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METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

THE PREPARATION OF THORIUM METAL
POWDER BY FUSED SALT ELECTROCHEMICAL
TECHNIQUES

By
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THE PREPARATION OF THORIUM METAL POWDER
BY FUSED SALT ELECTROCHEMICAL TECHNIQUES

A Paper
Prepared for Presentation
at the AEC
Metallurgy Technical Information Meeting
at Wilmington, Delaware
August 3, 1955

by

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THE PREPARATION OF THORIUM METAL POWDER BY FUSED SALT ELECTROCHEMICAL TECHNIQUES

INTRODUCTION

In April, 1952, Horizons Incorporated was awarded a small research contract by the New York office of the AEC to determine the feasibility of producing thorium metal in a high degree of purity by fused salt electrochemical techniques.

During the past three years the program has undergone several modifications and changes in emphasis, ranging from pure research requirements through process development to actual small scale production commitments.

At the present time the contract is under the auspices of the Savannah River Operations Office, technical cognizance being provided by the du Pont Atomic Energy Division.

The purpose of this paper is to present a resume of the developments under this contract, (AT(30-1)-1335), describe the present status of the work and outline briefly the program for fiscal year '56.

Program

The early portion of this program was exploratory in nature, numerous potential systems for metal preparation being evaluated in the laboratory on a small scale. The process which showed greatest promise, and which ultimately was selected for an extensive and intensive evaluation, was the production of thorium metal powder from a fused all-chloride salt bath.

Major emphasis during the first two years of the contract was placed on electrolytic aspects, preparation of suitable feed materials being somewhat secondary. The process for the preparation of small quantities of feed materials was selected largely from the literature and carried out in the

chemical laboratories on a beaker and test tube scale. Most of the electrolytic work was carried out in Horizons' Mark II electrolytic cells, these having a capacity of approximately one quart of electrolyte and running at a level of 40 to 80 amperes. Somewhat later in the program, after major variables had been established, Horizons' Mark XX type electrolytic cell was used extensively, this unit operating at a level of 400 amperes and capable of producing from four to eight lbs. of metal per working day.

In the late spring of 1954 cognizance of the program was transferred to the Fernald group, and emphasis was switched from research approaches to sub-pilot plant activities with definite production requirements being established. This immediately necessitated the setting up of moderate capacity facilities for the preparation of electrolytic cell feed, time being of the essence. While admittedly the wet chemical technique which had been utilized up to that time for the preparation of cell feed lacked much to be desired, there was no immediate choice but to make an installation based on the procedures which had been established in the chemical laboratory. To make matters worse, the unit had to be operating within a month's time, which limited the choice of process equipment to that which could be purloined from other areas of the laboratory, or which could be obtained from manufacturers out of stock.

Simultaneously with the setting up of cell feed facilities, a research program was initiated whose goal it was to evaluate other techniques for cell feed preparation, with the ultimate hope in mind that a more economical and straightforward system could be developed in due course of time.

It happened that Horizons had a fairly large electrolytic cell on hand which had been built under the Navy auspices on a different research contract. It had been used for the preparation of zirconium metal powder satisfactorily

on previous occasions, and the decision was made that, despite the fact that the design lacked much to be desired, it would be most expedient to convert this unit to the preparation of thorium metal powder.

The Mark VI cell has a capacity of approximately 375 lbs. of molten salt, the crucible being 18" diameter and 36" deep. Heat is provided by an external graphite resistor heater surrounding the crucible, and a metal cathode centrally located is utilized on which to plate the metal. This cell previously had been operated at levels up to 2000 amperes.

Simultaneously with the Mark VI cell activities a development program was initiated on cell design. This was considered mandatory since previous experience had indicated that the Mark VI could not readily be scaled up. Many different types of graphite crucibles have been used in this unit, including such dense grades as graphitite. Without exception salt leakage occurred sooner or later, not necessarily on the first run in the crucible, but generally after three or four runs in the cell. One therefore could not be in a position to count on having perfect operating conditions during any heat, and hence it was considered necessary to redesign for larger cells using a completely different cell concept.

The basis for the revised cell design centered largely around a prototype variety that had been developed previously on a small scale in Horizons' metallurgical laboratories. In general the concept is a modification of a frozen salt crucible principle, heat being supplied to the cell by internal electric resistors. The preferred design consists of graphite or carbon slabs to form the anode crucible, this being backed up by a layer of insulating carbon black and surrounded externally with a nickel shell. Experimentally it was found that the molten salt permeates the graphite but solidifies in

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Figure 1 presents a schematic drawing of the flow sheet for the original wet process as devised at Horizons and installed on a sub-pilot plant scale. In general the procedure was as follows:

1. Crystalline thorium nitrate was placed in water solution in a large rubber-lined tank. In a similar sized tank, positioned at a somewhat higher elevation, soda ash likewise was dissolved in water, at approximately 80°C. The resulting soda solution was drained by gravity into the thorium nitrate tank, where thorium oxycarbonate precipitated out. After a short period of agitation, this precipitate was allowed to settle, the upper solution decanted, fresh water introduced and the material re-suspended.

2. The thorium oxycarbonate suspension was pumped into a vertical Oliver leaf filter, where the oxycarbonate formed a suitable filter cake without benefit of pre-coat. The filtrate usually was completely free of thorium. As a precaution, however, the liquid was pumped into a large sump tank and treated with additional quantities of soda ash before being pumped to sewage.

The filter cake was then thoroughly washed with fresh water and air blown.

3. Because of the design of the vertical filter it was not convenient to remove the filter cake as a solid. A procedure therefore was worked out whereby most of the filter cake was knocked off the leaf surfaces to the lower portion of the filter body and dissolved in concentrated hydrochloric acid. The thorium chloride solution resulting was pumped to an evaporator for the next stage in the process.

4. The ultimate goal in this process was to produce an anhydrous thorium chloride. Because of the properties of hydrated thorium chloride it is substantially impossible to dry the material alone. However, thorium chloride forms a compound with ammonia which can be dehydrated, the ammonium chloride

Fig.1. Flow sheet of wet chemical process for producing electrolytic cell feed.

later being driven off to yield a high purity, anhydrous thorium chloride.

