SRO-11

METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

RESEARCH AND DEVELOPMENT IN THE FIELD OF THORIUM CHEMISTRY AND METALLURGY. VOLUME I. PREPARATION OF ELECTROLYTIC CELL FEED FOR PRODUCTION OF THORIUM METAL

Final Report

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June 30, 1956

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Other issues of this report may bear the number HZ-98.

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Printed in USA. Price $2.75. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

AEC Technical Information Service Extension
Oak Ridge, Tennessee

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Final Report

Research and Development in the Field of Thorium Chemistry and Metallurgy

Volume I

Preparation of Electrolytic Cell Feed for Production of Thorium Metal

June 30, 1956

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ABSTRACT

From 1952 through 1956 Horizons Incorporated, under Contract AT(30-1)-1335, conducted a research and development program in the field of thorium chemistry and metallurgy. Most of this activity prior to the summer of 1954 was directed toward the development of techniques for the production of metal by fused salt electrolytic approaches, little effort being proportioned to the preparation of an electrolyte for the process.

In the summer of 1954 an aqueous method for the preparation of an anhydrous cell feed was set up and operated for several months. Relatively high operating expense and difficulties with materials of construction prompted the development of a more direct approach for the production of electrolytic cell feed.

The system established for cell feed preparation converts thorium nitrate to a basic carbonate via the reaction between the nitrate and sodium carbonate, this precipitation being quantitative. Following a suitable filtration and drying operation, the thorium oxycarbonate is converted directly to the chloride by reaction with carbon and chlorine, forming a cell feed containing between 40 and 45% thorium in a molten matrix of sodium and potassium chlorides.

The preparation of cell feed by the described process has been carried out on a small-tonnage basis, in 1,000-pound batches. The entire process is capable of being operated on a continuous or semi-continuous basis and presents a commercially feasible approach for the

preparation of high quality anhydrous electrolytes suitable for conversion to A.E.C. grade thorium metal by electrolytic techniques.

A brief description of small-scale research and development experiments leading to the established system also is included in this report.

RESEARCH AND DEVELOPMENT IN THE FIELD OF THORIUM CHEMISTRY AND METALLURGY

Volume I

Preparation of Electrolytic Cell Feed for Production of Thorium Metal

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I. INTRODUCTION

A. Historic Background

Since 1948 Horizons Incorporated has been active in the field of high temperature fused salt electrochemistry, most of the research pertaining to titanium and zirconium. Familiarity with the chemistry and metallurgy of the various elements represented in groups IV and V of the periodic table tended to indicate that fused salt techniques might be applicable for the production of thorium metal. Accordingly, a proposal to study possible production methods was prepared and submitted to the Atomic Energy Commission; the first contract in this field was awarded in April, 1952, and has continued in various forms through June 30, 1956.

During the first two years of the contract major activities and goals were proportionated toward a rather complete and thorough examination of all possible systems for the preparation of thorium metal, elimination of those systems which did not appear too feasible either technically or economically, and cursory evaluations of several of the more promising processes. Following this stage rather concentrated efforts were applied to investigations of fused salt electrolyses. Both fluoride and chloride systems were evaluated, it being established ultimately that the chloride system was the more feasible approach. A great deal of effort was directed to the establishment of major parameters which pertained to production of the metal by this technique. Included in the early studies were fundamental aspects of the electrolytic process such as determinations of decomposition potentials as a function of temperature, phase diagrams in systems which would be appropriate for electrolysis, kinetics of electrochemical reactions, effects of current density, temperature and cell geometry on the crystal structure of metal produced, and many other aspects which were important to a complete understanding of the process.

Small scale cell feed preparation was carried out at the bench level, and many electrolytic operations were conducted in research size laboratory cells, largely ones which were originally designed and constructed for titanium and zirconium preparation. No major effort was extended toward developing a process for the production of cell feed, rather complex aqueous systems being carried out in the chemical laboratory for the preparation of small quantities as required.

A complete report on the first two years' activities under Contract AT(30-1)-1335 has been prepared and submitted to the Savannah River Operations Office.(1)

In the spring of 1954 a major resurgence of Atomic Energy Commission interest in thorium metal occurred. At that time the contract operations at Horizons were transferred from the New York Office of the A.E.C. to the Fernald Area which organization was producing small quantities of thorium by the Ames process and wished to have a secondary production means should major difficulties arise in scaling up the Ames pilot operation.

The nature of the program from April until October, 1954, during which time cognizance was maintained by Fernald, was that of a "crash" program, expedition being given to setting up moderate scale pilot operations for the preparation of cell feed, and for the production of several hundred pounds of thorium in order that it might be evaluated from a nuclear standpoint. Because of the time factor it was necessary to purchase equipment items that were available on an immediate basis without too much regard to suitability to the process, and to establish a process which lacked much to be desired for the preparation of electrolytic cell feed. Similarly, in the electrolytic area it was necessary to press into service a large cell of an externally heated design which had been used previously for zirconium preparation. Neither the cell design nor available auxiliary equipment were particularly suited to the job, but despite this fact quantities of metal were turned out which were of reasonably acceptable quality.

During the early part of 1954 the Atomic Energy Commission contracted with R. B. MacMullin Associates of Niagara Falls to make a cost estimate on the electrolytic process for the production of thorium metal. Despite the fact that a relatively minor amount of actual operating data was available to this engineering organization, they nevertheless came up with quite a comprehensive treatise on the preparation of cell feed by an aqueous system and electrolysis in moderately-sized electrolytic cells, the cost estimate resulting in a figure of approximately $1.43 per pound in order to convert thorium nitrate to finished metal, with a requirement of approximately 6-1/2 million dollars for capitalization.(2) This report undoubtedly was at least in part responsible for larger-scale pilot production of thorium by the electrolytic process, inasmuch as the estimated cost of production was a very small fraction of the actual costs estimated and found for the Ames operation.

In October of 1954 cognizance of the program at Horizons was transferred to the Savannah River Operations Office, which organization maintained supervision throughout the remainder of the contract life. Under Savannah River jurisdiction an entirely different philosophy was encountered, emphasis being placed on the development of a more feasible process rather than attempting to produce quantities of metal expeditiously. A research program was set up in order to evaluate various other methods of cell feed preparation and a rather broad program of cell development was simultaneously initiated. It is to a large extent the activities carried out under the Savannah River cognizance that this Final Report covers.

B. Program Goals and Scheduling

1. Process

In October, 1954, a rather awkward and labor-consuming facility was in existence which converted thorium nitrate to thorium chloride by means of precipitating thorium oxycarbonate, dissolving the latter in hydrochloric acid, complexing the thorium chloride with ammonium chloride, drying the complex, decomposing the complex to recover thorium chloride with ammonium chloride as by-product, and finally fusing the thorium chloride with sodium and potassium chlorides to form a suitable cell feed electrolyte.

While reasonably adequate quality cell feed had been produced in moderate quantity up to that time, materials of construction for several of the process steps continued to prove to be quite complex, the entire system was batch-type and radiation hazards were more severe than ordinarily are desired.

Early in the summer a research program had been initiated for determining the feasibility of converting thorium nitrate directly to cell feed by the mechanism of chlorination. This program was accented in October, major effort being expended in determining the most feasible method of producing a suitable electrolyte without the necessity of resorting to the aqueous process which had been set up on a hasty basis. The program goal for preparation of cell feed therefore was to develop a simplified, and if possible, direct, approach to the preparation of cell feed; the desired system would treat thorium nitrate in a crystalline hydrated form by conventional chemical engineering approaches to convert it to an electrolyte without the necessity of major equipment development and expensive materials of construction. Cost factors were to be borne in mind, since the anticipated result would be a full-scale production plant based on the developments.

Operation of an externally heated electrolytic cell had been carried out for some months in various sizes of equipment, but again difficulties had been encountered on scaling up the units to anything approaching a feasible commercial size. Among the major difficulties encountered were salt leakage through graphite crucibles, atmosphere contamination of the product, heat dissipation during electrolysis and recovery of cathode deposits without excessive losses into the electrolyte.

Simultaneously with the research and development program on preparation methods for cell feed production a parallel program was initiated to develop suitable electrolytic cell designs which could be scaled up to any desired size for commercial production of thorium metal. Process-wise, additional data obviously were necessary in order to determine the effects of temperature, current density and cell geometry on particle size, current efficiencies, and metal quality of the product turned out.

As a correlative program, which proved to be vitally necessary, the technique used for recovering metal contained in the cathode deposit also came in for much research and development activity. Evaluations numbering in the hundreds were ultimately resorted to in order to determine the most feasible method of washing out occluded salts and recovering a high-quality granular metal powder product from the deposited mass. Techniques for drying, metal consolidation, and physical evaluation also were included in the program in order that a fully-rounded picture of the preparation of thorium cell feed, and metal by fused salt electrolysis, might result.

2. Equipment

As mentioned earlier, many of the equipment items selected for the preparation of cell feed lacked something to be desired. For example, the only filter press which was available to the project from industry at the time it was necessary to procure one was a vertical leaf filter with substantially non-removable leaves. It was necessary to utilize this unit for filtering a thorium oxycarbonate precipitate, and to devise techniques for removing the filter cake mechanically from the pressure filter. Techniques also had to be devised for converting a solution of thorium chloride in ammonium chloride to a solid, this necessitating a physical change from a thin liquid through a pasty state to a solid cake, on a somewhat continuous basis. Equipment consisted of a variety of graphite-lined vessels, mostly heated externally, which did not appear to be susceptible of scaling up to a large size because of crucible leakage.

Under the program initiated with Savannah River, and as a result of the development program, a continuous drum-type filter was ultimately procured and placed in service, as were a continuous belt drier and other associated equipment which simplified the wet chemical process noticeably. In addition, techniques ultimately were developed wherein most of the aqueous processing was eliminated and replaced by fused salt chlorination in order to produce the desired cell feed material.

In order to eliminate the problem of salt leakage through graphite crucibles in electrolytic cells, an entirely different concept of cell design was resorted to. This fundamentally consisted of the frozen salt principle which has been used for many years in other types of applications. By using internal heating and a frozen-salt principle for salt leakage control, adequate devices were designed and ultimately operated for the production of a high-quality thorium metal powder. This type of equipment is not limited in scaling up, any desired size of cell being susceptible of operation.

Metal recovery facilities to a large extent were limited to small cone washers of the laboratory variety at the onset of the program. At a somewhat later date larger-scale equipment was installed in order that sizeable deposits, weighing upwards of 200 pounds, could be processed satisfactorily. Again, many batch-type equipment devices for the metal recovery processes were evaluated before final selection of a countercurrent cone washer technique was finally established.

Complete historic development of the electrolytic, metal recovery, and physical metallurgy phases of the program are presented in Volume II of the Final Report under Contract AT(30-1)-1335.(3) It is the purpose of this volume to present data and information which will describe the research and development activities carried out under the cell feed preparation program, and to describe in complete detail the final pilot equipment and operations which were utilized successfully to produce moderate quantities of electrolytic cell feed in a high degree of purity and appropriate thorium concentration.

Volume III of this report presents a very brief resumé of the entire thorium process, together with a cost estimate for the production of thorium metal at the rate of 1,000 tons per year.(4) Briefly, it has been estimated that the conversion cost per pound of metal in going from thorium nitrate to granular powder would be approximately $1.00, with a capital investment in the range of 4-1/2 million dollars.

It is suggested that the reader refer to either Volume II or Volume III for more complete details on these phases of the project activity.

II. EARLY METHODS OF CELL FEED PREPARATION

With the onset of a program for preparation of thorium metal and establishment that fused salt electrolysis of the chloride was a practical approach, it became necessary to produce on a laboratory scale small quantities of adequate quality cell feed.

Initial program requirements necessitated Horizons procuring a thorium-bearing raw material, nitrate supplied by the Commission not entering into the picture until a somewhat later date. Accordingly, thorium carbonate was procured from Lindsay Chemical Company and used as a starting raw material for the preparation of a suitable cell feed.

Two different grades of thorium carbonate were evaluated, one contaminated with silica, the other with only minor traces of this impurity. Both compounds were utilized in an attempt to produce thorium chloride by aqueous techniques, for example, by reacting the carbonate with hydrochloric acid to produce thorium chloride in accordance with the following reaction:

$$ThOCO_3 + 4\ HCl \rightarrow ThCl_4 + CO_2 + 2\ H_2O$$

The resulting liquor was filtered free of silica and evaporated in a graphite crucible to form a hard, dry thorium tetrachloride which it was thought possibly could be mixed directly with sodium chloride and electrolyzed to produce metal.

Analysis and experimental data, however, showed that during the evaporation process the liquid thorium chloride took on oxygen to form an oxychloride which was insoluble in the molten salt bath. It therefore was not possible to produce metal from a feed material prepared in this manner.

A study of the chemistry of thorium chloride indicated that it might be possible to produce a complex compound which would exclude oxygen from the final chloride. Ammonium chloride as a complexing agent was selected for this purpose.

In operation the same steps were carried out as before, i.e., thorium oxycarbonate was reacted with hydrochloric acid to convert this material to the chloride. While in aqueous acid solution ammonium chloride in a ratio of approximately 3 mols per mol of thorium was added and the material evaporated to dryness at approximately 120°C. It was then necessary to remove the ammonium chloride by sublimation, which was carried out at a temperature ranging as high as 650°C. During this operation an inert atmosphere or a hydrogen chloride gas atmosphere also was necessary.

Soon after the establishment of a definite method for the preparation of thorium chloride from the basic carbonate the Atomic Energy Commission modified the program to include supplying Horizons with a starting material in the form of thorium nitrate solution. The feed preparation facility therefore had to be altered to incorporate conversion of a nitrate solution to oxycarbonate in order to carry out the established process.

Again an investigation of the chemistry concerned indicated that the most feasible method for preparation of thorium oxycarbonate would be a reaction between thorium nitrate and sodium carbonate in accordance with the following equation:

$$Th(NO_3)_4 + 2\ Na_2CO_3 \rightarrow \text{"}ThOCO_3\text{"} + CO_2 + 4\ NaNO_3$$

The thorium nitrate supplied to Horizons in liquid form contained approximately 25% thorium by weight and was generally free from contamination.

Small-scale operations utilizing the chemistry described above were carried in the laboratory during the first two years of the Contract. In May, 1954, it was necessary to scale up the operation in order to produce much larger quantities of material for a semi-pilot plant operation. The first actual batch precipitation on an expanded scale was undertaken on May 25th, some three weeks after the "crash" program had been initiated. The first batch produced was carried out as follows:

A 5% solution of Na_2CO_3 was made using 44 pounds of Na_2CO_3 in 105 gallons of water at 76°C.

143 pounds of thorium tetranitrate solution containing 33 pounds of thorium as metal were slowly pumped into the Na_2CO_3 solution. The reaction was not quite complete and 2 additional pounds of Na_2CO_3, dry, were added. The pH of the solution was 7.5.

Filtration was accomplished in a 20-frame 12" hard rubber filter at 30 psi, washing with cold tap water to a wash water final sp. gr. of 1.001.

The filter cake was deposited into a rubber-lined portable trough and reacted with anhydrous HCl.

This method was rather time-consuming and hazardous from a health standpoint and was soon modified to incorporate dissolution by direct reaction with 37% HCl and subsequent evaporation of the resultant chloride.

Evaporation was first undertaken in 20-gallon, glass-lined, direct fired pots, hand stirred and regulated to 120°C maximum temperature. This method proved to be costly since thermal strains and improper operator care shortened the life of the glass linings. The material had to be chipped out of the glass-lined pot, and mortality rate on linings was high.

Numerous types of vessels for evaporation were suggested and tried, including ceramic troughs, porcelain pots and graphite containers. Ultimately a stainless steel vessel, under-fired, lined with graphite was selected for the job. The latter proved to be the most efficient and was adopted.

Early in the program the thorium chloride-ammonium chloride evaporation liquor was hand stirred, using glass rods; somewhat later, a 4-blade graphite agitator, powered by a variable speed air driven motor, was adopted and very successfully used. The evaporator was heated by two crows-foot burners from beneath, the gas flow being hand regulated by needle valves, giving the operator a fair measure of temperature control.

Evaporation was continued to the point where a "drop sample" hardened upon a metal plate, at which point the gas was shut off and the heavy liquid, resembling syrup in consistency, was "cast" into a water-cooled stainless steel pan. When thoroughly hardened and cooled, the "cast" thorium ammonium chloride complex was carefully chipped out to walnut-sized pieces and placed in the complex salt dryers.

Drying devices used for dehydration consisted of graphite crucibles approximately 16" ID x 26" high, set in Glo-bar type resistance heated, ceramic-insulated ovens. A thermocouple of platinum, platinum-10% rhodium was inserted in the center of the complex salt, extending to two-thirds of the depth. Anhydrous HCl was passed through the crucible contents during the drying stages. The crucible was covered with a split lid of graphite to prevent gross air diffusion and an exhaust tube was provided which ducted acid gases to a caustic scrubber. The drying cycle was 16 hours in duration and was divided into two parts:

(1) Pre-heating to 220°C - 8 hours
(2) Heating at 220°C - 8 hours

The Globar furnace was powered by a 7.5 KW power unit, thermostatically controlled.

When the drying cycle had been completed, the furnace front was removed and the crucible allowed to cool to near room temperature. The contents of the crucible were then chipped out, jaw crushed and mixed on a drum roller with NaCl in the weight ratio of 5: 3. At a later date, the ratio was changed to 2: 1.

The final step in thorium feed preparation involved sublimation of ammonium chloride from the salt mix at 600°C under a partial atmosphere of HCl. An all-nickel unit was constructed for this operation, it being lined with ceramic insulating brick, holding a graphite crucible of the size used for dehydration and being equipped with a graphite resistor heater which was positioned between the insulated shell and the pot. Condensers for collecting the sublimed chloride, as well as an exhaust port and sparger inlet, were provided in the equipment design.

A normal cycle, producing up to 100 pounds of cell feed, consumed 2 to 4 days and required 2 men full time for the operation.

The procedure described was operated at various production levels for more than 6 months, during which time numerous process modifications were made and operational capacities increased. Immediately prior to shutting down the facility and replacing it with direct chlorination procedures, thorium nitrate was being processed at a rate of 100 lbs. per day.

The wet process for feed preparation, in addition to presenting difficulties in scaling up and in materials of construction, was also labor-consuming and produced in very low yield. Despite extreme care in atmosphere control and process supervision, usable thorium yields ranged from a low of 20% to a high of 80%. Much of the "cell feed" was high in oxide content and was extremely difficult to chip from the sublimation pot. Mortality rates on graphite pots also were high, and exposure of personnel to radiation hazards left much to be desired.

It was concluded that the process should be abandoned in favor of direct chlorination, since the overall feasibility for production appeared slight.

III. DEVELOPMENT OF FEED PREPARATION PROCESSES

A. Small-Scale Chlorination Experiments

1. Direct Chlorination of Thorium Nitrate

In previous sections a rather complete discussion of the wet chemical process for the preparation of electrolyte for electrolytic purposes was presented. General operational difficulties, the lack of adequate cell feed quality, poor recovery yields, and materials of construction problems for processing equipment necessitated the development of a different approach for the preparation of cell feed.

