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INVESTIGATION FOR THE PRODUCTION OF THORIUM METAL

Technical Progress Report – Fifth Quarter

By
M. Merlub-Sobel

AEC RESEARCH AND DEVELOPMENT REPORT

December 17, 1953

Horizons Incorporated

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INVESTIGATION FOR THE PRODUCTION OF THORIUM METAL

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By
M. Merlub-Sobel

Photostat Price $4.80
Microfilm Price $2.70

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

December 17, 1953

Horizons, Incorporated, Cleveland, Ohio

Technical Information Service Extension, Oak Ridge, Tenn.

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SUMMARY

The research program during this quarter was devoted almost entirely to discovering and developing an effective process for preparing a suitable chloride source electrolyte free of water and combined oxygen.

A large number of possible processes were investigated or considered, including chlorination with carbon-chlorine, chlorination with sulfur chlorides, chlorination in sodium chloride and preparation from anhydrous solvents, The most successful method and the one finally selected consisted of reacting $ThOCO_3$ with concentrated HCl, addition of NH_4Cl and subsequent heating in an inert atmosphere to drive off the NH_4Cl. The resultant anhydrous $ThCl_4$ was found to contain only 0.14% insoluble matter. This may be considered a suitable starting material for electrolysis.

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INVESTIGATION FOR THE PRODUCTION OF THORIUM METAL

Technical Progress Report – Fifth Quarter

By M. Merlub-Sobel

I. Introduction

The most pressing problem facing the research program, at the beginning of this quarter was the need for an effective process for preparing thorium tetrachloride in an anhydrous form and free of any combined oxygen for use as an electrolytic cell feed material. The work during this quarter has therefore concentrated almost entirely on developing such a process.

Thorium tetrachloride, among a relatively few others, is intermediate between the two extremes of metal halides -- those that are completely stable in water solution and can be recovered undecomposed from such solution (such are the alkali metal chlorides) -- and those which, once in water solution, can in no known direct manner be recovered undecomposed -- these latter being typified by the chlorides of aluminum, beryllium, zirconium, tantalum, etc.

In this intermediate position, thorium resembles cerium and, to a lesser extent, magnesium. Evaporation of a solution of the chloride yields first a hydrated salt; when this latter is heated, what at first ensues is the usual series of partial dehydrations:

$$ThCl_4.9H_2O \rightarrow ThCl_4.8H_2O \rightarrow ThCl_4.7H_2O \rightarrow ThCl_4.4H_2O \rightarrow ThCl_4 2H_2O$$

The final dehydration step is not, however, the desired

$$ThCl_4.2H_2O \rightarrow ThCl_4 + 2H_2O$$

but, rather, a series of partial hydrolyses, to yield, in sequence,

$$Th(OH)_2Cl_2,\ Th(OH)_3Cl,\ ThO_2.xH_2O,\ \text{and, finally}\ ThO_2.$$

In this, of course, the action of thorium is directly parallel to that of aluminum, zirconium, and the other metals whose chlorides hydrolyze completely. Where thorium differs (together with cerium and, to an even

[redacted]

greater extent, magnesium) is in the fact that the last-step hydrolysis can be repressed by the use of hydrogen chloride, either as such or in the form of high-temperature-decomposable ammonium chloride. In the case of thorium, repressing the chloride hydrolysis is a difficult task, considerably more difficult than for magnesium chloride. These difficulties have been sufficient to have resulted in thorium chloride being frequently produced through non-aqueous procedures, just as with aluminum and similar elements whose chlorides are not at all obtainable via aqueous processes.

Of the non-aqueous methods for thorium chloride, some are manifestly out of the question for all practical purposes. Foremost in any such list would, of course, be the interaction between elementary thorium and chlorine gas or hydrogen chloride gas. Another in the obviously impossible class is the formation of thorium chloride by reacting thorium bromide with chlorine.

However, the concept of reaction with elementary chlorine or with hydrogen chloride can be extrapolated to thorium carbide, a material which, if not as common as the dioxide, is still within reason; thorium chloride was obtained in this manner by Moissan, as part of his classical work on carbides during the closing years of the past century.

As far as practical methods go, most of the procedures suggested to date use the relatively cheap dioxide as a starting material. Attempts at making the chloride from the dioxide by reaction with PCl_5 under pressure and at low temperatures did yield some thorium tetrachloride, but yields have been found to vary and the procedure has neither economy nor practicality to recommend it. Substituting sulfur chlorides as reactants and operating at higher temperatures, without pressure and in the vapor phase, has been shown to give reasonably good results as far as yields go, both with and with-

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[redacted]

out the addition of excess chlorine to the stream of sulfur monochloride (the latter, in effect, creating SCl_2 and SCl_4 in the vapor phase). However, unpublished experimentation, several decades ago, has shown that chloride so made is impure and is likely to contain sulfur contamination, and so must be subjected to redistillation or resublimation to be at all usable for metal extraction.