With this process in mind, the thorium chloride solution was admixed with ammonium chloride in the evaporator and boiled down to a thick, sirupy constituency at a maximum temperature of approximately 146°C . It was found expedient to cast the sirup onto a quench tray and allow it to solidify before further treatment. The quenched cake was crushed, mixed with sodium and potassium chlorides and placed in a drier for the next step.

5. Experience showed that the hydrated ammonium thorium chloride, admixed with sodium and potassium chlorides, on heating did not go back through a liquid stage. Thus it was possible to dehydrate completely in the drier without too much difficulty, maximum temperature required being approximately 260°C . The batch was held at this temperature for a prolonged period of time in order to eliminate the last traces of moisture throughout the batch. Following this treatment the material was transferred to a sublimation vessel for additional processing.

6. At this stage of the process an ammonium thorium chloride, containing approximately two mols of ammonia per mol of thorium, existed in the anhydrous state. The last step in the process involved subliming off the ammonium chloride, leaving as a final product dry, anhydrous thorium chloride in the presence of sodium and potassium chlorides. The sublimation was accomplished by heating to approximately 600°C . for a prolonged period of time, during which the ammonium chloride was distilled off and collected in a condenser.

On occasion it was found convenient to fuse the thorium, potassium and sodium chlorides into a homogeneous menstruum, siphoning the liquid off into a casting pot. The material after solidification was then crushed and stored in polyethylene bags for further use as cell feed to the electrolysis process.

Remarks on the Wet Chemical Process

At first glance the process outlined above may appear to be relatively uncomplicated. However, in actual practice just the reverse is true. Because of the purity requirements imposed on the final product, materials of construction posed a major problem in many of the steps. Not the least of these was the evaporation stage. A water-like solution of concentrated hydrochloric acid containing thorium chloride, to which was added ammonium chloride, had to be converted to dryness and ultimately calcined to remove the ammonium chloride. To devise a continuous process for this operation undoubtedly would be something of a chore. Steel and cast iron pots with glass liners initially were selected for the evaporation stage, but the mortality rate on linings was extremely high. The unit finally evolved for the operation consisted of a stainless steel hemi-cylinder lined with a hemi-cylinder of graphite, carbon black insulation being placed between the stainless steel and the liner. With a unit of this type it was possible to heat externally, evaporating down the thorium chloride solution at a fairly rapid rate without introducing any contaminants into the bath. The carbon black insulating medium acted as a sort of sponge to collect any solution which leaked through the graphite, thermal gradients preventing the liquid ever from reaching the stainless steel shell.

Drying operations were carried out in graphite pots 18" in diameter and 24" deep, similarly sized units being used for the sublimation process. It was found necessary to maintain a hydrogen chloride gas atmosphere over both of these operations in order to prevent moisture pick-up from the atmosphere and ultimate hydration or oxide formation in the product. Even under the best of conditions, however, a sizable proportion of the total product reported

as insoluble oxide, and hence the ultimate requirement of fusing the bath prior to casting the material for use as a cell feed. Under molten conditions the oxide in the mix settled to the bottom, where it could be collected and removed after siphoning the liquid portion.

By and large the wet chemical process for the preparation of cell feed, while capable of producing adequate quality material, is afflicted with a great multiplicity of steps, too many handling problems, severe corrosion conditions and high losses. For these and other reasons it was not considered a feasible approach to the preparation of cell feed, despite the fact that several tons of adequate material were prepared in this manner in the early stages of the program. Fortunately much simpler and more direct approaches to the preparation of cell feed were ultimately developed and the wet chemical process has long since been discontinued. The details of this process development are presented in the following section.

Preparation of Cell Feed by Direct Chlorination

Process Development

The establishment of a more direct method of producing cell feed involved a rather prolonged program, one which is only now coming to fruition. Major emphasis was placed on reactions in fused salt systems, since this appeared to be the most logical approach to the solution of the problem.

Most of the experimental work was carried out in externally heated vycor test tubes 1-1/2" in diameter and 14" long. In those reactions involving gases, either a quartz or a vycor sparger was used to disperse the gas reactant as completely as possible.

The program included evaluations of various thorium bearing compounds, such as thorium nitrate, thorium hydrate, thorium oxide, thorium oxycarbonate,

etc. In every instance there was involved a reducing agent and a chlorinating agent, generally these two being incorporated in the single material. For example, hydrogen chloride gas serves the dual purpose of reducing an oxidized compound and providing the chlorine for converting to the chloride. Such reactants as hydrogen chloride gas, phosgene, carbon plus chlorine, carbon tetrachloride and combinations thereof were evaluated on each compound under consideration, other variables including the temperature of the operation and the composition of the fused salt. Literally hundreds of experiments of this type were run, the more promising ones being broadened out to include evaluations of the effects of multiple passes on the gas reactants in order to improve gas consumption efficiencies, cascade systems for accomplishing the same goal, etc.

Inasmuch as thorium nitrate was the material being supplied Horizons as a raw material, much work was done in determining the feasibility of using the nitrate for chlorination in a fused salt system. It was found that phosgene was reasonably effective in converting the material to chloride, and a sizable unit was operated for several months on this system. One of the sublimation furnaces, which was capable of producing between 250 and 300 lbs. of cell feed per batch, was converted to this chlorination operation.

There are a number of inherent difficulties in the use of thorium nitrate as a starting material for purposes of this type. On heating, the material undergoes decomposition, giving off copious quantities of moisture and nitrogen oxides of various types. Additionally, at least 10% of the nitrogen-bearing gases remain with the thorium, being driven off during the initial stages of chlorination with phosgene. The actual use of phosgene also is somewhat undesirable, inasmuch as the poisonous nature of the material necessitates rather concise safeguards and handling procedures. The corrosive fumes

resulting from heating, together with the phosgene problem, strongly suggested that a different approach be utilized.