Inasmuch as a fused salt product for electrolysis was desired, it seemed logical to determine whether or not a spent electrolyte might be rejuvenated by the direct expedient of adding thorium nitrate to it and converting the nitrate to a chloride by a suitable chlorinating agent. Accordingly, a program for evaluating the feasibility of chlorination in fused salt systems was set up on a small scale. Chlorinating agents investigated included carbon tetrachloride, hydrogen chloride gas, phosgene, ammonium chloride, and chlorine in the presence of carbon. The starting material in each case during the early research period was wet thorium nitrate tetrahydrate.

a) Experimental Equipment

Past electrolytic runs for producing thorium metal had been based on a sodium chloride-thorium tetrachloride binary system. Cursory evaluation runs using a potassium chloride-sodium chloride-thorium tetrachloride ternary system previously had indicated the feasibility of this system also. The direct chlorination program therefore was established utilizing a KCl-NaCl binary, to which thorium nitrate tetrahydrate was added. The prime reason for selecting the ternary system was the decreased melting temperature exhibited by a NaCl-KCl binary eutectic, which melts in the range of 600°C. To prevent loss by volatilization of the thorium values it was considered desirable to take advantage of lower temperatures.

An initial series of runs was made in 1-1/2" diameter vycor test tubes, externally heated and open to the atmosphere. More than 60 runs were made in this type of apparatus.

Based on the experiments performed in the 1-1/2" diameter vycor tubes, a scale-up of the process was completed and operated for approximately three weeks. The latter unit consisted of a 6" diameter fused quartz tube, with a capacity for chlorinating the equivalent of 400 grams of thorium metal per batch. The large experimental unit was externally heated, and differed only in minor respects from the small-scale unit. The top of the 6" tube was closed with graphite segments, and had openings only for a gas sparger, discharge tube and thermocouple well.

Equipment modifications on the large scale included the introduction of graphite liners within the quartz tube to prevent tube breakage on salt solidification, use of various sparging devices, etc.

The size ratio between the two unit volumes was 20 to 1.

b) Experimental Procedures

Most of the thorium nitrate tetrahydrate which was available for this program contained excess quantities of nitric acid and water. Reagent grade sodium and potassium chlorides constituted the remainder of the batch in each case.

Proportionate weights of potassium chloride and sodium chloride were weighed out in advance on a rather large scale, an intimate mixture of the two being used as the base material for making up the various runs. A typical heat in the 1-1/2" diameter unit required 85 grams of the sodium chloride-potassium chloride eutectic mixture and 55 grams of thorium nitrate tetrahydrate. These were blended and added to the vycor crucible.

After bringing the mix to a molten state, a suitable sparging device was inserted, reaching to the bottom of the crucible, and phosgene or other chlorinating agents added at a rate of approximately four cubic feet per hour. In most instances approximately one hour of chlorinating time was utilized. At the end of the chlorinating period the sparger was removed, the contents of the tube poured into a cooled Petri dish, and the material allowed to solidify under a watch-glass cover. After solidification and cooling the sample was broken up, sampled and a sample submitted for analysis of per cent soluble and insoluble thorium.

In general, the same procedure was followed throughout in operating the larger sized research unit, with the exception that the material after completion of the chlorination phase was not poured, but was allowed to solidify in the crucible itself. This was necessitated because of the physical size and weight of the unit.

Certain experiments were run in which ammonium chloride in the presence of carbon was utilized for chlorinating purposes. In these instances, the reactants were placed in a zircon crucible, which in turn was positioned within a plumbago crucible, the entire assembly being covered over with a silicon carbide slab. These experimental heats were run in Globar furnaces, but aside from the different type of crucible, all other experimental conditions were maintained constant.

The choice of one hour for chlorinating time in the 1-1/2" diameter unit was purely arbitrary, since results on this size of batch indicated that approximately 60 minutes were required to complete the chlorination run in the most optimum experimental heats. The 6" diameter unit was operated until samples contained no unconverted thorium, (based on a water solubility test), the normal time requirement being six hours.

c) Experimental Results with Discussion

Initial experiments carried out under the research phase of the program were somewhat exploratory in nature, involving one, or at most a few, runs in each system, in order to determine the feasibility of various chlorinating agents for reducing thorium nitrate tetrahydrate to the tetrachloride in a fused salt bath. In some instances mechanical difficulties were encountered, efficiencies were poor, excessive foaming and frothing were encountered, or yields were exceptionally poor. It was thus possible to eliminate from the series of experimental runs a number of the potential chlorinating agents, after which the program concentrated on two different systems. Tables I and II in the Appendix summarize data generated in the small scale chlorination experiments, groups of which are discussed below.

i) Chlorination with Ammomium Chloride in the Presence of Carbon

Twelve experimental heats utilized ammonium chloride in the presence of carbon as a chlorinating agent. These runs were made in a zirconia crucible, and each was run for a period of 60 minutes. Three different temperatures were investigated, four samples at each temperature constituting a series, as follows:

1. Stoichiometric quantities of ammonium chloride and carbon
2. Stoichiometric quantity of ammonium chloride with 100% excess carbon
3. Stoichiometric quantity of carbon and 100% excess ammonium chloride
4. 100% excess of both ammonium chloride and carbon.

Calculated weights of ammonium chloride and carbon were based on a charge weight of 55 grams of thorium nitrate tetrahydrate, which contained approximately 42% by weight of thorium as metal.

Foaming and frothing were quite noticeable in these experimental heats, and in most cases the bath overflowed the crucible walls. Total weight yields therefore were unobtainable in most instances.

As a result of the 12 heats which were run, it was concluded that temperature apparently has no major effect on the rate of chlorination. Similarly, the carbon content of the bath did not appear to be a determining factor, though if anything, excess amounts of carbon would appear to be detrimental, decreasing the yield of soluble, chlorinated thorium. The relative proportion of ammonium chloride also appeared to be somewhat unimportant, though there was perhaps an insufficient number of runs to allow one to draw final conclusions with respect to this. In general, the scatter of yield in per cent soluble thorium ranged from 10 to 50 per cent, though there was no definite correlation between this factor and any of the three major variables.

Because of the relatively high expense of the reagents, the physical difficulties of furnacing and the relatively poor yields obtained, no further experiments in this system were made.

ii) Chlorination with Carbon Tetrachloride and Chlorine

An attempt was made to use carbon tetrachloride as a reducing agent, transferring this material over in vapor form in a carrier stream of chlorine gas. In one series the temperature was approximately 750°C, the other, 850°C. Times ranged from one hour to two hours and 40 minutes for the chlorinating cycle. While no major difficulties were encountered in furnacing the mix, problems were confronted in maintaining carbon tetrachloride in the gas flow system, and the results were relatively poor. In no instance did the fraction of recovered thorium exceed 30 per cent of the total charge.

Because of the low yield in this system, no additional experiments were carried out.

iii) Chlorination with Hydrogen Chloride Gas

Several runs were made in the 1-1/2" diameter unit, in which hydrogen chloride gas was utilized for the chlorinating agent. Temperatures ranging from 650°C to 950°C were tried, and in all cases the percentage yield for a given time of chlorination was substantially constant. Thus, thorium nitrate chlorination with hydrogen chloride gas is not temperature sensitive, as was found with phosgene. Further the conversion of thorium nitrate tetrahydrate to thorium tetrachloride was limited to approximately 60 per cent.

Since hydrogen chloride gas is somewhat more expensive than phosgene, and inasmuch as conversion efficiencies were found to be very much lower when the hydrogen chloride gas was used than when phosgene was used, it was concluded that further experimentation with hydrogen chloride was not warranted.

iv) Chlorination with Chlorine in Presence of Carbon

Some 20 heats under varying conditions were run utilizing chlorine as the chlorinating agent. For the initial series a chlorine gas flow rate of approximately 3.5 cubic feet per hour was maintained, the amount of carbon present being the major variable. In most of these series, finely divided lampblack was the form in which the carbon was introduced. Additional experiments were run in which finely divided carbon black was replaced by various types of carbon rods, porous carbon shapes, carbon rods in conjunction with graphite crucibles, and similar arrangements.

In addition to changing the relative quantity of carbon black in these melts, the time and the temperature of reaction were variables in some instances.

There was no apparent change in thorium conversion as a function of temperature, all heats going to completion within a 60 minute period when finely divided carbon black was utilized in excess in conjunction with chlorine as a reducing agent. This was true regardless of the temperature, which ranged from 600°C to nearly 1000°C.

Some additional runs were made in which carbon plus chlorine was utilized in a bath of pure sodium chloride, and here again excellent results were obtained.

In those runs where a stoichiometric quantity of finely divided carbon black was used, and in cases where less than the theoretical quantity was utilized, all of the carbon added to the bath was consumed in the reaction. In each of these instances, incomplete conversion of the thorium nitrate to tetrachloride was experienced. Thus, an excess amount of carbon appeared to be necessary in order to convert completely the thorium nitrate which was added into the bath. The use of carbon black as a reducing agent for chlorination therefore posed an immediate problem: It is most undesirable to have excess carbon in the salt bath when electrolysis takes place, so it becomes necessary to effect a carbon removal prior to electrolysis by some physical means. High temperature filtration would appear to be the only obvious solution. While efficiencies have been quite good in a number of experimental runs utilizing finely divided carbon black as the reducing agent, the necessity of filtering out the excess would appear to place this system in the category of a last resort, to be used only if no other system works, though filtration at 700 to 800°C may be within the realm of feasibility.

In the early stages of heating up a reaction mix, quantities of water and NO_2 are given off, causing excessive frothing and bubbling to occur. Similarly, at a temperature between 600° and 700°C, the charge goes through a pasty state, which, coupled with further evolution of gases due to calcination, causes severe bloating of the bath. A volume in excess of two times the required capacity for the liquid melt has been found necessary in order to contain the mixture properly. Furthermore, heating must be done extremely slowly in order to prevent the material from foaming out of the pot. While the process is unquestionably effective in the long run, it lacks much to be desired with respect to operation, even on a small laboratory scale, and many practical difficulties would be anticipated should the process be scaled up to a production capacity.

Additional runs were made in which a combination of chlorine plus carbon, and phosgene were used for chlorination. To the potassium chloride-sodium chloride eutectic, containing suitable quantities of thorium nitrate tetrahydrate, there was added a deficit amount of carbon black as a reducing agent. The batch was heated up in the usual manner and held for approximately 30 minutes to allow reaction, chlorine being bubbled through the melt during the entire period. At this stage most of the carbon black had reacted or was outside the zone of reaction due to frothing of the bath. A sparger was then placed in the bath and phosgene bubbled through for an additional 30 minute period. The results of one such run indicated approximately 60% conversion of the total available thorium. Based on a few experiments of this nature, it was concluded that the duplex type of operation, in which a deficit quantity of carbon is initially used, followed by completion of chlorination by means of phosgene, is not too feasible an approach. More overall time would be required, and the problem of frothing, attributable to a large extent to the carbon black, would contribute further to the infeasibility of this system.

v) Chlorination with Phosgene

Approximately 30 runs were made in which phosgene gas was used as the reduction and chlorinating agent. Initially an attempt was made to use a pure sodium chloride bath, at temperatures between 800 and 950°C, for phosgene chlorination. Because of the extremely poor results, it was necessary to resort to sodium chloride-potassium chloride eutectic systems, since it was soon found that lower temperatures increased the conversion yield noticeably. Fig. 1 shows a plot of four experimental melts, the graph indicating percentage of thorium converted to tetrachloride as a function of temperature, all experiments being run for 60 minutes. It

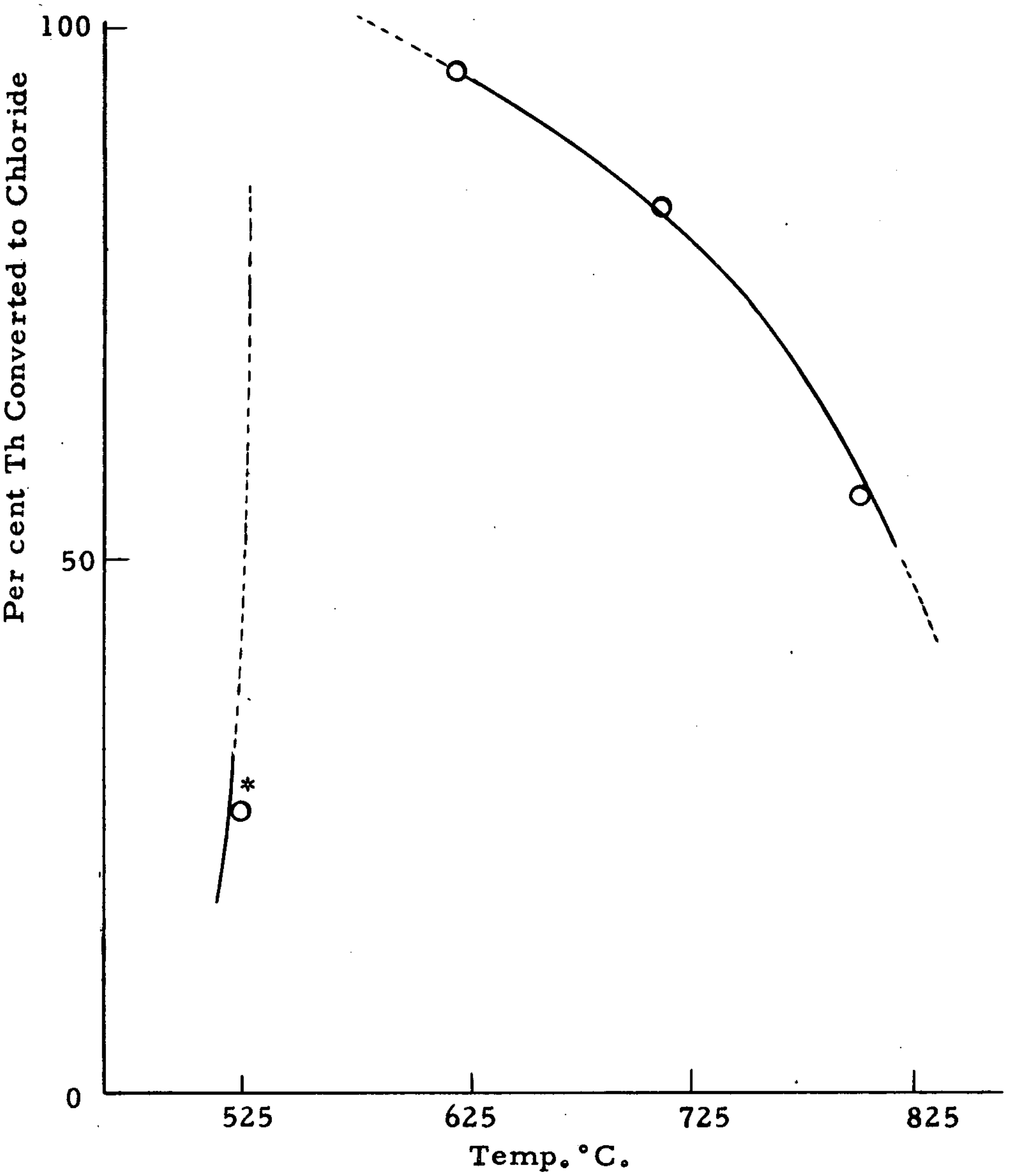


Fig. 1

Effect of Temperature on Fused Salt Chlorination of Thorium Nitrate with Phosgene.

* Solid charge; other points represent molten charge.

may thus be seen that the efficiency of phosgenation is inversely proportional to temperature, as long as the system maintains a molten state.

Both the mechanics and the chemistry of phosgenation appeared to be such that this particular system was the most desirable of those investigated for use as a commercial operation to convert thorium nitrate directly. Based on this conclusion. rather detailed studies of the system were made, and a number of the large scale experimental runs were electrolyzed in Horizons' Mark II size electrolytic cells. In every case excellent quality metal, based on hardness, resulted. It was therefore considered completely feasible to utilize phosgenated thorium tetrachloride-potassium chloride-sodium chloride eutectic systems as feed stock for electrolysis to produce thorium metal by the Horizons' process.

In a typical run, the thorium nitrate tetrahydrate was mixed with suitable quantities of the potassium chloride-sodium chloride eutectic mixture, and the batch placed loosely inside a vycor or graphite crucible. The unit was then heated slowly from the outside. When the temperature reached approximately 95°C, noticeable quantities of water began to evolve, and continued to evolve until a temperature of approximately 275°C was reached. On further temperature increase, nitrogen dioxide, NO_2, began to evolve, going through a maximum evolution at temperature ranges between 300 and 400°C, and coming to an apparent completion at approximately 450°C. There was no visible evidence of NO_2 elimination beyond temperatures of approximately 500°C until after chlorination had been initiated with the phosgene. In actuality, it appears that up to 8% of the NO_2 in the mixture remained until phosgenation was initiated, the latter quantities coming off with the first portion of phosgene sparged.

A pasty stage was encountered during melt-down at approximately 600°C, and this, together with some additional evolution of gases, caused the material to foam and bloat to a minor degree. A total volume of crucible approximating two times the original occupied volume has been found adequate in order to insure that no loss of a charge is encountered. By heating slowly through certain ranges the foaming can largely be eliminated.

On raising the temperature to between 650° and 700°C, the material in the crucible became completely molten, the thorium decomposition product, obtained from dewatering and denitrating thorium nitrate, being present as a suspension of solid particles. At this point a gas sparger was placed in the crucible and the reacting gas flow started. As the phosgene sparging was initiated, a slight temperature drop in the bath was recorded, followed by a later thermal increase, indicating that the reaction is somewhat exothermic. The initial thermal drop possibly results from the cooling effect of the incoming gases prior to the actual initiation of reaction, or an endothermic heat of solution of phosgene in the melt.

Visual observations have shown that on completion of chlorination, the bath has the same visible coloration as water, being completely clear and extremely fluid.

Determinations of insoluble thorium content have been run by taking a sample and dissolving it in water. After a one hour phosgenation in the 1-1/2" diameter tube, it has been found in most instances that there is no evidence of any water insoluble material remaining.

2. Direct Chlorination of Thorium Intermediates

a) Program Technology and Procedures

The feasibility of producing a high-quality thorium cell feed by the mechanism of directly chlorinating thorium nitrate was established as described in previous sections. However, certain aspects of the process left much to be desired, primarily as a result of the rather corrosive fumes which result from the chlorination reaction. For example, nitrogen monoxides and dioxides, possibly nitrosyl chloride, hydrogen chloride gas, moisture, and various acids resulting from interreactions, were constituents of the effluent gases resulting from the operation. Severe corrosion and erosion of equipment components were encountered, to the extent that rather major difficulties were anticipated in scaling up the system.

In addition to the corrosive nature of the off-gases, floating of the charge, excessive frothing and loss of bath constituents further accented the necessity for system improvement.

One of the intermediates produced earlier in the aqueous system for preparation of cell feed was a thorium oxycarbonate, and it was to this material that further experimentation was turned.

Thorium oxycarbonate presents many advantages for direct chlorination over those exhibited by thorium nitrate. Most, if not all, of the nitrogen-bearing gases associated with thorium nitrate are removed as a result of thorium oxycarbonate formation; further, the material may be dried to a very low water level and still be amenable to direct chlorination without major difficulties. Off-gases resulting from the reaction are predominantly carbon monoxide and carbon dioxide, relatively innocuous gases with respect to corrosive conditions.

Experimental approaches, equipment and techniques used in the evaluation of thorium oxycarbonate as a raw material for direct chlorination were substantially identical to those reported on in earlier sections and will not be repeated here.

b) Experimental Results with Discussion

i) Experiments with Ammonium Chloride

A series of experiments was run in which 1) ammonium chloride and thorium oxycarbonate were ground together in a mortar and pestle, 2) ammonium chloride and thorium oxycarbonate were ball milled for 90 hours, and 3) thorium oxycarbonate was calcined for one hour at 900°C, followed by mixing with ammonium chloride and grinding in a mortar and pestle. Table III in the Appendix summarizes the results of these runs. It may be noted that the most optimum yield of soluble chloride from this series of experiments was obtained at approximately 450°C, and that the method of mixing of the two components apparently was not too material.

ii) Chlorination in the Presence of Carbon

In Table IV , page 123 in the Appendix, experiments are reported which attempted to convert thorium oxycarbonate to chloride, using phosgene in the presence of carbon. In the first of three experiments porous carbon rods were placed in the molten salt menstruum.