The most practical reductant for thorium dioxide, to achieve chlorination, is carbon; for this purpose elementary carbon or carbon monoxide can both be used, with chlorine, or the reducing action can be combined with the chlorination by using carbon chlorides (such as CCl_4) or phosgene:

$$ThO_2 + 2C + 2Cl_2 \rightarrow ThCl_4 + 2CO$$

$$ThO_2 + 2CO + 2Cl_2 \rightarrow ThCl_4 + 2CO_2$$

$$ThO_2 + CCl_4 \rightarrow ThCl_4 + CO_2$$

$$ThO_2 + 2COCl_2 \rightarrow ThCl_4 + 2CO_2$$

It will be noted that either CO or CO_2 can be the by-product; whether CO will act as a further reductant on ThO_2 will depend on the concentration of the reactants. The purest thorium chloride, least contaminated with by-products (such as C_2Cl_6, as occurs with carbon tetrachloride use) results from operating with phosgene or carbon monoxide with chlorine (same unpublished experimentation). The toxicity of phosgene or of the monoxide-chlorine combination, is however, so great a drawback to broad utilization of this procedure that it has not found favor, either for thorium or for any other metal halide.

II. Experimental

A. Chlorination with Sulfur Chlorides

In preliminary exploratory tests in this project, interaction of basic thorium carbonate with sulfur monochloride, in the liquid state, by simple

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refluxing, with a stream of gaseous chlorine passing through the suspension, was tried; it resulted in a mass which was substantially insoluble in the sulfur chloride solvent. Filtration, and analysis of the residue, showed that approximately 70.5% of the original basic carbonate had been converted into chloride. Undoubtedly, longer operation, and changes in details of procedure, could raise the yield, perhaps even to quantitative proportions, but the difficulty of handling the monochloride, together with inevitable partial hydrolysis, with elementary sulfur as a by-product, as well as the many complicated operating steps involved, all made it evident that there was little reason to expect that this procedure could prove practical on a large scale. A similar experiment, with the sulfur chloride diluted with an inert hydrocarbon solvent, was not as successful, nor did it overcome any of the major problems. Some thought was given to the possibility of using the oxy-sulfur chlorides (thionyl and sulfuryl chlorides), but their low boiling points made it quite unreasonable to expect reaction, and there was also danger of further reaction between any thorium chloride formed and the mother solvent or by-products of the initial interaction (for example, sulfur trioxide). The whole concept of low-temperature conversion by sulfur chlorides was therefore abandoned.

B. Chlorination with Carbon-chlorine

Instead, attention was directed to the standard chlorination technique of carbon-chlorine combination action at elevated temperatures. While such chlorination is quite simple and effective in the case of certain elements (it is being done on high-tonnage scale with aluminum, for example), thorium presents unusual problems in consequence of the inconvenient melting and sublimation points of the chloride. Most anhydrous chlorides, when formed

[redacted]

by carbon-chlorine or equivalent techniques, readily volatilize away from the zone of interaction, for the chlorination reaction usually takes place most favorably in the 800°C.-1000°C. range, while the vaporization point of the resultant chloride is far lower (e.g., 178°C. for aluminum chloride, 520°C. for beryllium chloride, etc.). When operating with metallic chlorides of this type, the chlorides are readily carried away in the gas stream, immediately as formed, and are caught in collection chambers at a convenient distance away from the reaction furnace. As long as the boiling point of the chloride is reasonably below the temperature of chlorination, the carbon-chlorine procedure works well, and this holds true for the greater majority of elements.

Thorium unfortunately is the major exception to this rule; both its melting and boiling points are such as to impede easy chlorination of the oxide by the standard chlorination techniques. Published data on thorium chloride are, actually, none too definite at best, with reports on the melting point varying from as low as 567°C. to as high as 820°C., and with the zone of volatilization even more nebulous. What is known, particularly from the unpublished work previously referred to, is that the normal chlorination procedure will, if temperatures exceed about 730°C., cause the thorium chloride, as formed, to fuse (either as a pure compound, or by virtue of thorium chloride in solution), and, in fusing, "blind" the rest of the raw thorium oxide, effectively preventing further contact of the oxide with the chlorinating gases. Under such circumstances, the rate of thorium chloride formation becomes dependent upon the vaporizing away of any chloride formed, which is at best a slow process, even at temperatures in the 1000-1100°C. range. Actually, what thorium chloride does vaporize during chlorination is not carried over very far, but condenses almost immediately outside of the actual heating zone. It having proved so difficult to obtain the thorium chloride either in volatilized or in fused state, the best procedure worked out in the past involved chlorination with carbon tetrachloride and chlorine at a temperature rigidly held between 720°C. and 740°C. This control of temperature prevented fusion of the chloride, and was, in effect, the solid-state conversion of thorium oxide to the chloride. It had the important advantage of producing the chloride in massive crystal-like form, rather than the feathery form characteristic of the sublimed material, which latter is so readily hydrolyzed by the moisture of the air because of its extensive surface area. The temperature of operation being so low, however, rates of production are low; in the technique as developed, horizontal quartz tube furnaces, with thin layers of the oxide in quartz boats, were exposed to the chlorine-carbon tetrachloride stream. The scheme did not permit of any large scale production at the time, and what was true at the time of the original development is still valid.