Small scale experiments using thorium oxycarbonate indicated that the reactivity of this material was considerably higher than that of the nitrate. Further, the gaseous product of thermal decomposition is quite innocuous, consisting largely of moisture and CO_2 . By a rather simple chemical conversion from nitrate to oxycarbonate, therefore, the major corrosive problem can be eliminated.

Experimentation showed, rather surprisingly, that some of the combination reducing and chlorinating agents were far more effective on thorium oxycarbonate in a fused salt system than on the nitrate. For example, in a recent small scale experiment it was possible to form a 45% thorium cell feed by reaction with carbon and chlorine in less than 10 minutes. The chlorine conversion efficiency was extremely high. Comparable tests using phosgene had required more than one hour, with very low conversion efficiency.

The sublimation furnace, utilized to produce sizable quantities of high thorium concentration cell feed during the past six months, now has been shut down and is being held in stand-by condition should a recently installed internally heated chlorinator not prove satisfactory. The details of the latter unit will be presented below.

Modified Feed Preparation Process

Figure 2 shows a drawing of the proposed flow sheet for a modified process to product cell feed by a combination of portions of the wet chemical process and direct chlorination techniques. In essence, the procedure consists of the following steps:

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Fig. 2. Flow sheet of chlorination process for producing electrolytic cell feed.

1. Thorium nitrate hexahydrate crystals are placed in solution in a tank and reacted with soda ash solution to precipitate an oxycarbonate of thorium, in the same manner as described in the wet chemical process above.

2. The oxycarbonate suspension is filtered on a continuous Eimco filter, the washed filter cake being repulped without adding any water, the only additive being a small quantity of a pelletizing aid, such as starch or dextrin solution.

3. The repulped filter cake is fed directly to a continuous stainless steel belt drier which dehydrates the oxycarbonate to less than 5% water. The product from the belt drier, a porous and friable white solid, is crushed, mixed with quantities of sodium and potassium chlorides and pelletized into small briquettes.

4. The pelletized material is fed semi-continuously to an internally heated chlorinator, where the thorium oxycarbonate is converted to a thorium chloride. This, together with sodium and potassium chlorides, forms a fluid bed which is periodically tapped off, cast into an enclosed cooling mold, crushed and bagged for feed into the electrolytic process.

From the point of dissolving the thorium nitrate to the blending of the final product prior to pelletizing, the process will be completely integrated and continuous. The repulped filter cake, for example, is fed continuously to the belt drier directly from the repulp tank by means of two Moyno pumps, which extrude the cream-like oxycarbonate material through a nozzle system onto a continuously moving stainless steel belt drier.

At this writing the integration of the various processes has not yet been accomplished. The Eimco filter, key to integration, was recently received and is scheduled to be installed in the very near future. The belt drier,

completed three months ago, has been operated continuously by feeding from a batch-charged repulp tank; however, so there is no anticipated difficulty in this proposed integration. The drier, a rather versatile unit designed at Horizons, may be run at any desired belt speed, at variable cake thickness, and over a wide range of temperatures. The approximate capacity of the system, running around the clock, is rated to handle some 400 lbs. of contained metal. This would represent a consumption of 1000 lbs. of thorium nitrate per day.

The Chlorination Process

A schematic diagram of the internally heated chlorinator is presented in Figure 3. Basically this unit was designed after the chlorinator utilized in a commercial installation for the production of magnesium chloride at the Basic Magnesium Plant, Henderson, Nevada. The units at Henderson are approximately 12 ft. in diameter and 25 ft. high, a single chlorinator supplying the requirements of four magnesium cells, each producing approximately one ton per day of magnesium metal. In the magnesium chlorinator heat was supplied by two sets of three large electrodes set into a bed of carbon rondelles, so that in essence a graphite resistor pile served as the heat generator on the inside of the chlorinator unit. Pelletized magnesium oxide, in combination with peat moss and other carbonaceous materials, served as the feed to the unit. Chlorine gas evolved from the magnesium cells was used as the chlorinating agent to convert the magnesium oxide to the chloride. The material was periodically tapped from the chlorinator and carried in heated buggies to the cells where it was poured in for make-up purposes.

The chlorinator designed at Horizons is a vertical shaft furnace with inside hearth dimensions approximately 18" in diameter and a working depth of 24". Two sets of two electrodes each are positioned at different levels

Fig.3. Internally heated chlorinator.

in the chlorinator at 90° positions, four arc welders supplying the power.

A maximum power input of approximately 60 kilowatts could be achieved providing resistance of the bath were properly adjusted.

The last mentioned point is a rather critical one, and one which, unfortunately, one can do very little about. The internal resistance of a unit of this type consists predominantly of contact resistance between the electrodes and the multiplicity of carbon or graphite chunks which constitute the resistor bed. When the bed is covered with a molten bath of chlorides, the contact resistance appreciably decreases, thus resulting in a rather low over-all resistance in the system. Under operating conditions with molten salt covering the graphite bed, the power input on each set of electrodes was 600 amperes at 12 volts. The desired operating temperature for the unit is approximately 800°C., a thermal condition easily achieved in the unit which has been fabricated.

An actual chlorination run in the chlorinator has not as yet been carried out, some minor difficulties with the lower electrode being encountered during the first salt melt-down. This necessitated redesign of the electrode ports, and the unit has not been returned to service as of the present writing. It is anticipated that the first chlorination campaign will take place early in August.

Electrolytic Division

In the second portion of this paper a brief description of the cell development program was presented. For the past several months major activities in the electrolytic section have dealt with continued experimentation on cell design, the development of internal heaters for use in fused salt systems and the design of auxiliary components for use in conjunction with electrolytic

operations. Fundamentals of the process were covered fairly thoroughly in the early years of the process, and will be recounted only briefly here.

Process Fundamentals

A proportionately large amount of the work in the electrochemical section was done on the binary system thorium chloride-sodium chloride, the thorium content ranging from zero to as high as 20 weight per cent. The decomposition potential of anhydrous thorium tetrachloride in sodium chloride was determined at a concentration of 15 weight per cent thorium as a function of temperature over quite a wide range. A temperature coefficient of 2.25×10^{-3} volts per degree Centigrade was determined, Th decomposition voltages varying from approximately 2.5 at 700°C. to 2.0 at 900°C.

