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UNITED STATES ATOMIC ENERGY COMMISSION

TID-5246

INVESTIGATIONS FOR THE PRODUCTION
OF THORIUM METAL

Final Report — May 1, 1952 to April 30, 1954

By

B. C. Raynes
J. C. Bleiweiss
M. E. Sibert
M. A. Steinberg

November 1, 1954

Horizons Incorporated
Cleveland, Ohio

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AEC RESEARCH AND DEVELOPMENT REPORT

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SUMMARY

A research program has been carried out to develop a new electrolytic process for the preparation of pure thorium metal. Aqueous and organic methods were ruled out by virtue of the oxyphilic properties of thorium and its ions, as evidenced by prior work. Therefore the program was devoted to applications of fused salt electrolysis for thorium metal preparation.

During the course of this investigation, two practical methods were developed for the preparation of thorium by fused salt electrolytic means. One was a modification of a previously reported method, and the other a new development.

The former method was the electrolysis of KThF_6 in sodium chloride. This double fluoride had previously been used in mixtures of sodium chloride and potassium chloride. The simpler electrolyte behaved as well, or better, than the eutectic mixture previously used. However, this process has the disadvantage of limited life of the electrolyte. The refractory fluorides accumulate in the melt, since only chlorine gas and thorium metal are produced in the process. These refractory fluorides serve to raise the melting point of the bath and to decrease the electrical conductivity of the melt to a point where further electrolysis is impractical after three to four cathode withdrawals.

The new process for the electrolytic production of thorium metal developed in the laboratories of Horizons Incorporated is based upon an all-chloride electrolytic system. In this system, thorium chloride, ThCl_4 , dissolved in sodium chloride, is employed in a process which

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produces thorium metal at the cathode, chlorine gas at the anode, and has, therefore, the ability to operate indefinitely.

For both processes, electrolytic cells of special construction were used to provide both an inert cell atmosphere and also corrosion resistance to the reactants and to the product. Such cells employ all graphite internal construction wherever possible, to eliminate any corrosion problem

Thorium chloride can be prepared by wet chemical procedures from thorium nitrate or from thorium oxycarbonate by treating an HCl solution of these salts with ammonium chloride to produce ammonium thorium chloride. This is followed first, by evaporation and drying, and then by sublimation of the ammonium chloride in the presence of sodium chloride to produce the all-chloride source electrolyte. The purity and physical properties of the product thorium metal are largely dependent upon the purity of the thorium chloride, particularly with respect to oxide and moisture content.

High purity thorium metal was repetitively produced from both source electrolytes. The thorium could be readily arc melted, rolled, drawn, and swaged. Thorium metal with an as-cast hardness of Rockwell B 5 (Vickers 78) has been produced. Complete data on both processes are given in this report. Included also is the design of the laboratory cell and an intermediate size cell used in an expansion of the all-chloride process to a larger scale. Operational data, preparation of source electrolytes, physical data on the melts, and procedures for recovery and evaluation of the thorium metal produced are also included. This report also includes a literature summary of thorium metal preparation and a summary of the properties of some compounds of the metal.

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INVESTIGATIONS FOR THE PRODUCTION OF THORIUM METAL

I. INTRODUCTION

This investigation was undertaken to develop a new process for the preparation of high purity thorium metal. In order to be commercially useful, such a process must be economically competitive with existing methods, must produce a high purity product metal, and should preferably be a continuous process.

A survey of the literature of thorium chemistry and of the disclosed methods of preparation of the metal indicates that electrolytic methods appear to offer the most promise for meeting these requirements. Thorium forms a number of ionizable compounds which are potential source electrolytes. There has been relatively little work done on the electrochemical preparation of thorium, whereas chemical and thermal methods have received considerable attention. Thermal reduction methods do not readily lend themselves to continuous processing and they are further limited by the relatively high costs of metal reductants (i.e., high purity calcium, magnesium, etc.).

Electrochemical methods offer the prospects of utilization of readily available or readily processed economical materials, continuous operation, and a product of controlled high purity.

In consideration of electrochemical methods alone, the field was further narrowed to fused salt electrolysis. As borne out by the literature, the prospects of producing thorium from aqueous or other oxygen bearing media are extremely remote. The metal is strongly electropositive and possesses a high affinity for oxygen and nitrogen; it will oxidize in air even at room temperature. The

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use of a fused salt under a controlled inert atmosphere alleviates all of these difficulties.

Thus, the basic problem toward which this program was directed was the development of a suitable melt which could be economically electrolyzed to produce thorium metal, along with determination of the requisite operating conditions to accomplish this in a straightforward efficient manner.

The first portion of the work was devoted to a small scale investigation of the electrolysis of potassium thorium fluoride under a variety of conditions. High purity thorium was prepared in this manner, but the process is not a continuous one due to the gradual buildup of by-product refractory fluorides in the melt (NaF, KF, etc., dependent upon the particular melt employed).

Thus, the bulk of the research effort has been concerned with an all-chloride system employing thorium chloride as the basic source electrolyte. The ThCl_4 has been used in the form of an anhydrous stabilized material in molten sodium chloride. This material was further diluted with NaCl and subjected to electrolysis. This process has been extensively studied in cells capable of holding 5 and 50 lbs. of salt charge. High purity ductile thorium metal has been reproducibly obtained in both scales of operation. Operational procedures have been completely established, and the process is now believed ready for large scale development.

A considerable portion of the research effort has been devoted to preparation of source electrolyte materials, both chlorides and

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fluorides. The principle requirements in such procedures are that the product be free of moisture, oxide, carbonate, nitrates, and certain metallic and non-metallic impurities. The latter are largely removed through use of high purity starting materials, generally $\text{Th}(\text{NO}_3)_4$, ThOCO_3 , or ThO_2 . Oxide and moisture are removed by chemical and drying techniques.

The KThF_6 has generally been prepared from $\text{Th}(\text{NO}_3)_4$ by a simple precipitation from aqueous solution by KF , followed by washing and drying.

The bulk of this phase of the effort has been devoted to the chloride preparation. An HCl solution of ThOCO_3 was generally treated with NH_4Cl and NaCl and evaporated to dryness producing $(\text{NH}_4\text{Cl})_2 \cdot \text{ThCl}_4$. The NH_4Cl was then sublimed to yield the anhydrous ThCl_4 in NaCl .

Some work was carried out on preparation and electrolysis of other salts, but these gave generally inferior results. Such salts included NaThF_6 , KThCl_6 and ThOCl_2 .

A concurrent and important portion of the effort concerned recovery and evaluation of the thorium metal produced. The thorium is cathodically deposited in all cases as a coarsely crystalline powder interspersed with residual salts. Thus, a recovery procedure is necessary to remove all occluded salts without damage to the metal powder.

Aqueous procedures have been successfully applied to this problem in a simple but effective manner. The principle factors govern-

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ing success of the method are continuous washing of the powder, and specific final treatment to remove any hydrolytic products.

The metal powder obtained has been evaluated relative to hardness, ductility, density, workability, and chemical purity. The metal is compacted and are melted to ingot form. It may be cold-compacted to 97% of theoretical density. Samples have been fabricated to sheet, wire, bar, etc. Metallographic data, chemical and spectrographic analyses have been assembled.

A survey of applicable literature and a summary of all phases of the work accomplished during this contract period are given in the following section.

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II. THORIUM AND ITS COMPOUNDS

A. Thorium Metal

1. Properties

Thorium is generally considered as the first member of the actinide series, but it also bears a close resemblance to Ti, Zr, and Hf of Group IV, as well as to tetravalent cerium. It is predominantly tetravalent and in general displays few characteristics of the rare earth series.

Thorium is the most metallic of the + 4 metals. Its hydroxide is distinctly basic unlike those of Ti, Zr, and Hf; this follows a normal trend to increasing basicity going down a sub-group of the periodic table, if thorium is considered with the other + 4 metals. Its hydroxide reacts to give a variety of salts. The salts readily hydrolyze to give thoryl compounds such as ThOCO_3 and ThOSO_4 . Its salts can, however, be recrystallized from aqueous solution unchanged, using moderately strong acid.

The metal has a density of 11.7 g/cc. (calculated) and melts at $1690 \pm 10^\circ\text{C}$. It is very electropositive and falls between Be and Mg in the Emf series. The pure metal reacts readily with HCl, HF and H_2SO_4 , but is only slightly affected by HNO_3 .

Thorium metal is a naturally radioactive substance. Six natural isotopes are known, Th^{227} , Th^{228} , Th^{230} , Th^{231} , Th^{232} , and Th^{234} . Th^{232} , the normal form, has the longest

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half life of all members of the Th decay series, 1.34×10^{10} years. The thorium series is illustrated in Figure 1.

Note: Half life given below each series number.
y = years; d = days; m = minutes; s = seconds.
Figures below radiation are Energies in Mev.

The Thorium Series

Figure 1

The naturally occurring isotope found in monazite, Th^{232} , decays by an emission of a 3.98 Mev magnitude. This is comparable both in half life and radiation to U^{238} . About 24% of the α radiation is accompanied by conversion electrons of a 55-kev gamma ray. The Th^{232} decays to Ra^{228} with a half life of 6.7 years. This Ra isotope has a weak β activity (0.053 Mev) going to Ac^{228} . Ac^{228} is strongly β active (1.55 mev) going to Th^{232} (Radiothorium). Radiothorium decays by successive

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emission to Pb^{212} through a series of short-lived isotopes, all strong α emitters. The Pb^{212} goes to Bi^{212} by β emission followed by a branching to Po^{212} and Tl^{208} . This latter activity is 65% β and 35% α . These in turn decay to the stable Pb^{208} .

Throughout the series, the energy of radiation is quite comparable to the uranium series. However, the first Th decay product has a half life of 6.7 years while the Th^{234} from U has only 24.1 days, and the daughter, Pa^{234} is a strong β -active material. In both the U and Th series, the half life of the heavy isotope is greater than the geological age of the earth.

Thus, there is little hazard associated with recently prepared Th^{232} . If the isotopic composition of a material is unknown or if material has been in storage over a period of time, precautions are necessary for protection against the β and γ activity. The α activity is hazardous only in close proximity to the human body.

Thorium, in the pure state, is a silvery-white metal changing rapidly to gray in air. Physical and chemical constants for the metal are shown in Table I (as).

The crystal structure is face-centered-cubic, and until recently no allotropic modifications have been observed. Recent studies at Iowa State College indicate that a transformation to body-centered-cubic structure occurs between 1400° and $1500^\circ C$. The lattice constant observed at 1400° on the FCC

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structure was 5.18 Å. The BCC at 1140°C had a lattice constant of 4.11 Å (26). Evidence of an allotropic modification at high temperature has also been observed by McCaldin and Duwez (36).

TABLE I

PHYSICAL AND CHEMICAL CONSTANTS OF THORIUM

Density, g/cu.cm.	
Theoretical	11.71
Arc-melted iodide	11.66
Melting point, °C	1690 ± 10
Boiling point, °C	>3000
Heat of vaporization, kcal/mole	145 - 177
Specific heat, cal./(mole)(°C.)	
99.3°C.	6.59
198.7°C.	6.61
Entropy, cal./(mole)(°C.)	
25°C	13.6 ± 0.8
Coefficient of thermal expansion, °C x 10 ⁶	
30° to 100°C.	11.5
30° to 500°C.	11.9
30° to 1000°C.	12.5
Thermal conductivity, cal./(sec.)(cm.)(°C.)	
100°C	0.090
650°C.	0.108
Electrical resistivity, ohm-cm.	
20°C.	18 x 10 ⁻⁶
Thorium is superconducting below 1.70°K.	
Crystallography	
Lattice constant a ₀ , Å.	
26.2°C.	5.0871 ± 0.0002
Atomic diameter, Kx	3.59
Coordination number	12
Structure	FCC

Thorium is comparable to mild steel in machinability. It can be rolled, extruded, forged, swaged, and drawn. It forms many alloys with the following elements: Al, Ag, Au, B, Be, Bi, Co, Cu, Fe, Pb, Pt, Ni, Mo, Na, Hg, Si, Se, Ta, W, Zn, etc. Simple eutectics are formed with uranium and with chromium.

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2. Preparation

Thorium metal has been prepared by a variety of methods. These fall into four general categories:

1. Thermal reduction of halides or double halides.
2. Thermal decomposition of halides.
3. Thermal reduction of the oxide.
4. Electrolytic methods.

The largest variety of recorded attempts to prepare the metal is found in the field of thermal reductions. The first such work was that of Berzelius (10) who reduced ThCl_4 with sodium or potassium. Many other investigators followed with modifications of this reaction (31, 32, 41, 49). Some used the simple chloride, and others the double chloride, KThCl_5 . Chauvenet (13) improved on the method by using a hydrogen atmosphere. Marden (32) reduced KThF_5 with Al in an electric furnace under vacuum or an inert atmosphere. Lautie (30) reduced NaThCl_5 with potassium vapor produced from KCl and CaC_2 . Westinghouse Electric Ltd. (50) has a patented process for a calcium reduction of ThCl_4 (70%) in ThOCl_2 (30%).

The thermal decomposition process is exemplified by the Van Arkel hot wire method (4) whereby thorium tetraiodide is broken down on a hot refractory metal filament in a sealed bulb. It has been claimed that this method operates at lower temperature (800°C) producing ThI_3 . ThI_3 disproportionates in water to yield Th and ThI_4 .

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A number of investigators have tried to reduce ThO_2 with various reductants, including magnesium (51), silicon (22), aluminum and carbon (36), and calcium (23, 29). Of these, the calcium method has been the most successful. A mixture of ThO_2 , CaCl_2 and Ca are reacted under argon at 1400°C . In a similar manner, Cachimaille (12) used BaCl_2 and Na. Von Wartenburg et al, (47) tried a reduction of the ThO_2 at 2500°C . under pressure of $\text{H}_2 + \text{N}_2$. Schlecht and Jahrstofer (45) used a carbon reduction under hydrogen at $800-1000^\circ\text{C}$.

The electrolysis of aqueous solutions to yield thorium metal has not been successful. Marden et al (35) have patented a method for preparation of thorium by electrolysis of $\text{Th}(\text{OH})_4$ in HBF_4 , but the claims are doubtful. Piontelli and Builotto (43) claimed electrolytic thorium deposits from a solution of a thorium salt in HSO_3-NH_3 . Chester (16) claimed thin plates from acid and alkaline plating baths.

In the organic field, Atanasin and Babor (8) tried to electrolyze thorium salt solutions in $\text{C}_2\text{H}_5\text{OH}$, CH_3OH , $\text{C}_6\text{H}_5\text{N}$ and other alcohols, but obtained only organic compounds. Koizumi (28) claimed deposition of thorium coatings from complex thorium salts of organic acids. Cachimaille electrolyzed thorium lactate salts and other similar organics (11). Cotelli and Haissinsky (17) used $\text{Th}(\text{NO}_3)_4$ in $\text{C}_2\text{H}_5\text{OH}$ with 15-20% Me_2CO_3 and obtained only ThO_2 . Distillation of $\text{Th}(\text{CH}_3\text{COCHCHCOCH}_3)_4$ and Na metal in a hot tube gave the carbide or high carbon metal.

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Probably the most promising method of thorium production as evidenced from the literature is fused salt electrolysis. Various electrolytic experiments have offered promise for the past 50 years, but little sustained investigation has been done, due to lack of demand for the metal, until recently.

Moissan and Honigschmidt (32) electrolyzed ThCl_4 in $\text{KCl}=\text{NaCl}$ in 1904. They obtained a high oxide and high carbon material due to lack of a protective atmosphere, and the use of a carbon cathode. Driggs and Lilliendahl (19) and Marden (34) used KThF_6 in $\text{NaCl}=\text{KCl}$ with molybdenum cathodes, obtaining much better results. They did report difficulty in recovering the thorium from the deposit due to hydrolysis of residual thorium salt to ThO_2 .