The problem being essentially physical rather than strictly chemical -- its major aspect being how to remove the thorium chloride, after formation, from the reaction zone, so as to prevent its blinding of the remainder of the thorium oxide -- logic seemed to dictate the use of a vertical tube furnace, with the thought that the liquid thorium chloride would drain away, as rapidly as formed, from the reaction mass, leaving the oxide free again.

Any vertical furnace of the sort is faced, however, with the question of a grate arrangement to hold the thoria-carbon mixture against the gas stream, while at the same time permitting any liquid chloride formed to drain down into a receiving vessel. In the first furnace designed in this project, a vertical tube of fused silica, approximately six inches in diameter, was externally heated electrically; an intimately ground mixture of two parts of thorium oxide and one of charcoal was made up into small briquettes about 1-1/4 inches in diameter and about 3/4 inches in thickness, with polystyrene-xylene as binder These briquettes rested on a round plate, which filled substantially all of the inner circle of the quartz tube, the plate being of porous carbon (made by National Carbon Co.). The porous plate rested on a short block of carbon shaped like a flattened funnel; this in turn, topped a long deep crucible of graphite. Chlorine was led in from the top of the furnace, and it was expected that the interaction of the gas with the thoria-carbon mixture would yield thorium chloride liquid enough, at the high temperature of operation, to filter through the porous carbon into the receiving crucible, aided somewhat by the slight pressure of gas above the porous plate. A total of 1470 grams of thoria-carbon mixture was used, and the mixture was preheated, in a slow stream of chlorine, at about 200°C. to drive off the xylene and polystyrene. Thereafter the furnace was brought up to 1000°C. and held at that temperature, within about ten degrees, for approximately one and one-half hours. At this point, the top carbon plug (see Fig. 1) blew out, and it proved impossible to refit it to hold chlorine pressure, the plug blowing out immediately after repair. The run was therefore stopped and cooled as rapidly as possible, with a slow flow of chlorine (flowing out past the plug instead of through the furnace, of course), so as to prevent any air intake.

Examination of the apparatus, after standing overnight and complete cooling, showed that no thorium chloride whatever had collected in the crucible, but a trivial amount had sublimed up on to the silica tube just

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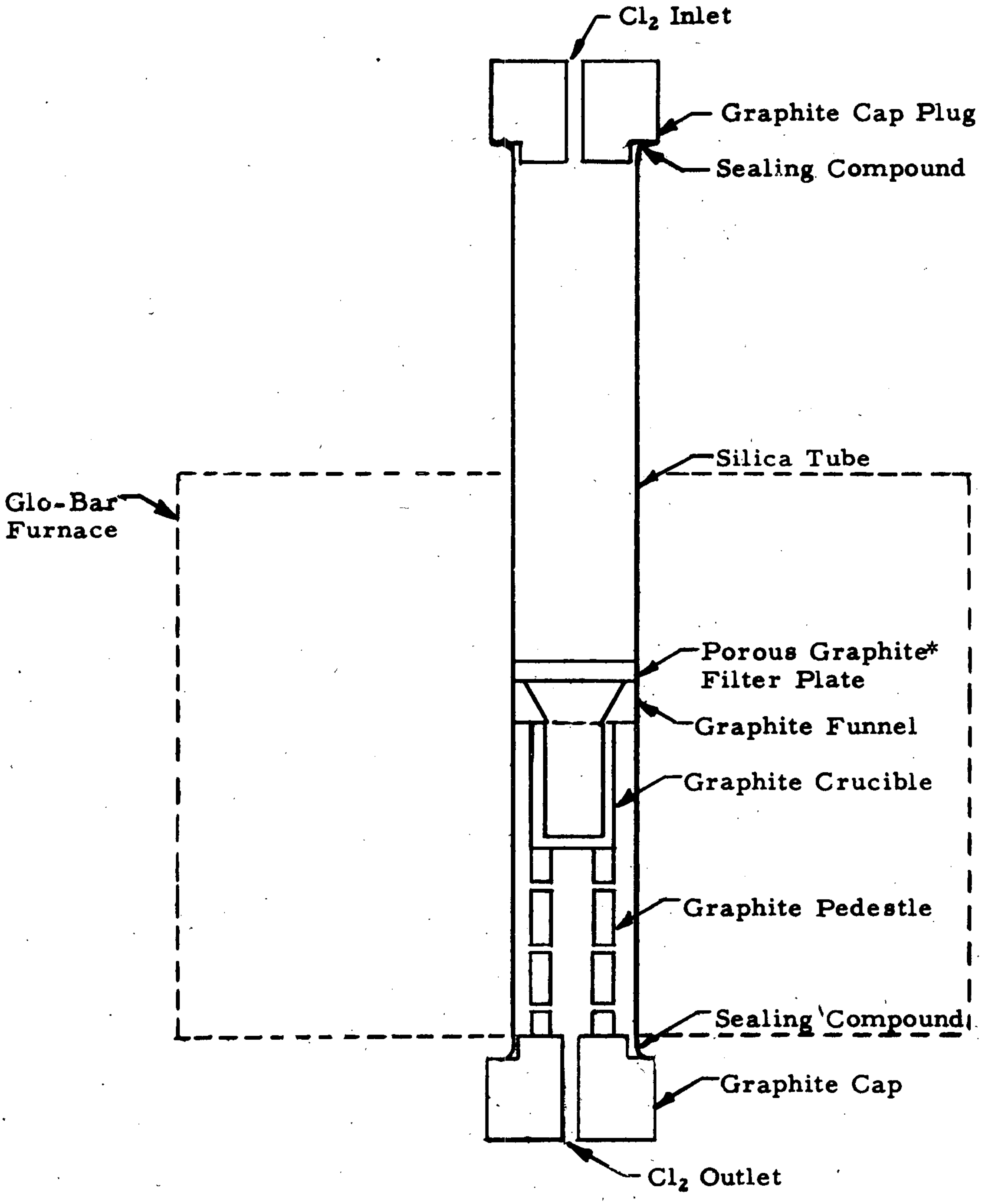
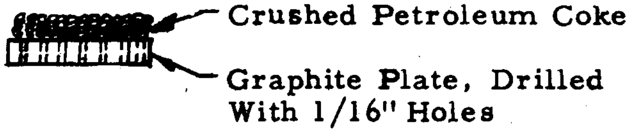
Fig. 1