The phase diagram for the system, sodium chloride-thorium tetrachloride, also has been determined, up to approximately 35 weight per cent thorium. The liquidus temperature in this phase diagram is characterized by a continuous drop with increasing thorium content, the solidus probably being in the range of 600°C. The compound, $4\text{NaCl} \cdot \text{ThCl}_4$, exists as the first compound on the sodium chloride side.

Experimentally, in the preparation of cell feed by chlorination techniques it has been found that the rate of chlorination is far faster in a sodium chloride-potassium chloride system, preferably the 1:1 molar eutectic system, than in straight sodium chloride baths. This possibly is related to the formation of potassium-thorium double chlorides, comparable units of which may not be formed with sodium chloride. The addition of potassium chloride to the system also effects a lowering of the temperature, which has the added advantage of lower thorium chloride losses due to direct vaporization. The vapor pressure of thorium chloride, for example, drops from a value of approximately

250 millimeters at 850°C. to 50 millimeters at 750°C.

Much of the recent experimental work in electrolysis has been involved with the determination of whether or not suitable deposits can be made in a sodium chloride-potassium chloride eutectic containing thorium chloride. It has been found that, while deposits of metal are obtained from such a composition, the outer portions of the deposit are extremely friable, giving rise to high loss percentages due to portions of the deposit falling into the bath.

Good quality metal, with no losses of the metal deposit, has been produced in a straight sodium chloride-thorium chloride bath. A series of experiments therefore was performed in which small additions of potassium chloride were added to sodium thorium chloride systems in order to work up as closely as possible to the most easily chlorinated composition, thus approaching a compromise with respect to electrolysis. In general it was found that a fused salt system containing approximately two times as much sodium chloride by weight as potassium chloride provided satisfactory operating conditions without major difficulties being encountered with the physical attributes of the metal deposit itself.

In practice it is found that the cathode deposits average nearly 50% metal by weight, the remainder of the mass being salt. For continuous operation, which is envisaged for the process, it is necessary to add make-up salt periodically in order to counteract the "drag-out" losses and to replenish the bath in thorium ion. Recent experience on a concerted campaign has indicated that the cell feed requirement will be met if a charge material can be provided which contains between 49% and 50% thorium by weight. A eutectic KCl-NaCl cell feed prepared by direct chlorination, and containing 50% thorium by weight, can be admixed with sodium chloride to bring the sodium chloride to potassium chloride ratio up to a value of 2:1, and at the same time provide for

precisely the amount of make-up salt needed to replenish the cell. This would assume an electrolytic operation with a thorium concentration in the bath ranging between 8% and 12% during the major portion of the electrolysis. It has been found feasible to produce the thorium metal from a bath containing as high as 20% thorium by weight and as low as 1% to 2%, the latter being a function of cell geometry and current density.

Cell Design Concepts

As mentioned earlier in the paper, two basic cell design concepts have been evaluated on a fairly sizable scale under the present contract. Representative of these two are the Mark VI and Mark XXV cells, schematic views of which are shown in Figure 4. By way of comparison, these two cells are of like capacities, both volume-wise and power-wise, though the external sizes are complete different orders of magnitude. The Mark VI cell is approximately 6 ft. in diameter and 6 ft. high, whereas the Mark XXV has dimensions of 16" x 32" x 40" high.

The Mark VI type of design involves heating a graphite crucible by external means, a preferred method involving the use of graphite resistor heating elements, heat insulation being provided by one or more courses of insulating fire brick. This type of design suffers from a number of shortcomings including the following:

1. The unit is difficult to evacuate and maintain completely inert with respect to atmosphere; the insulating brickwork provides oxygen and moisture due to adsorbed gases, and absorbs vaporized salt, which also acts as a potential supply of moisture and other gases.
2. For a given capacity the exterior cell dimensions are relatively large, requiring a great deal of floor space per unit of productive metal capacity.

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Mark VI cell design

Mark XXV cell design

Fig. 4. Schematic sections through externally and internally heated electrolytic cells

3. The most serious drawback of all, salt leakage from the crucible, has been a continual problem, graphite containers not being impervious to molten materials of these types. The latter factor would be a deterrent for scale-up of the unit to commercial or near-commercial sizes.

4. While the Mark VI type of design obviously provides for very good insulation during heat-up, at the same time it prevents heat transfer outward during electrolysis, during which period of operation it is desirable, and indeed oftentimes necessary, to dissipate large quantities of heat at a fairly rapid rate.

By way of comparison, the Mark XXV does not suffer from most of the items listed above, it taking up a relatively small floor area per unit of productivity, the capacity or size of the unit could be increased to any desired level, salt leakage ceases to be a problem and any desired heat transfer rate can be designed into the unit. The Mark XXV may, however, suffer from gassing problems in the same manner as the Mark VI, inasmuch as carbon black is a noted adsorber of gases and could potentially provide a continuous supply for atmosphere contamination during electrolytic campaigns. The Mark XXV basic design also is characterized by one additional factor which is debatable as regards its desirability. For a unit of power capacity the quantity of molten salt required is considerably more than for the Mark VI type of cell. This is necessitated by the fact that the heating elements also require a volume inside the cell proper and must be surrounded by the molten salt bath. While the quantity of salt required is therefore considerably more, at the same time it provides a greater reservoir of thorium ions, possibly preventing the necessity of a DC shutdown for an extended period of time should something go wrong with the cell feed charging device. In a cell of the Mark XXV basic design it may also

be possible to operate at a constant or nearly constant thorium ion concentration, thus eliminating one specific variable from the electrolytic operation. The details of how this may be accomplished will be presented a bit later.