In general it appeared that there was a definite decrease in the oxycarbonate conversion rate when porous carbon was present in the salt bath. By way of explanation, it was thought that perhaps these conclusions were somewhat erroneous, the temperature of the bath possibly having been severely decreased as a result of large masses of graphite protruding from the material and extracting heat.

Listed in the same Table are further heats in which thorium oxycarbonate was reacted directly with phosgene without benefit (or detriment) of carbon. In this series of runs it was demonstrated that it is possible to chlorinate thorium oxycarbonate with phosgene, running the reaction to completion in order to arrive at a cell feed containing in excess of 45% thorium.

This series of experiments also served to demonstrate that the thorium oxycarbonate could be added gradually to the molten bath in increments simultaneously with sparging, giving rise to the possibility of continuous or semi-continuous operations of the chlorinator. The problems encountered in the use of thorium nitrate, largely concerned with dewatering and denitration, were thus not encountered in the direct chlorination of thorium oxycarbonate.

Further runs in this series showed that even thorium oxycarbonate as taken off the filter, i.e., in a very wet condition, can be chlorinated reasonably well, though a somewhat longer time is required than when dry thorium oxycarbonate is used.

iii) Chlorination of Thorium Oxycarbonate with Anhydrous HCl

Further runs tabulated in this group of data represent information obtained when hydrogen chloride gas was substituted for phosgene as the chlorinating agent, thorium oxycarbonate being converted to chloride in a comparable manner. In these instances, both Horizons-produced oxycarbonate and materials obtained from Lindsay Chemical Corporation were used. It may be noted that no difficulty was encountered in completely converting these materials with hydrogen chloride.

iv) Chlorination of Thorium Oxycarbonate with Carbon and Chlorine

Because of the toxicity of phosgene and the comparative inefficiency of hydrogen chloride as chlorinating agents the system thorium oxycarbonate-carbon-chlorine was investigated as a possible alternative system for the preparation of cell feed. In these groups of experiments dry thorium oxycarbonate was ground together with varying amounts of lampblack, pelletized and added to molten mixtures of sodium and potassium chlorides, the entire system being sparged with chlorine gas for a predetermined period of time at a fixed flow rate.

Early experiments dealt primarily with the relative quantity of carbon to be used as an additive with respect to the quantity of thorium in the system. Pellets containing between 200 and 500 per cent of the theoretical amount of lampblack were used, 1-1/2 hours of chlorine flow being standardized upon. No difficulty was encountered in complete conversion of the oxide, though large excesses of lampblack were found on completion of each cycle.

Carbon rods as the source of carbon also were used in a group of experiments, though with much poorer results than those obtained when lampblack was present.

In another group of experiments in which pelletized oxycarbonate interspersed with carbon served as the feed material, one group of pellets was converted in which no carbon was present, a second group in which 50% of the theoretical lampblack requirement had been added, a third group in which 100% of theoretical was present, and a fourth group in which 125% of theoretical lampblack had been added. Table V below presents the results of the latter four groups of experiments.

Table V

Effects of Pellet Composition on Chlorination of Thorium Oxycarbonate

Sample Number	Percent Theoretical Carbon	Soluble Thorium Percent	Insolubles Percent	Carbon Percent
A	50	28.9	4.39	0.31
B	75	34.5	0.054	0.054
C	100	35.3	0.073	0.073
D	125	34.8	0.068	0.068

In reference to the table above it may be observed that in Sample A there was an appreciable residue of unconverted thorium oxide remaining in the bath, whereas in the latter three samples the entire insolubles residue was excess carbon. It did serve to point out that it is possible to convert the entire thorium value in the bath to chloride by supplying the proper proportion of lampblack and sparging with chlorine gas.

By way of explanation, the calculation of theoretical carbon required for the reaction assumes that all thorium present in the bath is in the form of thorium dioxide, and that the theoretical quantity of carbon would be the quantity required to convert the thorium oxide to thorium chloride with carbon monoxide being the by-product gas. According to the Table above, it may be deduced that a carbon additive in the range of 75% of the theoretical value is required for complete conversion; i.e., the chemical reaction apparently produces a gaseous by-product which is approximately 50% carbon monoxide and 50% carbon dioxide at a temperature in the range of 700 to 750°C.

Later experiments served to confirm that it was possible to adjust the bath composition, either by the minor addition of additional oxycarbonate or lampblack so that all oxycarbonate in the bath was completely converted to chloride, and all carbon in the bath was completely consumed. Thus, a perfectly clear bath of cell feed was obtainable, with thorium contents as high as 45%.

v) Effects of Drying Variables on Chlorination Rate

A group of experiments was completed in which the drying conditions for thorium oxycarbonate filter cake presented the major variable. In this instance a standard hot air furnace was used, thorium oxycarbonate being spread in glass trays at varying thicknesses and dried over a range of temperatures and times. Some 20 experiments of this type were run, indicating that a wide variety of time-temperature-thickness parameters may be used satisfactorily to produce an adequate thorium oxycarbonate suitable for chlorination with hydrogen chloride gas or chlorine.

In another group of experiments the rates of chlorination on thorium oxycarbonate dried under varying conditions were compared with material obtained from Lindsay Chemical Company. Table VI in the Appendix presents the results of these data, indicating that thorium oxycarbonate dried at 250°C was converted with hydrogen chloride gas at a more rapid rate than the material which had been obtained from Lindsay.

vi) Comparative Rates of Chlorination

In order to evaluate the relative effects of hydrogen chloride and phosgene as chlorinating agents, duplicate sets of experiments were run in which these two reactants converted Lindsay oxycarbonate and Horizons oxycarbonate to the chloride. Table VII below presents the results of this group of experiments.

Table VII

Comparison of Reaction Rates of Phosgene and Hydrogen Chloride Gas

Chlorinating Agent	Basic Th Carbonate	Reaction Time (minutes) for Each 5-gram Addition 1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
$COCl_2$		44	36	31	33	31	30	30	25	20	23
HCl	Lindsay	17	41	74	128	*					
$CoCl_2$	Wet chemical process pre-dried	52	61	37	38	47	26	29	33		
HCl		20	36	65	114	**					

* 5th addition incompletely reacted after 165 minutes.

** 5th addition was completely reacted in 117 minutes by dropping the reaction temperature to 600° C.

With reference to the Table above, it may be noted that during the early portion of the chlorination cycle hydrogen chloride gas appears to be more efficient than phosgene; however, as the thorium content of the bath increases, phosgene appears to have an edge over hydrogen chloride gas as a conversion medium.

3. Miscellaneous Research Activities

a) Cascade Chlorination Systems

At one stage in the program for preparation of fused salts by direct chlorination it appeared that phosgene was the only suitable reagent which would allow preparation of a high-thorium fused salt for electrolysis. Because of the relative inefficiency of the reaction,(e.g., maximum phosgene utilization was in the order of 10%,)it was deemed advisable to evaluate methods of recycling the effluent gases from the system in order to increase the overall phosgene utilization.

Facilities were not available which would satisfactorily handle phosgene by condensation from the chlorination off gases. As a rather simple alternative, a multiplicity of chlorinating vessels was set up in tandem with arrangements being provided for ducting the off gases from each unit into the sparging system of the next succeeding unit. Up to six furnaces were operated in series in this manner, in order to determine whether or not additional phosgene utilization was accomplished by the multiple-pass approach.

As actually operated, the entire group of furnaces was charged, all units brought to temperature with a minor amount of phosgene sparging on an individual basis in order to effect dewatering and de-nitration. Once the bath was de-nitrated and fully molten the series system of phosgene introduction was initiated and the units run for a prescribed period of time, in general one hour. Phosgene and minor quantities of gases resulting from the chemical reaction from the first furnace were then passed into the second furnace, etc., in series. Each unit was pressure-tight, though some difficulties were encountered in attempting to maintain this condition throughout the run.

In one specific group of experiments, in which four furnaces were used in series, the respective quantities of thorium converted from nitrate to chloride, in grams, were 10.0, 10.1, 9.4, and 8.2. The overall phosgene utilization efficiency was between 30 and 35% in this particular experiment. It thus is obvious that by the medium of recycling phosgene, or by the use of a suitably designed chlorinator with the equivalent of a sufficient number of contacting stages, it should be possible to achieve a reasonably acceptable phosgene utilization efficiency.

At the time of these experiments the system was not followed up, primarily because of the difficulty in continuously feeding a chlorinator using thorium nitrate as the raw material. The quantity of nitrogen-bearing gases and water accompanying the off gases from phosgenation was too large to consider recycling, and hence a refrigeration system or other variety of separatory arrangement for collecting unused phosgene would have been necessary. The advent of successful chlorination systems using carbon and chlorine as the reactants obviated the necessity for further evaluations of the cascade flow system using phosgene.

b) Direct Chlorination of Thorium Oxide

In order to alleviate the difficulties inherent in direct chlorination of thorium nitrate a quantity of this material was dewatered and de-nitrated by heating to an elevated temperature (500-600°C). The material resulting from this operation was intimately ground with lampblack in proportion approximating 200% of the theoretical requirement based on a thorium oxide-carbon reaction to yield carbon monoxide as the by-product, the solid blend pelletized into small pellets and packaged into tubular containers suitable for feeding into a small experimental chlorination unit.

Two such sets of experiments were run using different kinds of experimental arrangements. These two will be covered separately.

i) Co-current Chlorination

In the first system evaluated, a totally enclosed furnace unit lined with graphite crucible and external heater was utilized to hold a molten batch of sodium chloride-potassium chloride eutectic. Inserted in the molten bath was a hollow graphite tube, to which was attached a porous graphite, blind end cup. The entire porous graphite section and a portion of the solid cylindrical graphite tube were immersed in the molten bath. Pellets of de-nitrated thorium nitrate and carbon mixture were inserted in the central portion of the tube and chlorine flow initiated at the upper perimeter of the graphite sparger system. Experimentally, the chlorine passed through the quasi-thorium oxide-carbon mixture, effecting a solid-gas reaction in certain portions of the unit and providing a partially chlorinated mix for reaction at the sparger head between the molten salt and the charge. Further chlorination was effected by the action of chlorine bubbling through the molten salt and sparger head around the immediate vicinity of the partially chlorinated solid charge.

Experimentally it was shown that quantities of thorium could be transferred from a solid charge into the bath as thorium chloride at a relatively low rate, but numerous difficulties were encountered from a practical standpoint. Chlorine efficiencies were not particularly high and the mortality rate on graphite sparger tips precluded scaling up this type of system.

ii) Extraction Chlorination

The possibility of modifying a co-current system of chlorination somewhat, at the same time maintaining the continuous feed approach, was tried on a small scale. This system incorporated a long, vertical tube with a central shaft and agitator affixed at the bottom. Supported concentrically inside the tube was a graphite cylinder with a pervious graphite plug at the lower end. A charge of pelletized quasi-thorium oxide plus carbon was placed inside the central cylinder, molten salt levels being adjusted such that the upper end of the cylinder was slightly below the salt level. Agitation of the impeller in the proper direction forced molten salt downward through the central tube, up the outer walls and into the top of the central tube, thus contacting pellets while trickling through the central column. Simultaneously with the salt movement downward a sparger introduced chlorinating agents, such as phosgene or chlorine, beneath the tip of the agitator in such a manner that it passed vertically upward through the column in a counter-current fashion to the molten salt movement. By the combined techniques of rather vigorous agitation and good contacting in the column, much faster chlorination rates were achieved than by the direct passage of a chlorinating agent co-currently, using solid state reaction, as described in the previous section.

A system of the type presently being described could be operated on a continuous or semi-continuous basis, withdrawing a quantity of the molten salt under scheduled conditions and continuously or semi-continuously charging pellets into the central column. Materials of construction, however, would be something of a problem. Agitators, shafts and concentric cylinders, while readily constructed and operated on a small scale, pose major problems on scaling up to commercial or semi-commercial sizes.

In view of the results which were obtained in using the carbon plus chlorine system and direct chlorination of thorium oxycarbonate in a molten salt bath, which development paralleled the present one, it was decided that scaling up of the agitated counter-current system should not be undertaken.

c) Preparation of Pure Thorium Tetrachloride

A group of experiments was carried out in order to determine the feasibility of chlorinating thorium oxycarbonate in the solid state as compared with chlorination in a fused salt bath. In this system a vycor tube was used to house a mixture of thorium oxycarbonate and small ceramic raschig rings, the latter acting as spacers. The desired chlorinating agent was passed upward through the tube by sparging, the entire column being heated in a temperature range from 400 to 650°C. Chlorine flow rate was 10 cubic feet per hour through a column size 1-1/2" in diameter and 4 ft. long.

Table VIII below presents data resulting from five typical runs in this system.

Table VIII

Solid State Chlorination of Thorium Oxycarbonate

Sample No.	Temperature	Chlorinating Agent	Time	% Soluble Thorium	% In-solubles	% Chlorine
1	600-625°C	chlorine saturated with carbon tetrachloride	1 hr.	13.9	68.6	
2	600-625°C	hydrogen chlorine gas	1 hr.	22.6	54.1	21.4
3	425°C	chlorine saturated with carbon tetrachloride	1 hr.	74.7	0.56	15.3
4	525°C	chlorine saturated with carbon tetrachloride	3 hrs.	72.0	0	24.6
5	525°C	chlorine saturated with carbon tetrachloride	1 hr.	61.0	0.35	35.8

It may be observed that Sample No. 5 in Table VIII comes closest to approximating the theoretical composition of thorium tetrachloride. However, the fact that the thorium present was in soluble form did not necessarily prove that it was in the form of a tetrachloride, an equally probable system being thorium oxychloride which is known to exist in the thorium-oxygen-chlorine system. As a quality evaluation test, a sample of the product from Run No. 5 was added under an argon atmosphere to a molten bath of sodium and potassium chlorides at 725°C. The product was analyzed and found to contain only 17.6% soluble thorium, along with 24% insolubles. From this it was concluded that the product resulting from solid state reaction was an oxychloride rather than a true chloride of thorium, and hence would be unsuitable for electrolytic purposes.

d) Recovery of Scrap Thorium

Under normal operating circumstances it would be expected in a production plant that some minor fraction of the product would be lost through fires, or contamination of one form or another. For example, in pilot operations on preparation of thorium, under three separate circumstances a small fire occurred which consumed minor quantities of thorium metal. In each instance the pyrophoricity of the material was readily explainable; in two cases finely divided thorium ignited spontaneously and in a third, an alloy of iron in thorium, producing a pyrophoric alloy, was handled in such a manner that it spontaneously ignited.

In order to determine the feasibility of recovering the material after burning, a quantity of thorium oxide resulting from these fires was crushed, mixed intimately with lampblack, pelletized, and fed into a molten salt bath through which was sparged chlorine. It was found that the material chlorinated at approximately the same rate as thorium oxycarbonate, thus demonstrating that it is completely feasible to return to process any oxides resulting from inadvertent combustion of finely divided or off-grade thorium metal. Even if moderately contaminated with impurities such as iron, it should be accommodated readily in the process by suitable blending techniques.

e) Evaluations of Ceramic Materials for Fused Salt Applications

With the advent of direct chlorination as a feasible system for the preparation of electrolytic cell feed, a research program was initiated in Horizons' Ceramics Department to determine which ceramic compositions were most resistant to fused salt baths.

The system utilized for initial evaluation consisted of eutectic sodium chloride-potassium chloride; more promising materials also were exposed to sodium-potassium chloride baths which contained up to 15% thorium as thorium tetrachloride.

Times of tests ranged from 24 hours to one month, at temperatures between 700 and 800°C. The first series of tests was largely screening in order to eliminate materials which obviously were infeasible. Those materials which showed promise were then given longer tests at temperature in order to determine at least in a relative manner the most logical systems for consideration.

Evaluations were based on weight gain or loss, appearance of specimen, depth of penetration, appearance of reaction zones and actual composition of molten salt baths following tests.

Of the materials which were found to be satisfactory, fused quartz or fused silica appeared to be among the best. Other satisfactory materials for most applications were U. S. Stoneware's "elite", Star Porcelain's No. 148 and McDaniel mullite. Possibilities also worthy of some consideration were acid-proof bricks manufactured by Harbison-Walker and A. P. Green Company, commonly known as "acido" and " duro".

Use of fused quartz for heater protection tubes and thermocouple wells was found to be adequate in chlorination systems, but difficulties were encountered when similar applications were made in electrolytic cells. A metal "fog" of thorium, present in the electrolyte, reacted with the quartz to produce a thorium oxide outer coating and effect devitrification in a thickness of as much as 1/8" in two weeks at 800°C. Fused quartz or silica is therefore not recommended for use in the electrolysis of thorium chloride unless protected by a suitable shield, such as graphite.

4. Bench Scale Phosgenation Experiments

Following the series of successful experimental runs in a 1-1/2" diameter tube, a 6" diameter unit was procured and set up for further experimental runs. A unit of this size was selected because the capacity was adequate to produce a sufficient quantity for evaluation in the Mark II electrolytic cells in a single run.

A total weight in the small test tubes approximating 110 grams was ordinarily obtained from a phosgenating run. In the scale-up to a 6" unit, normal yield was 2200 grams of product per batch, a twentyfold increase. A proportionate scale-up in area was not obtained, in this case the relative openings of the two tubes being in the ratio of approximately 11: 1. Hence, the bath depth in the larger tube was approximately twice that which had been obtained in the smaller unit. In the 1-1/2" diameter tube the normal operating depth varied from 3 to 4", whereas depths from 7-1/2" to 10" were utilized in the larger unit.

In the small unit, a phosgene flow rate of 4 cubic feet per hour was maintained, and reactions were complete within 60 minutes. In the larger unit, utilizing the same flow rate, it was found that approximately six hours of reaction time were required. Since the amount of total gas flow in the small unit was approximately 20 times the volume required theoretically, the ratio of theoretical to actual in the large unit approximated 6: 1, i.e., some six times as much total phosgene was used in the large unit for a batch containing 20 times as much thorium, so that the relative concentration per unit time was in a ratio of approximately 3: 1 in the two units. One would therefore have expected approximately 18 times the chlorinating time in the large unit, whereas a sixfold increase was actually experienced.

One heat in the large unit was run with a phosgene flow rate of two cubic feet per hour, and it was found that the bath still contained large quantities of thorium oxide after nine hours of phosgenation. This would tend to substantiate the thought that increased flow rates would reduce the phosgenation time drastically.

a) Effects of Gas Bubble Size and Related Variables

In order to ascertain whether or not other factors were influencing the relatively long phosgenation time in the larger unit, several experiments were run in which a number of variations were made. A series of three heats was run, the first utilizing a 1/4" diameter open end tube as a sparger, the second utilizing a tube with one millimeter diameter openings, approximately 8 in number, and the third utilizing a 1-1/2" diameter sparging disc at the bottom end of a conical-shaped tube, the average opening approximating 100 microns. For a constant phosgenating period it was found that the relative conversions for the three heats were approximately 60, 97 and 100%. It thus may be concluded that the smaller the bubble size, the better the recovery per unit of time, and hence the higher efficiency of utilization of the phosgene. Any commercial or large scale type of chlorinating unit therefore should be equipped with spargers which will produce extremely fine bubble size.

