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Process Report

**PRODUCTION OF ELECTROLYTIC THORIUM CELL
FEED BY A WET CHEMICAL METHOD**

For: Manager
U. S. Atomic Energy Commission
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PRODUCTION OF ELECTROLYTIC THORIUM CELL FEED BY A
WET CHEMICAL METHOD

Introduction

Electrolysis of thorium chloride in a fused alkali chloride bath appears to be an economical procedure for the isolation of metallic thorium in a state of purity adequate for mechanical processing. A presupposition, of course, is the availability of anhydrous thorium chloride, either as such or as a mixture with one or more of the alkali chlorides.

The most common method of forming the anhydrous chlorides of metals of this type is the interaction of the oxide - the only readily-available compound stable at reaction temperatures - with chlorinating agents of the type of phosgene, carbon tetrachloride, carbon plus chlorine, etc. This procedure has proven very successful with the chlorides of aluminum, beryllium, zirconium, tantalum, and others, which chlorides are volatile below 600°C. Reaction of the oxide at 750° to 900°C., the generally-optimum chlorinating temperature range, acts to remove the resultant chloride from the reaction zone and thereby facilitate the operation.

In this regard, thorium is at a great disadvantage in chlorination. The chloride is much less volatile than the parallel chlorides of the other metal mentioned; it does not melt until about 740°C., and its vapor pressure does not become adequate for volatilization below 1000°C. Worst of all, it is a characteristic of the thorium chloride formed, if operations are above or about 740°C., to coat the surface of the remaining oxide, and thereby "blind" such oxide against chlorination.

Fortunately thorium shares with magnesium and cerium the ability to be recoverable, in the anhydrous state, from the hydrated chloride. In the case of magnesium and cerium this has been done by heating the hydrated chlorides in either an HCl gas stream or by heating with ammonium chloride; with

thorium, only an ammonium chloride technique appears to operate. In order to produce a substantially oxide-free chloride, a specialized technique, based on the chemical characteristics of the ammonium thorium chloride complexes, has been found optimum.

The Wet Chemical Process

Broadly stated, the procedure involves the formation of a solution of thorium chloride and ammonium chloride (at least two mols of the latter to each of thorium), evaporation of the solution to form a hydrated ammonium thorium chloride complex, dehydration of the complex by low temperature drying, and ignition of the complex, after inter-mixture with an alkali chloride, to remove ammonium chloride and to form a thorium alkali chloride mixture for electrolysis.

Process Development

Since the compound regularly available to Horizons' program was hydrated thorium tetranitrate, a preliminary conversion to the chloride was necessitated. Chemically the most feasible procedure involved dissolving the nitrate in water and converting it to a basic carbonate by treating with soda ash, followed by dissolution of the oxycarbonate in concentrated hydrochloric acid. The addition of ammonium chloride prior to the evaporation of the resulting thorium chloride solution brought the procedure in line with the process indicated above.

Preliminarily, this phase of operations was accomplished at Horizons on a relatively small scale, using a 150-gallon tank, neoprene lined, for the precipitation of basic carbonate. The original thorium nitrate was obtained as a 25% thorium solution; after reaction with soda ash and precipitation of the carbonate, the slurry was filtered on a rubber-coated plate-and-frame press (12" x 12"). The carbonate was then dissolved by passage of anhydrous HCl gas into the wet filter cake.

Since this latter procedure proved to be unduly time-consuming, a change was made to concentrated hydrochloric acid (37% HCl) as a solvent medium, which proved far more practical.

The concentration step also was started on a tentative basis equipment-wise, with the use of gas-fired, glass-lined pots of 10-gallons (later 20-gallons) capacity. Under the combined adverse influences of strong hydrochloric acid and thermal strains incident to heating and cooling, the life of the glass linings was quite short; it was soon recognized that this type of equipment was out of the question for even moderately sized batch operations. A further objectionable factor pertaining to quality also entered, in that failure of the glass lining frequently introduced chips of glass into the ammonium thorium chloride complex, thereby introducing iron, (from the underlying metal base), boron and similar contaminants from the glass.

The evaporation cycle initially carried the chloride solution to a semi-plastic consistency, (135°-145°C.), after which it was allowed to solidify in the glass-lined pots. Subsequent chipping also added to liner breakage. The process was later modified both equipmentwise and in technique to include casting the thick chloride solution into a cold metal trough. This greatly simplified product recovery from the evaporation phase.

Drying of the ammonium thorium chloride complex was, from the very beginning, done in pure graphite crucibles heated by means of Glo-bar units. Changes in the location and number of Glo-bars was soon found necessary in order to obtain adequate and uniform heating, it proving necessary to achieve an inside temperature of 260°C. in order to obtain optimum results from subsequent operations. Initially the drying was done with direct atmospheric contact, but when it was found that considerable oxide was being formed, mostly at the surface but also throughout the mass, a change was made to include a covered crucible with anhydrous HCl gas passing through the mass throughout the drying cycle.