*Later substituted Drilled Graphite Plate with a layer of crushed petroleum coke on top as a filter.



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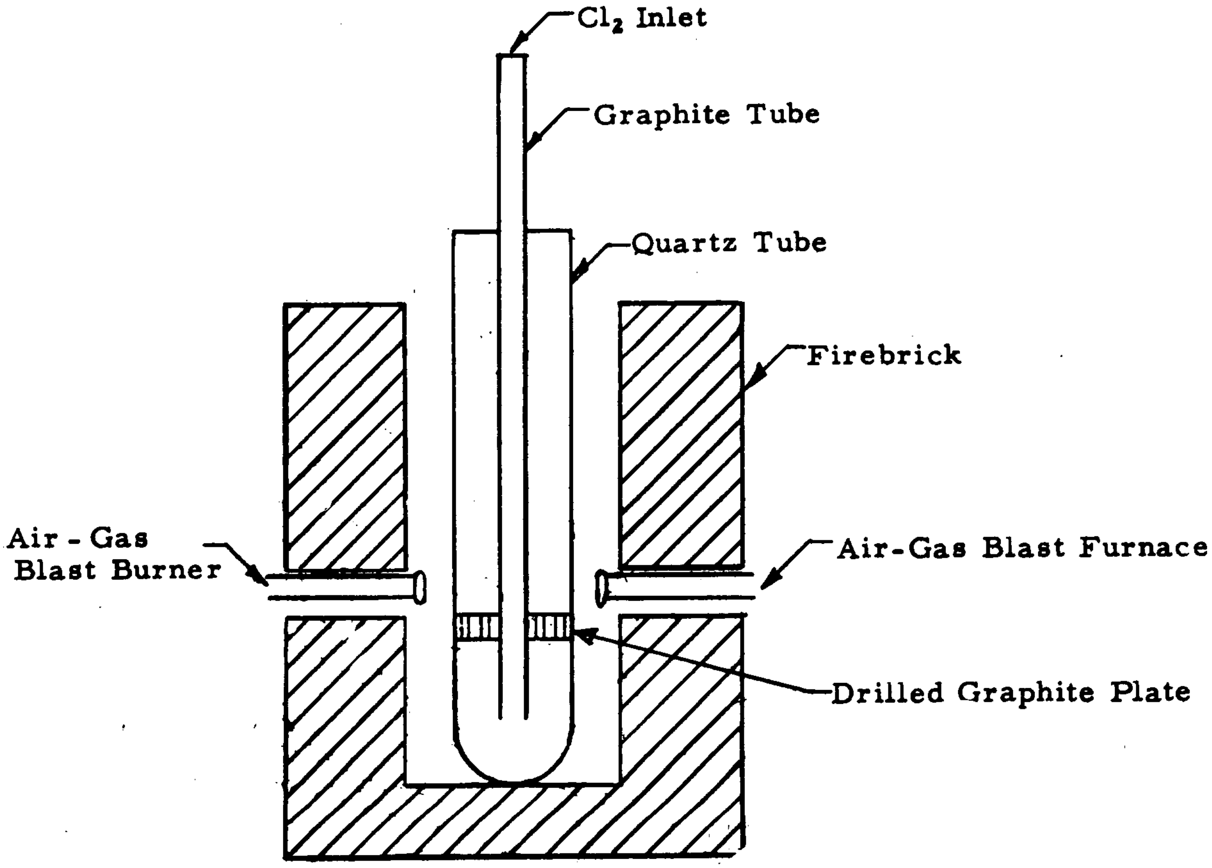
outside the heating zone, and a slight amount had also settled on the upper carbon plug as well. In both cases, the thorium chloride was in the cottony, highly reactive form characteristic of the vaporized material, and hydrolyzed rapidly when exposed to the air. The filter block of porous carbon was found to be saturated with thorium chloride; on standing for some time, the chloride hydrolyzed in the air, and, by expansion, disintegrated the block. Quite evidently, some chloride had formed, as expected, but its flow characteristics were not adequate to allow free flow through the porous carbon. It was concluded, therefore, that the concept of a porous filtration plate which would hold back any excess oxide and carbon, while allowing free flow of thorium chloride, was not workable; instead, a grate, with visible-sized holes, would have to be substituted.