Electrolytic Cell Superstructure

A very thorough investigation of the effect of cell atmosphere contamination has been carried out during the past many months. It has been established without question that it is necessary to operate the electrolytic cells under an oxygen-, nitrogen- and moisture-free atmosphere. Much time and effort have gone into the design of suitable auxiliary components for use in conjunction with various electrolytic cells which would accomplish this rather rigid requirement. The cell atmosphere must be limited to chlorine which is given off in the operation and either argon or helium, which is introduced to maintain the working atmosphere.

Figure 5 depicts the system which ultimately has been arrived at, this unit having actually been used for one campaign in Horizons' Mark VI cell. The same unit will be used on the Mark XXVI cell as soon as its fabrication has been completed.

Directly above the electrolytic cell is positioned an 18" all nickel gate valve of a design developed at Horizons. This unit, one of the largest ever cast of pure nickel, required some 3000 lbs. of nickel stock to make the castings. It is a completely vacuum tight valve, capable of being operated under either positive or negative pressure, components being designed so as to prevent or minimize to the maximum extent condensation of volatilized salts on the working components. The valve is actuated by a gear which meshes with a rack attached to the valve gate, the latter being on wheels for ease of

Fig. 5. Schematic drawing of Mark ~~XXVI~~ cell and removal chamber assembly

movement. Positive sealing in the closed position is assured by vertical action of a group of six hydraulically actuated rams and compressor rings which are affixed to the ram pistons.

In a commercial installation a valve above the cell would not be an absolute necessity. However, it was considered desirable to have one in this installation inasmuch as it provides a means for isolating the removal chamber assembly from the cell proper without having to shut down the operation, a desirable convenience for an experimental unit of this type.

Attached to the upper portion of the horizontal gate valve in an eccentric position is a circular plate nearly 6 ft. in diameter. A pivot is provided in the center of the plate, around which rotates a matching circular plate, the latter supporting two removal chambers as shown in Figure 5. During electrolysis the upper removal plate sits flat on the lower one, positive vacuum sealing being provided by a double O-ring around the perimeter of the plate. After an electrolysis, the entire upper assembly is lifted approximately 1/8" off the lower plate by means of lever actuated wheels around the perimeter of the upper plate. It is then manually rotated to the desired position. During this lifting and rotating operation a positive seal still is maintained by means of an oil channel built into the lower plate, into which dips a metal ring welded to the upper plate. Thus, the design incorporates positive sealing at all times to prevent entry of air into the system, within the limits of normal operating pressures.

Provision was made for charging make-up salt from the removal chamber level by positioning a charging port over the center of the cell. Experience in the Mark VI during a recent campaign showed, however, that severe splashing of the molten bath occurred when charging was carried out at this level. The

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the melting rate is approximately 1 lb./min. There therefore is necessitated a period of between 30 and 45 minutes between cathodes in order to melt down the make-up cell feed. In practice, turn-around times less than 45 minutes were achieved during the first campaign using this system.

The cathode on which the deposit was plated would now be in the cooling position, with cooling air and water flowing through the cathode itself. It has been found that less than 1-1/2 hrs. are required to cool the deposit to a temperature below 80°C. Once this temperature has been reached the removal chamber is removed from the upper plate by quick acting clamps and the entire assembly lowered to a working platform below the cell. The removal chamber is positioned on a rack which allows lowering the cathode deposit below it into a chipping chamber, where the metal deposit is quickly chipped into a receiving basket by means of an electric hammer. The cathode is then retracted into the removal chamber and the assembly replaced on the upper removal plate.

The empty chamber is then evacuated and flushed with argon, and is ready for the next cycle in the process.

Semi-continuous Mark VI Electrolytic Campaign

Early in June, 1955, the first semi-continuous operation was completed utilizing the complete removal chamber assembly and the Mark VI electrolytic cell. The campaign was carried out with completely inexperienced crews and under conditions which were considered to be other than ideal before the electrolytic campaign began.

The primary purpose of this campaign was to train operating personnel and to check out the operation of the removal chamber assembly. The desired concentration of cell feed was not available, so a somewhat lower concentration was used. A stockpile of some 800 lbs. was prepared prior to the inception of

the Mark VI campaign, which was adequate to run for approximately three days continuously.

As is customary in campaigns of this type, the hottest three days of the year, boasting the highest humidity, were selected for the actual operation. The moisture problem, coupled with a somewhat inadequate air supply, prevented adequate cathode cooling during electrolyses in all but three instances, so that the results from the campaign were not particularly outstanding. Despite this fact and other obstacles which were encountered during the run, the results were quite gratifying in some cases. During a continued campaign of 78 hours, 14 cathodes were pulled, ranging in size up to 57 lbs. Current efficiencies approaching 80% were encountered, and in one run, which has just been completely evaluated, the softest metal ever produced at Horizons by electrochemical techniques resulted. This material, arc-melted and annealed, had a recorded Brinell hardness of 46.

Table I presents a brief summary of information on this campaign.

Table I

Statistics on First Continuous Mark VI Electrolytic Campaign

Total weight of thorium charged to cell	442 lbs.
Total weight of deposits recovered (metal + salt)	532 lbs.
Total weight of thorium metal recovered	261.5 lbs.
Deposit weights (metal + salt)	{ least 22 lbs. average 38.1 lbs. largest 57 lbs.
Metal weights	{ least 5.9 lbs. average 15.6 lbs. largest 31.2 lbs.
Current efficiencies	{ lowest 21% average 44.5% highest 79%
% metal in deposits	{ lowest 27% average 41.2% highest 55%
Total time for electrolytic campaign	78 hrs.
Total number of cathodes produced	14 hrs.
Average electrolytic cycle	5.5 hrs.
Cumulative current efficiency for entire campaign	54.2%

The sodium chloride to potassium chloride ratio decreased throughout the run, to the point toward the end where a dangerous proportion was being approached. Under normal operating conditions this would not happen, inasmuch as the charge feed would have a composition necessary to maintain the ratio constant.