One-hundred micron size spargers, some facing down, some sideways, and others in various positions, did not seem to alter the results on another series of runs that was made. Further, the use of cone-shaped bottom crucibles as compared with flat bottom crucibles did not appear to make any appreciable change in the chlorination rate. It would appear that the only major criterion for effective chlorination is an ample concentration of gas, fine bubble size and rapid agitation, in order to maintain the thorium oxide particles in a semi-fluidized state.

b) Effects of De-watering Thorium Nitrate

A few runs were made in which the thorium nitrate tetrahydrate was de-watered, and in some instances de-nitrated, prior to mixing with the potassium chloride-sodium chloride eutectic mixture for phosgenation. In all cases, a much longer chlorination time was required than when the material was mixed directly without de-watering or de-nitrating. It would therefore appear that the reaction between thorium nitrate and phosgene is related in a very definite manner to the surface properties of the decomposition product itself.

c) Thermal Effects

A potassium chloride-sodium chloride eutectic system, containing approximately 18% thorium metal in the form of tetrachloride, was found to have a freezing point of approximately 500°C.

d) Volatilization Losses

While the number of experiments run at temperatures in excess of 800°C was not great, it was evident from the results obtained that a sizable proportion of the total thorium content of the bath is lost by volatilization at higher temperatures (as much as 3% per hour at 900°C). Therefore, chlorination in a low melting point eutectic system is desirable from an over-all efficiency standpoint.

B. Pre-Pilot Production of Cell Feed by Phosgenation

1. Process Description

Shortly following completion of the early small-scale experimental work, in which phosgene was shown to be a good chlorinating agent, a scale-up of the process was effected. It was during the operations of the scaled-up process that further small-scale research work leading to the use of carbon plus chlorine was carried out.

The process used in the pre-pilot scale-up of the operation involved a direct conversion of thorium nitrate to thorium chloride in a fused bath of sodium chloride and potassium chloride, phosgene being utilized as the combination chlorinating and reducing agent. Thorium content in the chlorinated product ranged generally from 20 to 30%, though latter runs during this phase of the campaign in certain instances were increased in thorium content to as high as 40%.

2. Process Equipment

The pre-pilot production of cell feed using phosgene as the chlorinating agent was carried out in a reaction vessel which consisted predominantly of a cylindrical nickel shell lined on the inside with firebrick. A graphite crucible was positioned concentrically, the latter being surrounded by a graphite resistor heater. The size of crucibles used in this operation was approximately 18" in diameter and 28 to 30" deep, capable of taking a charge weighing between 200 and 300 pounds. The top of this unit was partially enclosed, outlets being provided for a thermocouple well, gas exhaust and sparging tubes.

On completion of a chlorination cycle, the molten salt was removed from the chlorination vessel by means of a vacuum siphon technique. A vacuum vessel slightly larger in volume than the graphite crucible contained in the chlorinator, fitted with a completely enclosed head and quick-opening valve, was pre-evacuated, after which a nickel connecting tube between it and the chlorinator vessel was opened. The differential pressure between atmospheric and the pressure in the vacuum vessel was sufficient to initiate a siphon action, readily transferring molten salt from the chlorinator to the vessel, where it solidified. The frozen product was then chipped mechanically, crushed and stored for use in electrolytic operations.

3. Operations

The pre-pilot scale of cell feed preparation was operated for approximately 9 months on a somewhat sporadic basis in order to stockpile a quantity of cell feed for electrolytic operations. More than two tons of adequate quality cell feed were made in this manner, though operations were not without major difficulties.

Table IX is a summary presentation of typical data from a group of runs in a chlorinator of the type described. From this information it may be observed that the phosgene efficiency was relatively low, and that the time cycle for conversion was quite long. In theory, for each 100 pounds of thorium converted to chloride by means of phosgene, some 85-1/2 lbs. of phosgene are required. The efficiency of phosgene utilization ranged from 5 to 10%. Feed rate on a typical heat ranged from 2 to 5 pounds of thorium nitrate per hour, giving a production rate on the average of approximately 2 pounds per hour of thorium in the form of cell feed. Table X presents a more detailed operating summary of a typical heat.

Table IX

Summary of Direct Chlorination Runs

	Run Number					
	14	15	16	17	18	19
Total weight of charge	285	325	336	336	336	425
Pounds of TNT charge	90	150	175	175	175	275
Pounds of thorium charge	78	74	70	70	70	149
Time required to melt charge, hrs.	16	15*	15	15	15	8
Pounds of phosgene used	517	551	560	750	880	1725
Time phosgene flowed	22	29	24	36	37	103
Avg. flow rate phosgene lbs./hr.	23	19	23	21	23	17
Pounds of salt recovered	208	264	248	217	260	--
Concentration of product	26.5	25	26	20	26	--
Thorium recovered in product	55	66	64	44	68	--

* Charge for Run No. 15 added to hot crucible after completion of Run No. 14.

In general, while the quality of cell feed produced in these units was reasonably adequate, production rates were quite low. As an example, during the nine months' period of operation, less than two tons of total cell feed were produced. In view of the fact that the electrolytic cell contemplated for the latter stages in the program was designed to consume approximately 1,000 lbs. of cell feed per day, an entirely different approach to the production of cell feed obviously was called for. The

Table X

Run No. 19 (291-20) Summary

Cumulative Hours	Cumulative Lbs. TNT	Cumulative Lbs. Th.	
0	30	51	Plus 150 lbs. of 26% Th feed
6	35	53	
6.5	40	55	
7	55	61	Started chlorinating after 8 hrs.
22	85	73	
32	95	77	
34.5	125	89	30 lbs. TNT in 10-lb. increments
47.5	130	91	Approx. 20 lbs. salt erupted from unit
68	230	131	100 lbs. TNT in 5-lb. increments
70	235	133	Approx. 5 lbs./hr.
72	240	135	
76	245	137	
80	250	139	
81	263	144	
82	269	146	
83	275	149	
111			Siphoned

Phosgene usage = 1,725 lbs.

Recovered salt:

siphoned =	145 lbs.
crucible =	125 lbs.
salt eruption=	20 lbs.
Total	290 lbs.

difficulty in furnacing the charge, bloating and boiling over, as well as the very low phosgene efficiency, necessitated that this system be abandoned as soon as a more feasible preparation method was devised.

Through the latter portions of the program in intermediate scale chlorination, hydrogen chloride gas was resorted to in an attempt to get higher rates of conversion and yields. This did not prove to be a satisfactory system because of the relatively slow conversion rate at higher thorium contents.

IV. DEVELOPMENT OF A COMMERCIALLY FEASIBLE SYSTEM FOR PRODUCTION OF ELECTROLYTIC CELL FEED

In Section II, page 10 , a complete description of the wet chemical process for the preparation of electrolytic cell feed has been presented. In subsequent sections a review of small and intermediate-scale research experiments also has been presented, these pertaining to the development of a system for cell feed production which encompasses direct chlorination of thorium nitrate and certain thorium intermediates. Among the materials which proved to be the most feasible was thorium oxycarbonate, which was an intermediate material produced in the existing wet chemical operation for cell feed preparation. The modified feed production system was therefore predicated on the use of existing facilities insofar as possible, with changes largely dictated by equipment size and capacity rather than any other factor.

A. Evolution of Thorium Oxycarbonate Preparation Process

1. Process Development

Facilities were at hand for the precipitation of thorium oxycarbonate in 1200-gallon tanks by interaction between solutions of thorium nitrate and sodium carbonate. This reaction is quantitative, sodium nitrate solution being the primary by-product.

As previously operated prior to the chlorination installation, thorium oxycarbonate slurry, after decanting and repulping in fresh water to remove most of the sodium nitrate solution, was transferred to a vertical

Oliver pressure filter. In the aqueous approach the filter cake was dissolved off in hydrochloric acid and the resulting solution transferred to an evaporator kettle for concentration to a syrupy stage. In the modified process it was desired to recover thorium oxycarbonate as a solid, dry cake in order that it might be used for direct chlorination. Accordingly, modifications to the equipment and operational procedures were necessary, as will be described below.

The remainder of the process following filtration necessitated only moderate temperature drying of the thorium oxycarbonate to yield a material capable of being chlorinated which contained a minimum amount of moisture. The dried product, somewhat like chalk in character, was found to be very suitable for continuous feeding into a high temperature fused salt chlorination unit using standard available equipment devices such as screw feeders or star valve systems for continuous or intermittent charging.

Chlorination of this material was carried out much in the same manner as described in the research aspects of earlier work, equipment being delineated in much detail in a later section. Suffice to say here that a reaction between thorium oxycarbonate, carbon and chlorine ultimately proved to be a very satisfactory approach for the preparation of cell feed, at temperatures in the range of 725 to 750°C.

On completion of a chlorination cycle, which would produce approximately 1,000 lbs. of cell feed containing 40 to 45% thorium by weight, the molten salt was tapped into a water-cooled nickel receiver where it was allowed to solidify. The development of the chlorinator and auxiliaries is covered in a later section and will not be dwelt upon here.

2. Process Equipment Changes and Modifications

The use of a vertical pressure filter of the leaf type soon was seen to be completely infeasible, since difficulties in removing solid thorium oxycarbonate from the leaves in a very restricted area was extremely difficult and time consuming. Accordingly, a drum filter manufactured by the Eimco Corporation, 3 ft. in diameter and with a 2-ft. face,was procured for the operation. The use of a drum filter posed problems in precipitation of thorium oxycarbonate, since contrary to experience in the leaf filter, a thick cake could not be built up. It was necessary also to underleaf the drum filter covering with filter paper in order to prevent some contamination of the filtrate solution with very finely divided thorium oxycarbonate.

A portion of these difficulties was alleviated by the mechanism of introducing heaters into the thorium nitrate dissolution tank and in the thorium oxycarbonate precipitation tank. By maintaining the temperature during precipitation at a minimum of 80°C it was found that a coarser, more crystalline precipitate was formed which was much more easily filtered than material which had been precipitated at a somewhat lower temperature.

At a somewhat later date a process modification was made, in which lampblack was suspended in the sodium carbonate solution prior to precipitation of thorium oxycarbonate. This produced a precipitate with a very intimate mixture between the thorium oxycarbonate particles and the lampblack which ultimately acts as a reducing agent in the chlorination cycle. The combination of nucleation precipitation, combined with a dispersing agent and flocculating agent, gave rise to very coarse, crystalline material which were much more readily filtered on the drum filter than any other previously processed materials.

The results of drying experiments showed that a suitable product for chlorination could be obtained by added drying at temperatures below 300°C. Quite arbitrarily a continuous belt dryer designed to take a filter cake approximately 12" wide and 1/2" thick over a heated belt length of approximately 12 ft. Unfortunately it was found that suitable stainless steel belting in this width was not immediately available, and it was necessary to modify the dryer design to incorporate the two 6" width belts and run them in parallel, since the narrower belt was available in a matter of days.

Transfer of the filter cake from the drum filter onto the continuous belt dryer posed a number of mechanical problems, accentuated because of space limitations in the laboratory area where the system was installed. The length of the room was insufficient to allow end-to-end installation, it being necessary to position the drum filter beside the dryer, hence giving a flow of filter cake 90° from the flow direction of the dryer.

In order to make the process substantially continuous it was decided that the filter cake, which is a thixotropic material, should be repulped in its own water of hydration into a pasty form and extruded through Moyno pumps onto the belt dryer. In this manner the relative locations of the filter and dryer were somewhat immaterial.

In principle the Moyno pump extrusion system worked quite satisfactorily, it being used for several months to provide a continuous feed of thorium oxycarbonate onto the belt dryer. However, the mortality rate on Moyno pumps proved to be quite severe, apparently as a result of the somewhat refractory nature of thorium oxycarbonate in particulate form. Further, adjustment of flow rates and the spreading characteristics of the thoxotropic material lacked something to be desired, occasional pipe stoppages and caking of the material in transit through the piping system giving rise to a more than average amount of maintenance and supervision.

The first alternative to extrusion which was attempted concerned itself with the use of a string filter principle. An extra filter cloth was installed on the filter, extending outward from the filter drum over a series of rollers which provided for distributing the filter cake at proper positions with respect to the belts on the continuous belt dryer. This system was operated for a short period of time with reasonable success, though major difficulties were encountered in obtaining a clean removal of the filter cake from the extra filter cloth. On one of the return rolls the material not effectively scraped off had a tendency to build up and ultimately require additional labor in order to maintain it in operating condition.

As finally modified and successfully operated, both filter and dryer were modified so that, by shortening the dryer approximately 2 ft. in length and lowering it approximately 10", it was possible to scrape the filter cake directly onto the dryer belts without any necessary additional equipment in between.

As first designed and operated the continuous belt dryer did not prove too satisfactory. The original belting used for this application was 3 mils thick and ultimately proved to be unstable. Edge kinking of the metal strip caused much difficulty in the dryer operation, occasionally tearing the belt and wedging. In the series of experimental belt evaluations the thickness of sheet used for belting was varied up to 15 mils, which thickness ultimately proved to be satisfactory. Once belts of that weight were installed, no further difficulties with kinking or lodging were experienced.

In order to obtain the desired throughput of dried product it was necessary to increase the heat capacity of the dryer, especially after shortening it 2 ft. in order to accommodate the filter. The mechanism evolved for supplying additional heat concerned itself with the addition of an air blower and preheating air which was blown into the tunnel dryer about 2 ft. from the exit end. By establishing a positive air movement across the cake and introducing additional heat in the form of sensible heat in the drying air, adequate drying was ultimately achieved.

B. Development of Direct Chlorination Equipment and Procedures

On completion of successful small-and intermediate- scale laboratory chlorination researches the decision to design, construct and operate a pre-pilot sized chlorinator was made. As originally planned, the unit was to have a capacity of 250 pounds of cell feed per batch, with a 2-day operating cycle.

The chlorinator consisted of a two-section cylindrical steel shell, flanged and bolted together using an asbestos gasket. Positioned concentrically was an internallining of acid-proof ceramic brick, cemented together with silica cement. The 2" space between the brick and inner wall of the shell was packed with carbon black to act as an insulating material primarily.

Chlorine was introduced into the vessel through a 1" graphite tube passing down inside a notched recess along the inner face of the brick and connecting with a circular perforated hollow graphite plate. This arrangement permitted chlorine to be disseminated throughout the molten bath in tiny bubble form. The down pipe was protected by a vycor tube.

The vessel was internally heated by a graphite resistor bed consisting of irregular chunks of carbon. These made contact with two sets of graphite resistor electrodes placed 180° to each other, one set being 6" off the bottom and the other 16" higher and 90° around with respect to the lower set.

Two sets of AC welders capable of delivering 400 amperes at 80 volts were connected to the electrodes as separate circuits.

The temperature was determined from a thermocouple placed in the center of the graphite chunks, a vycor protection tube of suitable size serving adequately.

The lid of the chlorinator was of nickel clad steel, water-jacketed and flanged to the body.

A tapping device was provided in the bottom of the chlorinator, consisting of a Y-shaped affair connecting the interior at the bottom through a graphite tube within a ceramic insulator tube. Frozen salt constituted the plug, which could be melted out at tapping time. The melting system consisted of a wire-wound resistor, which was capable of reaching a temperature of 750°C in 15 minutes. This was deemed sufficiently high to melt a frozen salt plug and permit the vessel to tap out.

A preliminary heat-up of 59 hours' duration was made to determine the power requirements of the unit. There was considerable arcing of the electrodes and between graphite blocks. Following a bake-out at 800°C the unit was cooled to room temperature, opened and inspected. An area 1-1/2" deep by the width of four bricks was found to have been burned away by the very high arcing temperatures adjacent to two of the electrode ports, but no other damage was sustained.

The unit was repaired, thoroughly cleaned out, new ceramic-graphite protection tubes for the electrodes were installed and a charge of more uniformly sized carbon chunks put in for the resistor bed.

Experience showed that a re-positioning of the thermocouple was expedient. Four closed end ceramic wells were installed at different positions in the body of the unit so as to record temperature at several heights and angles. This installation required a lot of time because of the difficulty in drilling through the acid-proof brick.

During the down time on this chlorinator, some trials were run with the pelletizing of spent cell feed and thorium oxycarbonate to ready these materials for chlorination feed. The tests proved fairly successful and a quantity of pellets was stockpiled for future use.

Just prior to the first chlorination run the vessel was charged with 1-1/2" uniform graphite cubes to a depth of 24" so that the level was approximately 5" below the top pair of electrodes. Then 20.4 kg of spent salt pellets were charged in on top of the graphite cubes, followed by a second layer of graphite cubes, to a level 8" above the upper electrodes.

In order to determine the approximate temperature near the top of the bath, a closed end vycor tube with thermocouple was inserted through a port in the lid assembly so that it was just penetrating the top layer of graphite cubes. This aided in determining the proper time for charging, since there was a temperature drop after each addition and recovery of original temperature was used as a governing indicator.

To insure complete thermal saturation of the internal vessel, the temperature was slowly raised over an 8-hour period to 500°C, then for 30 hours gradually raised to 600°C. Somewhat later the temperature was raised to 800°C and the run initiated.

Thermal conditions were maintained at 800-900°C, while adding pellets of salt. A total of 80.3 kg was charged in the first run.

During the course of the run one of the lower electrodes arced quite badly, suddenly giving way. Approximately 30 kg of molten salt poured out before the operators were able to seal it off. The balance of the bath was tapped and the run concluded.

Data indicated that 6 to 8 KW of power were sufficient for internal thermal equilibrium, this being fairly evenly distributed between the upper and lower sets of electrodes. It was also noted that when the lower electrodes were immersed in the molten salt bath the voltage dropped from 35 to 40 volts to 10.5, and the amperage increased to a range of 500 to 600. Two welders were used in parallel to maintain the 6-8 KW necessary for good operation. A thermal equilibrium of 300°C at outer shell was reached when bath temperatures were 850°C.

Prior to re-use the chlorinator resistor electrodes were re-designed, embodying a larger diameter graphite rod surrounded by a copper cooling sleeve bolted in between flanges to keep it in place and provide an extra precaution against molten salt leaks around the electrodes.

The next run was in progress for 48 hours when a cooling gland failure caused the operation to be terminated.

On a new run a temperature of 745°C had been reached in 8 hours when arcing, due to lug corrosion, became violent. Shortly after this had been remedied, steam was noticed around one of the electrodes, necessitating termination of the run.

Examination of copper cooling glands showed that three of the four were badly pitted and one leaked badly. The combination of moisture and chlorine apparently was the cause of the corrosion. It was decided to refabricate the units from nickel, with a slight modification to improve the cooling efficiencies. After suitable changes were made the program again was initiated.

During the course of an 8-day run, wherein one tapping had taken place, one of the AC welders burned out, resulting in a severe temperature drop.