The blowing-out of the carbon plug high-lighted one of the major mechanical difficulties of the whole procedure -- that of sealing the ends of the fused quartz tube against gas leakage. Various methods were tried preliminarily; the one finally adopted involved the use of graphite plugs with a sealing compound cement of graphite-latex composition. This latter material was quite satisfactory as long as the joint was not subjected to undue heat, and as long as no undue pressure developed inside the tube. (The seal could not, however, withstand the pressure of chlorine gas once the filter plate plugged up with fused thorium chloride). The worst feature of the seal problem, however, was the fact that the cementing material hardened sufficiently, under the influence of heat and chlorine, so as to make very difficult the removal of the plug after completion of the run; in point of fact, it did not prove possible, in any preliminary or experimental run, to remove both plugs from the tube without at least one breakage of the highly fragile silica tube, with consequent need for recutting the tube and shortening its operating length.

With the substitution of a perforated round disc for the porous plate, it was deemed desirable to overlay the disc with crushed petroleum coke, starting with relatively coarse material in contact with the plate (plus six mesh) and decreasing in size to about twenty mesh at the top; on this the thoria-carbon briquettes were laid. Other than this one change, and a raising of the temperature to 1100°C. (measured externally against the side of the silica tube at the level of the plate), the run was substantially identical with the previous one. Unfortunately, the results were also the same; no thorium chloride was collected in the crucible, and there was only a small amount to be found, in the coke and sublimed on to the wall of the tube and on to the graphite plug. Here, too, there was evidence of clogging, since, after about an hour of operation, the top plug was forced off by chlorine pressure; evidently, the fused thorium chloride, though far above its melting point (which, in any event, is below 850°C.) is quite viscous and does not flow readily through even the coarse coke layers. A further, and major, break in the silica tube resulted when dis-assembling the unit, in consequence of the hardening of the graphite cement, making further use of the tube impossible.

With the thought that bringing chlorine from below, and thereby operating countercurrently, some improvement might be attained, a smaller-scale experiment was tried, using a quartz tube with one end closed, and arranged as in Fig. 2, the chlorine gas coming in from under the drilled graphite plate and rising through the thoria-carbon mixture. Here, no coke was used on the plate, and the briquettes were laid directly on it. A total

Fig. 2


Cl_2 Inlet
Graphite Tube
Quartz Tube
Firebrick
Air - Gas Blast Burner
Air-Gas Blast Furnace
Drilled Graphite Plate

of 89.4 grams of briquettes were used, made from a mixture comprising 100 grams of thoria-coke (two parts thoria to one of petroleum coke), 4 grams of dextrine, and 14 grams of water. Chlorination was continued for about one and one-half hours, at which time it was assumed that the reaction would logically be complete. Although it had been hoped that considerable molten thorium chloride would collect at the bottom of the tube, no material was found there at all. A few grams of thorium chloride were found above the heating zone in semi-fused form, but the greater amount of thorium oxide was not affected and remained unreacted.

C. Chlorination by Carbon-chlorine (volatilization procedures)

In order to determine whether it might not be more feasible to recover the thorium chloride by sublimation and vaporization techniques, a small (approximately 1-1/2" I.D.) horizontal electrically-heated porcelain tube was arranged, with a mixture of thoria and petroleum coke, as before, held in two small zirconia boats. Chlorine as brought in through one end of the tube (the stoppers, on both ends, being protected by a firebrick plug preventing heat access); the effluent gases were caught in a caustic solution. The thorium oxide was made by igniting Lindsay Light thorium carbonate at 500°C.; this oxide was mixed, volume for volume, with petroleum coke. The temperature of operation was 1000°C., being held within ten degrees. A mass of fine white needle-shaped crystals collected near the outlet firebrick plug; it proved to be pure thorium chloride, completely soluble in water. The total quantity was small, approximating two grams in all (exact weighings were difficult because of the highly hygroscopic nature of the material, a basic characteristic of all volatilized metal chlorides).

A second run, of more quantitative character, involved the use of twenty grams of thorium oxide (made as above) with the ten grams of coke; both materials were passed through a forty-mesh screen and then blended through the same screen. The mixture was pelletized, under pressure, using a polybutene-xylene mixture as a binder, approximately five grams of the binder being used for thirty of the thoria-coke mixture. The reaction mass (thirty grams in all) was heated in two zirconia boats, at 1000°C., as in the previous run. Mechanical back-pressure interfered frequently with the run; no reason for such back-pressure could, however, be found. On weighing the boats after completion of that run, it was found that the charge had increased in weight, instead of suffering the expected decrease, the total weight having risen from 30 grams to 32.2 grams. Evidently, therefore, considerable conversion of the thorium oxide had actually occurred, forming thorium chloride, but such chloride had remained in the boat instead of volatilizing over, as hoped for. This was substantiated by the comparatively small amount (about one gram only) of volatilized solids obtained. All this is in close confirmation of earlier researches, published and otherwise, that the volatilization of thorium chloride does not take place on sufficiently high a scale to yield a workable process, even when the operation is conducted at as high a chlorinating temperature as 1000°C.