Figure 6 shows a photograph of four typical cathode deposits made in the Mark XXV cell. They are generally carrot-shaped, with slightly irregular protrusions on the outer perimeter, and are characterized by an over-all length approximately twice that of the cathode tip itself. These deposits, which were grown on a 3-1/2" O.D. cathode 9" long, range in outer diameter from 9-1/2" to 10". A 3-1/2" to 4" thickness of deposit on the surface of the cathode appears to be the maximum desirable from a strength and heat transfer standpoint. In larger cells, therefore, cathodes are planned which will be much larger in diameter in order to provide adequate surface for growth of much heavier deposits.

Proposed Electrolytic Cell

As indicated above, the removal chamber assembly was designed for ultimate use with a cell other than the Mark VI. Immediate future plans under the present contract provide for the design, fabrication, installation and operation of an electrolytic cell of the Mark XXV basic design which will have a capacity of 7500 amperes. This unit, which is presently under construction, has crucible dimensions of approximately 22" width, 44" length and 48" height, and will hold 2500 pounds of molten salt. In theory it will be capable of producing between 20 and 25 lbs. of metal per hour of operation, and during a campaign such as recently was run in the Mark VI, between 300 and 400 lbs. of metal should be produced per 24-hour working day. It was on

Figure 6
Typical Examples of Thorium Cathode Deposits.

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this basis that the cell feed preparation department was designed.

The Mark XXVI cell will have heating chambers on either end, each chamber housing two separate graphite resistor heating elements. These will have an approximate capacity of 10 kilowatts each to provide heat for melting down salt and for overcoming heat losses should this prove necessary during the electrolytic cycle. It is anticipated that salt could be melted at a rate of two to four pounds per minute by feeding between two of the heating elements on one end of the cell. Designs will be provided for continuous feeding of cell feed during electrolysis, so that no down-time will be required for charging make-up feed. Provision also will be made to introduce approximately twice as much power on the charging end of the furnace as is used on the non-charging end.

The removal chamber and valve assembly presently used on the Mark VI cell will also be used on the Mark XXVI unit. The only changes will be minor in nature, a few modifications being required on the top of the removal chambers themselves, in order to house cathodes of a much larger diameter and greater weight. The Mark XXVI cathodes will have a tip 16" long and 8" in diameter, and each cathode will weigh approximately 1100 lbs. Operating techniques will be substantially identical to those outlined above for the Mark VI campaign with the exception that no time will be required between cathode changes for salt melt-down. It therefore is expected that, barring unforeseen difficulties, turn-around time between electrolyses should be no more than 30 minutes. An average electrolysis may range between 2-1/2 and 5 hrs., between 50 and 150 lbs. of metal being pulled per cathode.

In theory this type of cell should be able to be operated indefinitely without shutdown. Heating element designs are such that they can easily be

changed without shutting down the cell, and also without introducing any air contamination into the cell. Unless a power failure occurs, there should be no necessity for shutting down the operation providing adequate cell feed is available for its continued running. Unfortunately the scope of the program presently being conducted at Horizons does not provide for adequate funds to allow running this unit on a continuous basis, so it will be necessary to make sporadic runs of relatively short duration. On completion of the campaign, which will be dictated by the quantity of cell feed which will be stockpiled, the cell will be tapped through a taphole provided in the base of the unit.

DC Power Supply

Prior to the present installation all electrolytic cells have been powered with either motor generator sets or rectifiers with constant voltage controls. For the Mark XXVI installation a constant amperage control system has been installed. This was considered desirable, inasmuch as the resistance continually decreases during the run as the result of decreasing distance between anode and cathode surfaces (deposit growth toward anode) and the fact that a bath low in thorium ion is more conductive than one high in thorium ion. For example, in a Mark VI electrolysis the initial voltage may be in excess of 12 volts, while the final voltage will be no more than eight assuming constant amperage flow. With a constant voltage control, therefore, there is required continuous operation of the controls in order to decrease the voltage to compensate for decreasing resistance. By operating at a constant amperage substantially no attention is required on the DC circuitry, and at the same time a more uniform deposit of metal is produced. The power system for the Mark XXVI will consist of a DC constant amperage control unit which feeds five 1500 ampere selenium rectifiers. These units, in parallel, will provide

the cell with up to 7500 amperes on a continuous basis. In all probability the running level will range between 6000 and 7000 amperes.

Product Recovery Division

The deposit formed in the electrolytic process consists of an agglomeration of thorium crystals interspersed with frozen salt. As a rule the proportion of salt to metal is approximately 50% by weight. It will consist of sodium chloride and potassium chloride in the approximate ratio of 2:1, together with small percentages of thorium chloride which remain in the bath at the end of the electrolysis. Analyses taken of the salt at various points in a deposit have shown that the salt remaining on the inner portion of the cathode approximates in composition the early concentration of the bath, this leading to the conclusion that actual metal deposition takes place on the outer perimeter of the deposit, not in the interstices. Since the bath does not become depleted within the metal deposit itself, there is available on and within the metal structure some thorium chloride which, when exposed to moist atmosphere, hydrolyzes. It is believed that, on heating to melt or sinter, the adsorbed or absorbed hydrated thorium chloride converts to thorium oxide, which ultimately reports in the final consolidated metal as an insoluble oxide phase. The section dealing with metal recovery has concerned itself with the problem of how this hydrated chloride may be eliminated from the metal structure, literally hundreds of washing and leaching experiments having been carried out. Much progress has been made in this direction, but the problem as yet is not considered completely solved.

Metal Recovery Procedures

Early in the paper it was mentioned briefly that the metal deposit is chipped from the cathode with an electric hammer. The product, consisting of

large chunks of salt interspersed with crystals, is fed to a jaw crusher for major comminution, followed by treatment in a roll crusher to reduce the average particle size to approximately 40 mesh. These crushing techniques have been selected as the ones which give the maximum crushing action with minimum smearing, since any tendency to shear or smear the metal would effectively incorporate quantities of salt into the metal where it would be unavailable for any type of surface treatment.

Following roll crushing the material is fed into one of a variety of countercurrent washing devices. As a result of extensive evaluation tests, two primary designs appear to be the most feasible. These are cone washers and pachuca tanks.