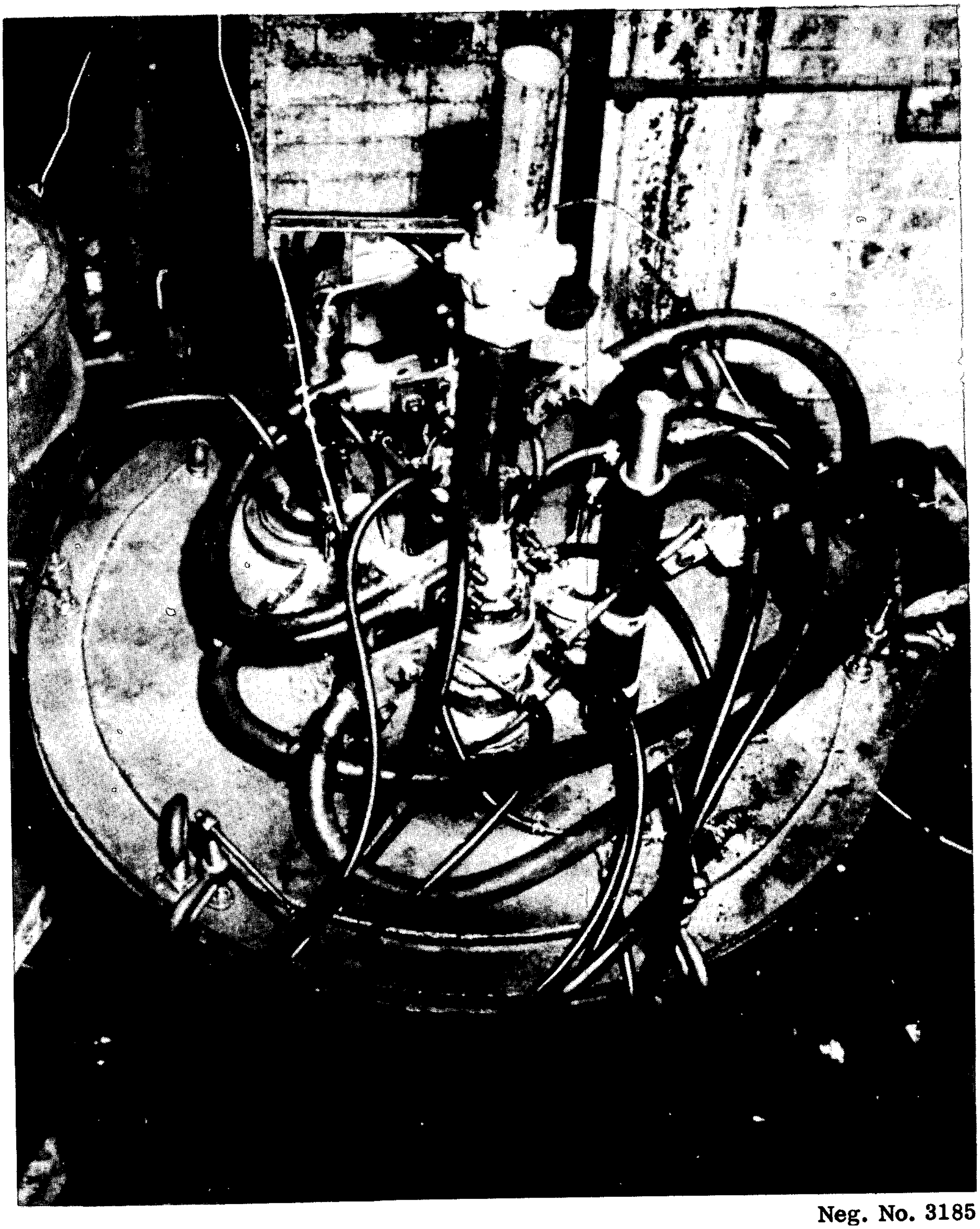
One of the upper electrodes became immovably frozen in the bath, probably due to seepage into the ceramic protector well. It was necessary to connect power leads to three electrodes only, cutting the power input and greatly inhibiting the thermal recovery time after each charge. Shortly following this setback, leaks developed in two of the cooling spades, necessitating tapping and termination of the campaign. Removal of cooling glands revealed that in all cases the welds had failed.

A redesign meeting was held and the following drastic changes were considered.

1. Elimination of heating elements at levels below the molten bath.
2. Redesign of heater elements to incorporate a center rod surrounded by a very thin wall resistor tube, to be inserted through the lid and extend to the bottom of the vessel.
3. Auxiliary arcing resistor heaters placed in the lid extending to graphite resistor bed to be used for heating the top surface of melt only.
4. Re-fabrication of the shell using nickel.
5. Using graphite crucibles for the inner vessel.
6. Incorporation of a manually operated bottom tap, using a side tap heated by resistance for normal operations, the manually operated bottom tap for emergency.

Fig. 2 shows a top view of the chlorinator as modified.

The first run made in this new "B" chlorinator was partially successful in operation, it being a "clean-out" run using only sodium and potassium chlorides. The resistance tap failed and it was necessary to resort to the bottom tap to remove the molten salt. A new type of side



Neg. No. 3185

Fig. 2

Top View of Internally Heated Experimental Fused Salt Chlorinator tap was designed and fabricated, consisting of a Graph-i-tite tube passing through a ceramic insulator into the crucible near the bottom. A protective structure was placed over the inner end to prevent particles from clogging the outlet. The Graph-i-tite tube was fitted into a graphite tee section. A short graphite tube led from the bottom of the tee to a molten salt receiver. Later modifications were found to be necessary, but basically the design proved to be quite effective. Tapping was initiated by using the Graph-i-tite tube as a resistor, melting out a frozen salt plug.

Three runs in the next series were completed, using thorium carbonate-eutectic salt mix. The results of these three runs may be found in Table XI.

The thorium carbonate used contained 55% thorium and the charge calculated out to 36.5% metal in the bath.

Table XI

Summary of Early Pre-Pilot Chlorination Runs

	Run Number		
	1	2	3
Weight of material charged	250 lbs.	236 lbs.	222 lbs.
Weight of material recovered	176	111	99.2
Weight of product "lost"	74	125	133.8
Weight of Th charged	91.0	84.96	79.92
Per cent Th in product	15.9	6.31	3.74
Weight Th 'lost'	63.02	77.92	76.22

The losses were 70%, 47%, and 44%, respectively, which may be explained by severe volatilization of the charge compound mostly mechanically entrapped in exit gases, and by "skull" formation in the chlorinator.

Several modifications were made as a direct result of the runs summarized above. These included the following:

1. Removal of one auxiliary heater.
2. Extension of vycor thermocouple tube to reach the bottom of the chlorinator vessel.
3. Placing of three thermocouples within the vycor tube at depths of 6", 12" and 18" from the bottom, respectively. Placing of thermocouple tube 6" radially from center of chlorinator.
4. The remaining auxiliary heater element was extended to the bottom of the inner vessel and was to serve as one electrode for the tapping power, the other power lead being connected to the side tap resistor heater.
5. Most of graphite cubes were removed to achieve earlier fusing of the salt and, by so doing, also enlarging bath capacity to 550 lbs.
6. Incorporation of a long charging tube reaching nearly to the top of bath. This was initiated because pellet charging had been found to be inadequate. When the pellets reached the molten bath there was a tendency for the salt to melt, air floating some of the carbon and thorium carbonate, which was lost through the vent.
7. A six cubic foot salt receiver was fabricated, thus providing for batches of nearly 1,000 lbs. if such could be achieved in the chlorinator.

After several runs, the chlorinator was shut down and opened for observation. It was found that the graphite sparger was badly eroded and one of the heat shields had dropped due to corrosion of the nickel bolts which held the shields to the head of the chlorinator.

It was observed that the newer types of electrodes, while electrically efficient, were not sufficiently strong to withstand constant usage. These accordingly were replaced with two 1" graphite rods 30" long, joined at the bottom to form a U-shaped heater, the whole assembly being encased in a ceramic insulator tube which reached to the bottom of the internal vessel. These units were made to be interchangeable.

During previous chlorination operations the head of the chlorinator had been water cooled. In the next trial run, where the new type heaters were being evaluated, it was necessary to shut down because of steam emanating from the chlorinator. A large volume of water was found in the unit and ultimately traced to leaks in the water jacket on the head. This required partial disassembly, rebuilding and redesign of the head to incorporate air cooling. The new air cooled head was installed and a 4" layer of graphite chunks was put into the vessel to protect the bottom and sparger, after which a further operation was initiated. Rather sporadic cycles were scheduled, several further modifications being made following each campaign in order to achieve a more workable unit. The sparging devices were changed to three open end graphite tubes to give better agitation of the bath; originally a build-up of thorium oxide in the lower crucible seemed to come from the relatively low turbulence of the bath, but later the reason was conceded to be feeding of powder in 1-lb. bags too frequently. This also resulted in pressurizing the vessel with subsequent expulsion of carbon and $ThOCO_3$, and was soon replaced by a continuous feed system.

A screw feeder was used to spread the material evenly over the surface of the bath and eliminate the severe loss of carbon by blowing out. Once installed, it continued to be used as a standard charging device, with satisfaction.

During the runs following the use of the screw feeder, the feeding rates were very noticeably slowed down. The first thought was faulty charging techniques and heavy sparging, but the difficulty was finally traced to the relative inertness of the carbon black. A new source for this material had been used, and the reactivity of the carbon powder was markedly different from that which had been used before. Reversion to the previous supplier solved this problem.

Because of the marked differences observed among various grades of carbons, it is apropos to list the chemical and physical properties of the grade which was found to be satisfactory. Table XII presents the available data, as obtained from the manufacturer.

Table XII

Physical and Chemical Properties of Lampblack

Moisture content	0.2%
Ash content	0.01%
Benzol extractable	0.19%
Free carbon	99.1%
Volatile	0.68%
Apparent density	17 lbs./ft.^{3}
Grit	40 ppm on 325 mesh
Particle size	0.1 to 0.5 microns

This material is manufactured from creosote oil derivatives by the Monsanto Chemical Company, and is listed as Monsanto Standard 10-C.

It is entirely possible that other carbons might be equal or superior to this grade; however, the carbon and graphite blacks evaluated from other sources did not compare favorably, and the information included above might be helpful as a guide for further evaluations.

The next phase of development concerned the design of spargers. The first improvement over open end tubes consisted of graphite cylinders with one solid end, the cylinder body perforated with 1/16" holes. The smaller bubble size was calculated to give greater Cl_2 efficiency in the molten bath, and indeed the desired result was obtained. Even finer bubble sizes seemed warranted, so the chlorinator was shut down in order to incorporate a sparger of suitable type. Opportunity was also taken to modify the crucible assembly.

Rebuilding the unit embodied these new principles:

1) The upper section of the crucible was machined in three descending diameter steps to support graphite heat shields, so that they no longer were dependent on nickel bolt suspension.

2) A finger-type fritted quartz sparger assembly was installed in place of the perforated graphite type. The quartz system consisted of a 1" O.D. vycor downpipe with five branch lines, each with a 20 micron porous fritted quartz disc at its terminus.

Initial operation of the chlorinator as modified showed excellent results, feed rates as high as 40 lbs. per hour being achieved regularly. Unfortunately a pressure surge experienced while changing chlorine cylinders caused a severe fracture of the sparger head and necessitated further system modifications.

As a temporary expedient individual quartz closed-end tubes, drilled with a multiplicity of small diameter holes were used as spargers, but were ultimately replaced by porous graphite spargers. The latter were used satisfactorily throughout the remainder of the program. A complete description of the unit as finally developed is provided in Section V.

V. PILOT FACILITY FOR PRODUCTION OF CELL FEED

In earlier sections of this paper information has been reported which pertains to the various stages of research and development which finally led to a commercially feasible process for the production of electrolytic cell feed. In this section will be presented a complete description of process, equipment and operations as they were set up and utilized during the latter stages of the development program for quantity processing of thorium-bearing materials.

A. Process Description

The process for producing high quality electrolytic cell feed may logically be divided into three separate categories. Each will be reviewed individually.

1. Precipitation of Thorium Oxycarbonate

The starting raw material for processing during the entire pilot production operation was crystalline thorium nitrate hexahydrate. Reagents used for preparation of the oxycarbonate included commercial grade sodium carbonate and lampblack purchased from the Ohio Carbon Company.

Sequentially the precipitation of thorium oxycarbonate was carried out in a batch type of operation, as follows: A suitable quantity of thorium nitrate was dissolved in hot water and the solution pumped directly into a tank containing dissolved sodium carbonate. Prior to the mixing operation a quantity of lampblack was suspended in the sodium carbonate solution through the use of a wetting agent in order that oxycarbonate precipitation might be nucleated by the lampblack particles.

Precipitation of the thorium oxycarbonate is qualitative, in accordance with the reaction,

$$Th(NO_3)_4 \cdot xH_2O + 2Na_2CO_3 \xrightarrow{C} ThOCO_3 \cdot x'H_2O + 4NaNO_3 + 2CO_2 + x''H_2O$$

As described in the Operation section below, particular attention to details such as water temperature and pH of the solution is required in order to produce a filterable material. If the proper conditions are maintained, however, no difficulties are experienced in precipitating a material which can be handled adequately on normal filter equipment.

2. Filtration and Drying of Thorium Oxycarbonate

Thorium oxycarbonate as precipitated consisted of a slurry containing approximately 15% solids. The dispersing medium was a sodium nitrate solution averaging approximately 8% in strength. In order to minimize the quantity of sodium nitrate carried further into the process it was the practice to decant this solution following a settling cycle for the precipitate. Fresh water was then added, the precipitate agitated and re-settled, after which a further decantation was made.

Following the decantation cycles, an additional quantity of water was added, the slurry agitated and fed continuously or intermittently to the drum filter, which was covered with vinyon cloth.

Filtering techniques were varied from time to time, on some occasions using a water spray, on other occasions eliminating this source of dilution. Following a short period for pre-coat, the oxycarbonate cake blinded the filter cloth to solid-particle passage and a completely clear filtrate solution was obtained which could be discarded directly. Cake removal was accomplished in a normal manner, scraping the entire deposit with the aid of a blowing cycle on the filter drum.

The filter cake as scraped from the drum surface was dropped directly down a chute to a stainless steel continuous belt dryer which served to remove the majority of moisture contained in the cake. Passage time through the 10-foot dryer was approximately one hour, at a maximum temperature of 260°C, this yielded a relatively dry thorium oxycarbonate containing a maximum of 5% moisture and approximately 55% thorium by weight. The character of dried thorium oxycarbonate was somewhat chalk-like in nature, being a very open, friable type of solid which was easily comminuted but somewhat abrasive in nature. The dried material was stored directly in polyethylene-lined containers for ultimate disposition as a feed material to the chlorination cycle.

3. Chlorination of Thorium Oxycarbonate

Thorium oxycarbonate in the form obtained directly from the drying operation was fed continuously into a chlorinating vessel which is described in the Equipment section below. Introduction of the rather finely divided oxycarbonate was by means of a screw feeder of standard design, the rate being adjusted to match the approximate conversion rate to tetrachloride, this being dependent to a large extent on the rate of chlorine introduction through spargers and the bath depth.

Chlorination of the thorium oxycarbonate to yield thorium tetrachloride in accordance with the reaction,

$$ThOCO_3 + 2C + 2Cl_2 \rightarrow \rightarrow ThCl_4 + 2CO + 2CO_2,$$

was carried out in a fused salt bath consisting of eutectic sodium and potassium chlorides at a temperature between 725 and 750° C. Chlorine gas was sparged through a graphite sparger head, ultimately interacting with the carbon and thorium to produce a thorium chloride which dissolved readily in the bath.

Cycle times for the production of 1,000-pound batches of cell feed, containing 40 to 45% thorium by weight, ranged as low as 60 hours. The latter portion of each cycle was spent in adjusting bath composition, adding minor quantities of lampblack or thorium oxycarbonate, whichever was necessary, in order to have a completely clear bath, devoid of all oxide and carbon.

On completion of the cycle the molten salt bath was tapped directly into a closed container, where it was cooled, chipped and crushed for feed into the electrolytic cell.

B. Pilot Plant Equipment

A sequential description of the equipment and processes used to produce 100 pounds per day of dried thorium oxycarbonate-lampblack coprecipitated chlorinator feed may be found in Section V-C, wherein the pilot plant operations are described in detail.

In this discussion the processing equipment will be reviewed under two separate categories: wet chemical processing equipment, and chlorination equipment.

Because of the contamination problem which confronted the process due to extremely rigid product purity specifications, the materials of construction were limited to rubber-lined, neoprene-lined, plastic, and in some cases, either nickel or nickel-clad equipment.

For the most part, the large equipment used in the wet chemical process was constructed of steel covered with 1/8" bonded neoprene; valving, piping and pumps were of polyvinyl chloride plastic construction. In cases where waste liquors were pumped to recovery units, mild steel, cast iron and stainless steel construction was specified, since corrosive conditions were not too prevalent in these steps.

1. Thorium Oxycarbonate Processing Equipment

The solution of sodium carbonate and suspension of the lampblack were effected in a 1,250-gallon capacity neoprene-lined tank. (Specification Item B_1) *

The auxiliary equipment necessary to effect the solution of sodium

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* All Specification Items referred to may be found in the Appendix.

carbonate, etc., consisted of a gear-reduced 420 RPM mixer. (Specification Item B100); one No. 355 Palmer dial type thermometer mounted in the tank cover (Specification Item B-101); one electric immersion heater mounted in the lid of the tank (Specification Item B-102); one 1-1/2" Y-valve (Specification Item B-103); Agilux pipe, rigid polyvinyl chloride (Specification Item B-104); and a sump pump for "skimmer" decantation with bypass to sump for washing down tank (Specification Item B-105).

A similar tank and auxiliaries were used for dissolving crystalline thorium nitrate (see Specification Items A_1, A-100, A-101, A-102 and A-103).

After precipitation and decantation washing has been effected, the dewatering of the slurry was partially effected by passing over a rotary vacuum filter as described in Specification Item C_1, with auxiliary equipment as therein appended.

Secondary dewatering was accomplished by depositing the filter cake on each of two stainless steel endless belts which were conveyed through a tunnel type of dryer. The belt dryer was designed and fabricated by Horizons Incorporated.

Essentially, the dryer construction and operation were as follows:

Two parallel stainless steel endless belts each 6" wide and .015" thick, traveled over a pair of pulleys centered 11 ft. apart. The belts were driven by a 1/4-HP variable speed motor, with an appropriate gear reducer selected to give a belt speed of 0.3" to 2.5" per minute. This corresponded to a time cycle of residence in the heated zone ranging from 6.65 hours at lowest speed to 0.8 hour at the highest, ranges being subject to change by the simple expedient of changing sprocket gear sizes.

The endless belts passed through a pair of parallel tunnels in the top of which were two banks of 10 exposed element resistance heaters, 220V-7.5 KW rating, regulated by a powerstat. The operating load setting was 220V at 28 amperes. This was not peak capacity but insured longer life of the heating elements.

Removal of supersaturated air was effected by introduction of a counter-current stream of air introduced into each drying tunnel at approximately one-third the distance from the discharge end. At the feed end the saturated hot air was vented to an exhaust line which ducted the gases and dusts through a caustic soda solution in a Clarage scrubber.

The feed of wet thorium oxycarbonate from the drum filter and the belt speed of the dryer were so regulated that a production rate of 10 lbs./hr. throughput of material containing a maximum of 5% moisture was achieved.

The vapor, fume and dust exhaust system in use for both wet chemical and chlorination processes consisted of two stages of scrubbers, both exhausted through the same duct work and using the same exhaust fan. The first stage, (located indoors), depended upon the second stage Clarage scrubber, (located outdoors), for its exhausting force.

The primary scrubber was constructed from two 55-gal. drums welded together, the bottom of the upper drum being removed and lugs being welded in at appropriate levels to support perforated plates. All internal surfaces were rubber-covered. A conical cap completed the basic shell. Two beds of burl saddles, each 8" deep, sprayed from above by recirculating caustic solution, served to remove entrained solids and to provide surface area for chemical neutralization of acid gases.

A separate caustic sump tank was provided to hold the caustic solution, it being recirculated at a rate of 20 gpm through the scrubber.

The duct work from the top of the scrubber cone was directly connected to a Clarage scrubber unit (See Specification Item D_1).