One other method of interest is that of Marden (33) whereby NH_4ThCl_5 was reacted with Al metal to give an alloy. Then the Al was either distilled out or dissolved out with HNO_3 .

B. Thorium Compounds

This survey is concerned only with such compounds as might be useful as electrolytes or as source materials for preparation of such electrolytes. A desirable electrolyte must be of an ionic nature, have a reasonable melting point or form a reasonably low temperature eutectic, be stable at elevated temperature, and exist in the anhydrous state.

1. Thorium Oxide

Thorium forms only one well-established, stable oxide, the dioxide, which is distinctly basic in character. It melts at

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about 4000°C. It is derived from the metal by air oxidation or thru use of oxidizing agents. The hydroxide $\text{Th}(\text{OH})_4$ calcines to ThO_2 (21, 24). Most salts and thorium organics also calcine to the oxide (25). It may also be prepared by ignition of the hydroxide formed by the action of NaNO_2 , NH_4OH , and the like, on soluble thorium salts.

Thorium oxide is reduced with difficulty. It is reduced with W and H_2 at 2000°C (48). Action with carbon forms ThC_2 at 1600°C (44). Alkali metals are ineffective reductants. Calcium and magnesium will reduce the oxide at high temperatures.

Chlorination is accomplished with CCl_4 , $\text{CO} + \text{Cl}_2$, COCl_2 , PCl_5 , $\text{S} + \text{Cl}_2$, etc. to give ThCl_4 . Other halogenations behave similarly.

ThO_2 is substantially inert to acid action. It is slowly soluble in H_2SO_4 . It may be fused with NaHSO_4 . Thoria is somewhat hygroscopic.

Peroxides of thorium have been reported. When H_2O_2 is added to a thorium salt solution, a precipitate forms which has been identified as Th_2O_7 . It is also formed by the action of H_2O_2 or NaClO_2 on $\text{Th}(\text{OH})_4$. It is insoluble in water and dilute acids, but concentrated mineral acids readily dissolve it. Recent work has demonstrated that these peroxides are a function of the particular system involved; e.g., from a sulfuric acid solution, $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$ was identified.

The hydroxide is insoluble in water and other alkalies, but is readily acid soluble. It reacts with HF , H_2MoO_7 , and

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$(\text{COOH})_2$ to give insoluble salts. The precipitation of $\text{Th}(\text{OH})_4$ in thorium salt solutions may be avoided by the addition of polyalcohols ⁽⁴²⁾. $\text{Th}(\text{OH})_4$ is formed anodically in the electrolysis of $\text{Th}(\text{NO}_3)_4$ solution.

2. Thorium Fluoride

The tetrafluoride is formed by the action of F_2 or HF on the metal, HF or F_2 with other halides ⁽⁵²⁾ or the hydride, or by the fluorination of the carbide. The octahydrate is prepared by an HF treatment of $\text{Th}(\text{OH})_4$ ⁽⁵³⁾ in solution. This is readily dried to the tetrahydrate, and at 100°C , it goes to $\text{ThF}_4 \cdot 2\text{H}_2\text{O}$. At 250°C , $\text{Th}(\text{OH})\text{F}_3 \cdot \text{H}_2\text{O}$ results, and at red heat ThOF_2 forms. This is decomposed with steam at 900°C or by H_2SO_4 or alkali hydroxides to ThO_2 .

A number of double fluoride salts of thorium exist. With alkali metals, anhydrous salts form with alkali to thorium ratios of 1:6, 1:2, 1:1, 2:1, 4:1, and 5:1, although all of these have not been prepared for all alkali metals. ⁽³⁾

In the case of alkaline earth metals, the ratio is generally 1:1, other ratios are known in both cases as hydrates. Such salts are usually prepared by fusion of the component salts, acid fluoride action on ThO_2 or ThCl_4 , or reaction of alkali fluorides with soluble thorium salts.

The phase relationships in the system $\text{KF}-\text{ThF}_4$ have been determined by Dergunov and Bergman ⁽¹⁸⁾ up to 80% ThF_4 . This diagram is shown in Fig. 2. Four eutectics were found up to

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Fig. 2 - The System KF-ThF₄

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80% ThF_4 : 664°C. at 17 mol % ThF_4 , 750°C. at 33%, 878°C. at 51% and 954°C. at 80% ThF_4 . Three compounds were noted, K_3ThF_7 at 870°C., KThF_6 at 906°C., and $\text{KF} \cdot 3\text{ThF}_4$ at 960°C. These data do not correspond to Seaborg's statement above, regarding alkali to thorium ratios, nor does it account for K_2ThF_6 commonly reported in the literature.

No lower fluorides of thorium are known. An attempt to prepare ThF_3 from ThF_4 and the metal was not successful (3).

3. Thorium Chlorides

The tetrachloride is formed by chlorination of the metal, the carbide or the hydride. The oxide may be chlorinated with $\text{Cl}_2 + \text{S}_2\text{Cl}_2$, CCl_4 , COCl_2 , or PCl_5 (5, 6). If moisture or oxygen is present, ThOCl_2 forms preferentially. Physical properties of ThCl_4 are shown in Table II. The vapor pressure-temperature curve for ThCl_4 (20, 48) is shown in Fig. 3. The vapor is dissociated somewhat above 1000°C. A number of hydrates are known. It forms salts in water, ammonia, alcohol and other systems.

A large number of alkali double chlorides are known. The type M_2ThCl_6 forms with all alkali metals, MThCl_5 for Li and NH_4 , and M_4ThCl_8 with Rb and Cs. A number of hydrated double salts have been prepared from aqueous solution.

Berzleius (10) originally prepared KThCl_5 by evaporation and ignition in HCl atmosphere of a solution of ThCl_4 and KCl. Nilson (41) later showed that this preparation was probably ThOCl_2 .

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TABLE II
PHYSICAL PROPERTIES OF THORIUM CHLORIDE (ThCl_4)

Atomic Weight: 373.95

Physical Form: Tetragonal, prismatic crystals

Density: 4.59 g./cc (solid at 25°C)
3.32 ± 0.03 g./cc (Liquid at 770°C) (as)

Melting Point: 770 ± 2°C (19)

Vapor Pressure: See Fig. 3. $\log_{10} P(\text{mm}) = 14.30 - \frac{12,900}{T}$ (974-1043°K)

Boiling Point: 922°C (19) (45)

Specific Heat: For crystalline solid at 30°C; $c_p = 0.406 \text{ cal/gm.}^\circ\text{C}$ (ICT)

Electrical Conductivity: For molten pure salt (ICT) (43)

Temp °C	K (1/ohm cm)	ρ (ohm cm)
814	0.61	1.64
843	0.67	1.49
866	0.71	1.41
889	0.76	1.31
922	0.78	1.28

Heat of Formation: ($\Delta H_{f,298}$): (-285 to -335 K cal/mol)

Entropy: $S_{298} = 54 \text{ cal/}^\circ \text{ mole}$ (K and E)

Latent Heat of Vaporization: 36.5 K cal/mol. (19)

Heat of Solution: (14) (15)

ThCl_4	56.7 K cal/mol	
$\text{ThCl}_4 \cdot 2\text{H}_2\text{O}$	41.1	00 00
$\text{ThCl}_4 \cdot 4\text{H}_2\text{O}$	21.2	00 00
$\text{ThCl}_4 \cdot 7\text{H}_2\text{O}$	14.7	00 00
$\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$	11.4	00 00
ThOCl_2	28.2	00 00
$\text{Th}(\text{OH})\text{Cl}_3 \cdot \text{H}_2\text{O}$	47.6	00 00

Latent Heat of Sublimation: (ΔH_s) = 59.0 K cal/mole at 770°C (K and E)

ICT - International Critical Tables

K and E - Kubaschewski and Evans

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Fig. 3 - Vapor Pressure - Temperature
Curve for Thorium Chloride (ThCl₄)
(20, 46)

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Chauvenet (13) later prepared the double chloride in a pure form using dry fusion methods. He prepared compounds of the type M_2ThCl_6 with Li, Na, K, Rb and Cs; for Rb and Cs only the type M_4ThCl_6 was found, and for ammonium, only NH_4ThCl_5 was obtained. The latter was prepared by dehydration at $150^\circ C$ of $ThCl_4 \cdot 2NH_4Cl \cdot 10H_2O$. The resultant $ThCl_4 \cdot NH_4Cl$ was calcined further to yield anhydrous $ThCl_4$.

$ThOCl_2$ may be prepared from $ThCl_4 \cdot xH_2O$ or $Th(OH)_4$ by heating to $250^\circ C$ in a stream of HCl. $Th(OH)_2Cl_2 \cdot xH_2O$ is formed by hydration of $ThOCl_2$. Hydrated Li and Na double salts hydrolyze to $M(OH)_2Cl_2$ when dried at $200^\circ C$ in an HCl atmosphere.

$ThCl_4$ is readily water soluble giving an acid solution, and may be water recrystallized as a hydrate. At red heat, it readily oxidizes. It is reduced by Ca and K. Alkali chlorides form completely miscible solutions with it in the fused state.

4. Other Halides

$ThBr_4$ is prepared in a manner similar to the chloride. It likewise forms a variety of hydrates, and also an oxybromide, $ThOBr_2$, and a hydroxybromide, $Th(OH)Br_3$. It decomposes slowly in light (52) and is readily attacked by F_2 and Cl_2 (52). It is highly hygroscopic and readily hydrolyzes to the oxybromide. A few double salts are reported, among them being the potassium salt.

The tetraiodide results from the action of I_2 on the metal or from the reaction of HI with ThH_3 . Light and heat

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readily decompose the salt, and it readily hydrolyzes even as a solid. Oxyiodides and a series of hydrates are known. Mercury double salts have been reported.

Reduced iodides, ThI_3 and ThI_2 , have been prepared from ThI_4 with Th, but little is known of their nature. It is also claimed that ThI_3 can be prepared by dissociation of ThI_4 on a hot filament at 800°C (4).

5. Thorium Nitrate

The action of nitric acid on the hydroxide yields the nitrate as a hydrate. Drying over H_2SO_4 gives the tetrahydrate. Penta- and tetrahydrates are also common. The nitrate is very soluble in water, alcohol, and a number of organic solvents. Thorium nitrate forms double salts with a number of monovalent cations, as well as with Mg, Ni, Co, Mn, etc. Thorium nitrate begins to decompose to the oxide at about 200°C ; it is completely decomposed at 800°C . Anhydrous $\text{Th}(\text{NO}_3)_4$ has not been prepared. Solutions of the nitrate are acidic, so some hydrolysis apparently occurs. Electrolyses of $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ solutions are reported to yield thorium at the cathode and ThO_2 at the anode. The thorium nitrates are among the most soluble of thorium salts.

6. Thorium Carbonate

Basic thorium carbonate forms spontaneously from the action of atmospheric CO_2 on the hydroxide. Hydrated oxy-carbonates also form where sodium or ammonium carbonates act on thorium salt solutions. The ThOCO_3 is soluble in excess

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7. Thorium Sulfate

8. Thorium Carbides

9. Other Compounds

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III. THE RESEARCH PROGRAM

The first portion of the contract period was used to design and to construct a suitable electrolytic cell for fused salt electrolysis on the laboratory scale. Initial research was concerned with the use of thorium double fluorides as source electrolytes. This work was a modification of previously reported methods whereby $KThF_6$ was electrolyzed in various melts under generally poor conditions. After experience had been gained in this approach, the procedure was modified to an all chloride process with which the bulk of the effort has been concerned. A second and larger cell unit was utilized in this phase of the work in addition to the laboratory cell. Experimental work and equipment are completely described below.

A. The Laboratory Electrolytic Cell

The general requirements for the thorium cell were based upon experience with other refractory metals and knowledge of the general temperature range required for possible thorium salt baths. These requirements included:

1. Provision for inert atmosphere operation.
2. Operation at temperatures to 1000°C .
3. Materials of construction inert to thorium halides, common alkali halides, and halogen gases.
4. Provision for continuous operation.
5. Freedom from moisture and moisture-bearing materials.

The cell was built along the lines of previous refractory metal electrolytic cells used in the laboratories of Horizons

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Incorporated. All internal parts, as well as the crucible, are constructed of graphite. The outer shell is made from 14-inch steel pipe. An inner graphite liner is provided, separated from the steel by a layer of silica powder insulation. A graphite heating element is located within the graphite liner supported by the power leads at the side of the cell. These power connections are electrically insulated and vacuum sealed. The crucible rests inside the heating element on a graphite pedestal. The pedestal fits over a nickel post welded through the cell bottom forming the DC positive power connection. A removable, insulated, water-cooled head completes the assembly. Alternatively, a slide gate cooling chamber arrangement may be used in place of the head for continuous operation. A vacuum head is also provided for removal of moisture and other contaminants by hot evacuation. A cross section of the cell design is shown in Figure 4. This cell design was later modified and expanded to an intermediate scale. The laboratory cell takes a charge of 5 lbs. of salts and produces about 300-350 grams of thorium metal per cathode deposit.

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B. Preparation of Thorium from KThF₅

1. Preparation of KThF₅

KThF₅ was prepared from the hydrated nitrate by a simple precipitation procedure using KF. About 450 g. of thorium nitrate tetrahydrate were dissolved in 2.5 l. of water and precipitated with a solution of KF·2H₂O (320 g./500 ml.). The gelatinous precipitate was filtered and thoroughly water washed. It may either be vacuum-dried hot, or air-dried at a low temperature.

One lot of double fluoride, prepared directly from ThO₂, was fused with NH₄HF₂ and KF. The process is carried out under an argon atmosphere at 700-800°C, liberating NH₃ and H₂O. This may have yielded K₂ThF₆ instead of KThF₅. viz:

This material proved to be inferior to the material produced from the nitrate when used as a source electrolyte.

The precipitation process, equation 1, was carried out in polyethylene or rubber-lined vessels, while the fusion process, equation 2, was run in graphite crucibles. Near theoretical yields are obtained in both cases.

a. Decomposition Potential of KThF₅

One very desirable piece of information on a source electrolyte is its decomposition potential. For these measurements a small counterpart of the larger cell,

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capable of holding 100 gms was employed. Graphite cathodes were used instead of steel. The cell was equipped with a constant voltage controller and recorder arrangement to control the output from a 12 amp DC selenium rectifier at a constant selected voltage value.

A series of voltage-current readings was taken on a given melt at a given constant temperature. These values, plotted as current density vs. voltage, give a curve with a straight line portion, which, when extrapolated along a straight line to zero current, gives an approximate value for the decomposition voltage. A series of runs was made at different temperatures to obtain the E_D value as a function of temperature. Determinations were made using 20 and 25% by weight melts of $KThF_5$ in $NaCl$.

All of the curves obtained by this technique, using $KThF_5$, showed two distinct breaks, but later work with the chloride gave but a single break. These two breaks are probably due to incomplete conversion of the nitrate to $KThF_5$ and consequently residual ThO_2 formed at 800-1000°C which could account for the lower of the two apparent values. Experience indicates that thorium metal is not produced at values of 1-2 volts from $KThF_5$, so that this phenomenon is probably due to the presence of small amounts of oxide. It is also known that the inert atmosphere in the small cell is less pure than in the larger cells, which might

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account for the presence of oxide. A value of 2.8 volts was obtained at 850°C for a 20% melt and 2.7 volts for 25%, indicating that the concentration factor is small. A typical curve obtained is shown in Figure 5 and a plot of decomposition potential as a function of temperature is given in Figure 6. It should be noted that these determinations represent only an approximation of the decomposition potential, and are subject to error due to depolarizations, since no diaphragm was used in the experimental set-up.

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80% NaCl
20% KThF₅

Fig. 5 Typical Curve of Current Density as a Function of Voltage

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Fig. 6 - Temperature Variation vs. Decomposition Potential of $KThF_5$

$KThF_5$ 20%

$NaCl$ 80%

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

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2. Electrolysis of $KThF_6$

Nearly all of the electrolytic work was carried out using a melt of NaCl as a bath flux, since this material is readily obtainable in very pure form, can be made anhydrous, and is reasonable in cost. Because of its essentially anhydrous nature and also of its relatively high decomposition potential (ca. 3V at 800°C), it is a very satisfactory electrolytic bath constituent. Such a diluent is necessary to reduce the bath thorium concentration to a point where satisfactory cathodic crystal growth may be obtained at reasonably high current densities. It also serves to stabilize the $KThF_6$ at higher temperatures.