The design of the cone washer is shown in Figure 7 schematically. It consists of a simple cone with an included angle of between 25° and 30° , the unit being equipped with a valve at the bottom for withdrawing the deposit. A water inlet at the apex of the cone and suitable overflow devices are provided. By adjusting the water flow it is possible to maintain a fluid or semi-fluid metal suspension, effecting a very complete washing action in a fairly short period of time.

Experimentally a small pachuca tank also has been used for accomplishing the same goal. This consists of a vertical cylindrical tank inside which is suspended an open cylinder with a downward impeller positioned in the center. Agitation suspends the metal powder, forcing it underneath, up around the outside, and down the center of the suspended cylinder much in the same manner as the action achieved in an agitator type washing machine. Either of these two units appears to be equally satisfactory, the choice of cone washer installation being based on simplicity of design and elimination of the necessity for motor driven agitators.

Fig.7. Typical equipment designs used for washing crushed cathode deposits to remove occluded salts.

A vertical tower column washer also has been experimented with, this involving the upward movement of water countercurrently with a slow downward movement of the metal which is to be washed. While in principle this type of washer works adequately well, difficulties are encountered in localized overheating as a result of occasional spot formations of thorium carbide, which react with water to produce gaseous products with accompanying evolution of heat. At the present time it is not considered safe to use this type of washer, since severe localized overheating might give rise to an explosion. Neither of the other two washing choices is afflicted by this deterrent.

Figure 8 presents a schematic flow sheet of the entire metal washing process. The washed material resulting from the cone washer action normally consists of metal powder ranging in size from 20 to 200 mesh, 80% in the range from 40 mesh to 160 mesh, together with some occluded graphite which results from minor attrition of a graphite protector sleeve attached to the lower end of the cathode shaft.

Two methods have been used successfully to remove the occluded graphite. One involves the technique of heavy media float separation, bromoform having been used extensively to float the graphite from the metal. This process unfortunately suffers from the obvious drawbacks of an expensive reagent and the necessity for recovering the material by fractional distillation at a later stage. The other alternative, involving a mechanical separation, has been proven experimentally to be satisfactory. This involves wet agglomerate tabling on a Wilfley table, a very clean separation between heavy metal particles and lighter graphite being achieved without major difficulties.

Following the graphite separation step the metal may or may not be given any of a number of chemical treatments to attempt some degree of purification. Several hundred experiments have been run in which varying concentrations

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Fig.8. Flow sheet showing method of handling cathode deposits in metal recovery section.

and mixtures of acids have been used to treat the metal in order to lower the HCl-insolubles level of the resulting metal. It has been possible to treat the metal powder so as to yield a powder product having no measurable HCl-insolubles as determined by the standard process used by the AEC. However, the same situation does not prevail on specimens which have been melted in a water-cooled copper hearth furnace. On occasion HCl-insolubles have been as low as 0.3% on the melted buttons, but as a rule they analyze quite a bit higher. This appears to be a somewhat anomalous situation, and at first glance would tend to indicate possible air leakage into the melting furnace. However, leak rate tests on the furnace being used in the operation have shown pressure changes in the order of only three to five microns per minute, a rate which hardly would account for major increases in oxygen content. Recent vacuum treatment studies tend to indicate that the increased hardness may result from surface adsorbed moisture on the metal powder which is compacted for melting. Appreciable quantities are evolved on heating prior to melting, and it is suspected that this combines with the metal during melting, ultimately reporting as a higher oxide content than normally would be expected.

Suffice to say at this moment that the remainder of the flow diagram for processing the metal deposits is still subject to some question. There obviously will be a necessity for drying the metal after wet agglomerate tabling, and whether or not this requires a low temperature vacuum drying is yet to be determined precisely. Likewise, the factor of chemical treatments to increase purity still is in the late exploratory stages and may largely be a function of the operation of the electrolytic cell itself. The concentration of thorium remaining in the salt dragged with a deposit undoubtedly has a profound effect on the HCl-insolubles which ultimately report in the metal, and the degree of

atmosphere purity above the cell also is known to play a vital role. Once the Mark XXVI cell has been operated successfully it will be possible to evaluate these unknown factors in the metal recovery section much more completely.

Table II presents a typical spectrographic analysis of the thorium metal product which has been obtained in the electrolytic program. In the same table is shown the analysis of the thorium nitrate starting materials, and of chlorinated cell feed, a comparison among the three being generally indicative of the degree of purification attainable in the process and the impurities which are likely to be increased as a result of electrolysis.

It may be noted that rare earths, sulfate ion, boron and several other normal impurities are removed in the preparation of the cell feed, and additional purifications are achieved by electrolysis. Depending upon the purity specifications placed on the metal, therefore, it may be possible to use a lower grade starting raw material in the Horizons' process than has been required in other metal production operations.

Physical and Chemical Evaluations

Chemical Analyses

A considerable amount of development work has been carried out in the analytical chemical laboratories over the past year in order to improve upon and establish the dependability of the HCl-insolubles analysis. In a general way the HCl analysis seems to have been standardized upon by the Commission as a gross indication of metal quality. This would perhaps seem to be an unfortunate choice, inasmuch as the properties of thorium metal are totally unrelated to the HCl-insolubles analyses, oxygen apparently having little or no solubility in the metal lattice itself. The oxides segregate as minute inclusions, and, based upon rather extensive physical metallurgy evaluations

Table II

Comparative Spectrographic Analyses of Thorium Nitrate, Chlorinated Cell Feed and Melted Thorium Metal

	Typical Analysis Thorium Nitrate	Cell Feed	Melted Metal, ppm
Thorium	41.6%	20-50%	Major
Boron	* .4	< 0.2	< 0.2
Silicon	5	10-50	10-50
Iron	100	50-300	50-300
Magnesium	20	< 10	< 10
Aluminum	60	10-50	10-100
Nickel	125	10-50	10-100
Cadmium	* .5	< 0.1	< 0.1
Zinc	* 17	< 10	< 10
Manganese	10	< 10	< 10
Lead	* 10	< 10	< 10
Tin	* 10	< 2	< 2
Copper	5	0-10	< 0.5
Cobalt	* 5	< 5	< 5
Chromium	* 10	0-20	< 10
Zirconium	* 10	< 10	< 10
Titanium	17	< 10	< 10
Calcium	* 50	10-500	20-50
Molybdenum	* 10	< 10	< 10
Tungsten	* 10	< 10	< 10
Vanadium	* 10	< 10	< 10
Sodium	-	5-10	1-20
Potassium	-	10-15	1-50
Chlorine	-	-	< 10
Beryllium	-	1-10	1-10
Bismuth	-	< 1	< 1
Lithium	-	< 1	< 1
Arsenic	-	< 10	< 5
Rare Earths	200	1-20	Not detected
Sulfate ion	9,000	Not detected	Not detected

* Less than

of the metal product, hold no bearing whatsoever to properties such as yield or tensile strengths, extrudability, hardness, etc.