The rate of chlorine flow and the production of acid vapors during the chlorination process determined the frequency with which the caustic soda solution had to be changed; in normal operation, the first stage scrubber was flushed out at least once every 12 hours, while the second stage (Clarage unit) ran for 36 to 48 hours without either renewal of caustic or flushing and changing of the solution.

2. Chlorinator and Auxiliaries

The chlorination equipment utilized for conversion of thorium oxycarbonate to thorium chloride was designed and fabricated at Horizons Incorporated. The body of the chlorinating unit consisted of a two-piece cylindrical shell, 31" diameter, each half being fabricated from 1/4" nickel. The bottom and top shells were joined by nickel clad flanges, 3-1/2" by 1", acid gasketed with a 1/4" woven asbestos flat ring type of gasket, the top half having flanges at both top and bottom. Overall height was 63". The head of the vessel, fabricated from 1" nickel, was secured to the top flange of the upper section by means of C-clamps.

A detailed drawing of the chlorinator shell and components is shown in Fig. 3.

Index to Chlorinator, Fig. 3

(1) Upper nickel shell
(2) Lower nickel shell
(3) Support legs
(4) Asbestos gasketed flange
(5) Lampblack insulation
(6) Upper graphite shell liner
(7) Graphite crucible
(8) Chlorine sparger tube
(9) Porous graphite sparger
(10) Chlorinator lid
(11) Transite gas exhaust
(12) Ball valve
(13) Screw feeder
(14) Feed hopper
(15) Charging port
(16) Graphite heat shields
(17) Quartz heater tubes
(18) Graphite resistors
(19) Graphite terminal blocks
(20) Copper power spades
(21) Rubber seal boot
(22) Transite spacer
(23) Clamps
(24) "O" ring seals
(25) Tap-hole power connection
(26) Cooling coils
(27) Tap-hole chill rod
(28) Tapping port
(29) Tapping tube
(30) Ceramic insulator
(31) Thermocouple well
(32) Sampling port
(33) Graphite brick supports
(34) Tube insulator
(35) Resistor jumper block
(36) Graphite cross
(37) Power lead insulator
(38) Ceramic insulation

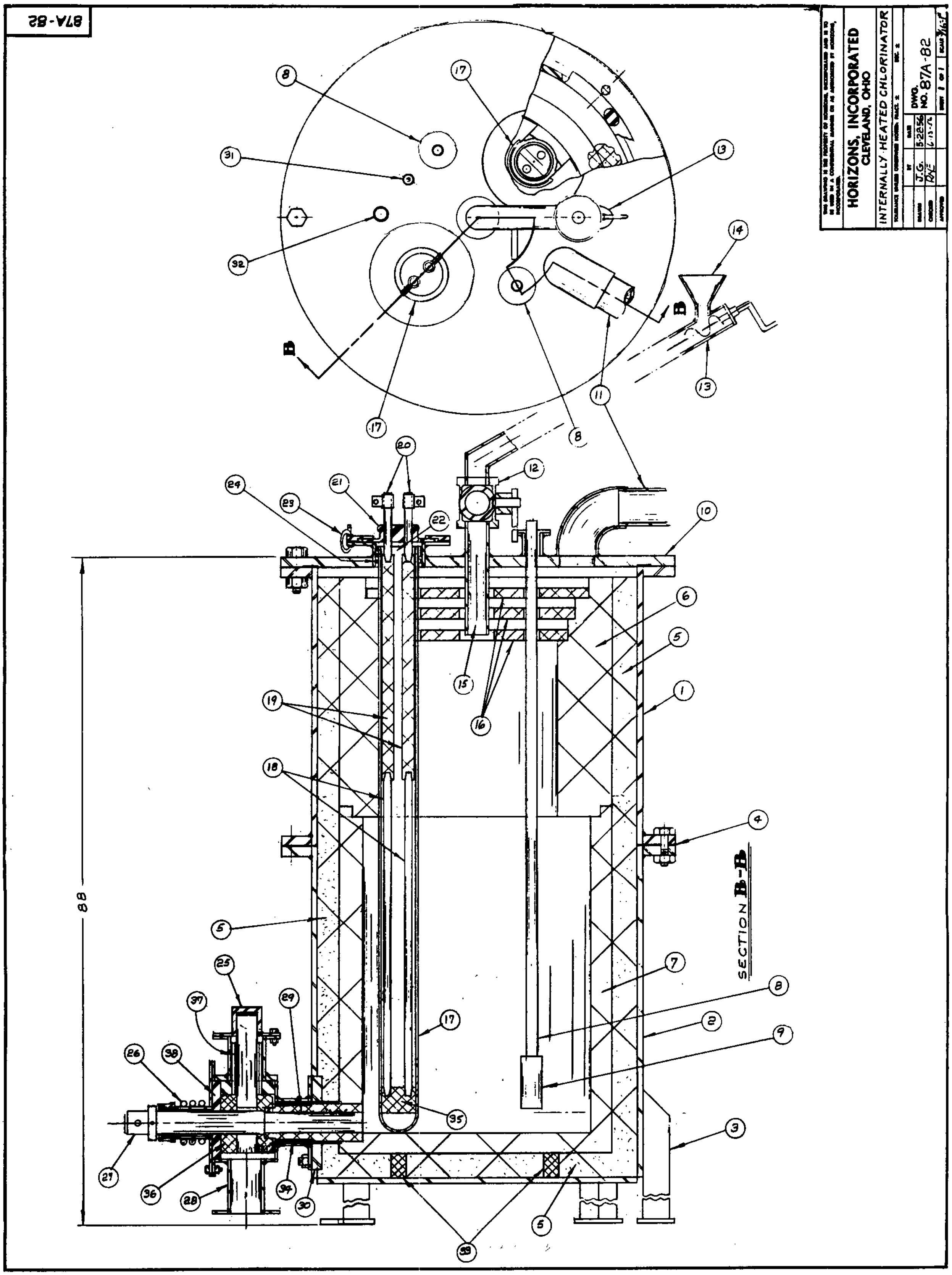

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Fig. 3

Cross-Section Sketch of Modified Experimental "B" Chlorinator

A graphite crucible was used to line the nickel shell, approximate dimensions being 26" O.D., 22" I.D., and 32-1/2" deep. The bottom was 3" thick. An extension cylinder of graphite mated the crucible top with a step joint, providing a liner for the remaining height of the chlorinator shell. Both sections were insulated with lampblack, packed to a density of 40 lbs./ft^3.

The upper shell liner was machined in steps of varying dimensions to provide support for three disc-type graphite heat shields.

The chlorinator was provided with a taphole as previously described, using the electrical resistance of an impregnated graphite tube as the tapping device. General appearance of the chlorinator may be clarified by reference to Fig. 10, page 97.

The chlorinator vessel was supported by four I-beam legs, placed in proper position to provide clearance below for a mobile tapping vessel of 1000 lbs. capacity.

Two bayonet type heating units, constructed of graphite and series rated collectively at 0.5 ohm resistance, were positioned in the crucible, extending through the lid. These were placed within fritted quartz tubes which were closed at the bottom and sealed at the top so that a very small flow of an inert gas such as argon could be bled into the shells, displacing oxygen and preventing the breakdown of the elements by oxidation. The heaters were positioned on opposite sides of the head 180° apart, on a concentric circle 10" in diameter.

Similarly situated, at 90° to the heater units and at 180° relative to one another, were two sparging tubes, consisting of a porous graphite head, attached by threads to 5-1/2 ft. x 1" I.D. impervious graphite tubing. These were connected to individual banks of chlorine cylinders by copper compression-type fittings through a system consisting of 3/8" nickel piping. A needle valve, flowmeter and manometer were provided in each line to register pressure and flow data for control purposes.

On one side of the head a thermocouple well was set, reaching to the bottom of the inner vessel and containing two sets of thermocouples, one 6" off the bottom and the other 12" off the bottom. These were connected to a multipoint recorder for continuous registry of bath thermal conditions.

The feeding of thorium oxycarbonate was accomplished through a 2" ball valve set in the center of the chlorinator lid. A ceramic tube extension through the heat shields served as a feed guide into the bath. Charging of material was regulated by the use of a manually operated combination hopper-screw conveyor which was set into the nipple above the ball valve. Provisions for introduction of argon or other inert gas into this system were also made, preventing air from being introduced to any marked extent into the chlorinator vessel.

At one side of the chlorinator head, a vent port connected to a 3" I.D. transite vent pipe. Off-gases were piped through this to an expansion box for settling solids and draft adjustment, then to the bottom part of the primary scrubber mentioned in the previous section on wet chemical process equipment.

It was mentioned above that there were two banks of chlorine tanks with the necessary nickel piping, valves and flowmeters. This type of setup was also employed in the connection of the argon cylinders for purging of the heater shields and filling port, and for sparging argon through the bath during tapping. Standard flowmeters were used in these systems.

On completion of a chlorination cycle the molten salt was tapped from the chlorinator into a water-cooled nickel receiver, the unit being mounted on wheels for mobility. A gas-tight connection between the two vessels was made by means of a flanged pipe, provision being made for fume removal at a separate point. The lid was easily removable, being held in place by bolts or C-clamps.

Design of the receiver was similar to an elongated, truncated pyramid to provide easy removal of the solidified cake. One end was mounted on pivots, the other provided with a lifting lug, should it be desirable to dump the cake whole. In general, however, the salt cake was chipped by hand and scooped out into storage drums.

The receiver is also shown in Fig. 11, page 97 .

The only auxiliary equipment items required by the chlorinator were the scrubbers which already have been described, and a power source for heat. The latter made use of two welders connected in parallel, characteristics of which are discussed in the section on Operations. A detailed description of these units is presented in Specification Item E_1 -E_2.

C. Operations

The pilot process, which has been developed at Horizons for the production of high thorium content electrolytic cell feed, has proven itself to be quite satisfactory in design and operation. A flow sheet depicting the sequence of operations is presented in Fig. 4.

The pilot plant as operated during the latter phase of the program was scaled to accommodate production of 165 kg of contained thorium per batch. Operational details are presented below.

1. Precipitation and Filtration of Thorium Oxycarbonate

City water heated to approximately 80°C was run into the oxycarbonate precipitation tank, to a level of 44" (equivalent to 510 gals.). The agitator was started and the immersion heater turned on. While thermal equilibrium was being established at 80°C, 179.5 kg of light soda ash were weighed up and 156-3/4 kg of the material dissolved in the hot water. The holdout of 22-3/4 kg was found necessary by practice, since the free acidity of the thorium tetranitrate was somewhat variable. The holdout material was used to complete the reaction when near equilibrium was approached.

The soda ash solution was formulated for approximately 7.5% by weight, a concentration which proved to be one of the determining factors for achieving desired physical properties in the precipitated thorium oxycarbonate.

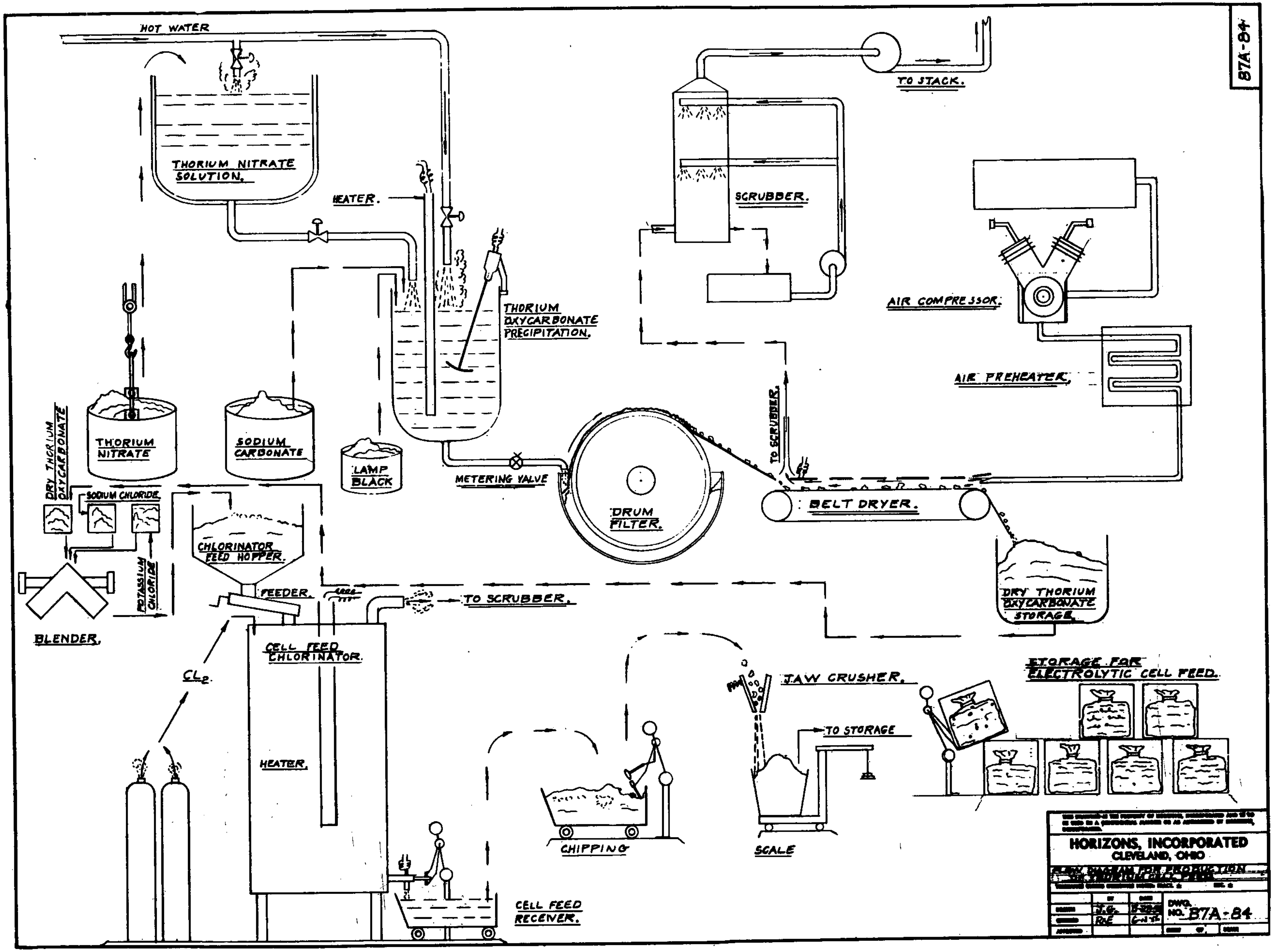

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Fig. 4
Flow Diagram for Pilot Production of Electrolytic Cell Feed

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As previously mentioned, the most efficient product for chlorination feed was formed when the thorium oxycarbonate was precipitated upon carbon black particles. This technique was used throughout the pilot program.

When the soda ash solution had been completed, temperature being maintained at 80°C, with constant agitation, 13.4 kg of No. 4 carbon black (Monsanto Chemical Co.) were charged into the solution followed by 600 ml of Wyandotte Chemical Co. Pluronic L-61, a wetting and dispersing agent. The selected quantities represent 8.5% of carbon black by weight with reference to the contained thorium in the final precipitate, while the dispersing agent weight was based on 0.15% of the total weight of carbon to be dispersed.

Simultaneously with the above operation, hot water was run into the thorium nitrate dissolver tank to a level of 50" (equivalent to 420 gallons), and the heater and agitator turned on. When the temperature came to equilibrium at 80°C, 410 kg of thorium tetranitrate were added to the hot water and completely dissolved. This amount is equivalent to 165 kg ± 2 kg of contained thorium and yields a solution of approximately 10% thorium by weight. Here again, the concentration of the solution is one of the principal factors in determining the physical properties of the precipitate.

When solution was completed, the thorium nitrate was pumped into the soda ash-carbon black slurry at a rate of 20 gpm through an all-plastic piping system, to avoid metallic contamination, maintaining both reacting solutions under constant agitation.

There was no noticeable reaction until chemical equilibrium was approached. At this time a fine precipitate began to form followed shortly thereafter by foaming. Careful regulation of the rate of introduction of thorium nitrate solution must be practiced at this point. It was generally necessary to stop the thorium nitrate addition several times to permit the foam to subside because of the limited tank volume.

Upon reaching equilibrium, the foaming entirely subsided; however, equilibrium was seldom reached until some or all of the additional 22-3/4 kg of soda ash was added incrementally. Completion of the reaction was determined by the pH as measured by pHydrion paper of short range, 6.0-9.0, the final pH being adjusted to the range, 7.6-8.0. Along with concentration and temperature, the final pH is the third determining factor governing the physical properties of the precipitate.

It has been determined that thorium oxycarbonate when freshly precipitated is a somewhat slimy, difficultly filterable material, but strict adherence to the concentration, temperature and pH specifications will result in a product which is only moderately slimy and not too difficult in filtering.

The precipitate slurry, containing approximately 15% solids, was agitated for 5 to 10 minutes, the heat and agitator shut off, and the precipitate allowed to settle for 6 hours, at which time there were approximately 30" of clear supernatant liquor. This was carefully pumped off to the sump tank, using a skimmer, tested for thorium and precipitated with soda ash if radioactivity was found present. An equal amount of hot water was then pumped into the slurry, the batch agitated thoroughly and allowed to settle, as before, for 4 hours. This decantation-wash cycle was repeated once and the final supernatant liquid tested for thorium. The specific gravity of this water generally was very close to 1.000 and contained only a very small amount of sodium nitrate.

The slurry was made up to the original volume with cold water and filtered on a rotary vacuum filter, first recycling the filtrate back to the precipitation tank until a clear sample was obtained, then pumping from the combined vacuum filtrate-wash receiver to the sump tank. The filter cake is approximately 30% solids. Fig. 5 shows a view of the drum filter used in the program.

All of the liquor in the sump tank resulting from decanting and filtration was precipitated with soda ash and kept at a pH of 7.6 to 8.0. The resulting slurry from this treatment was filtered on the rotary vacuum filter periodically and the thorium carbonate set aside for further processing.

The filtration rate of the co-precipitated thorium oxycarbonate-carbon mixture was regulated by and adjusted to the throughput rate on a two-belt stainless steel tunnel type dryer. Satisfactory operation was characterized by removal of a 1/8" cake from the drum with the latter revolving at 4 rpm.

2. Thorium Oxycarbonate Drying Procedure

Thixotropic thorium oxycarbonate, in cake form, continuously discharged from the drum filter onto two stainless steel belts, each 6" wide. Thickness of the layer varied from 1/4" to 3/4", averaging 1/2".

In appearance the material was black, resembling rich earth. The belts carried the oxycarbonate through a tunnel-type dryer, shown in Figs. 5 and 6 , which was operated under thermal conditions calculated to dehydrate the cake and raise the temperature to 260°C at the discharge end. Passage time was approximately one hour, 10 feet of the cake being continuously exposed to heat.

The dryer was provided with an air jet system to insure positive air movement through the tunnels. Provisions were made for preheating the air, but operational results negated requirements for this additional heat input.

Dryer capacity ranged as high as 30 lbs./hr. of oxycarbonate, but generally operated well below this level in order to prolong the life of heater elements. Average output was governed by the chlorinator requirements, and approximated 10 lbs./hr. The dried oxycarbonate normally contained 55% thorium minimum and had a moisture content of 5% maximum, when all of the proper regulating factors were in force.

The thorium oxycarbonate-carbon mixture as it came off the dryer belts was packed in 35 kg lots in polyethylene-lined fiber containers. The dried material was used as feed to the chlorinating unit, which will be discussed separately.