Normally a 10-20% by weight concentration of $KThF_6$ in NaCl was employed. The mixture is charged to a clean, degassed cell heated to 800-900°C and melted under a positive pressure of argon gas.

Initially a pre-electrolysis was carried out on the melt to remove residual moisture and other impurities. This was done using a graphite cathode at a voltage below the decomposition voltage of $KThF_6$. During such a procedure, several characteristic voltage rises occur spontaneously, presumably being indicative of removal of a given impurity species. Such a procedure is initiated at about 1 volt, carried to 2 volts and finally to about 2.8 volts where some thorium metal is plated out. This cathode is then removed hot and discarded. It was shown later in the program that such a procedure did

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not sufficiently benefit the quality of the metal produced to justify its use, and the baths were subjected to electrolysis immediately after melting.

The electrolysis proper is run at 800-850°C using a steel cathode of cylindrical or conical shape. The cathode is attached to a nickel shank which in turn is protected by a graphite sleeve for maximum resistance to anodic chlorine produced in the process. This chlorine can permeate throughout the bath and the cell atmosphere. Runs were made at 3-4 volts with 100-750 amp/dm² starting cathode current density. When the bath thorium content is essentially exhausted, a characteristic voltage rise occurs. If the run is continued beyond this voltage rise, sodium metal is produced. After completion of electrolysis, the cathode is raised from the melt and allowed to cool above the melt in the argon atmosphere, or isolated in a cooling chamber under a positive argon pressure. After cooling to room temperature, the cathode deposit is chipped off and recovered by an aqueous procedure as described later. Yields of metal up to 85% and current efficiencies of the order of 40-45% are normally obtained in this procedure. Table III gives specific operating data for a number of runs using the KThF₆-NaCl electrolyte.

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TABLE III
ELECTROLYSIS OF $KThF_6$

Run and Series No.	Th Conc %	T °C	Cell Voltage	c.d. Amps/dm ²	Amp hrs	Yield %	Current Eff. %	Hardness R_E	Remarks
(97-1(1)	8	850	3.4	375	225	58	22	81	2 amp hrs. pre-electrolysis
(97-5(2)	9	840	3.8	375	270	69	24	100	Na produced, ThC present
97-3(1)	8.5	800	3.2	375	263	68	21	(B88)	(5 amp hrs. pre-elect; Produced (sodium. Deposit in crucible (formed carbide
(97-7(1)	8.5	810	3.2	300	200	58	27	--	First run in a series of six.
(97-9(2)	ca. 7	810	3.0	300	263	58	18	--	
(97-11(3)	ca. 7	860	3.0	300	260	65	20	86	Deposit hydrolyzed before recovery
(97-13(4)	ca. 8	860	3.2	375	260	68	23	89	
(97-15(5)	ca. 15	855	3.2	375	450	39	15	87	
(97-17(6)	ca. 8	855	3.2	375	340	37	9	--	
97-25(1)	8.5	860	3.6	750	300	80	25	79	
97-27(1)	8.5	860	2.8	190	263	82	29	75	
97-29(1)	8.5	945	2.9	375	300	--	--	(B76)	(High temp run, heavy fuming, (poor deposit, formed carbide (in crucible
(97-117(1)	9	855	3.0	100-85	115	43	33	(B93)	(6 A. hrs pre-elect; $KThF_6$ (not washed or vacuum-dried.
(97-121(2)	ca. 9	840	3.7	220	180	89	43	79	5 A. hrs. pre-electrolysis
97-119(1)	9	850	3.6	220	112	33	26	96	(Lost 1/2 of deposit in melt, (3 A hrs pre-elect; some (carbide formed in bath.
(97-123(1)	8.5	845	3.7	225	186	87	44	82	
(97-125(2)	ca. 9	845	3.8	220	157	72	40	81	
97-127(1)	9	835	3.7	220	180	82	41	84	($KThF_6$ used in 97-117 washed (and vacuum-dried
(97-129(1)	10.5	850	3.6	220	205	71	39	78	
(97-131(2)	ca. 10	820-750	3.8	220	187	47	29	91	Deposit in bath formed thorium carbide.
97-133(1)	11.5	845	3.6	220	180	35	22	78	(NO_2 fumes; $KThF_6$ not free of (NO_3 . Deposit in bath.
97-137(1)	11.5	850	3.5	220	160	53	39	84	

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During this work it was shown that the purity of the starting KThF_6 was of prime importance. Material which was not adequately washed following precipitation gave a product metal which was harder by 15 points average (R_E) than thorium obtained from thoroughly washed KThF_6 . Material not washed well and not vacuum dried gave metal up to 45 points harder (R_B). Properly washed and vacuum dried KThF_6 generally yielded metal of about R_E 80 hardness (R_B 40).

There was no noticeable improvement either in hardness or in particle size of the metal as a result of a pre-electrolysis step. In fact, many runs without a pre-electrolysis gave higher current efficiencies.

The principle objection to the fluoride method is the fact that it cannot be run continuously. Some difficulty is encountered after 8-10 runs on a melt. Fluorides, of course, accumulate in the bath thereby decreasing its current carrying capacity. Carbon contamination is also encountered by corrosion of the crucible and cathode sleeves probably through intermediate formation of potassium carbides. For these reasons an extensive research program was not carried out on this system. The work was done primarily to gain general information about electrolytic thorium preparation.

A cursory survey of operating variables revealed little change in results of the electrolysis. Temperature variations from 760-860°C appeared to have essentially no effect on the process. From the standpoint of viscosity, temperatures of

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at least 800-850°C are preferred. There is a minimum loss of thorium as volatile material below 850°C.

Current density variation from 100-750 A/dm² produces some change in current efficiency. There is a tendency toward higher current efficiency and larger particle size at the lower current density values (less than 300 Amps/dm²).

Concentration of thorium in the melt did not affect the process appreciably within the limits studied. A concentration of 8-12% Th ion was satisfactory.

Experiments which were over-run producing sodium metal, always yielded inferior results due to carbide contamination. Such deposits frequently slipped off the cathode on withdrawal.

3. Recovery of Electrolytic Thorium

Cathodes are removed as porous salt-metal agglomerates in an approximately cylindrical form. A cathode from a KThF₃-NaCl electrolysis is shown in Figure 7. The mass of salt-metal mixture is chipped from the base steel cathode and crushed to minus 10-20 mesh. This material is then soaked in cold water through a series of leaching and decantation steps until most of the occluded salts are removed. A hot water leach is then employed followed by a dilute HCl treatment for removal of any hydrolysis products. The metal crystals are then filtered, acetone or alcohol-washed, and dried in a low temperature oven (30-40°C). This procedure was later modified through use of a continuous counter-flow cone washer

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made from a separatory funnel, water entering from the bottom and overflowing at the top. A trap was provided to catch any metal powder overflow. As-recovered thorium metal gramules produced by $KThF_6$ electrolysis are shown in Figure 8.

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Fig. 7 Typical thorium cathode deposit obtained by electrolysis of KThF_6 in NaCl (Run No. 97-1).

(1/3 actual size)

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Mag. 20X

Fig. 8 As-recovered thorium crystals from electrolysis
of KThF_6 in NaCl .

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4. Evaluation of Thorium from $KThF_6$

Electrolytic thorium samples were evaluated by arc melting 20-30 g. buttons for testing. The thorium metal powder was cold pressed in a steel die. Using 25 t.s.i., the powder may be cold pressed to 88% of theoretical density or 10.05 gms./c.c. These pressed pellets were melted by the cold-mold method using a water-cooled tungsten electrode with a water-cooled copper-hearth anode under $1/4$ atm. of argon.

Hardness values ranged from Rockwell B 30-90. The hardness is largely a function of the impurities. The interstitial impurities analyzed about 0.03 - 0.04% oxygen, 0.002 - 0.003% nitrogen, and 0.01 - 0.3% carbon.

A thorium pellet of hardness R_p 18 was cold pressed from 0.410 inch to a 48% reduction and then cold rolled to 0.092 inch (hardness after rolling was R_p 62). This was further cold rolled to a 0.0023 inch strip demonstrating the easy working of this product.

Thorium wire of 0.030 inch diameter, was prepared from a similar ingot. Figure 9 shows "as recovered" powder, a pressed pellet, an arc melted button, and wire and sheet products.

No chemical analyses were accomplished on thorium metal produced from the fluoride electrolysis.

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(reduced approx. 1/2 in reproduction)

Fig. 9 Electrolytic thorium powder, arc-melted ingot,
and cold-rolled wire and sheet.

(from electrolysis of KThF_6 in NaCl)

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C. Preparation of Thorium Chloride Source Electrolytes

Having once established that high purity, high quality thorium metal can be produced by fused salt electrolytic means, it was then axiomatic to consider methods by which a fused salt electrolytic process can be made a continuous operation. The by-product anode gas, even in the electrolysis of $KThF_6$, is chlorine. Obviously, if an all-chloride electrolytic bath can be made to produce high quality thorium metal, then continuous operation becomes immediately practical.

Therefore, a number of procedures and methods to prepare stable, anhydrous chloride salts of thorium were investigated or considered. These possible processes included chlorination with various chlorinating agents, chlorination in fused salts, and preparation from anhydrous solvents.

1. Chlorination with Sulfur Chlorides

Basic thorium carbonate, $ThOCO_3$, reacts with sulfur monochloride, in the liquid state, and in the presence of gaseous chlorine to produce thorium chloride in about a 70% yield. Despite obvious advantages of low temperature conversion with sulfur chlorides or oxysulfur chlorides, it was decided that these procedures would not be applicable to large scale production of pure thorium chloride.

2. Chlorination with Chlorine-Carbon

Thorium chloride was prepared in small amounts by standard high temperature chlorination techniques from thorium

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oxide briquetted with charcoal and reacted with chlorine gas. The thoria-carbon mixtures were chlorinated at temperatures as high as 1000°C . This procedure was not pursued extensively in this laboratory, but is being studied at the AEC Laboratories of Iowa State College, Ames, Iowa.

3. Chlorination in Fused Salts

Thoria and petroleum coke mixtures were chlorinated with gaseous chlorine in fused sodium chloride at about 900°C . Electrolyzable thorium chloride was made by this procedure and about 100 grams of thorium were electrolyzed and recovered. The metal obtained in these experiments was hard (about Rockwell B 100) and contaminated with carbon.

4. Thorium Chloride from Aqueous Solutions

Thorium chloride, ThCl_4 , cannot be directly recovered undecomposed from water solutions as the alkali metal fluorides can. Evaporation of a solution of the chloride yields a hydrated salt which on further heating yields partially hydrated salts and, finally, ThO_2 .

However, in the case of thorium, it is possible to obtain the anhydrous chloride by forming a hydrated ammonium chloride in water solution, dehydrating this compound, and finally, decomposing the double salt by subliming away the ammonium chloride component. In this respect, thorium chloride differs sharply from many other metal chlorides (Al, Be, Ta, Zr, etc.), where it is impossible to obtain the anhydrous chloride from aqueous solution by any known means.

Various methods for the preparation of anhydrous thorium chloride were investigated using hydrated thorium chloride,

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$\text{ThCl}_4 \cdot 3\text{H}_2\text{O}$, and thorium oxycarbonate, ThOCO_3 , as the source thorium materials. These methods, summarized in Table IV, indicated that anhydrous thorium chloride or sodium thorium chloride can be prepared by employing ammonium chloride to suppress hydrolysis during drying of the salt. The most satisfactory method was found to be the formation of ammonium thorium chloride $(\text{NH}_4\text{Cl})_2 \cdot \text{ThCl}_4 \cdot 4\text{H}_2\text{O}$ in a hydrochloric acid solution, and the subsequent drying of this salt.

In the method finally adopted, thorium oxycarbonate is dissolved in an excess of concentrated HCl to give a clear yellow solution. Two mols of NH_4Cl (minimum) are added to the solution per mol of contained thorium. Ammonium thorium chloride hydrate is crystallized from solution by cooling and saturation with HCl , or it can be obtained by partial evaporation of water and HCl from the solution. The resultant complex, $(\text{NH}_4\text{Cl})_2 \cdot \text{ThCl}_4 \cdot \text{XH}_2\text{O}$, can be dehydrated by evaporation at $130\text{--}150^\circ\text{C}$, followed by thorough drying at about 250°C . The dried ammonium thorium chloride is then mixed with sodium chloride in proportions to form NaThCl_6 or to produce a $\text{ThCl}_4\text{--NaCl}$ mixture with a given thorium content. The ammonium chloride is sublimed off at temperatures above 500°C in an inert atmosphere furnace to give an anhydrous chloride source electrolyte, free of ThO_2 and NH_4Cl .

A flow diagram of the wet preparation of $\text{ThCl}_4\text{--NaCl}$ is shown in Fig. 10. Table V. is a tabulation of analyses of

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TABLE IV

PRELIMINARY METHODS FOR PREPARATION OF THORIUM CHLORIDE CELL FEED MIXTURES

Run No.	Type No.	Temp °F	Time Hrs	Reaction	Remarks
69-109	1	600	4	$\text{ThCl}_4 \cdot 3\text{H}_2\text{O} + \text{NaCl} + 3\text{NH}_4\text{Cl} \longrightarrow$ $\text{NaThCl}_5 + 3\text{NH}_4\text{OH} + 3\text{HCl}$	ThCl_4 was dried prior to reaction.
69-124	2	600	16	Same as (1)	Heated in pyrex container.
69-126A	3	200	To dry- ness	" " "	Yellow-tinted product. Heated in graphite crucibles.
69-126B	4	600	16	" " "	White product. Heated in graphite.
69-127A	5	200	To dry- ness	" " "	Product contains much NH_4Cl .
69-128	6	600	16	$\text{ThOCO}_3 + 4\text{NH}_4\text{Cl} + \text{NaCl} \longrightarrow$ $\text{NaThCl}_5 + 4\text{NH}_3 + 2\text{H}_2\text{O} + \text{CO}_2$	
120-36	7	600	4	$\text{ThOCO}_3 + \text{NaCl} + 6\text{NH}_4\text{Cl} \longrightarrow$ $\text{NaThCl}_5 + \text{CO}_2 + 6\text{NH}_3 + 2\text{N}_2\text{O} + 2\text{HCl}$	Micropulverized before heating in graphite crucibles.
128-36	8	600	4	Same as (7)	Same as (7)
128-37	9	300 600	2 14	$\text{ThOCO}_3 + 3\text{HCl} + \text{NaCl} + \text{NH}_4\text{Cl} \longrightarrow$ $\text{NaThCl}_5 + \text{CO}_2 + \text{NH}_3 + 2\text{H}_2\text{O}$	HCl solution evaporated to dryness prior to heating in graphite crucibles. Gray color.
164-85	10	300 900	2 20	$\text{ThOCO}_3 + 10\text{HCl} + 3\text{NH}_4\text{Cl} + 2\text{NaCl} +$ Anhydrous HCl to saturation $\longrightarrow$ $(\text{NH}_4\text{Cl})_2 \cdot \text{ThCl}_4 \cdot x\text{H}_2\text{O} + \text{etc.}$	Heated in air. Top crust high in ThO_2 . Bottom was fused mass containing 90% ThCl_4 and 0.29% ThO_2 .
164-89	11	300 650	17 69	Same as (10)	Heated in air. Top crust, 5% of total, was high in ThO_2 . Remainder contained 85% ThCl_4 , 15% NH_4Cl , no ThO_2 .
164-94	12	300 650 1000	37 100 50	Same as (10)	Heat in air-argon atmosphere. Contained 1.8% ThO_2 .