D. Chlorination in Sodium Chloride

In consequence of the above, it was viewed desirable to test the feasibility of chlorinating under conditions which would allow for dissolving away the chloride as rapidly as formed. After preliminary cruder tests had showed positive results, a graphite crucible was charged with 360 parts of sodium chloride and 42.4 parts of a 2:1 mixture of thoria and petroleum coke (the mixture being equivalent to about 10% of $ThCl_4$ in the bath if

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chlorination were complete). The crucible was heated, by means of an electric furnace, to 900°C., and chlorine gas was bubbled through the suspension for one hour, by means of a porous carbon sparging tube. On completion of the chlorinating step, it was observed that a great deal (most, in fact) of the petroleum coke excess floated on the surface of the bath, together with a good deal of unreacted thoria; much of this carbon and thoria could be removed mechanically from the surface. The salt bath itself, on analysis, showed 2.21% water-soluble thorium in the bath, with only 0.08% insolubles, the latter proving to be practically all carbon, since, on ignition, it left no residue. With this indication that the procedure could give soluble, and therefore electrolyzable, thorium in a salt bath, a series of runs were undertaken to determine the electrolytic characteristics of materials so made.

In the first run, four pounds of sodium chloride were melted down in a graphite crucible, together with 154 grams of thoria and 28 grams of carbon (this being equivalent to 100% excess carbon). The mixture was treated with chlorine gas for about two hours, using a graphite tube with small, drilled outlet holes. Operating at 886°C., with an average voltage of 3.8 carrying 50 amperes of current, 80 ampere-hours sufficed to bring the end of the run (as indicated by the appearance of sodium). No thorium was obtained on the cathode, but a small quantity (5.5 grams) of hard metal (Rockwell A, 68.5) was recovered from the bottom of the crucible. Quite evidently, thorium had been formed at the cathode, but it had dropped off and was partially reoxidized, and partially it had reacted with the carbon of the crucible (hence the hardness of the metal). There was a large

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quantity of sludge floating at the surface of the bath; examination showed it to be mostly carbon.

A second run, again with four pounds of sodium chloride, but with an increased amount of thorium dioxide together with 550% of theoretical carbon (190 grams of the mixture being used) involved treatment with chlorine for two hours, followed by overnight cooling. The top layer (about 1-1/2 inches) was removed, thereby removing most of the excess carbon and unreacted thoria. An electrolysis at 25 amperes and 3.2 volts gave a run in which 75 ampere-hours were required, but no metal resulted at the cathode. A good deal of carbide was found at the bottom of the crucible, indicating that metal, again, had formed, but that it did not adhere and had been converted to carbide when it fell to the bottom of the crucible.

The next run was made with only 100% excess carbon, using the same quantity of sodium chloride, but with 462 grams of thoria-carbon and four hours chlorination, followed by skimming off excess carbon and floating thoria. A pre-electrolysis at about 7 amperes for 40 minutes and 50 amperes for 10 minutes was followed by electrolysis proper at 50 amperes and 3 volts. about 150 ampere-hours being required till sodium appeared. A good-appearing deposit was obtained, totaling, however, only 53 grams in all. The Rockwell B hardness was 98, much too high for good thorium. The presence of considerable carbon in the metal as evidenced by gassing during washing of the metal, was undoubtedly the main cause of the high hardness.

In the last run of this series, carbon was limited to its theoretical ratio, and a large quantity (1050 grams) of the thoria-carbon mixture was used (962 thoria and 88 carbon). Chlorination was for 3-1/2 hours, and the bath was subjected to a pre-electrolysis varying from 0.5 amperes to 16 amperes over a period of one hour. Thereafter, the electrolysis itself was conducted at 50 amperes, requiring 2.6 to 3.0 volts; after 150 ampere hours had been passed through the bath, the deposit apparently shorted across between its cathode origin and the anode pot, so that the run had to be stopped. The deposit fell into the bath, and showed extensive carbonization (again, as evidenced when treated with water). A yield of 43 grams of metal was obtained, having a Rockwell B value of 102, essentially the same as before, and far too hard for usable thorium.

E. Thorium Chloride from Aqueous Solutions

Since neither the formation of pure anyhdrous thorium chloride by high-temperature chlorination procedures, nor the in-situ formation of thorium chloride in sodium chloride, had yielded results justifying carrying into pilot scale operations (although the latter represented qualitative success along the lines of a technique which had hitherto not proven at all workable) and since preliminary experimentation had simultaneously shown that the dehydration of hydrated thorium chloride was feasible on both laboratory and pilot plant scales, it was decided to forego further experimentation on the former techniques, and to determine, instead, operating characteristics for forming thorium chloride in electrolyzable form, by dehydration procedures.