Early in this program great difficulty was encountered in attempting to achieve reproducibility in the HCl-insolubles analysis. At the suggestion of the Oak Ridge National Laboratories Horizons' techniques were modified to include reflux condensers for the digestion step, Whatman paper filtration instead of Gooch filtering, and a calcination operation at 900°C. which should be effective in the elimination of any carbonaceous materials present. It is now possible to get reproducible results on melted pellet samples of thorium metal, though as yet there appears to be absolutely no correlation between the HCl-insolubles value and the properties of the metal. Similarly, there has as yet been developed no correlation between process variables and HCl-insolubles. The importance of this test is perhaps subject to question, since the addition of a very minute quantity of hydrofluoric acid to the digestion unit completely eliminates all insoluble materials, everything going into solution.

In a routine manner the analytical laboratories have been required to run carbon analyses by combustion techniques, nitrogen analyses by the Kjeldahl process, total thorium by wet chemical approaches, and vacuum fusion analyses for oxygen, nitrogen and hydrogen. The latter operations are in their infancy, reportable results as yet not having been certified. Most of the vacuum fusion analyses so far determined have been based on titanium, inasmuch as standard samples for this metal are in existence. As soon as the equipment is known to be reasonably trustworthy, thorium analyses will be initiated.

Physical Metallurgy Evaluations

In order to melt representative samples of electrolytic deposits it has been the practice for some years to pre-pelletize the powder under nominal

pressures. Density determinations on green compacts as a function of pressure have been run, 10,000 lbs./in², for example, yielding a product with a density ranging between 65% and 70% of theoretical. Twenty-five to thirty tons/in² will yield approximately 85% green density.

Recent experiments have shown that even without sintering the green compact structure has reasonable strength for handling purposes. Quite recently some experimental work was initiated in which both green and sintered compacts were utilized as starting slugs for extrusion purposes.

On a purely arbitrary basis a die was designed with a 16:1 extrusion ratio, the starting slug having a diameter of 1" and producing a 1/4" diameter extrusion. The design was such that the entire operation could be carried out under an inert atmosphere and at temperatures up to 1300°F. In actual practice it apparently does not matter whether the slug is sintered or whether a green compact is used as the starting material. In either case very satisfactory extrusions have been obtained, with densities in the range of 11.60 grams/cm² and physical properties comparable to those reported for the best quality iodide thorium metal.

Table III presents a few of the physical properties of thorium metal extrusions which have been obtained during recent weeks.

Table III
Physical Properties of Horizons' Thorium Metal

<u>Physical Property</u>	<u>Value</u>
Tensile strength	28,000 lbs./in ²
% elongation	36%
As extruded hardness	VPN 69
Specific gravity	11.60

'As yet no tensile or elongation values' have been obtained from arc-melted and fabricated specimens, inasmuch as the larger melting furnace which

presently is being installed has not yet been placed in operation. However, hardness values on very small pellets have ranged as low as Brinell 46 in recent evaluations.

Both melted and extruded thorium rods have been cold-rolled without annealing from 1/4" thickness to 6 mils, representing a 98% reduction, without any evidence of major loss in ductility. Foil resulting from these experiments still exhibits excellent ductility and only nominal edge cracking. Small diameter wire likewise has been rolled from both melted and extruded pellets without any difficulty. In general it is concluded that the product resulting from direct extrusion at relatively low temperatures from the powder has properties identical to those resulting from melting and subsequent fabrication. The implications here are fairly obvious, since a major economic saving in the preparation of thorium fabricated parts could be achieved by the elimination of the melting stage, extruding the end product directly from the powder.

Metallographic studies have been made on both extruded and melted specimens of thorium. There are only nominal differences in appearance between the metallographic structures of the two processing methods, as shown in Fig. 9. Oxide inclusions in the extruded specimen appear to be somewhat more agglomerated, as compared to precipitation around grain boundaries in the melted specimen. However, the quantities in general appear to be about the same. In addition, one may notice by careful observation the presence of a light-colored second phase, which conceivably could be a thorium nitride, though this still is subject to verification. A similar phase also is present in the melted specimen, though in elongated form to such an extent that it is difficult to ascertain at a magnification of 250X.

a. As extruded from powder at 1275°F.

b. As arc-melted in water-cooled copper hearth.

Figure 9.

Typical Photomicrographs of Thorium Metal

8. VVI

Program for Fiscal Year 1956

The anticipated program for fiscal year 1956 will involve the semi-continuous operation of all aspects of the program. These will include semi-pilot production of cell feed by direct chlorination techniques, the operation of a 7500 ampere electrolytic cell, metal recovery operations to produce high quality thorium metal powder and additional physical metallurgy evaluations of the metal product resulting.

Project allocations dictate that only one portion of the project be active at any particular time. For example, it will be possible to start up and operate the cell feed preparation section for a continued campaign in order to stockpile cell feed for electrolysis. Operations then will be suspended in that area and transferred to electrochemistry, where the Mark XXVI cell will be operated until the cell feed inventory is completely consumed. Thus one may envisage a series of sporadic semi-continuous operations in both of these areas beginning in the very near future and running until late Spring of 1956.

It is anticipated that several tons of high quality thorium metal will be produced before the end of fiscal year 1956.

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