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Figure 10. Flow Diagram for Wet Preparation of NaCl-ThCl₄ Cell Feed.

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TABLE V

SUMMARY OF ANALYSES CELL FEED

<u>NH₄Cl-ThCl₄</u>	<u>NaCl-ThCl₄</u>					Na	<u>Total</u>
		<u>Total</u>	<u>Cl</u>	<u>NH₄</u>	<u>Insol</u>	<u>based on Chloride Balance</u>	
	164-110	2.52	60.1	0	0	37.9	100.5
164-121A		38.2	46.6	14.3	0	0	99.1
	164-121B	27.5	53.0	.006	0	23.3	103.8
	164-128	25.9	52.5	0	*	23.8	102.2
164-135B		42.2	41.8	5.23	*	3.7	92.9
	164-135C	44.3	41.0	0	*	9.0	94.3
	164-138	34.8	--	--	*		
	164-140A	18.4	55.2	0	*	28.0	101.6
	164-140B	31.5	51.1	0	*	20.6	103.2
	164-142	27.5	50.5	0	*	21.8	99.8
164-145A		51.1	40.6	6.9	0	0	98.6
	164-145B	38.7	46.2	0	0	14.6	99.4
	164-147	18.0					
164-150A		51.5	40.7	7.5	0.7	0	99.8
	164-150B	26.9	50.0	0	0.6	22.0	99.0
	164-150C	33.2	46.4	0	9.3		
164-154A		34.0	47.6	8.2	0.5	7.0	96.8
	164-154B	26.6	50.5	0	2.6	23.0	100.4
	164-155A	28.7	51.3	0	0	21.8	101.8
	164-156A	27.6	51.3	0	*	22.2	101.1
	164-156B	16.4					
	164-158B	8.6	57.8	0	*	34.0	100.4
	164-158C	8.2	57.5	0	*	34.0	99.7
	164-159	25.7	52.0	0	0	23.5	101.2
	164-160	30.5	48.0	0.01	3.6	20.3	99.2
	164-161	35.8	44.8	0.8	0.9	14.1	95.6**
164-162A		52.3	40.3	7.2	0	0	99.8
	164-162B	40.9	43.0	0	2.0		
	164-164				2.0		

* Very slight turbidity.

** 0.1% Fe.

Blank spaces indicate that the analysis was not carried out.

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ThCl₄-NaCl cell feed preparations indicating the quality of material which can be produced by this method.

This thorium salt is electrolyzed in sodium chloride to yield high quality thorium metal. A number of chloride source electrolytes prepared by variations of this method were electrolyzed and are described below.

The all-chloride source electrolyte prepared as described above, or by modifications of that procedure, is the material with which the majority of the electrolytic work was done. This system, ThCl₄-NaCl, with the cathode product thorium and the anode product chlorine, is amenable to continuous operation and represents the goal of the investigation for the production of thorium metal.

a. Decomposition Potential of ThCl₄

The decomposition potential of anhydrous ThCl₄ in NaCl was determined in the manner as previously described for KThF₆ at a concentration of 17% by weight ThCl₄ and as a function of temperature from 820°C to 1130°C. A temperature coefficient of 2.25×10^{-3} volts/°C was obtained. Figure No. 11 shows a typical curve plotted as current density vs. voltage. The variation with temperature is given in Figure No. 12.

b. The System NaCl-ThCl₄

The phase diagram of the system NaCl-ThCl₄ was determined up to 36 weight per cent ThCl₄. Points were obtained by standard cooling curve methods. A nichrome

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Fig. 11 - Decomposition Potential of ThCl₄-NaCl

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Fig. 12 - Variation of Decomposition Potential with Temperature

ThCl₄ 18%
NaCl 82%
 $a = 2.25 \times 10^{-3} \text{ V/}^\circ\text{C}$

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heated furnace was employed, the nichrome being wound over an alundum coated stainless steel tube. Melts were made in vycor test tubes fitted with graphite caps. The unit was insulated with firebrick and contained in a large pyrex tube. Facilities for a stirrer, power leads, and a thermocouple, were provided. A diagram of the furnace is shown in Figure No. 13.

A series of melts was run to give the phase diagram of the system. The diagram as determined from 0-36 weight per cent ThCl_4 is shown in Figure No. 14.

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Fig. 13 - Furnace for Phase Studies

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Fig. 14 - Partial Phase Diagram ThCl₄-NaCl

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D. Preparation of Thorium Metal from Thorium Chloride Source

Electrolytes

1. Small Scale Laboratory Electrolytic Runs

The electrolytic work with the all-chloride system was carried out in the same equipment used with $KThF_6$, and later in large scale equipment. $NaCl$ was chosen as the solvent to present a simple bath composition and one which readily permitted a study of the effect of thorium ion concentration upon electrolysis. The phase diagram work and the experimental electrolytic work indicate that in the fused condition the bath is completely ionized, viz:

Following a number of exploratory runs to demonstrate that high quality thorium metal can be produced from a $ThCl_4$ - $NaCl$ system, a study of the factors affecting the electrolysis of this system was undertaken on the laboratory and on the intermediate scale. Since purity of starting materials is of fundamental importance, considerable experimentation went into the establishment of the procedure described immediately above to produce thorium chloride. Table No. V is a tabulation of analyses of thorium chloride-sodium chloride cell feed preparations indicating the quality of material which can be produced.

Table No. VI presents run summaries of small scale laboratory electrolytic runs made from questionable cell feed preparations, while Table No. VII presents run summaries of small scale laboratory electrolytic runs made from cell feed of good quality.

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TABLE VI

Electrolysis of ThCl_4 -NaCl. Salts of questionable quality from preliminary methods

Run No.	Thorium Salt No. *	Th Conc %	Temp °C	Volts DC	Amps DC	C.D. Amps dm^2	Amp Hrs	Metal Recov. gms %	Current Eff. %	Hardness R_E	Remarks
97-33	1	7	860	3.2	150	375	300	133 73	20	--	Heavy fuming due to NH_4Cl present.
97-37	1	6	880	3.2	150	375	375	47 35	6	--	Most of deposit fell into bath and formed carbide.
97-41	1	10	855	3.3	200	500	450	80 31	8	(R_B 98)	Made a lot of sodium.
97-43	1	10	860	3.2	200	500	350	95 36	13	(R_B 100)	Most of deposit fell into bath and formed carbide.
97-45	1	10		3.2	150	375	150	43 16	14	--	Made sodium metal.
97-47	1	7	845	3.2	150	375	185	-- --	--	--	Deposit fell into bath.
97-51	1	7	875	3.6	150	360	200	56 31	13	76	Part of deposit fell into bath.
97-53	1	7	870	3.5	150	360	185	-- --	--	--	Most of deposit fell into bath.
97-55	2	7	850	3.6	150	360	250	81 40	15	(R_B 94)	Part of deposit fell into bath.
97-57	3	9	850	3.7	150	370	185	161 80	40	87	Made sodium for about 35 amp hrs. **
97-59	2	10	860	3.7	140	390	225	25 10	5	--	Most of deposit fell into bath.
97-63	2	10	860	3.6	100	260	150	48 20	15	71	Part of deposit fell into bath.
97-65	6	7.5		3.8	150	370	185	20 11	5	--	Made much sodium.
97-67	6	7.5	855	3.0	50	130	150	121 60	37	88	Probably made sodium for approx. 50 amp hrs. **
97-69	6-b	7.5	840	3.2	50	120	140	-- --	--	--	This was another batch of salt using method (6). Heavy fuming during melting operation. Deposit fell into bath during electrolysis.
97-71	6-b	7.5	860	3.0	50	120	100	61 32	28	(R_B 78)	Lost part of deposit. Probably made sodium for 50 amp hrs. **
97-73	4	7.5	860	3.0	50	120	140	99 46	33	82	Probably made sodium for 30 amp hrs. **
97-75	5	7.5	850	3.0	50	120	125	129 70	48	88	Probably made sodium for 12 amp hrs. **

TABLE VI (continued)

Electrolysis of $\text{ThCl}_4\text{-NaCl}$. Salts of questionable quality from preliminary methods

Run No.	Thorium Salt No.*	Th Conc %	Temp °C	Volts DC	Amps DC	C.D. Amps dm^2	Amp Hrs	Metal Recov.		Current Eff. %	Hardness R_E	Remarks
								gms	%			
97-77	3	8.5	855	3.0	50	120	125	126	65	47	91	Probably made sodium for 25 amp hrs.***
97-79	3	9.5	855	3.6	150	370	100	64	25	26	91	Lost part of deposit into bath.
97-81	2	10	850	2.9	50	120	130	115	48	44	100	
97-83	2	10	855	3.0	50	120	135	85	35	29	100	Used truncated cone cathode. Lost part of deposit.
97-85	3	13.5	855	3.5	150	370	385	55	16	6	91	Most of deposit fell into bath.
97-87	7	8	855	3.2	50	120	100	--	--	--	--	Deposit fell into bath.
97-93	7	9	855	3.2	50	120	120	55	25	21	(R_B 82)	
97-95	9	10	860	2.9	50	120	125	154	71	56	87	Very nice concentric deposit.
97-97 (1)	9	10	855	3.0	50	120	110	137	63	57	81	" " " "
97-113 (2)	9	7.5	855	3.0	50	120	125	82	50	30	76	Second run in series using same salt bath and adding additional thorium salt. Lower portion of deposit fell into bath.
97-115 (3)	9	7	855	3.0	50	120	120	110	80	42	90	Third run in series.
97-139	5	7.5	855	3.6	50	120	85	110	65	59	72	Repeat of 97-75
97-143	11	8.7	850	2.9	50	120	86	110	59	23	86	Bottom portion of deposit fell into bath. Hardness of metal in the bath R_E 86. Metal in cathode R_E 96.
97-145	10	8.7	860	2.8	50	120	100	--	--	--	--	Deposit fell into bath during electrolysis and carbided.
97-146	10	7	850	3.5	100	240	75	11	--	5		Deposit fell into bath.

* No. refers back to Table IV

*** As evidenced by a voltage rise.

TABLE VII

Small Scale Laboratory Electric Runs Using ThCl_4 - NaCl Cell Feed of Good Quality

Run No.	Th Conc %	Bath Temp °C	Cell Voltage D.C.	Cell Current D.C.	Amp Hrs	Metal Wt. Gms	Process Efficiency %	Process Recovery %	Hardness R_B	Remarks	
97-149	2.5	840	3.0	25	45	13	13	28	104	There was only 0.3% thorium left in bath. Very low concentration run.	
97-151	2.5	850	3.0	25	45	14	14	30	(R_A 66)	Duplicate of 97-149. Cell feed was only 2.5% thorium.	
97-152	13.9	840	4.5	225	80	86	50	34	78.5	Deposit fell into bath. Part of it carbided.	
97-154	4.6	850	3.4	50	96	52	51	25	93	Deposit was large but showed indications of carbiding.	
97-156	6.8	850	3.2	75	124	106	40	64	36	(A 63)	Deposit fell into bath. Most of it carbided.
97-158	10	850	3.6	110	110	67	28	67			
97-160*	7	850	3.5	75	176	42	11	28	45	Used ceramic sleeve at bath interface instead of graphite. Otherwise a duplicate of 97-156	
97-162*	10	850	3.5	75	129	174	62	78	26	Large concentric deposit.	
97-166*	10	850	3.0	50	120	160	61	72	54	Lower part of deposit fell into bath and was recovered intact. Crystal size coarser than 97-162.	
97-168*	7	850	2.6	50	105	--	--	--	--	Low concentration--low current density--run unsuccessful. Deposit fell into bath and carbided.	
97-170*	15-17	850	3.0	75	210	326	72	ca. 90	10.5	Deposit very large and very coarse. Runs 97-152 through 97-170 all made using cell feed 164-121.	
97-172*	10	850	3.0	75	95	121	59.5	55	18	Salt 165-39. Salt made using method of 128-37 (Type 9) NH_4Cl driven off in cell. 2 mols NH_4Cl per mol ThCl_4 . Part of deposit fell off cathode but was recovered intact.	

TABLE VII (continued)

Small Scale Laboratory Electric Runs Using ThCl₄-NaCl Cell Feed of Good Quality

Run No.	Th Conc %	Bath Temp °C	Cell Voltage D.C.	Cell Current D.C.	Amp Hrs	Metal Wt. Gms	Process Efficiency %	Process Recovery %	Hardness R _B	Remarks
97-174	15	850	3.0	75	140	216	71	65	31.5	<u>Salt 165-39</u>
97-176*	15	850	2.9	75	280	111	18	33	82	<u>Salt 165-40</u> . Same method as 165-39 with 3 mols NH ₄ Cl per mol ThCl ₄ . Most of deposit fell into bath.
97-178*	20	840	2.9	75	208	276	69.5	61.5	46	<u>Salt 164-121</u> . Electrolyzed until deposit shorted out on crucible wall. Crystals were very large and were rolled in the pulverizer. Probably occluded salts when pulverized.
97-182*	10	845	2.9	50	106	158	69	72	36.5	<u>Salt 164-121</u> . Repeat of 97-166. Ceramic tube cracked during run. Possibility of contamination.
97-184* (1)	14.1	850	2.9	75	170	268	72.5	86.5	13.5	<u>Salt 164-128</u> . Start of continuous run with salt bath reused.
97-186* (2)	14.1	845	2.9	75	175	269	71.0	86.8	23.5	<u>Salt 164-128</u> . Ceramic tube split. Removed bottom of salt bath as possible SiO ₂ contamination.
97-188* (3)	9.5	840	2.9	75	175	184	49	88	28	<u>Salt 164-128</u> .
97-190 (4)	9.5	845	2.9-3.0	75	131	175.5	58	84	A=57 B=43	<u>Salt 164-128</u> . 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	<u>Salt 164-128</u> . 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	<u>Salt 164-128</u> . Same as 97-190. Continuous run stopped.

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TABLE VII (continued)

Small Scale Laboratory Electric Runs Using ThCl₄-NaCl Cell Feed of Good Quality

Run No.	Th Conc %	Bath Temp °C	Cell Voltage D.C.	Cell Current D.C.	Amp Hrs	Metal Wt. Gms	Process Efficiency %	Process Recovery %	Hardness R _B	Remarks
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.
196-14	15	790	2.8	100	180	274	71.5	83	30	Thermocouple in the cathode tip was about 40°C higher than the indicated bath temp. Higher current, same initial current density as runs above.
196-15	15	800	3.0	125	185	119	30	36	33	Same current density as 196-14. Lost part of deposit.

* Used 2-inch long porcelain sleeve at bath interface. Graphite sleeve on the rest of the nickel cathode rod.

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a. Operating Conditions

The following operating conditions and operating specifications are drawn from the results of the laboratory runs given in Table No. VII.

1. In order to produce thorium metal of high quality (R_B 30 or lower in hardness) the thorium chloride cell feed must be less than 0.1% in insoluble content.

2. The electrolytic cell atmosphere must be inert and free especially of oxygen or water vapor.

3. The operating temperature range for electrolysis is between 800 and 840°C.

4. The cathode temperature must be controlled at under 850°C during operation, either by cooling or by control of current passage.

5. Cathode current density and thorium ion bath concentration are mutually dependent functions. For a 12-15% thorium ion concentration, cathode current densities of about 210-250 amperes/dm² are optimum. (Current density based upon original cathode area.) In general, crystal size increases with higher thorium ion concentration and lower current densities.

6. The system $\text{ThCl}_4\text{-NaCl}$ is capable of being operated continuously by adding make-up cell feed of the proper thorium ion concentration. Make up salts can be added during an electrolysis, or following a cathode withdrawal.

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b. Results

When conditions of electrolysis in the laboratory (5 pounds total salt charge) cell are optimum, average results are:

1. Current Efficiency

a. 10% thorium concentration; 60-65%.

b. 15% thorium concentration; 70-80%.