Preliminary, exploratory efforts at forming Na_2ThCl_6 by dehydrating a mixture of salts resulting from evaporating down a solution containing sodium and thorium chlorides in the proper ratio showed that extensive hydrolysis takes place when the salt mixture is heated to 200°C. or beyond. This parallels the findings of Chauvenet that even in a stream of HCl gas, the compound $NaThCl_5 10H_2O$ cannot be dehydrated without hydrolytic decomposition yielding, instead of the anhydrous double salt, an oxychloride of the formula

$NaTh(OH)Cl_4$. Although it might have been of some merely-theoretical interest to determine the characteristics of the potassium analogues (and especially so in view of conflicting reports in the literature), it appeared far more immediately fruitful to follow the line of dehydration technique which had already proven successful in the hands of other researchers -- that involving the use of ammonium chloride as a hydrolysis-repressant.

The theoretical basis for the procedure lies in the fact that the compound $(NH_4)_2ThCl_6 . 10H_2O$ can be deposited out of a solution containing 3 mols of the ammonium salt to one of thorium chloride. When heated to about 150°C., this compound loses its water, but, unlike the equivalent sodium and lithium compounds, no significant hydrolysis takes place during such dehydration. Much more important, heating to 500°C., or slightly above that point, decomposes the anhydrous double salt, resulting in the indirect formation of the desired anhydrous thorium chloride.

After some preliminary qualitative experimentation, a test was made to determine whether the drying could be done directly, without specific care as to drying conditions from the physical viewpoint. A quantity of 334 parts of thorium basic carbonate (79.1% ThO_2) was added at 50-70°C. to a mixture of 384 parts of 37% HCl and 500 water. To this was carefully added 190 parts of 28% ammonia water, which still left the solution highly acid; beyond this, thorium hydroxide was precipitated. To redissolve, sufficient HCl was added, bringing the solution back to a pH of about 1.0, after which the solution was filtered hot, and an additional 150 parts of ammonium chloride dissolved in the solution. This solution was then taken down to dryness; even in this state, the mass already showed considerable insolubles when tested by re-solution in water, indicating extensive hydrolysis. When this same residue was heated to 675°C.

[redacted]

for an hour in a covered crucible, strong hydrolysis and oxidation was found to have taken place, the material showing 84.5% insolubles and only 4.15% chlorine. This confirmed an earlier exploratory test which had shown that heating a high-thorium mixture of ammonium and thorium chloride at 500°C. yielded over 25% of insoluble matter. The basic purpose of the test had been to determine whether there was any constancy to the Th: NH_4 ratio.

To a solution of 330 parts of basic thorium carbonate dissolved in 395 parts of 37% HCl with 500 of water at 50-70°C. and then heated to 90-95°C., 161 parts of ammonium chloride were added. The first crop of crystals obtained on cooling the solution showed only 4.47% of thorium. When the same solution was boiled down to about half its original volume and similarly cooled, a large amount of yellow crystals resulted; on drying these at 110°C., analysis showed an increase in thorium content to 9.28%, with 19.9% as nitrogen and 33.9% chlorine. The mother liquor from this crystallization, when boiled down, gave a thick syrup, but did not crystallize, which action is characteristic of pure thorium chloride solutions. From this it is obvious that ammonium chloride tends to deposit separately and in excess of the equivalent quantity of thorium; any procedure based merely on concentrations of the two salts would also be subject to changes resulting from variations in solvent concentration, temperature, etc. It was to avoid this complication that the HCl gas procedure was resorted to, as will be discussed later.

F. Thorium Chloride from Anhydrous Solvents

In an effort to determine whether the problems of drying might not be entirely eliminated by the use of non-aqueous solvents, a series of essentially-qualitative tests were conducted, involving the use of anhydrous HCl gas dissolved in organic liquids as reactant on basic thorium carbonate. In the first

[redacted]

experiment of the series, 161 parts of basic thorium carbonate were added to 550 parts of methanol solution containing 142 grams of HCl per liter. After raising to boiling, and filtering, (discarding a small amount of insoluble gelatinous residue), a quantity of 52 parts of ammonium chloride was mixed into the solution (it being essentially insoluble); this mixture was evaporated down almost to dryness, cooled, and the crystal mass filtered off. The thorium constituent evidently contained methanol of solvation, for, on heating to 110°C. a great deal of charring resulted.

The same technique was tried with normalbutanol, with 143 parts of basic thorium carbonate, and 550 parts of the butanol containing 125 grams of anhydrous HCl per liter. The solution was raised to boiling and then additional HCl was bubbled through it, followed by filtration and the addition of 68.8 parts of ammonium chloride. Further evaporation, almost to dryness, was followed by cooling; the mass then solidified. When dried at 200°C., extensive charring developed.

In the hope of avoiding the formation of solvates, which appears to occur between thorium chloride and most alcohols, hexyl ether was tried as a reaction medium. A quantity of 100 parts of basic thorium carbonate was added to 500 of hexyl ether and then HCl gas was bubbled through the suspension. After all reaction has ceased, the hexyl ether was filtered off (since the reaction product proved insoluble). A portion of the product was heated carefully in a closed crucible. On analysis of this material for chlorine, it proved to contain only 58.3% thorium chloride, the remainder of the thorium having quite evidently gone over to oxide.