The calcination, or subliming, step has also remained basically unchanged. In a sense it is merely a continuation of the drying step; equipmentwise, however, a change was necessary because of the much higher temperatures necessary for the removal of the ammonium chloride. Originally this step was done in an atmosphere of HCl gas, but corrosion factors necessitated a change to argon. In practice, the dried ammonium thorium chloride was crushed, mixed with sodium chloride and placed in an all-graphite crucible identical in type to the one used for drying. It was then heated under argon in an electric furnace powered by means of graphite resistors. Heating to about $650^{\circ} - 700^{\circ}\text{C}$. caused decomposition of the complex into ammonium chloride, which vaporized, and thorium chloride, which remained united with the sodium chloride present to form a molten mass. Any oxide contaminant tended to drop to the bottom of the crucible and form a very hard material difficult at removal, so that separation of this last-mentioned from the more fusible double alkali chloride was readily effected by chipping. This latter mass, after crude jaw crushing, constituted the electrolytic cell feed.

The Wet Chemical Process for Producing Cell Feed

The procedure, as used at present, after many modifications in details of equipment construction and operation, may be summarized as being represented by the following stages:

- I. Preparation of thorium nitrate solution
- II. Preparation of precipitant and precipitation of basic thorium carbonate
- III. Filtration and purification of basic thorium carbonate.
- IV. Hydrochlorination of basic thorium carbonate filter cake.
- V. Conversion of hydrochlorinated thorium salt to complex ammonium thorium chloride and partial dehydration by evaporation.
- VI. Complete dehydration
- VII. Sublimation (removal of ammonium chloride and last traces of water).

The attached flow sheet, Figure 1, indicates how these stages have been integrated into current operation.

I. Since the thorium nitrate available to the project comes in the form of a crystalline tetranitrate, the first step required involves its solution in water. This is done in a neoprene-lined tank, the solution being made up to contain approximately 10% thorium metal equivalent. The exact concentration is checked by laboratory analysis.

II. In a second neoprene-lined tank, a 15% solution of sodium carbonate is made up from soda ash and water, the latter being heated to about 80°C. To the carbonate solution, while being strongly agitated, the thorium tetranitrate solution is slowly added. Final adjustment is made to a pH value of 7.5 - 8.1, which precipitates all the thorium values as a readily filterable basic carbonate. After completion of the reaction, the precipitate is allowed to settle, with some concomitant natural cooling, for about four hours; the supernatant liquor is then pumped to a sump tank for subsequent disposal and the precipitate reagitated with cold water of the same volume as that removed. The resultant slurry is ready for filtration.

III. Filtration equipment was selected primarily on availability. It was necessary to compromise and accept a relatively unusual type, an Oliver vertical-leaf pressure filter, for the filtration and re-solution steps. The filter body is completely rubber-lined, and all parts in contact with the slurry and filtrate are non-metallic, including auxiliary pumps, piping, valves, etc. Filtration is achieved, after recycling of the filtrate until completely clear by virtue of building up a "pre-coat" of the carbonate precipitate itself, then continuing until cakes of about 1-1/4" thickness are formed on each of the vertical leaves. The latter are of plastic construction, covered with Vinyon cloth. A batch equivalent to 36 Kg. of thorium metal requires, with the equipment currently available, about three hours for the actual filtration. A washing cycle, using heated tap water (about 120°F.) follows. This washing lasts from 1-1/2 to 3 hours, the length of

V. The apparatus now in use for evaporating the chloride consists of an all-graphite trough fabricated from one-half of a cylinder of graphite 18" I.D., with two semi-circular end plates cemented into two grooved joints. The hemi-cylinder is encased in a stainless steel shell, a mixture of graphite powder and sodium silicate solution filling the space between the steel shell and the graphite trough. The shell is directly heated by means of two 60,000 BTU per hour flat gas burners, with appropriate arrangements to take off

combustion gases. The vessel is semi-enclosed, with arrangements for removal of the HCl gases emanating from the evaporating liquid. A variable speed, air-driven graphite propeller agitator de-froths the liquid during evaporation, minimizing foaming and swelling, which represent real operating difficulties.

Evaporation is continued, with incremental additions of 2 to 2.5 mols of ammonium chloride per mol of thorium, until the fluid mass is in the 135° to 145°C. range and becomes almost plastic in nature. During the latter evaporation stage the agitator is no longer capable of operation due to high viscosity, and some amount of hand agitation must be relied on just prior to casting to prevent crusting of the surface. The casting is at present done by hand ladling; the semi-solid mass is cast directly onto a stainless steel shallow pan 4' x 2.5' in size where it solidifies at once in large masses. These are broken away from the pan, crushed to walnut size and used as feed stock for the next step in the operation.