2. Yield: $83 \pm 10\%$.

3. Thorium metal hardness: R_B 5-30.

Several samples of thorium metal were sent to the New Brunswick Laboratory of the AEC for spectrographic analysis. The results of the analyses are shown in Table VIII.

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TABLE VIII

Spectrographic Analyses of Thorium Metal Produced in Small Scale
Laboratory Electrolytic Runs

Horizons	97-162	97-170	97-174***	97-174	97-170
Run Number	Powder	Powder	Powder	Pellet	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 34 ppm	*310; 360 ppm 32 ppm	*290 ppm 27 ppm	--	**480 ppm 37 ppm

NOTE: a = approximate; -- = not detected

* Results of individual determinations

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

*** Thorium chloride used for 97-174 was prepared in glass and graphite. A nickel stirrer was used in the preparation of the cell feed for the other samples.

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When operating conditions for the ThCl_4 -NaCl fused salt system were established, the scale of operation was expanded about nine-fold. The laboratory work was performed in a cell whose crucible is four inches in inside diameter and which operates with about a six-inch bath depth. The intermediate scale of operation was performed in a cell whose crucible is eight and one-half inches inside diameter and which operates with about a ten to twelve inch bath depth.

In its essential principles, the intermediate scale electrolytic cell makes no major deviations from the laboratory cell. The crucible is a monolithic, machined shape of graphite. It also serves as the anode. The crucible is surrounded by a single-phase graphite resistor which is comprised of graphite links and rods. The shell of the cell is circular in cross-section, is all nickel, and is insulated with K-28 fire brick. The upper section of the shell is flanged; the lower portion is welded to a solid nickel plate. The anode connection to the crucible is made from this bottom plate by three graphite posts upon which the crucible rests. The entire shell of the cell is anodic in operation.

The cell is provided with an upper, water-cooled assembly and an operating head. The operating head is

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provided with heat reflector shields, an insulated port for a cathode, and a port for salt addition and chlorine evolution. An assembly drawing of this cell is shown in Figure No. 15.

The cell is provided with a DC source capable of delivering 1000 amperes at 12 volts, a 32 KW AC source capable of delivering 600 amperes, an argon metering system and a ventilating hood. The cell is both gas and vacuum-tight.

The cathode for this cell consists of a steel or Hastelloy "C" 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, about three inches long, protects the nickel at the bath interface. Above this, a graphite sleeve protects the nickel rod against chlorine attack and extends through the operating head. The cathode connection from the DC source is made directly to this nickel rod. An insulating bushing insulates the cathode from the operating head. The anode connection is from the bus bar to a steel boss welded to the bottom plate of the cell.

b. Electrolysis Procedure

Normal operational procedure for this cell, which is ordinarily operated as a batch unit, is accomplished in the following manner. A crucible is placed into the cell, upon the anode posts, and is charged with a batch of cell

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(Scale approx. 7.5:1)

Fig. 15 Assembly Drawing of Intermediate Size Electrolytic Cell.

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feed and additional sodium chloride to achieve the desired thorium ion concentration. The operating head is cleaned, positioned, and bolted down. The vacuum flange is bolted to the head and the cell is evacuated and flushed with argon several times. When an inert (argon) atmosphere has been established, the vacuum flange is removed, an argon flush is established, and heating of the cell charge is begun. The salts are melted in about two to two-and-one-half hours.

When the salts are molten and the bath is controlled at the chosen operating temperature (about 800°C), the cathode is inserted into the bath under a polarizing voltage of about 1.5 volts DC. When the cathode has reached bath temperature (which it approaches in about 5 minutes), the voltage is increased and electrolysis proceeds. When the electrolysis is halted, the cathode is again polarized and withdrawn from the bath but held in the inert atmosphere of the cell. The entire cell is cooled under an argon atmosphere overnight. For the next run, the operating head is removed, the cathode withdrawn, the crucible either removed or recharged and the unit reassembled. Figure No. 16 is a photograph of the cell.

With the scale up of some eight to ten times, it was necessary to establish certain operating conditions and to determine which factors, of little consequence on the small scale, are of importance on the larger scale. The

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Fig. 16 Photograph of Intermediate Size Electrolytic Cell showing cathode in place and some auxiliary equipment.

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main factors which were established were that the bath temperature must be controlled within the range 800-830°C and that the cathode temperature must also be controlled below 850°C. Those factors which were reaffirmed, were that the bath constituents must be anhydrous and essentially free of insolubles, that the electrolytic cell atmosphere must be inert and moisture-free, and that starting current densities (based upon initial cathode area) must be in the order of 150-250 amperes/dm².

c. Results

The initial electrolytic runs made in the intermediate-sized cell are summarized in Table IX. These runs were characterized by all, or most, of the deposit falling into the bath during electrolysis. This was partly due to poor temperature control, but was chiefly caused by high localized temperatures at the cathode due to the passage of a high DC current. In several runs in which the DC current was about 400 amps, the cathode became so hot that thorium alloyed with the iron cathode, and this alloy melted away from the cathode.

After temperature conditions of the electrolyte and the cathode were established and controlled, electrolyses were carried out in a rather routine fashion. Table X summarizes electrolytic runs made in the intermediate sized cell after the proper operating criteria had been established. These runs were successful.

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TABLE IX

Preliminary Electrolytic Runs in Intermediate Scale Cell

Run No.	Th Ion Conc %	Bath Temp °C	Cell Voltage D.C.	Cell Current D.C.	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. Deposit fell off cathode. Cathode badly corroded. Cathode temperature probably approached 1000°C.
184-25	15	850-860	3.5-2.9	250	800	--	--	--	--	Used salt bath from 184-22. Cathode 1" dia. x 5" long. Deposit fell off cathode.
184-27	15	850	3.9	380	1200	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" dia. 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/dm ² . Uniform deposit. Cathode 1" dia. x 5" long.
184-31	7	850	3.7	190-225	630	40	--	--	--	Salt bath from 184-29. Starting current density was 185 amps/dm ² . Most of deposit fell off. Metal on cathode would not melt. Cathode 1" dia. x 5" long.
184-33	10	850	3.5	240-300	1600	--	--	--	--	Salt 164-140. Cathode 1" dia. x 5" long. No deposit on cathode.

TABLE IX (continued)

Preliminary Electrolytic Runs in Intermediate Scale Cell

Run No.	Th Ion Conc %	Bath Temp °C	Cell Voltage D.C.	Cell Current D.C.	Amp Hrs	Metal Wt. Gms.	Process Efficiency %	Process Recovery %	Hardness R_B	Remarks
184-37	10	850	4.5	390-420	1500	--	--	--	--	Salt bath from 184-33. Cathode 1-1/2" dia. x 5" long. Deposit fell off cathode. Cathode was pitted slightly.
184-39	15	850	4.6	370-430	2270	--	--	--	--	Salt 164-140 and 164-142. Cathode 1-1/2" dia. x 5" long. Thorium alloyed with cathode and fell into bath. Cathode badly eaten away. Recovered thorium from salt bath loaded with iron.
184-42	14.5	820	4	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	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.
184-50	--	--	4.4-3.4	380-290	1269	--	--	--	--	Salt 21 lbs NaCl 14 lbs 164-150 Cathode 1 1/2 dia. x 5". Most of deposit fell into bath. Carbide, iron contamination.
184-55	--	--	3.6	200	775	303	--	--	99.5	Salt 27 lbs of 184-50. Bath pre-electrolyzed with steel cathode.

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TABLE IX (continued)

Preliminary Electrolytic Runs in Intermediate Scale Cell

Run No.	Th Ion Conc %	Bath Temp °C	Cell Voltage D.C.	Cell Current D.C.	Amp Hrs	Metal Wt. Gms	Process Efficiency %	Process Recovery %	Hardness R _B	Remarks
184-57	--	780-790	3.9	300	840	450	25	--	61	<u>Salt</u> 184-55 10 lbs of 164-150 Bath depleted, Na formed.
184-62	--	--	4.0	300	540	--	--	--	--	18 lbs 164-154 B 17 lbs NaCl Grooved cathode. Deposit fell into bath.
184-66	--	--	3.3	300	550	154	13	--	--	<u>Salt</u> 15 lbs 164-156 17 3/4 lbs 184-62 3 lbs 184-35 Cell not evacuated before run.

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TABLE X

Electrolytic Runs in Intermediate Scale Cell

Run No.	Th Ion Conc %	Bath Temp °C	Cell Voltage D.C.	Cell Current D.C.	Amp Hrs	Metal Wt. Gms	Process Efficiency %	Process Recovery %	Hardness R_B	Remarks
184-71	Initial 8.1 Final = 5.2	830- 800-	3.5	200-230	684	440	35	30	R_B 33	Salt 15 lbs 164-156-A 20 lbs Fused Salt Bath Bath Depth 8 1/2 inches in 8 1/2 inches diam. tapered crucible Cathode 1 1/4 inches diam. x 5 inches long grooved Conditioning: Cell hot evacuated. Allowed temp. to fall to 800°C. Deposit came out with a layer of salt across top. Initial current density = 180 amp/dm ²
184-73	16	820	3.5	230	1270	A=1870 B=1670	68.1	61	46	Salt 164-155; 35 lbs. total. Bath Depth 10 inches Cathode 1 1/4 inches x 5 inches with thermocouple 1 1/2 inches into cathode top. A=water-washed metal weight B=final acid-treated weight. Initial current density= 180 amps/dm ²
223-2	3.3	800- 820	4.2-4.4	230	380	171	40	35	54	Salt bath from 184-23 depleted bath to 0% Th. Sodium at end point.
223-4	10%	800	3.5	220-240	1100	A=1550	65.5	63	B=69.5 C=73.5 D=40 E=35.5	Salt 164-158 and fused salt from 184-171 (35 lbs total) Bath level: 10 1/2 inches Thermocouples in side wall and cathode. End Point: Voltage rose to 3.7 with current dropping to 180. A=water washed weight

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TABLE X (continued)

Electrolytic Runs in Intermediate Scale Cell

Run No.	Th Ion Conc %	Bath Temp °C	Cell Voltage D.C.	Cell Current D.C.	Amp Hrs	Metal Wt Gms	Process Efficiency %	Process Recovery %	Hardness R _B	Remarks
223-4 (continued)										B=5% acid washed metal C=10% acid washed metal D=B after 5% HCl-5% Formic acid E=C after 5% HCl-5% Formic acid
223-7	6.2		4.3	200-260	1230	772	29	29	A=60.5 B=50	<u>Salt</u> 17 lbs 164-158B 18 lbs Fused Salt (6.0% Th) <u>Bath level:</u> 11 inches Erratic temperature control. Bath temperature indicated was 800; bare thermocouple in bath was 890. A=after 10% HCl B=after 5% HCl-5% Formic acid
223-11	13.5	750	3.5	250-400	2190	A=883 B=385 C=350	18.7		A= B=48 C=40	<u>Salt</u> 18.6 lbs 164-159 16.4 lbs Fused salt (6.0% Th) Thermocouple in cathode gave inaccurate readings. Bath temp. higher than indicated by about 150 degrees. A=water-washed metal B=5% acid-washed metal C=10% acid-washed metal.
223-14	13.0*	780-800	4.1	300	1730	2270	61		54	<u>Salt</u> 15 lbs 164-160 24 lbs Fused Salt 223-11 Thermocouple in cathode. Depleted bath-sodium evolution. Initial current density= 230 amps/dm ² See Table XII for summary of various acid treatments.

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TABLE X (continued)

Electrolytic Runs in Intermediate Scale Cell

Run No.	Th Ion Conc %	Bath Temp °C	Cell Voltage D.C.	Cell Current D.C.	Amp Hrs	Metal Wt Gms	Process Efficiency %	Process Recovery %	Hardness R _B	Remarks
223-22	23	780-800	3.8	360-400	3035	3632	55.5	75	36	Crucible ID increased from 8 1/2 to 9 1/2 inches. <u>Salt</u> 22.7 lbs. 164-161 14 lbs. 164-150-C Total = 46.7 lbs. Bath level = 10 1/2 inches Bath level dropped two inches during electrolysis exposing portion of deposit to chlorine 1 1/4 inch x 5 inches Hastelloy C cathode
223-29	22	770-800	3.8	400	3500	3900	51.5	73	31	Crucible ID = 9 1/2 inches 1 1/4 inch x 5 inches Hastelloy C cathode Charge: 29 lbs. 164-162 25 lbs. NaCl Bath level: 12 inches Charged 2 lbs. fused NaCl every 600 amp hrs., Total of 8 lbs. Difficulty of deposit shorting against bottom of crucible at 2600 amp hrs. and at 3000 amp hrs. Raised deposit 1/4 inch both times.
223-33	19	800*	3.8	320-400	1780	1590	42		23	Crucible and cathode same as 223-29. (*) Thermocouples inoperative throughout electrolysis. Maintained approx. temperature by color of bath.

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With a thermocouple inside the cathode tip to indicate the temperature of the cathode, it is possible to obtain a fairly accurate measurement of temperature during the initial, critical period of electrolysis when it is essential that the deposit adheres to the cathode. As shown in Table IX, the early successful runs were made using a fairly low DC current averaging about 250 amps. Although the scale-up of cell capacity is approximately nine to one, the ratio of operating DC current was less than four to one. After additional experience had been gained, the temperature was more delicately controlled by AC input to the cell to accommodate 400-500 amps, D.C. with no deleterious effects. Initial current densities at the higher currents were about 300 amps/dm².

The higher current density runs were made using a cathode tip of Hastelloy "C". The formation of a high-melting thorium-nickel alloy at the cathode-thorium deposit interface greatly aided in making the deposit adhere strongly to the cathode. The alloy comes off as a thin shell with the deposit the first few times a Hastelloy "C" cathode is used, and must be separated from the main deposit before processing. However, after the cathode has been used several times, the thorium-nickel alloy adheres more strongly to the cathode than to the deposit and does not constitute much of a separation problem.

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During electrolysis in the small laboratory cell, the cathode had to be lowered approximately one-half inch into the bath during electrolysis to keep the upper portion of the deposit from becoming chlorinated. This amounts to an approximate 8% loss in volume during the average 150 ampere hour electrolytic cycle. However, in the larger cell the decrease in volume is such that the bath level drops about two inches in 2500 ampere hours of electrolysis, or a decrease in volume of about 17-18%. The two-inch drop in level occurred in runs where ten pounds of metal per deposit were desired. The drop in level for the two cells is proportionately the same based on initial volumes, concentrations, and ampere hours of electrolysis.

If the deposit is not lowered to accommodate the approximate two-inch drop in bath level, much of the deposit is chlorinated. An example of this is shown in Fig. 17 which is a photograph of the cathode produced in Run No. 223-22.

The crucible for the intermediate-sized electrolytic cell is too shallow to accommodate more than an inch of deposit lowering, since the cathode deposit might then be long enough to short out against the anodic crucible bottom. Addition of salt to maintain a constant bath level was satisfactory as evidenced by the deposit shown in Fig. 18. However, the additional salt was difficult to melt and introduced possible contamination since the

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Fig. 17 Thorium cathode deposit from Intermediate Size Cell showing effect of lowering of bath level and subsequent re-chlorination of upper portion of deposit.

Run No. 223-22

Approx. 8 pounds of metal in deposit.

Fig. 18 Thorium cathode deposit from electrolytic run in Intermediate Size Cell where salt additions were made during the run to maintain a fairly constant bath level.

Run No. 223-29

Approx. 8 pounds of metal in deposit.

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cell was not specifically designed to accommodate salt additions during a run.

The deposits shown in Figs. 17 and 18 were obtained when the electrolysis object was to produce a deposit containing ten pounds of thorium metal. Actually, only eight pounds were obtained in each run, and this appears to be the operational limit of this cell. When a deposit containing about five pounds of metal was made, little difficulty was encountered since the resulting one-inch drop in bath level can easily be accommodated. Fig. 19 shows a typical deposit, Run No. 223-14, containing about five pounds of thorium metal.