3. Oxycarbonate Process Yields

The facility described above was operated on an around-the-clock basis for several months in conjunction with the chlorination process, during which time several tons of cell feed were produced. Table XIII

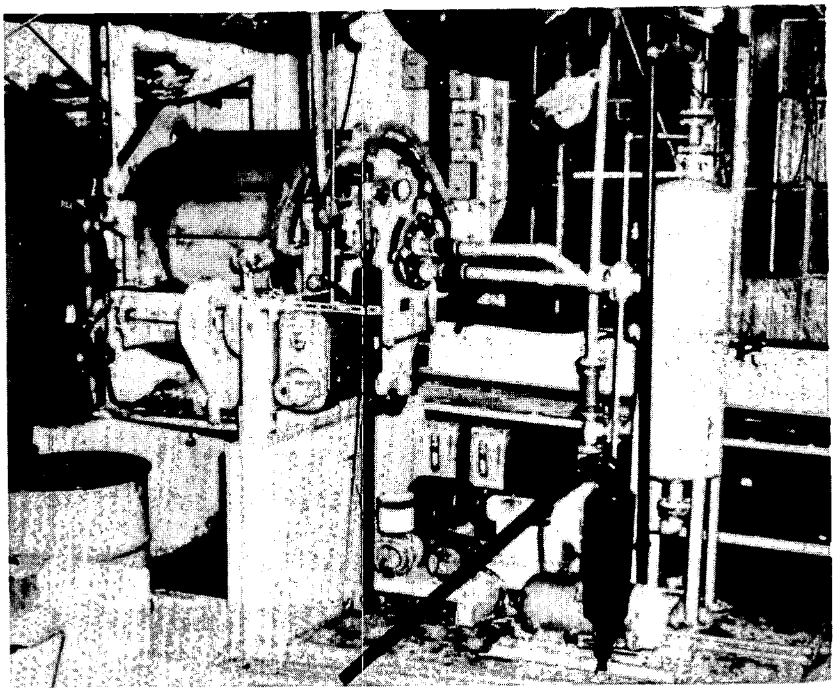

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Fig. 5

Drum Filter and Auxiliaries Used to De-Water Thorium Oxycarbonate.

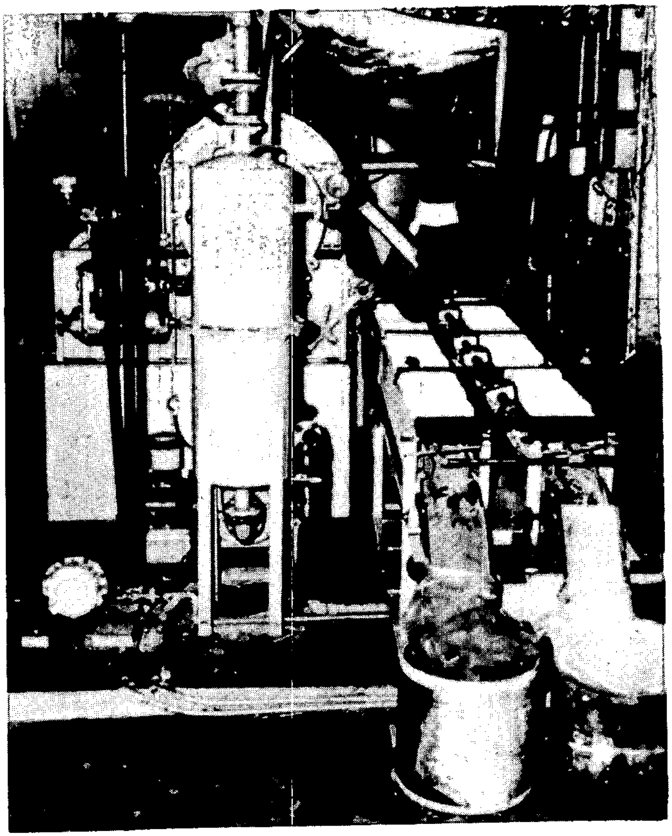

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Fig. 6

Continuous Belt Dryer Used to Dehydrate Thorium Oxycarbonate Filter Cake.

presents a summary of the thorium recovery efficiencies experienced, not including processing losses. Major spillages in a few instances, resulting from broken transfer line valves, pump leakage and other similar occurrences, were not accounted as recovered. If one discounts these anomalies, expected process recovery is in the range of 97.5 to 99.5%.

Table XIII

Thorium Yields Over a Series of Batches

Batch No.	Kg Th Input	Kg $ThOCO_3$	Av.% Th	Kg Th Output	% Th Recovery	Remarks
395-20	166.25	293.0	55.0%	161.1	96.9	
395-23	167.40	346.16	55.0	166.45	99.2	
395-27	168.03	303.5	55.0	166.42	98.4	
395-28	161.00	253.43	60.0	152.06	94.4	
395-32	166.85	271.9	60.0	163.14	97.6	
395-40	94.2	136.0	59.0	80.14	85.0 *	Some material left in filter
395-42	167.34	267.0	63.2	165.5	98.8	
395-44	165.5	263.2	63.4	164.4	99.3	
395-46	164.03	283.2	57.8	163.8	99.8	
395-47	167.13	262.4	55.0	149.53	89.4	
395-49	167.36	281.16	55.2	155.29	92.7 *	Some material on trays under belts--to be added to next batch.

4. Chlorination Operations

The equipment used for conversion of thorium oxycarbonate to the chloride has been described in Section V.B.2. Feed material consisted of dry thorium oxycarbonate-carbon aggregates, sodium chloride, potassium chloride and chlorine gas.

On installing a new crucible it was customary to run a "clean-out" heat of eutectic sodium-potassium chlorides, melting the batch completely, sparging with chlorine and holding at temperature for 8 hours. The purpose of this run was to establish steady state thermal conditions, saturate the crucible and insulation with salt and extract most of the impurities from the graphite shell. It is not uncommon to find as much as 3% iron and lesser quantities of alumina, silica and other metallic constituents as impurities in graphite, all of which serve as cell feed contaminants unless removed. This material, after the heat soak, was tapped and discarded, meanwhile maintaining the chlorinator at temperature.

Following the clean-out run the first productive heat was then initiated, the campaign running continuously thereafter on an around-the-clock basis.

Prior to the initial heat-up, the water was turned on to flow through the cooling coil on the tapping device, argon at 0.25 ml/min. was sent through the resistor-type heater shields to provide a non-oxidizing atmosphere, and the inner vessel was flushed with argon through the spargers at a rate of approximately 10 cfh.

Power settings on two AC welders in parallel, which served as the heat source, generally ranged from 500 to 700 amperes at 30 to 45 volts during the preliminary heat-up and salt-melting cycle. Once a completely molten bath was attained, the power requirements were reduced to 300 to 400 amperes and 20 to 25 volts in order to maintain

725 to 750°C in the bath.

During the tap and initiation of the next charge, power was maintained in order to prevent thermal loss from the interior and to serve as a heat sump to aid in melting the solid feed.

The initial charge for the conversion of thorium oxycarbonate will consist of either straight eutectic salt mix (0.8 NaCl: 1.0 KCl) or a mixture of spent cell feed from the electrolytic process and eutectic salt. This latter, however, would not be available until sufficient thorium chloride cell feed had been produced for electrolysis.

Starting with the eutectic salt mix, the initial charge was 175 to 225 pounds, added as rapidly as possible through the screw conveyor feeder.

This base charge permitted the final amount of thorium contained in the cell feed to range from 40 to 45% in a bath weighing approximately 1000 lbs.

Figs. 7 and 8 show the power source for the chlorinator, and the chlorinator receiving its initial charge. Chlorine was sparged through the bath at a rate of 15 to 40 cfh when it became molten, this generally requiring approximately four hours after initial charging. The temperature at this stage will be 650°C minimum. While charging, a flexible exhaust and fume hood duct are placed over the screw feeder to remove dusts from the air. A hopper capable of housing 100 lbs. of feed attached to the feeder, provided intermittent supply.

Once the bath was fully molten, charging of the thorium oxycarbonate-carbon co-precipitate was initiated. This was charged in

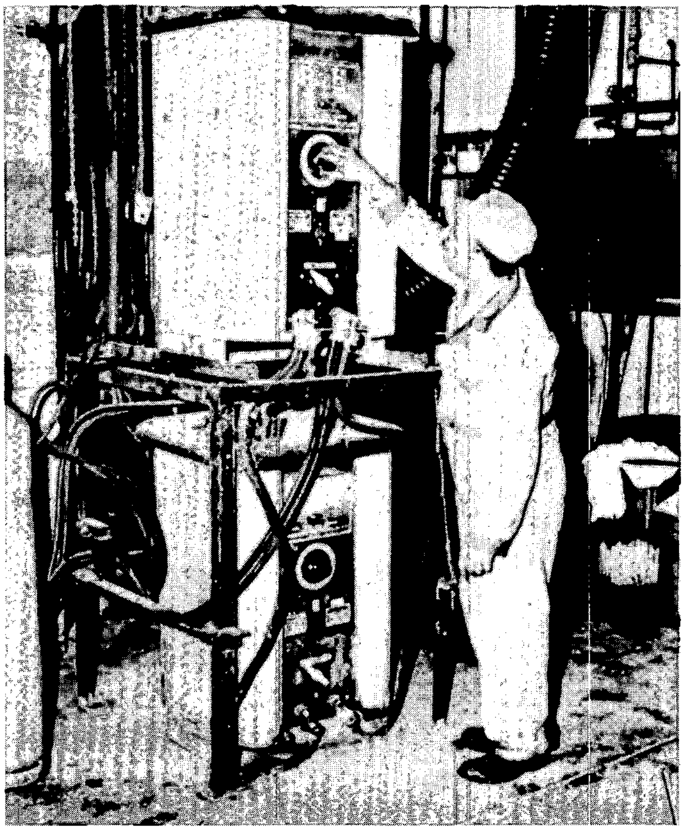

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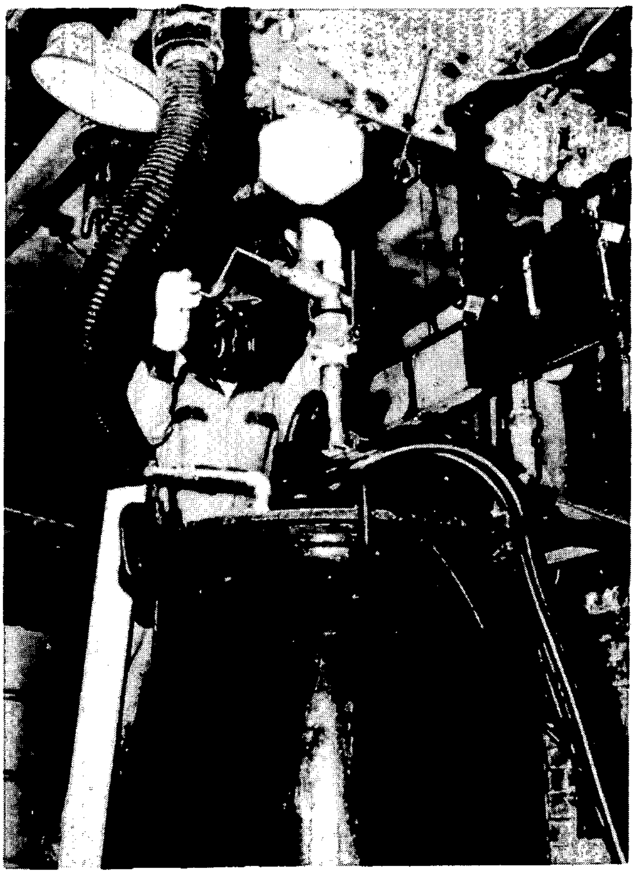
Fig. 7

Power Source for Experimental Chlorinator

Fig. 8

Partial View of Chlorinator, Showing the Feed Charging Operation



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through the screw conveyor at the rate of 10 to 20 lbs./hr., being governed by the reaction rate as observed visually and evaluated by sampling. The rate of charging on occasion was increased if reaction appeared to be rapid and no complication such as pressure build-up, "skulling" over of the molten bath or undue loss of temperature occurred following each addition.

The rate of chlorine sparging generally was increased as the bath depth increased. Increased bath depth provided greater contact time for reaction, higher chlorine efficiencies and increased product yields per unit of operating time. Excess chlorine was scrubbed from chlorinator off-gases by a caustic scrubber, shown in Fig. 9.

Temperature regulation so that a minimum of 725°C was maintained was readily attained by minor adjustments of the welder output current. Average settings for steady state operations were 325 amps at 22 volts, which maintained 735°C except during charging cycles.

It has been observed that there is a well-defined temperature drop during and immediately following charging, the time required to attain normal operating temperatures being largely a function of the quantity of material charged, as would be expected.

During chlorination, the primary scrubber system was carefully checked for pH and liquid level every 4 hours. When the pH dropped below 10 it was necessary to add caustic soda to render the scrubber effective for neutralization of Cl_2, $COCl_2$ and possibly HCl. A pH of 14 was desirable. Once each 8-hour shift, the scrubber was drained and refilled, taking precaution to shut off the chlorine to the chlorinator while so doing.

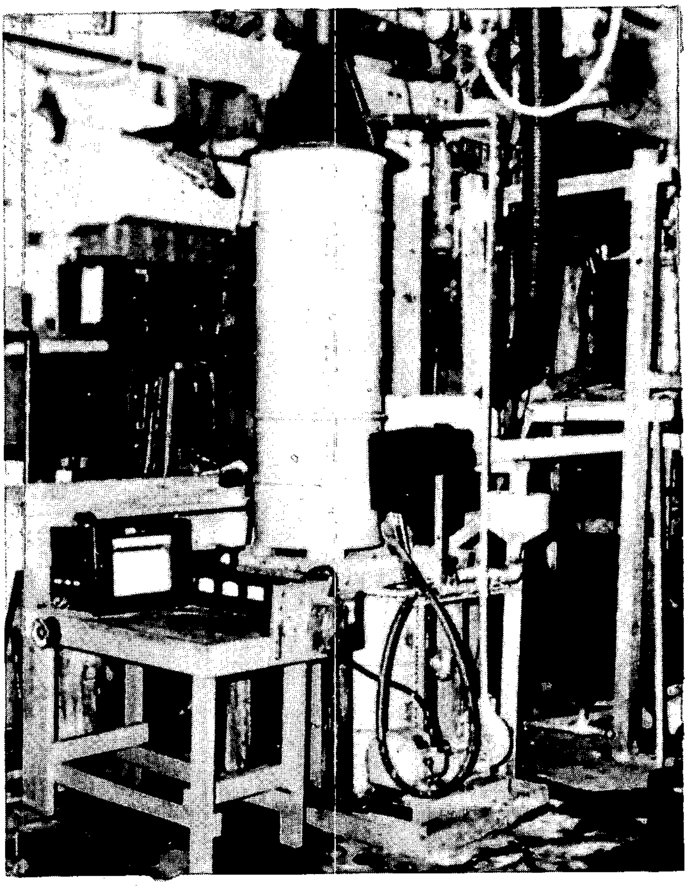

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Fig. 9
Caustic Scrubber and Auxiliaries Used to Remove Acid Constituents from Chlorinator Off-Gases.

Necessity for frequent scrubber attention was a result of rather inadequate capacity of the unit.

Feeding of thorium oxycarbonate was continued at the specified rate until a total charge of 1,000 pounds had been completed. At this time, the chlorination was continued for 4 to 8 hours, holding temperature at 725 to 740° and making tests every quarter hour with "dip" samples to ascertain whether the reaction mass contained any insoluble impurities. A typical method of testing was to insert a cold nickel rod through a port in the top of the chlorinator, making sure that the rod reached the bottom of the internal vessel, rapidly withdrawing the rod, removing the frozen salt adhering to it and dissolving in hot water. A visual test for insoluble thoria and/or unreacted carbon black was made. Some of the solution, or suspension, was centrifuged and an approximation of the per cent insolubles evaluated.

The corrections for excess of oxide or carbon were made during this period. In the first case, small increments of carbon black were added to reduce the thoria; in the latter, straight thorium oxycarbonate was charged, in proper amounts. As soon as the bath was clear, the tapping operation was begun (see Tapping Operation - Appendix). Immediately following the "tap", the same cycle was again initiated.

Figs. 10 and 11 show views of the chlorinator tapping operation, taphole assembly and molten salt receiver used in the feed production campaigns.

The operation of the chlorinator was scheduled on a continuous basis for several months, during which time more than 8 tons of cell feed were

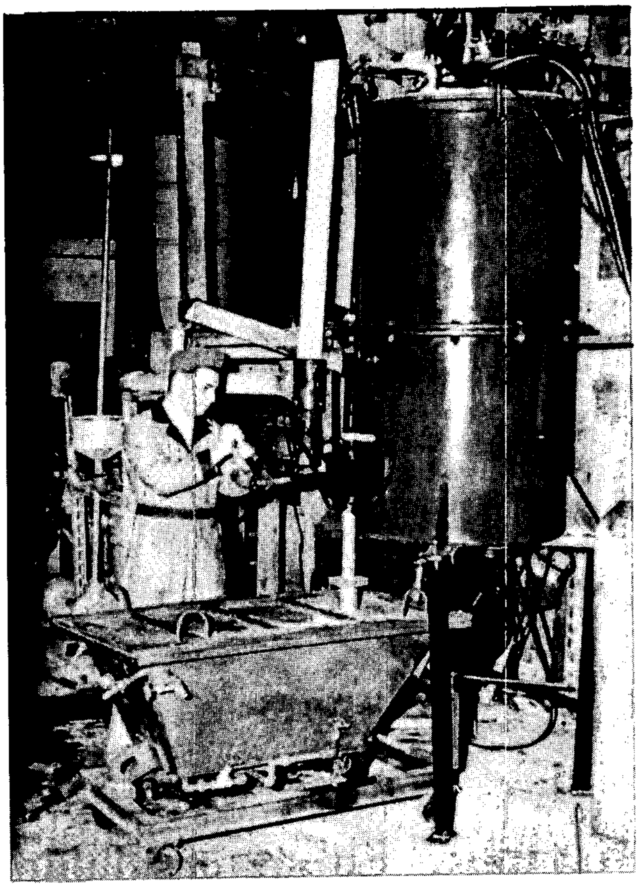

Fig. 10

General View of Chlorinator, Showing the Tapping Operation

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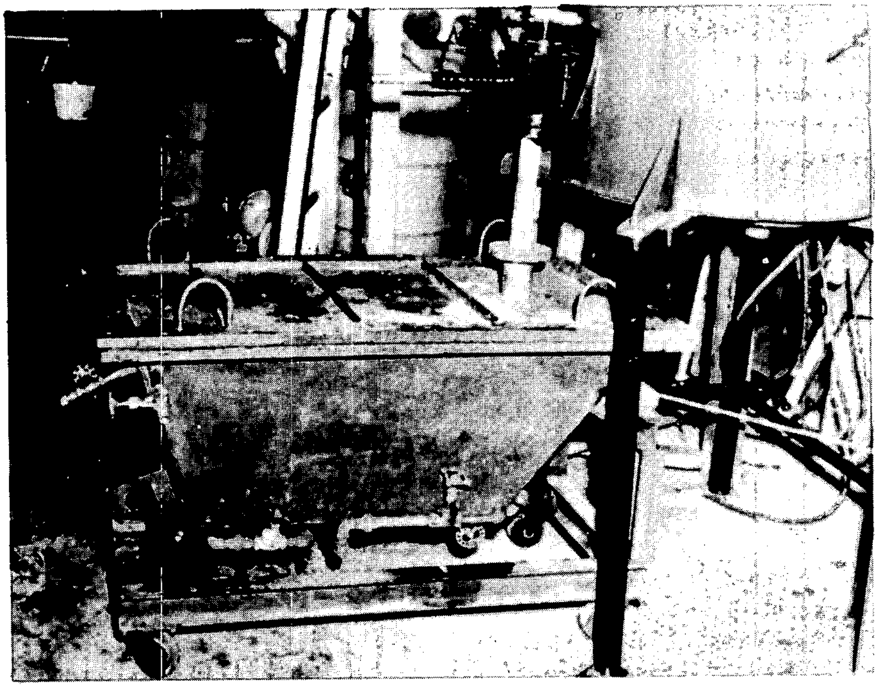
Fig. 11

Molten Salt Receiving Vessel Positioned Beneath Chlorinator, Ready for Tapping



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produced. Data to determine the life expectancy of the various components of the chlorinator were taken and evaluated on completion of the campaign.

