 B-57
97-81-83	Cold H ₂ O 10% HNO ₃ 10% HCl	B-94 B-89 B-76
97-73	Screening +200M -200M + 325M	B-40 B-41
97-67	Screening +325M -325M	B-52 B-95

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pellet and measuring its hardness. Most metal produced has been successfully hot or cold rolled. Values range from Rockwell B 24 to B 100 depending on free ThO_2 or dissolved carbon remaining in the powder. An average value for material prepared from a reasonably pure NaThCl_5 seems to be around Rockwell B 35-40. (Brinell 71-75) Values for the runs reported are given in Table V.

Softness in thorium is not necessarily a measure of ductility. Some pellets of B 30 hardness did not cold roll without cracking. This is presumably due to free ThO_2 present which is almost insoluble in thorium metal. Such inclusions create weak bonding areas and under stress, these result in fractures.

Some chloride produced thorium was induction melted in high vacuum using berylia crucibles as containers. This metal was not as soft as arc melted material, but was successfully rolled employing a canning technique. The melted ingot is sealed in a steel container and successively heated and rolled. A temperature of 750-800°C was used.

In this manner a strip .160" x 7/8" x 2-3/8", Rockwell B 56 was produced. This in turn cold rolled to a strip .042" x 15/16" x 7" long. Another sample .340" thick x 1-5/8" in diameter was hot rolled to a strip .060" x 4-1/4" x 3-1/2". Cold rolling was not attempted on this material.

Other standard rolling data is given in Table VI.

Electrolytic thorium powder may be cold pressed to very near theoretical density. At about 70,000 psi, 91% of the theoretical density is obtained. This is suggestive of considerable promise in the application of powder metallurgical techniques to this material.

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TABLE V

Rockwell Hardness - Electrolytic Thorium

<u>Run No.</u>	<u>R_H</u>	<u>Remarks</u>
97-51	B-27	
97-55	B-94	High oxide NaThCl ₅
97-57	B-50	
97-65	>B-100	High oxide NaThCl ₅
97-67	B-52	Fines B-95 (<-325M)
97-73	B-41	+200M B-40
97-75	B-52	Free C present
97-93	B-82	Moisture in NaThCl ₅
97-95	B-50	
97-97	B-40	

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TABLE VI

Rolling of Electrolytic Thorium

Sample 97-15

Thickness Ins.	Percent Reduction	Hardness RB	Remarks
.275	---	---	1-5/8" diameter All cold rolled
.160	24	---	
.0095	96.5	---	
.007	97.5	---	
.0035	99	---	1-3/16" w x 9" l
.0025	99.5	---	

Sample 97-27-1

.260	----	30	Slight edge cracking More edge cracking Heated 600°C - hot rolled. Slight edge cracking.
.220	15.5	55	
.208	20	55	
.182	30	56	
.156	40	57	
.130	50	67	
.104	60	64	
.078	70	68	
.052	80	69	
.040	84.5	71	
			Some cracking

Sample 97-27-2

.235	---	38.5	Slight edge cracking Slight edge cracking Edge cracking stopped Quite ductile strip
.212	10	52	
.189	20	54	
.167	30	55	
.135	40	59	
.117	50	63	
.093	60	64	
.070	70	65	
.047	80	66	
.024	90	69	
.003	98.7	---	

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Thorium sinters at relatively low temperatures, as low as 800°C, so near 100% density material should be readily obtainable. A plot of some cold pressing data is shown in Figure 3.

F. Decomposition Potential Determination

Decomposition potential measurements have been obtained on NaThCl_5 and KThF_6 by employing the small 100 g cell. This cell is equipped with a constant voltage controller and recorder. The unit maintains a constant voltage at a given setting regardless of bath resistance changes. A series of voltage settings are made and corresponding currents obtained. These are then plotted as current density (cathodic) vs. voltage, and extrapolated to zero current along the straight line portion of the curve. These data were taken from 800 to 1100°C so that the variation of decomposition potential with temperature could be obtained.

Plots of data for the fluoride are shown in Figures 4 to 6 and for the chloride in Figures 7 to 10. Variations of these values with temperature are plotted in Figures 11 and 12. In Figures 4 to 6, the decomposition potential of NaCl is also evident.

G. Conclusion

It has been shown in this phase of the work that ductile thorium metal can be produced by the electrolysis of NaThCl_5 in NaCl . The principal factors affecting the purity and crystal size of such cathode deposits are purity of the starting materials and cell voltage.

The best cell feed has so far been produced from ThOCO_3 by reaction with NaCl and NH_4Cl . Pre-treatment with concentrated HCl is indicated to be of value. Material made from ThCl_4 hydrate is poor

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Fig. 4 Decomposition Potential of KThF₅ T = 750°C

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Fig. 5 Decomposition Potential of KThF₆ T = 850°C

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Fig. 6 Decomposition Potential of KThF₅ T = 975°C

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Fig. 7 Decomposition Potential of NaThCl₅ T = 820°C

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Fig. 8 Decomposition Potential of NaThCl₅ T = 860°C

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Fig. 9 Decomposition Potential of NaThCl₅ T = 975°C

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Fig. 10 Decomposition Potential of NaThCl₅ T = 1130°C

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Fig. 11 Variation of Decomposition Potential with Temperature

KThF₅ 20%

NaCl 80%

$a = 2.27 \times 10^{-3} \text{ V/}^\circ\text{C}$

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Fig. 12 Variation of Decomposition Potential with Temperature

NaThCl₅ 20%

NaCl 80%

$a = 2.25 \times 10^{-3} \text{ V/}^\circ\text{C}$

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due to incomplete removal of oxygen and water of hydration.

The optimum cell voltage is indicated to be in the region of 2.5-3.0 volts. This is borne out by the proximity of the decomposition voltage of NaThCl_5 to that of NaCl , and also by the relative instability of the double chloride, NaThCl_5 . At high voltages, excessive sodium production results.

Other operating conditions such as thorium concentration in the electrolyte, current density and temperature have been previously well defined.

When good cathode deposits are obtained, little difficulty is encountered in recovering the metal. Coarse crystalline material is easily freed of entrapped salts through a crushing operation and continuous water wash. A cold 10% HCl wash has been shown to be beneficial. Fluosilicate and nitric acid washes have been shown to be unsatisfactory.

Metal with low carbon content and a minimum of ThO_2 contaminant yields hardnesses in the Rockwell B 30 hardness range and is easily rolled and fabricated.

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