Electrolyses made with pure constituents, and properly controlled, produced thorium metal at current efficiencies of about 60% and with Rockwell B hardnesses under 30. Additional electrolytic runs made after the conclusion of this contract proved conclusively that thorium metal of R_B 10-25 can be made.

The hardness of metal made in the intermediate-sized cell was generally not quite so good as those made in the small laboratory cell. However, most of the thorium chloride cell feed for the larger cell was prepared from Lindsay Chemical Corporation grade 150H thorium oxycarbonate. The difference in quality between the 150H and 151H thorium oxycarbonate is shown in the spectrographic analyses in Table XI. In each case the metal was made from the cell

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Fig. 19 Typical cathode deposit containing approximately
5 pounds of metal from Intermediate Size Cell.

Run No. 223-14.

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TABLE XI

Spectrographic Analysis of two grades of Thorium Carbonate and Product Thorium Metal

151 H				150 H			
Element	Thorium Carbonate	Cell Feed 164-121	Metal Average from Table VIII	Element	Thorium Carbonate	Cell Feed 164-155	Metal Run No. 184-73
Ag	0.2	10	1	Ag	0.5	10	0.1
Al	800	100-1000	25	Al	500	100-1000	50
B	10	--	5	B	10	--	0.5
Be	--	--	--	Be	--	--	1
Bi	50	10	5-10	Bi	50	10	1
Ca	1000	1000	100	Ca	500	1000	100
Cd	0.1	--	0.2-0.3	Cd	0.1	--	0.1
Cu	50	10-100	80	Cu	30	10-100	10
Fe	200	100-1000	600	Fe	200	10-100	800
Mg	200	10-100	10	Mg	100	10-100	8
Mn	10	10-100	5	Mn	5	10-100	5
Ni	15	100-1000	300	Ni	13	10-100	200
Pb	70	--	15	Pb	70	--	2
Si	2000	10-100	50	Si	2000	10-100	2000
Sn	100	10	5-10	Sn	15	10	2
V	--	--	--	V	--	--	50
As	5	--	5	As	5	--	5
P	50	--	--	P	50	--	--
Na	800	10%	150	Na	800	10%	

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feed listed in the adjoining column.

Thorium metal made in electrolytic run No. 223-33 had a hardness of R_p 23. The starting material was the better grade of thorium oxycarbonate, 151 H.

d. Electrolysis End Point

In the small scale laboratory electrolytic runs, the end point for the electrolysis was very pronounced. During electrolysis at a constant current input (motor generator), the voltage gradually decreased from about 3.0 to about 2.7 volts. At the end point, or when the thorium remaining in the salt bath is about 0.1 to 0.2%, the voltage rises very sharply to over 3 volts. The change occurs in a matter of several minutes. If electrolysis is allowed to continue, sodium metal is produced at the cathode. Some of the electrolytic runs summarized in Table V produced sodium metal for varying periods of time.

In the intermediate scale electrolytic runs, the end point was not as pronounced but this was due primarily to the type of electric equipment used. A rectifier was used which did not have very fine control. This gave a rather constant voltage, but the DC current varied with changing bath resistivity and changing voltage drop between the growing cathode deposit and the crucible walls. Thus, the DC current increased throughout the run. At low current density runs, the change in DC current was not

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appreciable. Several runs were made in the intermediate scale cell which reached an end point similar to that reached in runs made in the small scale cell. The end point consisted of a voltage rise accompanied by a sharp DC current decrease.

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E. THORIUM METAL RECOVERY

1. Crushing

Thorium cathode deposits made by the electrolysis of thorium chloride in sodium chloride are recovered when cold. Cathode deposits are a composite of about 50% thorium metal and about 50% salts. Of the salts, about 2-3% are soluble thorium salts, the remainder being sodium chloride. Figures No. 20, 21, and 22 are photographs of typical cathode deposits as withdrawn from the intermediate size cell. The cathode deposits are broken away from the cathode itself by means of a hammer and chisel or similar devices, and are then jaw crushed. The jaw crushed segments are then lightly pulverized in a secondary crusher to about -40 mesh.

Since pure thorium metal is very ductile, the secondary crushing operation should be single-impact, like a roll crusher, rather than shearing as in a pulverizer. A laboratory pulverizer used for some of the work, tended to "roll" the thorium crystals, occluding some salts inside the metal "cylinders". This occluded salt cannot readily be removed by washing.

2. Leaching

The particles of thorium-salt agglomerate are then water leached. This leaching is done either by a series of leaching and decantation operations in a beaker, or as a fluidized mass in an adaptation of counter-current leaching principles. In this case, the crushed deposit is placed into a cone shaped washer in which water continuously flows from the apex of the

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cone up through the fluidized deposit. A fractionating three-compartment catch basin collects any metal fines which may overflow. Such a device effectively removes all salts together with any low density impurities which may be present. When the soluble salts have been dissolved, the metal deposit is removed, drained free of excess water, and treated with a final acid pickle to remove any hydrolyzed thorium salts which may be present due to the reaction of thorium chloride with water. A photograph of this continuous counter-current cone washer is shown in Figure No. 20.

3. Acid Treatment

A number of final acid treatments have been investigated in the course of this project. The residual metal has been treated with varying percentages of HCl at various temperatures, with HNO_3 , $\text{HNO}_3 + \text{Na}_2\text{SiF}_6$, and $\text{HCl} + \text{HCOOH}$ mixtures. Time, temperature, and volume relationships have also been studied for this final acid treatment. It has been found that the final acid treatment can markedly affect the resultant hardness of the thorium product. In some cases, however, the hardness of the as-cast thorium metal cannot be drastically affected by any acid treatment. In these cases, the hardness is due entirely to impurities soluble in the thorium metal itself and not formed during the leaching operation or due to casual electrolytic impurities. Table XII presents the results obtained with varying acid pickle treatments on a single cathode deposit of thorium metal. It can be seen that the metal with no acid

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Fig. 20 Continuous counter-current cone washers
and auxiliary equipment.

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TABLE XII

Acid Treatment of Deposit No. 223-14

No.	Acid	Time	Initial Wt.gms	Final Wt.	Wt. Loss %	Hardness R _B
1	None					75
2	5% HCl	5	113.3	107	5.5	55
3	"	10	"	107	5.5	62
4	"	15	"	105	7.3	64
5	5% HCOOH	5	"	109	3.8	60
6	"	10	"	107.5	5.1	56
7	"	15	"	109.5	3.3	54
8	5% HCl-5% HCOOH	5	"	107	5.5	55
9	"	10	"	105.5	6.9	54
10	"	15	"	104.5	7.7	54
11	5% HCl-10% HCOOH	5	"	106.7	5.8	61
12	"	10	"	105	7.3	64
13	"	15	"	105	7.3	54
14	10% HCOOH	5	"	108	4.7	57
15	"	10	"	104.8	7.5	55
16	"	15	"	108	4.7	63
17	5% HNO ₃	5	"	106	6.4	54
18	"	10	"	108.3	4.4	59
19	"	15	"	104.1	8.1	53
20	10% HCl	5	"	100.8	11	56
21	"	10	103.0	87.5	15	58

Retreated 3, 4, 5, 11, 12, 14, 16, 18, 20, and 21 with 5% HCOOH +
2.5% HCl

Loss = 0.7%; Hardness = R_B 56.5

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treatment had a Rockwell B hardness of 75. However, by treatment with a mixture of 5% HCl and 5% HCOOH the final hardness was Rockwell B 54. In Table No. XIII a summary of various acid treatments with different thorium metal deposits indicates that a reduction of 50 per cent in hardness, in some cases, can be affected by proper acid treatments.

Additional work accomplished after the termination of the present contract period proved conclusively that the loss in acid-treatment (5% HCl-5% Formic for five minutes) is very small when the metal is of good quality. In one run, in which the as-cast hardness was $R_{\text{B}}-59$, the loss was only 0.8%. In other runs the maximum was only 3.5% weight loss, and the average weight loss was less than 2%.

Following the acid treatment the metal is washed free of any trace of acid and air-dried at 35°C. Figures No. 21 and 22 are photomicrographs and photomacrographs of thorium crystals produced by electrolysis of thorium chloride and appear below in this report.

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TABLE XIII

Summary of Acid Treating with 5% HCl; 10% HCl; and 5% HCl-5% Formic ⁺

Sample No.	Weight Before Acid Treatment	Weight After 10% HCl	% Wt. Loss	Initial Hardness R_B	Weight After 5% HCl-5% Formic	% Wt. Loss	Final Hardness R_B	% Reduction in Hardness	Actual Reduction in Hardness (R_B)
196-12	*	210		41.5	185	11.9	31.5	24	10
184-29	*	435		93	369	15.2	64.5	30	28
184-49				66		0	66	0	0
184-55	*	287		99.5	227.5	20.7	80	20	20
184-57	*	435		61	410.5	5.6	55.5	8	5
184-71	*	428		67	390	8.9	32.5	50	34
184-73	1870	1450	22.5	46					
223-4-A	388	375.5**	3.2	69.5	330	8.5	40	43	30
223-4-B	1162	1113.5	4.2	73.5	1068	2.9	35.5	51	38
223-7	*	755		60.5	682.5	9.7	50	17	10
223-11-A	435	401.5**	7.7	48					
223-11-B	435	366	15.9	40					

(+) Per cent acid is by volume.

* Metal was not dried and weighed before acid treatment.

** 5% HCl treatment.

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F. PROPERTIES OF ELECTROLYTIC THORIUM

1. Evaluation at Horizons Incorporated

a. Hardness

The primary means of product evaluation, at the laboratories of Horizons Incorporated, are Rockwell hardnesses taken on arc melted pellets of thorium. The electrolytically produced thorium is consolidated first by pressing into dense compacts one-inch in diameter and one-quarter-inch to three-eighths-inch in height. These compacts are then arc melted in a tungsten arc, water-cooled copper-hearth furnace under a quarter of an atmosphere of argon. The arc furnace, which is similar to many which have been described in the literature, is pictured in Figure No. 21. Electrolytic thorium metal has exhibited hardnesses in the as-cast state as low as Rockwell B 1.5 (Vickers 67). From consideration of the many runs reported upon, it is believed that a fair statement of the expected average hardness of thorium metal produced by the electrolysis of thorium chloride is Vickers 70 to 80. 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 or purity, electrolytic procedure, etc. The production of low hardness thorium in several instances alone establishes the capability of the process.

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Fig. 21 Arc furnaces and auxiliary equipment.

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b. Induction Melting

Some electrolytic thorium was induction melted in beryllia crucibles to determine melting characteristics of this type of thorium, and subsequently rolled by canning in a steel container and by hot rolling directly followed by cold rolling.

One and one-half pounds of thorium powder was cold pressed at 20 t.s.i. in a one and one-half inch die steel die to form completed briquettes. These briquettes were charged to a previously baked-out beryllia crucible and heated in vacuo by induction to the melting point of thorium. The ingot was allowed to solidify and cool to room temperature in vacuum.

The pressure, in microns, as a function of temperature is given in Figure No. 22 from 1000°C through the melting point. As can be seen from the graph, the rather high pressure in the temperature range of 1000°C to 1400°C is probably due to the sublimation of residual salts and gases not completely removed in the metal recovery step. Above 1500°C the pressure decreases to about the leak rate of the system. There is a slight increase in pressure above the melting point of the thorium metal.

c. Rolling

This thorium was hot rolled to 0.160 inches and then cold rolled to 0.04 inches in one case. The final thorium strip was Rockwell B-36 in hardness, ingot hardness was R_B 12.

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Fig. 22 - Temperature vs. Pressure Curve for Melting Thorium in Vacuum-Induction Furnace

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d. Tensile Properties

Two tensile specimens were prepared from thorium sheet of 0.040 inch thickness and tested to fracture. The sheet was rolled from a small ingot of thorium which was induction melted in a beryllia crucible under vacuum. The ingot was sealed in a steel jacket and hot rolled to a thickness of 1/8 inch which represented a reduction of about 50%. This sheet was then cold rolled to 0.040 inch thickness for the tensile tests. The specimens were vacuum annealed at 600°C for one hour prior to testing. The average values of ultimate strength, yield point (0.2%), and per cent elongation in a one-inch gage length are as follows:

Ultimate Tensile Strength -- 52,235 psi

Yield Point 41,675 psi

Per cent Elongation (one-inch length) 11.2%

A stress-strain curve for this material is shown in Figure 23.

e. Pole Figure Determination

The cold-rolled and cold-rolled plus recrystallized textures of thorium sheet were determined by x-ray diffraction photograms using MoK α radiation with a Zr filter. Four reflection patterns were used for each pole figure determination, corresponding to rotation of the specimen about axes 0°, 30°, 60°, and 90° from the rolling direction. Laue transmission photograms were also taken normal to the rolling plane. These photograms are shown in Fig. No. 24. The stereographic plots of the 110 and 100 poles are shown in Figs. No. 25 and 26, for cold-rolled and cold-rolled plus recrystallized thorium respectively.

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Fig. 23 - Stress Strain Plot for Annealed Thorium

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a

b

Fig. 24 Laue Transmission Photograms of thorium sheet: (a) Cold Rolled, (b) Recrystallized.

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Fig. 25 - Pole Figures Showing Preferred Orientation in Thorium Due to Cold Rolling.

Fig. 26 - Pole Figures Showing Preferred Orientation in Thorium Due to Cold Rolling and Recrystallization

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The principle textures developed in cold rolling were (100) (001) and (011)(211). Such duplex rolling textures are not uncommon in face centered cubic metals, having been found in most pure metals and alloys having the F.C.C. crystallographic structure.

The recrystallization textures were somewhat more difficult to define in terms of ideal textures. A considerable tendency toward randomness existed in the recrystallized sample. There were evidences, however, of a (100)(110) preferred orientation, and in addition, an indication of (111) planes in the rolling plane. However, this latter condition did not seem to be associated with a definite crystallographic orientation in the rolling direction.

f. Comparison of Horizons Electrolytic Powder with Ames

Thorium Billet (A-520)

Through the good auspices of the Atomic Energy Commission, the New Brunswick Laboratory has analyzed electrolytic thorium metal produced in several of the runs reported upon above. These analyses are shown in Table No. VII.

These analyses can be compared to the results published* on Ames Thorium (Billet A-520^h) in 1952. This bar had a hardness of R_E 44. Horizons electrolytic 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, both metals appear to be equivalent.

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

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g. Conversion Curve R_B vs. R_E for Thorium

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 No. 27.

h. Physical Evaluation of Thorium Produced from $KThF_6$

Figure No. 28 is a typical hardness vs. per cent reduction curve for thorium produced from $KThF_6$.

Photomicrographs showing the as-cast, cold worked, and annealed structure of this metal are shown in Figures Nos. 29 through 32.

Debye-Scherrer x-ray photograms have been taken of the metal powder. Calculation indicates the lattice parameter for FCC thorium to be $a_0 = 5.0735 \text{ \AA}$.

i. Correlation of Microstructures with Hardness and Chemical Properties

An attempt was made to relate the microstructures of arc-melted thorium pellets with hardness and chemical composition. A series of arc-melted thorium pellets ranging in hardness from R_B 1.5 to R_B 70 was examined metallographically for evidences of microstructural differences. The results of these observations are recorded in Table No. XIV and in the photomicrographs in Figures Nos. 33 through 36.

A general trend is evident in that a larger amount of precipitate phase occurs as specimen hardness increases.

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Fig. 27 - Hardness Conversion Chart for Horizons Incorporated Thorium

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Fig. 28 Hardness vs. Per cent Reduction

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Electrolytically Polished and Etched Mag. 250X

Fig. 29 As-cast thorium electrolytically produced from $KThF_5$ (Run No. 75-19). Melted in argon atmosphere. Large dendrites of ThO_2 apparent throughout structure. R_B-40 . Sol'n: 350 cc Butyl cellosolve; 590 cc Methanol; 60 cc perchloric acid (sp. g. 1.5).