Since both alcohols and others had failed to give satisfactory results the use of organic solvents was abandoned as an approach to the problem.

G. Drying Techniques

Returning to the concept of drying thorium ammonium chloride and igniting the resultant anhydrous double chloride, it was deemed advisable to test the possibility that the presence of sodium chloride might protect the thorium chloride at elevated temperatures, after the ammonium chloride had been sublimed away. In an experiment involving 334 parts of basic thorium carbonate dissolved in a solution of 409 parts of 37% HCl and 500 of water, 60 parts of sodium chloride were added at 95-100°C., followed by 165 of ammonium chloride. The mixture was then evaporated down to dryness, boiling beginning at about 107°C.; after being brought to the dry state, the mass was transferred to a casserole and heated to 600°C. to drive off the ammonium chloride. A sample of the resultant material, when dissolved in water, showed a great deal of insoluble matter, indicating that the technique used was probably at fault, since, theoretically, a fully-soluble product ought have been obtained. This only served further to emphasize the view that the problem was essentially one of care in drying and igniting, and of finding the proper physical conditions -- time-temperature chief among them -- for drying and igniting, rather than one of chemical concentrations.

After further tests had confirmed the fact that the presence of sodium chloride did not aid in protecting the thorium chloride against hydrolysis during any of the low temperature stages of drying, and especially in view of the danger that the thorium chloride might preferentially unite with the sodium chloride instead of with the ammonium chloride (the sodium double compound being known to hydrolyze even in the presence of HCl gas, as already cited), it was decided to limit any NaCl to additions only after the preliminary dehydration of the $ThCl_4$-NH_4Cl mass had been effected. It was similarly re-

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cognized that an essential part of any workable process would be the development of a procedure for overcoming the variability in salts ratio when crystallizing down a solution containing both ammonium and thorium chlorides.

This last was achieved by the use of HCl gas as a precipitant for thorium chloride. Normally, a solution of thorium chloride, when concentrated down, forms a syrupy liquid and then a semi-plastic mass, without any tendency to true crystallization; when the thorium chloride solution is saturated with HCl gas, however, a highly-crystalline, easily-filterable crystal mass is deposited, which can be drained of its adherent mother liquor as readily as any other crystalline material depositing out of water solution. Experimentally, a solution of basic thorium carbonate in an excess of strong hydrochloric acid, when saturated with additional HCl gas, does throw down most of the thorium content in finely-crystalline form, easy of filtration; the mother liquor can be used for the next cycle. It was further found that the addition of ammonium chloride (at least two mols to one of thorium, three being preferred, for safety) could be made either directly to the solution itself, or, alternatively, ammonium chloride in solid form, could be subsequently mixed in with hydrated thorium chloride crystals equally effectively. It may be assumed that the double thorium ammonium chloride compound forms on heating the solid mixture, with the water of hydration probably acting as reaction solvent.

In a typical run, the basic thorium carbonate, after solution in concentrated hydrochloric acid, was saturated with HCl gas and cooled by the addition of dry ice (merely to speed cooling). The hydrated thorium chloride (concentration 131 grams per liter) was mixed with 3 mols of ammonium chloride, dried carefully at 150°C., and then heated at 500°C. in a dry argon atmosphere until

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practically all of the ammonium chloride had been driven off. On analysis of the resultant anhydrous thorium chloride, it was found that only 0.14% was in insoluble form, thus representing a substantially pure thorium chloride, ready for electrolysis.

III. Conclusions

Further data on this procedure for making electrolyzable anhydrous thorium chloride, and the results obtained on electrolysis, will be found in the next report (No. 6) of this series. Here it is sufficient to anticipate that report only to the extent of indicating that chloride made in this manner, on a large laboratory scale, has proven fully amenable to electrolytic treatment, yielding metal of Rockwell B 10 hardness, with good yields and efficiencies. It should be added that the drying technique, as finally worked out, calls for the maximum practical drawing off of the mother liquor from the hydrated thorium chloride as thrown down by the HCl gas (ordinary suction filtration is adequate), preliminary drying above 100°C. and best at about 150°C., to remove free water and water of hydration of the double ammonium thorium compound. Sodium chloride can be added at any convenient point after this preliminary dehydration; possibly it helps in the subsequent dehydration too, but, in any event, its addition at some point of this operation fulfills conveniently all later electrolytic requirements. Heating of the mixed thorium-ammonium chlorides, with or without sodium chloride additions, in an inert dry atmosphere, to about 600°C. will drive off substantially all of the ammonium chloride. If sodium chloride has not been added prior to this stage, this represents a good point for such addition, best followed by melting the two salts down together to form the electrolyzable bath, ready for use.

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Layout and equipment needs for producing the electrolyzable mixture by the above techniques, on a pilot plant scale, will also be outlined in the next report. No particularly difficult problems of chemical engineering appear to be involved, and all equipment needed should prove either of standard type or, at worst, readily designed and cheap of construction.

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