VI. Dehydration of the cast complex salt, which may contain up to 10% water, is achieved by heating the material under an HCl atmosphere. It is placed in an all-graphite crucible 15" I.D. x 18" deep, holding about 17 Kg. of contained thorium. The crucible and its contents are heated by means of a Glo-bar furnace constructed of loose insulating brick, with two parallel banks, four each, of 40" x 1" Glo-bar units of 0.95 ohm resistance. A pair of similar units also passes beneath the crucible in order to obtain a more uniform heating. The spaces around the crucible where there are no heating units are well insulated with refractory brick to minimize heat losses. A graphite tube serves to bring in the HCl gas, reaching down to about half the depth of the charge. In the center of the charge, two-thirds of the way down, is a thermocouple protected by a closed-end graphite tube. A third graphite tube is provided for exhaust of moisture, some HCl gas, and a small amount of entrained ammonium chloride. Experience has shown that details of construction

and arrangement are of importance here; for this reason, a sketch, Figure 2, is appended. The lid consists of a split graphite disc.

The crucible and its contents are heated to 260°C. and held at this temperature for eight hours, which removes all but about 1% of the moisture in the chloride mass (as measured by the Karl Fischer method). After completion of the heating cycle, the bricks of one side of the furnace are removed and the crucible allowed to cool, HCl gas flow continuing until room temperature is reached.

The dried ammonium thorium complex is removed from the crucible by means of air-hammer chipping. It is then crushed in a jaw crusher to 1/2" size and sampled for moisture, total thorium, chloride, ammonia, and water insolubles. After sampling it is mixed with C.P. sodium chloride in the weight ratio of two parts sodium chloride to one part ammonium thorium complex, and homogenized in a rubber-lined drum on a barrel roller. After mixing, the material is packaged in polyethylene bags to avoid hydration.

VII. Calcination, or sublimation, is achieved in crucibles of the type used for drying. These form the core of Horizons' Mark XXIII sublimation furnaces, which are heated with graphite rod resistors, the whole apparatus operating in an atmosphere of argon gas. During the heating cycle, which requires 18 hours, ammonium chloride is driven off, most of it after the mass has reached temperatures in the range of about 600°C. The maximum temperature reached is 750°C., this maximum being held for three hours. The unit then cools gradually, aided by water-cooling of the head and furnace jackets. Argon is permitted to flow throughout the cooling step.

When at room temperature the crucible is removed from the furnace. The material, consisting of solidified sodium thorium chloride, is chipped out by air hammer and transferred at once to polyethylene bags, ready for electrolysis.

This material normally contains about 30% thorium.

After three runs, the oxide-containing bottom layer, which is glass-hard and almost impossible to remove by chipping, is dissolved by soaking the crucible with hot water under rapid agitation. This removes the matrix salt, allowing the oxide material to settle. The oxide is sent to scrap storage.

Production, Personnel and Problems

The process described above has been operated on a production basis for several months, and has been the supply source for most of the electrolytic operations on contract AT(30-1)-1335. When operated on a three-shift, five-day week with a crew of two men per shift and one operations supervisor, production under the most optimum conditions could approach 100 Kg. of contained metal per week. It has been our experience, however, that major maintenance on the sublimation equipment may effectively decrease the production figure to between 50 and 75 Kg.

For the entire life of the program the percentage recovery in the process has averaged 92.8%. During the past three months this average has been increased to 95%, and probably could be improved upon with special scrap recovery programs activated.

The Mark XXIII furnace shell, despite water cooling and nickel cladding inside, does not stand up under the service conditions encountered. Brick insulating materials inside the furnace decrepitate as a result of actions by ammonium chloride, moisture and temperature, and not infrequently graphite resistor heaters burn out from slow oxidation. Salt leakage out of the graphite crucible occasionally causes still further difficulties.

Process Evaluation and Proposed Modifications

In general, while the wet chemical process is capable of producing good

quality cell feed, there appear to be major problems in the path of any attempt to scale up the operation. It may be, however, that equipment constructed of acid brick, such as rotary kilns and the like, may be suited to this service. Unfortunately these approaches have not been evaluated in deference to what Horizons considers more promising approaches to cell feed production, such as direct chlorination. High maintenance, labor and capital costs would tend to discourage the use of the wet process in a production facility.

Recent experiments indicate that the basic carbonate produced in the first stages of the wet chemical process is of excellent quality, easily filtered and readily chlorinated. It is proposed that the process be modified to take the oxycarbonate from a continuous filter, run the wet cake through a continuous belt dryer and chlorinate the dried compound in a semi-continuous chlorinator.

Necessary equipment for these modifications is currently under construction. A description of this facility will be the subject of a separate process report when adequate operating data become available.

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March 18, 1955
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Figure 1 - Flow Sheet for Wet Chemical Process

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Figure 2

Cross-Section View of Equipment Used for Drying Ammonium Thorium Complex

Vertical Cross-sectional View

Top View Showing Split Cover