Electrolytically Polished and Etched Mag. 250X

Fig. 30 Arc melted as-cast thorium structure electrolytically produced from $KThF_5$ (Run No. 97-1), insoluble ThO_2 in dendritic form (not as contaminated as above). R_B-12

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Fig. 31 Section of thorium electrolytically produced from $KThF_6$. Arc melted and cold rolled to 80% reduction (to 0.050 inch).. The breaking up of the outside inclusions is shown. R_B-60 . (Run No. 97-1)

Electrolytically Polished and Etched Mag. 250X

Fig. 32 Section of thorium electrolytically produced from $KThF_6$. Arc melted and cold rolled to 99.2% (0.003 inch). Reduction annealed at 1000°C for 15 minutes. Annealed recrystallized grains and spheroidized oxide are shown.

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TABLE XIV

Comparison among Hardness, Chemical Composition and Microstructure
for Electrolytic Thorium

Spec. No. and Run No.	Hardness R_B	Analysis %	Amount of Gray Phase in Microstructure
633	1.5	HCl Ins. --- Carbon ---	Small amount of gray globules scattered throughout.
505 97-184	11	HCl Ins. 1.2 Carbon ---	Small amount. Particles much smaller in size than other specimens.
328 97-172A	20	HCl Ins. 2.94 Carbon 0.032	Medium amount. Some white phase in gray particles.
329 97-156	36	HCl Ins. 1.3 Carbon 0.02	Small amount.
500 97-192	37	HCl Ins. 2.2 Carbon 0.045	Medium amount white phase in part of gray particles.
501 196-9	37.5	HCl Ins. 0.8 Carbon 0.03	Small amount white phase in gray particles.
502 184-73	46	HCl Ins. 1.67 Carbon 0.027	Medium amount white phase in gray particles.
503 223-22D	53	HCl Ins. 4.2 Carbon 0.03 Si 0.1	Large amount. Gray particles are large in middle of pellet, small on outside white phase in gray particles.
499 97-166	59	HCl Ins. 4.95 Carbon 0.086	Large amount. About same as 503. Gray particles large in center. Small on outside. Some white phase in gray particles.
504 223-22E	70	HCl Ins. 11.1 Carbon 0.045 Si 0.3	Very large amount. White phase in gray particles.

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Unetched

Mag. 250X

Fig. 33 Structure of arc-melted thorium electrolytically produced from ThCl_4 -NaCl. Oxide phase present. Hardness R_p -60.

Etched

Mag. 250X

Fig. 34 Structure of arc-melted electrolytic thorium (Run No. 97-156) from ThCl_4 -NaCl with the oxide phase in a dendritic pattern. Hardness R_p -36.

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Mag. 250X

Fig. 36 Arc melted electrolytic thorium (Run No. 223-22-E using $\text{ThCl}_4\text{-NaCl}$). Microstructure from the highest hardness range showing large amount of dendritic pattern of oxides. Hardness $R_B\text{-70}$.

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Thus the specimen shown in Figure No. 33, having a hardness of R_p 1.5, shows randomly distributed gray particles of indefinite pattern. On the other hand, the specimen microstructure in Figure No. 36 shows a large amount of the gray phase in a dendritic pattern.

Thorium pellets shown in the photomicrographs in Figures No. 33-36, were analyzed for carbon content, and for total HCl insolubles, which would include SiO_2 as well as ThO_2 . From the results of these analyses, a relationship was found between the amount of gray phase present and the percentage of material insoluble in conc. HCl. On this basis, it is probable that the variation in hardness of these specimens was caused mainly by oxygen, although small differences in carbon content probably had some effect.

The photomicrographs in Figures No. 37 and 38 show the microstructures of arc-melted thorium after 90% cold-rolling and after cold rolling plus annealing at $1000^\circ C$ for one-half hour respectively. The initial hardness of the arc-melted pellet was R_p 1.5.

Hardness values were obtained as a function of cold reduction for a thorium pellet having an initial hardness of R_p 30. Values of hardness and per cent reduction in thickness are tabulated in Table No. XV following:

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Lightly etched

Mag. 100X

Fig. 37 Structure of as-cast electrolytic thorium that was cold rolled to 90% reduction. Initial hardness R_E-60 .

Etched

Mag. 100X

Fig. 38 As-cast electrolytic thorium recrystallized at 1000°C for 30 minutes after cold rolling to 90% reduction.

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TABLE XV

Hardness Versus Cold Reduction

<u>% Reduction</u>	<u>Hardness R_B</u>
0	30
15	55
20	55
30	56
40	57
50	67
60	64
70	68
80	69
85	71

i. Compactability

Compactability studies were conducted on electrolytic thorium powder by cold pressing in a one-inch diameter die. The results obtained are shown in Figure No. 39 which is a plot of green density vs. compacting pressure. The highest compacting pressure used was only 25 t.s.i., and the density at this pressure was 9.61 gm/cc, or 83.5% of theoretical density.

j. Observations on thorium crystals grown from fused-salt electrolytic bath

For the purpose of observing crystal growth features of thorium metal from a fused-salt electrolytic bath, larger and better developed crystals were selected after careful leaching in water. In general, it is observed that both flaky crystals with well-developed

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Fig. 39 - Green Density vs. Cold Compacting Pressure
Horizons Electrolytic Thorium Powder
(From Run 97-57)

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flat surfaces, and also massive clusters are obtained (see Figures No. 40 and 41).

An attempt was made to determine crystallographically the planes responsible for the flat and well developed faces by x-ray technique. A Laue back-reflection pattern was taken on the crystal shown in Figures Nos. 42 and 43 with the surface depicted in Figure No. 43 perpendicular to the x-ray beam. Stereographic plot of the resulting orientation showed that this plane corresponds to (221) which is about 16° from (111) plane. Since thorium is face centered cubic in crystal structure, ordinarily one would expect that (111), which is the most densely populated plane, would have the slowest growing rate, and therefore would be predominant. This behavior, however, is modified by the growth conditions and impurities present during crystal growth. In view of this, it is not remarkable that thorium crystals obtained from fused-salt electrolysis have well developed (221) faces.

2. Evaluation of Horizons Electrolytic Thorium Metal at other AEC Installations

Through the auspices of the Atomic Energy Commission, New York Operations Office, samples of Horizons electrolytically produced thorium metal were evaluated at various other installations and associated companies. These include, the

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Mag. 19X

Fig. 40 Electrolytically produced thorium crystals (from NaCl-ThCl_4) showing flat surfaces.

Mag. 18X

Fig. 41 A massive crystal of thorium produced by the electrolysis of $\text{ThCl}_4\text{-NaCl}$.

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Mag. 250X

Fig. 42 Layer structure of electrolytically produced thorium crystal. A Laue x-ray photograph was taken with the x-ray beam perpendicular to this face for orientation determination.

Mag. 250X

Fig. 43 Adjacent face of the crystal shown above. Notice that a ridge-like rather than a flat surface is observed, indicating faster growth in this direction.

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Brush Beryllium Co., Cleveland, Ohio, the AEC Laboratory of the Sylvania Electric Products Co., Bayside, L.I., the Brookhaven National Laboratory, Upton, N. Y., and the New Brunswick AEC Laboratory. The following data is abstracted from letter reports and interim reports which cover the data obtained. Table No. XVI is a list of shipments made through May of 1954.

a. Data obtained at the Brush Beryllium Co. on Horizons Incorporated Electrolytic Thorium Powder. Excerpted from a Brush Beryllium Company Report. (54)

A three-and-one-half pound lot of electrolytic thorium powder was shipped to The Brush Beryllium Co. for evaluation and for comparison with various grades of thorium powder produced by other methods, and to determine the applicability of these powders for fabrication by powder metallurgical methods. Horizons Incorporated electrolytic thorium powder was compared with:

- (1) Th metal produced by calcium reduction of ThO_2 (Westinghouse).
- (2) Thorium hydride powder (Metal Hydrides).
- (3) Special coarse thorium hydride (Brush Beryllium Co.).
- (4) Mechanically attritioned thorium powder made by grinding machined chips under inert atmosphere (Brush Beryllium Co.).
- (5) Scrap such as machine and saw chips from cast, rolled, and extruded metal.

The observations carried out on the various powders consisted of an evaluation of:

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TABLE XVI

Summary of Thorium Shipments to Sylvania and Brush
Beryllium Company

Jan. 13, 1954 - 3.5 lbs.

Lot A - to Brush Beryllium Company, Cleveland, Ohio

1.0 lbs. R_B 30-50

2.5 lbs. R_B 13-30

Lots 1-4 to Sylvania Electric Products Co., AEC Laboratory

(1) Feb. 15, 1954 - 2.61 lbs.

R_B 5-24

196-1-b	89 gms	R_B 18
97-170	30	10
97-192-b	75	5
97-172-b	<u>16</u>	24
	210 gms	

R_B 37 - R_B 50

196-1-a	92 gms	R_B 37
196-9	135	37.5
184-27	85	46
184-21a	217	45
184-21b	<u>85</u>	49
	614 gms	

R_B 54 - R_B 60

196-8	127 gms	R_B 53
196-10	108	57
97-166	<u>125</u>	54
	360 gms	

Total = 2.61 lbs.

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TABLE XVI (continued)

(2) April, 1953 - 4 lbs.

196-10	R _B 38
184-60	50
184-73	46
223-2	54

(3) April 13, 1954 - 5 lbs.

223-4-B	1000 gms	R _B 35.5
184-71	338	32.5
223-4-A	301	40
223-11-C	320	40
223-11-B	180	48
196-62	<u>143</u> 2277 gms	31.5

(4) May 7, 1954 - 17.9 lbs.

223-14	3.85 lbs.	(approx. R _B 55)
223-22	6.55	(" 65)
223-29	6.1	(" 30-40)
184-71	<u>1.4</u> 17.9 lbs.	Melted ingot R _E 87)

Part of Lot 4 to Brookhaven National Lab., AEC, Upton, N. Y.

TOTAL THORIUM SHIPPED -- 33 lbs.

Analytical specimens shipped to Dr. Harold Mullen at New Brunswick AEC Laboratory.

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- (a) Oxide content
- (b) Particle size
- (c) Apparent density
- (d) Flowability
- (e) Compactability
- (f) Sintering temperature
- (g) Ability to be hot-pressed
- (h) Extrudability of the powder metallurgy compacts
- (i) Tensile properties of the resulting rods from (h) above.

Because of the inability to get any of these powders to full density by pressing alone, all the powders were evaluated by extruding the compacts to full density into rods suitable for testing, using a reduction ratio of 2.5:1 at 425°C. All of the extruded rods were annealed for one hour at 660°C after extrusion. Data obtained are as follows:

(1) Oxide content

- (a) Cast metal = 1%
- (b) Material derived from cast metal = 1%
- (c) Special coarse hydride powder = 2%
- (d) Commminuted metal = .1.5%
- (e) Ca reduced powder = 0.2%
- (f) Electrolytic powder (Horizons) = 0.2%

(2) Particle size and apparent density and flow rate

- (a) Ca reduced metal - 5 microns
- (b) Metal Hydrides thorium hydride = 5 microns
- (c) All others including Horizons electrolytic powder -35 +325 mesh range

Apparent density of all particles was about 4 gms/cc with the exception of the calcium reduced metal which was 2.0 gms/cc.

All powders flowed well, with the exception of the calcium reduced and the commercially fine hydride powders.

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(3) Compactability

Density Obtained
Expressed as Per cent
of Theoretical Density
(11.59 g/cc)

<u>Powder Type</u>	<u>40 T.S.I.</u>	<u>90 T.S.I.</u>
(a) Ca reduced Th powder	75%	
(b) Commercial Th Hydride powder	75%	
(c) Special coarse hydride powder	80%	
(d) Comminuted powder	80%	
(e) Horizons electrolytic powder	88%	97%

(4) Sintering, Hot Pressing, and Extrusion

Little consolidation occurred in vacuum sintering of the special coarse hydride powder below 1100°C, while densities approaching theoretical were achieved at 1570°C. Densities of the order of 97-99% of theoretical (considered 11.59 gms/cc) were obtained at 1400°C after cold pressing at 85 T.S.I.

With the coarse Brush-produced hydride powder and the Horizons electrolytic powder, densities from 90 to 99% of theoretical were obtained by vacuum sintering at 1400°C after cold pressing at 85 T.S.I.

Hot pressing was carried out with graphite dies at 1100°C under vacuum. Pressures of 1000 to 1500 lbs. were used. In hot pressing at 1100°C, all of the powders except the commercial fine

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hydride could be brought to 98% of theoretical density.

With but slight reduction in area in extrusion (2.5/1) at 425°C, all the powders were brought to 100% of theoretical density (except the commercial-fine hydride powder which could not take even a slight reduction on extrusion without cracking).

(5) Tensile tests on Extruded Billets

After consolidation by compaction, extrusion and annealing, the rods were tested in tension and gave the following results:

	Ultimate Tensile Strength psi	Tensile Elongation %
Standard virgin cast thorium (also extruded and annealed)	41,800	38.6
-60 mesh special coarse hydride powder cold-pressed 85 TSI, sintered at 1400°C	48,900	11.4
-20 mesh saw chips, cold-pressed and sintered	32,700	11.0
Attritioned chips, cold-pressed and sintered, -35 mesh	32,000	1.4
Electrolytic flake, -35 mesh, cold- pressed and sintered (Horizons Inc.)	18,000	6.6
Special coarse hydride, -35 mesh, hot- pressed 1100°C	49,200	11.1
Calcium reduced, hot-pressed	42,600	20.2
Attritioned chip, 135 mesh, hot-pressed	51,400	4.9
Electrolytic flake, -35 mesh, hot-pressed	24,700	13.8

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The only type of powder tested as directly hot-pressed was lathe turnings, giving a 43,500 psi tensile strength and 5.2% elongation. Consequently, it was believed that values indicated from the slightly mechanically worked and annealed bars would be similar to those hot-pressed to full density.

(6) Conclusions

(a) It appears that vacuum hot-pressing is a superior consolidating method to cold-pressing and sintering, since more uniform as well as better properties were achieved at 1100°C processing temperature by the former method than by the latter at 1100°C. However, if some working is permitted, any of the powder metallurgy methods seem feasible for all of the powders tested with the exception of the fine, commercially available, hydride powder.

(b) None of the powder metallurgy products gave the elongation achieved with cast thorium, although higher strengths were obtained. This presumably was caused by the presence of foreign atoms, probably oxygen, in the case of the attritioned material, and other impurities in the case of the calcium-reduced oxide which showed extremely low thorium oxide content. The electrolytic powder, although not developing the elongation of the calcium-reduced

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material, showed equal or superior ductility to that of the attritioned powder and, in some cases, approached the calcium-reduced metal. However, the ultimate tensile strength of the electrolytic flake was only 40% to 60% of that found in other materials. This might be an indication of extra-high purity giving an extremely soft metal, as the electrolytic powder had the best cold compactability of any of the powders tested.

(c) The commercial hydride powder seems completely unsatisfactory for any powder metallurgical operations, although the reasons for this are not too readily apparent, since the oxide content is not excessively high nor the particle size excessively low. Generally, the coarser the powder the better the compactability, although some loss of consolidation in sintering is experienced with the coarser grains.

(d) The electrolytic powder produced by Horizons Inc., seems to be very satisfactory material for either vacuum hot-pressing or cold-pressing and sintering. It flows freely and is quite convenient to handle by any of the powder metallurgy techniques examined. Its extreme softness and low ultimate tensile strength would be an advantage for most

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mechanical fabrication methods, although it conceivably could be a disadvantage for direct use in structural applications without working. However, this is subject to further experimental verification. Powder was not available to carry out a low pressure hot-pressing test, unfortunately. This method of consolidation could conceivably be suitable for producing consolidated thorium in billets approaching 1-1/2 tons in size, with available commercial equipment, and could be considered an alternate process to vacuum melting which could compete on an economic basis. This has been demonstrated, however, in regard to scrap recycling of comminuted cast metal.

b. Evaluation of Horizons Incorporated Electrolytic Thorium Powder at the Sylvania Electric Products, AEC Lab. Excerpted from Sylvania Reports (SS).

(1) Materials and Methods

(a) Materials

The investigative work was conducted with three samples of Horizons Inc. thorium powder with as-cast hardnesses of R_B 55-60, R_B 37-50, and $R_B < 24$.

The comparative standard used was -100 mesh thorium powder as produced at Sylvania by hydriding Ames thorium chips.

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(b) Methods

The powder was processed entirely without the use of protective atmospheres, with the exception of the sintering which was performed in an argon atmosphere. Hot-pressing was carried out in vacuum.

(2) Experimental Results (ss)

(a) Powder Classification

TABLE XVII

<u>Batch of Powder</u>	<u>Ave. Particle Size Microns</u>	<u>Flow Rate gm/cc</u>	<u>Apparent Density g/cc</u>
R _B 55-60	105	2.00	3.66
R _B 37-50	150	1.62	3.46
R _B < 24	120	1.02	3.61

Spectrographic Analysis

Fe - 0.01 - 0.1

Mn - 0.0001 - 0.001

Na - 0.0001 - 0.001

Si - 0.001 - 0.01

Th - -10 - 100

Chemical Analysis

C - 0.05%

O - 0.5%

Cl - negative

(b) Cold Compacting

Cold compacting of 10.0 gm samples, nominally 1.50 inches x 0.25 inches x 0.20 inches, resulted in pressed bodies varying in density with compacting pressure as shown in Fig. No. 44. Fig. 44 shows, in addition, a comparative plot of

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Fig. 44 - Green Density vs. Cold Compacting Pressure, Horizons Batch R_B 55-60 and Sylvania Thorium Powder.

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results obtained compacting -100 mesh Sylvania thorium powder. A series of compacts pressed at 10, 25, 50, 65, and 75 tsi showed that the hardness of these bodies, while very erratic for any individual specimen, increases with compacting pressure from approximately R_E 10, for 10 tsi pressure, to R_E 45-50 for pressures above 50 tsi. The powder used for this study was that designated as R_B 55-60.

(c) Transverse Testing of Green Compacts

The cold compacted bodies were subjected to a standard transverse rupture test. The values for the modulus of transverse rupture obtained are shown in Fig. No. 45 as plotted vs. cold compacting pressures and green density.

(d) Sintering of Cold Compacted Bodies

A series of cold compacted bodies, pressed at 15 and at 25 tsi, was sintered in a tank argon atmosphere for one-half hour and subsequently cooled in argon. The temperature range investigated was from 400°C to 1350°C. Fig. No. 46 summarizes the data available and includes plots of sintering data obtained for Sylvania thorium powder compacts as processed in argon, compared with Horizons powder processed without protective atmosphere.

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Modulus of Transverse Rupture, psi

Fig. 45 - Modulus of Transverse Rupture vs. Cold Compacting Pressure and Green Density

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Fig. 46 - Sintered Density vs. Sintered Temperature
Horizons and Sylvania
Thorium Powder

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(e) Hot Pressing

A 175 gm slug, 1.44 inches in diameter, hot-pressed at 650°C and 12 tsi in vacuum using standard uranium hot-pressing equipment and procedures showed a density of 11.50 g/cc, or approximately 98% of the theoretical density.

The powder used for this pressing was $R_B < 24$.

(3) Summary and Discussion of Results (ss)

The apparent density of Horizons powder lies in the same range as that of Sylvania thorium powder, e.g., 3.50 to 4.00 g/cc (with the exception of -100 mesh Sylvania thorium powder which has an apparent density of 4.6 gm/cc).

Up to about 65 tsi the green densities of Horizons thorium powder were substantially higher than those obtained for Sylvania thorium powder. At this point the compacts from the latter powder exceeded those made from Horizons powder, and continued to exhibit an increase in density in the compacting pressure. The hardness of the green bodies at above 50 tsi cold compacting pressure was R_B 45-50.

The densities of cold pressed Horizons powder compared favorably with those of Sylvania processed in argon. Sylvania powder bodies pressed similarly

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to the Horizons powder bodies, e.g., without the use of protective atmosphere except during sintering, showed significantly inferior densities for most of the sintering range and did not reach the maximum density of Horizons powder.

The tests indicate that Horizons thorium powder will lend itself well to fabrication by hot-pressing. A density of 11.50 g/cc was obtained when the powder was pressed at 650°C and 12 tsi in vacuum.

(a) Density Determinations (56)

Melted Thorium Buttons

11.43 g/cc
11.51
11.58

Rolled Sheet

11.27 g/cc

Calculations of theoretical density of Horizons thorium powder, based upon Sylvania's chemical analysis, is 11.63 g/cc. The density achieved during hot pressing was 11.50 g/cc. This is approximately 99% of theoretical density.

(4) Additional Hot-Pressing Study (57)

A preliminary hot-pressing study was conducted by Sylvania utilizing Horizons thorium powder. 200 gram samples were hot pressed at different temperatures, pressures, and times-at-pressure. This was

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carried out in vacuo in a 1.440 inch diameter die. The resultant slugs were approximately 1/2 inch high.

Fig. No. 47 shows the relationship between hot-pressed density and temperature of hot-pressing using a pressure of 12 tsi held for 15 minutes at temperature. As can be seen, the knee of the curve was attained at approximately 625° to 650°C. At 600°C a density of about 97% of theoretical was achieved.

Fig. No. 48 is a plot of Rockwell F hardnesses of the hot-pressed samples vs. hot-pressing temperature. The indication was that at the low temperatures the hardness was probably low because of inherent porosity in the specimens. At approximately 600°C, apparently, these holes no longer materially influence the hardness and a maximum value was attained. The decline in hardness was attributed to possible grain growth.

The next reaction condition investigated was that of increasing pressure. Fig. No. 49 shows hot-pressed density vs. applied pressure, pressure being held for 15 minutes at 600°C. The knee of the curve occurs at approximately 6 tsi. Apparently not much is achieved in the way of further densification by using pressures above 10 tsi. This conclusion is based only on short slug lengths.

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Fig. 47 - Relationship Between Hot Pressing Density and Temperature of Hot Pressing Horizons Thorium Powder

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Fig. 48 - Hardness vs. Hot Pressing Temperature
Horizons Thorium Powder

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Fig. 49 - Hot Pressed Density vs. Pressure
Horizons Thorium Powder

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The next variable checked was that of time-at-pressure. Fig. No. 50 shows the relationship between hot pressed density and time-at-pressure. These specimens were hot-pressed at 600°C and held at pressure for 15 minutes. The knee of the curve appears to be located between approximately 5 and 10 minutes. The indication is that 10 minutes is just as satisfactory a holding time as is 15 minutes, based on short slug lengths.

(5) Cold Pressing (ss)

Horizons electrolytic thorium powder was cold-pressed into two specimens, one 3 inches long and the other 5 3/4 inches long, both of 1.370 inch diameter. They were compacted by double action pressing at 66 tsi. Aquadag was used as the lubricant on an oxidized 18-4-1 tool steel die wall. The overall density for the two specimens was 11.30 g/cc for the 3 inch long slug, and 11.04 g/cc for the 5 3/4 inch long specimen. The density of the former was 97% of theoretical; the latter 95% of theoretical.

(a) Density and Hardness Variations

A study was made of density and hardness variations within these two slugs. The results of this study were as follows:

Fig. No. 51 is a plot of density variation

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Fig. 50 - Hot Pressed Density vs. Time at Pressure
Horizons Thorium Powder

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Fig. 51 - Density Variation along Length of Cold Compacted Horizons Thorium Bar.

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along the length of the long bar. It is seen that density decreases from both ends as the center of the slug is approached. The lowest density obtained was 93% of theoretical, while the highest was 97% of theoretical. The low density obtained at the very end of the piece was believed caused, at least in part, by a crack imparted to the specimen while it was being ejected from the die.

Fig. No. 52 shows the relationship between exterior hardness of the bar and location along the length of the specimen. Little variation is seen to have taken place along the length of the 3 inch specimen; however, considerable variation was observed for the 5 3/4 inch specimen. As with density, the greatest hardnesses were found at the slug ends. As the center of the bar was approached, the hardness decreased until a minimum value was obtained at approximately the middle of the bar.

Fig. No. 53 shows the variation of interior hardness for the long bar. A similar effect is observed for these hardness values as was found for Fig. No. 52. However, the lowest value found in the interior of the slug was

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▲ Max } 3" long slug
 △ Min }

● Max } 5-3/4" long slug
 ○ Min }

Fig. 52 - Variation of Exterior Hardness of Cold Compacted Horizons Thorium Bar

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Fig. 53 - Variation of Interior Hardness of Cold Compacted Horizons Thorium Bar.

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considerably higher than the lowest hardness found for the exterior of the slug, specifically, R_F 58 vs. R_F 41, respectively.

Fig. No. 54 shows the relationship between interior hardness and the density of the long slug.

Both cold-pressed slugs could be readily cut up in a cut-off wheel, both could be centerless ground, and both could be turned down on a lathe.

(b) Transmission and Reflection of Ultrasonic Energy

Endeavors to transmit and reflect ultrasonic energy through the long bar were unsuccessful. The same was true for 1/2 inch long sections cut from this bar. However, it was possible to obtain transmission and reflection waves when hot-pressed slugs were investigated. Fig. No. 55 shows the relationship between the number of back reflections through these hot-pressed slugs versus the density of the specimens. The indication is that the number of reflections increases as the density of the specimens increases.

(6) Hot Pressing Study (ss)

1870 grams of Horizons electrolytic thorium

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Fig. 54 - Interior Hardness vs. Density of 5-3/4" long Cold Pressed Horizons Thorium Bar.

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Fig. 55 - Ultrasonic Transmission Through Hot-Pressed Thorium Slugs of Various Densities

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powder having an apparent density of 3.5 g/cc was charged into a 1.440 inch diameter die for subsequent hot-pressing. The material was tamped into the die. During hot-pressing the top punch hung up and it was not possible to apply the full pressure, 12 tsi, desired. During ejection of the semi-pressed specimen from the hot die the thorium burned upon exposure to the air.

In order to overcome the hang up problem the pressing techniques were changed. Powder was first cold compacted in a 1.353 inch diameter die at 3 1/2 tsi. The resultant preform was approximately 11 inches long and had a density of 7.63 g/cc. This specimen was then charged into a 1.440 inch diameter die and hot pressed so that its full length was 6 inches. Its density was 11.10 g/cc or 95% of theoretical. The hot pressing temperature desired was 625°C; however, a thermocouple failed during the run and it is believed that a temperature lower than 600°C was actually achieved. This would tend to account for the low density attained.

Another charge of 1690 grams was preform cold-pressed in a 1.353 inch diameter die to a measured 7.88 g/cc density. The specimen length was approximately 9 1/8 inches. The preform was then re-cold-pressed at 66 tsi in a 1.370 inch diameter die using

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double-action pressing. The slug's final length was 6 inches and its density was 11.20 g/cc or 96.5% of theoretical.

Hardness measurements of the hot-pressed and cold-pressed slugs are as follows:

TABLE XVIII

Hardness Measurement of Pressed Slugs

Type	Ave. R_F Hardness			Remarks
	Top	Bottom	Side	
Hot-pressed Specimen	69 1/2	58 1/2	57-66	Hardness decreased from top to bottom
Cold-pressed Specimen	53 1/2	64	58-62	Soft in center, minimum of 46 R_F

A considerable quantity of inclusions have been found in the structure of specimens pressed from Horizons powder. There is an indication that the amount lessens with hot-pressing temperature, i.e., possible volatilization of the impurity is occurring.

Photomicrographs taken are the following:

Figure No. 56 hot pressed specimen at 650°C/12 tsi 15 min. in vac.

Figure No. 57 hot pressed specimen at 515°C/12 tsi 15 min. in vac.

Figure No. 58 cold pressed specimen.

Spectrographic and chemical analyses of Horizons thorium Lot No. 4 are shown in Table XIX (so).

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Unetched

Mag. 500X

Fig. 56 Hot pressed Horizons thorium powder at 650°C/12 tsi/15 min. in vacuum. Particle boundaries are evident; the structure is fairly clean. Several large inclusions found which were white in bright field but showed fine grain structure in polarized light.

Unetched

Mag. 500X

Fig. 57 Hot pressed Horizons thorium powder at 515°C/12 tsi/15 min. in vacuum. Particle boundaries and many varied inclusions are evident.

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Mag. 500X

Fig. 58

Cold pressed Horizons thorium powder. Larger and more numerous inclusions are evident than in hot pressed specimens.

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TABLE XIX

Spectrographic and Chemical Analysis of Thorium Powder Lot No. 4

Element	Spectrochemical by Sylvania	Chemical by Sylvania	Chemical by Horizons		
			223-22**	223-29**	223-14**
Fe	0.01 - 0.1%	0.021%	0.1%	0.4%	
Mg	0.0001 - 0.001	--			
Na	0.0001 - 0.001	--			
Si	1 - 10	--	0.3%	0.1%	0.2%
O ₂	--	0.45%			
N ₂	--	0.002%			
Cl	--	0.068%			
C	--	0.11%			

** Individual batches of Lot No. 4

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IV. CONCLUSIONS

Investigations into various means for the electrolytic production of thorium metal, at the laboratories of Horizons Incorporated under Atomic Energy Commission Contract Number AT(30-1)-1335, have resulted in the development of a process for producing thorium metal. This process includes the preparation of anhydrous thorium chloride, the electrolysis of this salt in molten sodium chloride, and the recovery of thorium powder of high purity. Thorium metal of satisfactory purity can be prepared both from $KThF_6$ and from $ThCl_4$. The use of an all-chloride melt, however, results in a process which can be operated on a continuous basis. The largest part of the investigation was therefore concerned with the study of an all-chloride electrolytic system. In general, the primary factors contributing to the success of such a process are: (1) high purity source electrolyte, particularly with respect to oxides, insoluble matter, and moisture; (2) the use of an inert atmosphere electrolytic cell during the electrolytic step, and the cooling of the deposit in an inert atmosphere; (3) proper control of bath operating temperatures and cathode operating temperatures; (4) the use of electrolytic cells of such construction so as not to contribute impurities to the electrolytic bath; (5) proper metal recovery procedures to eliminate thorium hydrates and casual impurities.

A procedure has been established for the preparation of anhydrous insoluble-free thorium chloride and sodium chloride by

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wet chemical procedure, by means of which thorium chloride can be dehydrated by the use of an ammonium chloride hydrolysis repressant. Operating electrolytic procedures have been established for the process on both the laboratory scale, capable of producing about three quarters of a pound of thorium metal per run, and on the intermediate scale capable of producing about eight pounds of thorium metal per run. The electrolytic bath must be operated within the temperature range of 800°C to 840°C and the cathode must be controlled at temperatures below 850°C. The practicability of continuous operation of the electrolytic bath has also been established. In summary it may be considered that the process operates simply by adding thorium chloride to a fused sodium chloride electrolyte, depositing thorium metal as a solid cathode deposit, and producing chlorine as a by-product anode gaseous product.

Thorium metal has been produced on both of these scales of operation at current efficiencies of at least 55-65% and at high yield. The solid metal cathode deposits can be recovered by simple aqueous leaching procedures followed by a final acid pickle treatment which effectively removed any hydrates produced. Electrolytic thorium metal has been produced yielding a product of hardness of Rockwell B 5 (Vickers 68). The metal can be consolidated by standard arc melting techniques. It can be cold rolled, drawn, swaged, or otherwise mechanically worked with ease. It is ideally suited for powder metallurgy fabrication techniques.

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It is felt that the results obtained during this contract period on the complete thorium electrolytic process demonstrate that this process is ready for process development leading to pilot plant studies. R. B. MacMullen Associates, Consulting Engineers of Niagara Falls, New York, were engaged by the Commission to evaluate the Horizons electrolytic process for the production of thorium and to make preliminary estimate for a pilot plant and a production plant employing the process. This work was done under AEC Contract No. AT(30-1)-1677.

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