In the last consecutive feed production cycle, a series of eight consecutive runs was made. These produced about two tons of high quality cell feed averaging more than 40% thorium by weight. Data for these runs may be found in Table XIV .

a) Evaluation of Materials of Construction

On completion of the final chlorination series the unit was cooled to room temperature, opened up and inspected to determine the condition of all component parts. The findings were as follows:

(1) Ceramic heater protection tubes, which had been used for three consecutive campaigns, showed no signs of erosion, chemical attack or devitrification. They appear to be completely satisfactory for this application.

(2) Heater element components were intact, exhibited sharp corners, no pitting and no evidence of oxidation. The assemblies could have continued in service indefinitely.

(3) Taphole component parts, power leads and insulation showed no serious deterioration despite repeated use and many thermal cycles. The design appears to be completely satisfactory.

Table XIV.

Chlorination Run Data

Book No.	Run No.	Total Time (hrs)	Thorium Charge	Salt Charge	Product Yield	% Th	Kg Yield Th	Kg Th Hr	Kg Cl_2 Used	Cl_2 Efficiency
395-48	13	144	190.5	135.7	448.0	40.6	181.3	1.32	704.9	16.5%
395-51	14	176	217.1	105.	459.0	43.8	201.2	1.18	808	28.9
395-53[1]	15	62	180.7	--	390.0	39.6	154.4	2.49	--	Cl_2 leaks made accurate usage impossible.
395-54[2]	16	73	201.3	61.0	391.5	44.6	174.6	2.39	No account of chlorine used	
395-55[3]	17	101	192.3	22.7	393.2	43.9	172.60	1.71	495.0	23.08
395-56[4]	18	142	220.1	37.1	471.3	42.1	193.7	1.36	626.0	20.00
395-58[5]	19	120	170.0	18.0	346.0	46.39	160.2	1.33	370.0	28.4
395-59[6]	20	10	88.0	--	146.6	44.2	64.8	6.48	--	--

[1] Charge was a mixture of re-run from No. 14, and low Th cell feed plus $ThOCO_3$.
[2] Charge was a mixture of re-run from No. 14; some from No. 15 and eutectic salt plus $ThOCO_3$.
[3] Charge was a mixture of Run No. 16 and low Th cell feeds plus $ThOCO_3$ plus KCl.
[4] Charge was a mixture of Run No. 17, low Th cell feed plus $ThOCO_3$ plus KCl.
[5] Charge was a mixture of 190 kg Run No. 16, KCl and $ThOCO_3$.
[6] Charge was 190 kg of Run No. 16 (re-run because of high unreacted carbon).

(4) Graphite crucible linings showed a minor amount of pitting and surface oxidation, especially above the bath interface, and in the upper portion where air oxidation most logically could occur. Rate of oxidation with the design dimensions used would indicate that replacement might be required after 18 to 24 months of operation.

(5) Graphite heat shields showed evidence of oxidation. Expected life is estimated at 9 to 12 months, with increases possible as a result of minor design changes.

(6) Lampblack insulation was well saturated with thorium-bearing salts on the bottom, less extensively on the upper walls. Penetration nearly to the nickel shell was observed in localized areas, possibly a result of somewhat uneven lampblack density. The material served adequately as an insulator and is considered the best choice for this application.

(7) The nickel shell, used almost continuously for a year, showed evidence of some generalized pitting corrosion, probably a result of moisture adsorbed on the lampblack combining with chlorine under thermal conditions below 220°C. A shell 1/4" thick would have a useful life of 5 to 10 years based on the observed corrosion rate.

(8) Off-gas piping to the scrubber, which consisted of Transite, showed no evidence of deterioration except in the area immediately adjacent to the chlorinator shell. This appears to have resulted from excessive localized temperatures. With a minor amount of water cooling it is believed that the difficulty can be eliminated completely, with expected life limited only by mechanical breakage.

(9) Welders for power sources, while inexpensive, quickly available and capable of close control, are not particularly satisfactory. Continuous service, chlorine fumes and worker treatment combine to give an expected life of 3 months with minor repairs being necessary, 6 months with major repairs required and possibly a maximum life expectancy of 18 months. Multiple tap power transformers should be procured for continuous heating service.

b) Labor Requirements

The chlorinator was operated simultaneously with the thorium oxycarbonate production facility, both endeavors being handled by a 2-man crew on each shift. Labor was somewhat excessive because of the batch handling of feed to the chlorinator, lack of surge bin facilities, non-mechanized feeder and inadequate scrubber capacity. In a production facility a single operator should be able to handle the chlorination of large tonnages of feed providing supplies of raw materials are maintained.

c) Chlorinator Process Yields and Efficiencies

In Table XIV were presented data from a series of runs in the chlorinator. Table XV below summarizes and averages certain data from this campaign.

Table XV.

Average Operating Data from Chlorinator Campaign

Average Cycle Time-hrs.	Wt. Thorium Charged Kgm	% Th in Product	Wt. Th Recovered Kgm	Thorium Recovery %	Chlorine Efficiency %	Process Rate Lbs. Product per hour
116.6	196.0	43.0%	176.85	90.22	23.37	8.65

With respect to thorium recovery, it should be pointed out that actual process losses were negligible, the "unaccounted for" 10% residing largely in lampblack insulation and graphite crucible walls. For example, the average analysis of drillings from the crucible bottom was 10.3% thorium, and the lampblack zones varied from 27% to as high as 43% thorium, depending on the sample location. Over a prolonged campaign the thorium recovery should be at least 98%, providing an overall process recovery from nitrate to cell feed of approximately 95%. The remaining 5% to a large extent would be returned to process intermittently, following equipment teardown, processing of contaminated radioactive wastes and handling of spillages.

The chlorine efficiency is based on theoretical grounds, assuming 2 mols per mol of thorium in accordance with the reactions,

$ThO_2 + C + 2Cl_2 \rightarrow\rightarrow ThCl_4 + CO_2$ and

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

No allowance has been made for the fact that there is a relatively large solubility of chlorine in the fused salt, giving rise to a somewhat lower than theoretical yield, nor that the feed material contains finite quantities of sodium nitrate. Chlorination effects a denitration and converts it to sodium chloride, further consuming quantities of the chlorine fed. As an example, in batch 395-51, 808 kg of Cl_2 were consumed in converting 217 kg of thorium, giving an efficiency of 28.9% on chlorine. The product contained 56 kg more NaCl than charged, indicating that 31 kg of Cl_2 had been used for reaction with $NaNO_3$. Actual chlorine efficiency, based on the quantity used specifically for thorium conversion, was therefore about 31% instead of 28.9%. This increased efficiency could be achieved by repulping the thorium oxycarbonate filter cake and refiltering. Economics, however, indicate that the decrease in chlorine costs would only be about 2 mils per pound of thorium processed, and it would appear more feasible to use the slight excess of chlorine rather than increase the process steps and equipment.

Experience with the chlorinator demonstrated that increased bath depth, finer bubble size and good bath agitation result in increased chlorine efficiency. A pilot chlorinator with 25 to 35 feet of bath depth would be expected to increase chlorine efficiencies to a level in excess of 85%.

VI. AUXILIARY PROCESS PROCEDURES

A. Health and Safety Measures

Since the ingestion of thorium compounds into the body, particularly those of significant solubility, may be a serious health hazard to those who come in contact with this radioactive metal, it seems pertinent to place on record the facilities which have been in use at Horizons during the major part of the period when radioactive metal and metal salts were being handled.

The wet chemical process for thorium oxycarbonate presented several types of health hazards to those engaged in the production of this material, e.g:

1. Thorium nitrate dust and vapors which were airborne during the transfer of thorium nitrate to dissolving tank.
2. Vapors which were water vapor borne by agitation of the hot water-thorium salt solutions.
3. Thorium oxycarbonate dust evolved from a) counter-current air through dryer tunnels, and b) airborne dusts at discharge end of dryer.
4. Liquid thorium nitrate solution.
5. Liquid thorium carbonate slurry.
6. Airborne thorium carbonate dust from crushing and mixing operations.

These hazards have been mitigated, if not entirely removed, in the following manner.

1. The use of Comfo-respirators with special filters to prevent inhalation of dusts and vapors by personnel.
2. Proper exhaust systems installed over tanks, dryer inlet and discharge, crusher and mixer, scales and other sites where dusts and vapors could possibly be disseminated into the air and eventually be inhaled.

3. The use of gloves, caps, eye shields and special types of clothing (coveralls) to prevent liquid thorium salts or solutions from coming in direct contact with the body.

4. Regular scrub up-clean up campaigns to keep radioactivity and disintegration count within specified limits. Dust samples were taken at all points to enable management to take proper control action.

5. Direct contracts with industrial medical men, in case of accident, for immediate medical care should it be required. Physical examinations and various tests were used repetitiously.

6. Posted information relative to obligations of personnel in times of emergency, as well as individual information supply and training regarding dangers of radioactivity.

7. As a check upon the efficiency of the foregoing methods the use of radiation badges and counters was widespread.

The chlorination process also presented similar health hazards which are enumerated below.

1. $ThOCO_3$ dust from feeding operation.

2. $ThCl_4$ vapor from exhaust lines, feeder port and sampling port.

3. Mesothorium vapor from salt tap and salt receiver.

4. Chlorine and phosgene gases
   a) Chlorine from cylinder fed through system (leaks, surges through exhaust line, filling port and sampling port).

   b) Phosgene as a product of the carbon reaction, water vapor in the chlorinator, (noticeable at exhaust line), filling and sampling ports.

5. Possibility of burns and electrical shocks from (a) top and outer jacket of chlorinator (burns) and salt tap and receiver, and (b) heating element connection and taphole connections.

The elimination or minimization of these hazards was accomplished in the following manner:

1. Proper exhaust ducting was installed in correct positions to take care of items 1 to 4 inclusive.
2. Wearing of gloves, shields and other protective clothing to take care of items 5(a) and (b).

The overall health and safety precautions were apparently successfully conducted as may be concluded from the facts that less than 40 man-hours were lost due to injury or accident during 2-1/2 years of operation and the radioactivity was not in excess of levels deemed safe by the Atomic Energy Commission.

B. Accountability of S.F. Materials

The following procedures were established at Horizons Incorporated to insure proper accountability of S.F. materials.

The system has been divided into several categories, endeavoring to provide accountability by tracing the course of S.F. materials throughout the entire processing operations. In order to accomplish this purpose, a system of transfer forms was instituted whereby all movements of S.F. materials which were inter-departmental, might be traced.

The first category within the system was S.F. Raw Materials. The method for accountability for raw materials was as follows:

All receipts of materials were posted on a master sheet, the following data being regarded as essential:

1. Source of material.
2. Lot number, container number.
3. Analysis of each container.
4. Gross, tare and net weights of individual containers.

When any container or part thereof was removed from the storage area, a transfer form was filled out. At the same time, the transaction was recorded on the master sheet. These data include the feed batch number for which the material was to be used, the department and the date of transferral, so that there was an accurate record of S.F. materials in stock at all times.

The transfer form was then filed under the proper caption and was available for reference as a check on other data at any time.

A transfer record sheet was also kept in the accountability center, whereby all transfers were recorded, so that movements of S.F. materials could be pinpointed at any time.

The second category within the system was the transferral of partly processed S.F. materials to another department for further processing. These transfers were filled in, crediting the sending department and charging the receiving department, the transaction being similarly handled as described above.

The third category was that of semi-finished or finished products. Here a transfer from electrolytic area to metal recovery area was made and the last mentioned receiver was responsible for final accounting of the S.F. metal.

In each step of the process there were losses of one type or another. These were accounted for as either scrap awaiting recovery or, as in a minority of cases, chemical and mechanical losses unaccounted for.

At the end of each monthly accounting period, the supervisor of each operation received a request from the accountability center to forward information relative to amount of S. F. materials received, yields of batches, transfers to other departments, transfers to scrap recovery and losses of any nature. This information was checked against the master sheets and offers an accurate means of accounting for all S. F. materials.

Once checked out, it was necessary to consolidate the data pertaining to S. F. materials on hand as either raw materials or finished product in each department, material in process at the end of the period, and material awaiting recovery. Monthly accountability reports based on the system were submitted to the Atomic Energy Commission.

VII. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

To recapitulate briefly regarding the preparation of fused salt electrolytes, Horizons Incorporated was commissioned in April, 1952, to develop an electrolytic process and prepare on a small scale laboratory quantities of a suitable material for electrolysis. In 1954 it was necessary to scale up the laboratory method for cell feed preparation, and it was not until the summer of that year that progress was initiated in actual development of improved processes for making cell feed.

Evaluations of a multiplicity of systems for the preparation of cell feed by direct chlorination techniques, both in solid state and in fused salt baths, led to the ultimate conclusion that either the use of phosgene or carbon plus chlorine could effect the type of conversion necessary for an economically sound system of cell feed preparation. Because of health hazards and cost concepts, the carbon-chlorine system was considered to be the more feasible of the two.

A moderate-sized chlorinator, capable of producing approximately 200 pounds of cell feed per day, was designed, built, and operated successfully to turn out several tons of cell feed containing 40 to 45% thorium. This product was converted in a large electrolytic cell to produce thorium of as high a quality as has ever been reported in the literature. For example, metal with a hardness as low as Brinell 40 on melted ingots, with HCl-insolubles less than 0.5%, resulted.

Modifications to feed preparation process steps, including the precipitation of thorium oxycarbonate on lampblack to give more intimate contact, development of sparging techniques for chlorination, evolution of materials of construction and design concepts, all have resulted from the efforts which have gone into this program during the last two years.

Based on work completed up to the present time, it may be concluded that a commercially feasible process has been established. On a moderate scale it has been demonstrated that it is possible to produce a high quality cell feed capable of conversion to an excellent grade thorium metal. The achievement of high chlorine-utilization efficiency has not been accomplished, primarily because of equipment sizing and a lack of time and funds for scaling up the semi-pilot chlorination unit. However, with the present development of chemical engineering technology and the background of information developed on the internally heated chlorinator under the present program, there is little question but what acceptable conversion levels can be achieved in a suitably designed vessel.

It has been demonstrated that mechanical handling losses, recovery of by-products and general process efficiency may be maintained in the cell feed preparation process at a level acceptable by the Atomic Energy Commission. The accountability of radioactive materials has been maintained, health and safety standards have been met and processes have been developed for returning by-product materials and off-grade thorium-bearing materials to the process for return conversion to cell feed.

The process is characterized by major purification of raw materials, eliminating those elements whose chlorides are gaseous or are characterized by high vaporization points at temperatures in the range of 700° to 800°C; many of the elements normally present which would have high neutron absorption cross sections, such as boron, are completely expelled, and possibilities for more complete separations of undesired impurities are available in the process. Further, if a cell feed preparation plant were to be integrated with a fuel element recovery plant, several of the steps presently necessary to produce crystalline thorium nitrate could be eliminated at a decided savings to the Commission in overall processing costs.

All steps and procedures necessary for the production of cell feed have been handled on a routine basis by unskilled personnel with a minimum of supervision, demonstrating that special training for successful operation of a plant of this type is not required. The entire process could, if necessary, be handled by remote control, since continuous flow systems have been established for every step of the operation with the exception of batch-type precipitation of thorium oxycarbonate. Inasmuch as this precipitation step involves only charging of solid or liquid quantities into tanks and agitating solutions, this step, too, would lend itself readily to remote handling.

Techniques for handling molten salt systems have been worked out, including methods of intermittent and continuous tapping, atmosphere control during tapping operations, transfer of molten salts by siphoning and gravity techniques, etc.; similarly, materials of construction for every step in the operation are well in hand and there is no anticipated difficulty in scaling up the operation to any desired production level.

It is recommended that this process be considered for commercialization by the Atomic Energy Commission, should there at any time in the future develop a requirement for high-quality thorium metal; it has been proven without question that the presently developed process for the preparation of cell feed is completely adequate in all respects for turning out in quantity a high-quality cell feed capable of being electrolyzed to produce an excellent grade of thorium metal.

VIII. ACKNOWLEDGEMENTS

The entire staff of Horizons Incorporated has contributed to the success of the thorium development program. Individuals through whose leadership, planning and actions the success of the program was effected are listed in Vol. II of this Report.

IX. REFERENCES

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VOLUME I

APPENDIX

Table 1.

Laboratory Scale Direct Chlorination Experiments

(1-1/2" diameter unit)

Run No.	Wt. of $Th(NO_3)_4 \cdot H_2O$ (gms.)	Wt. of $NaCl \cdot KCl$ (gms.)	Wt. of NaCl (gms.)	Wt. of Carbon (gms.)	Wt. of NH_4Cl (gms.)	Chlorinating Agent	Wt. or Flow of Agent (ft^3/h)	Ratio of Wt or Flow to Theory	Temp. Range (°C)
271-1	55	85				CCl_4 Cl_2	38.6 gms. unknown	1.25:1	700-750
271-4	55	85				Cl_2	3.54	20:1	700-750
271-8	55	85				HCl	8.0	20:1	700-750
271-10	55	85			21.5	Cl_2	3.54	20:1	700-750
271-12	55	85		9.6		Cl_2	3.54	20:1	700-750
271-14	55	85		9.6	21.5	Cl_2	3.54	20:1	700-750
271-20	55	85		9.6	43.0	Cl_2	3.54	20:1	700-750
271-6	55	85				$COCl_2$	4.0	20:1	700-750
271-16	55	85				$COCl_2$	4.0	20:1	800-850
271-22	55	85				$COCl_2$	4.0	20:1	600-650
271-26	55	85				$COCl_2$	4.0	20:1	500-550
271-28	55	85				$COCl_2$	2.0	10:1	600-650
271-32	55	85				$COCl_2$	2.0	10:1	600-650
271-24	55	85				CCl_4 Cl_2	61.6 gms. 3.54	2:1 20:1	800-850
271-34	55	85		9.6		Cl_2	3.54	20:1	600-650
271-36	55	85		5.0		Cl_2	3.54	20:1	700-750
271-38	55	85		2.5		Cl_2	3.54	20:1	700-750
271-39	55	85		2.5		Cl_2	3.54	20:1	700-750
271-40	55	85		1.0		Cl_2	3.54	20:1	700-750
271-45	55	85		4.0		Cl_2	3.54	20:1	700-750
271-47	55	85		carbon brick rods		Cl_2	3.54	20:1	700-750
271-49	55	85		"		Cl_2	1.77	20:1	700-750
271-57	55	85		porous carbon rods		Cl_2	1.77	20:1	700-750

Table I. (cont'd)

Laboratory Scale Direct Chlorination Experiments (1-1/2" diameter unit)

Run No.	Length of Time (min.)	Possible Th Conc. (%)	Insolubles as ThO_2 (gms.)	% Th Converted	Soluble Th (gms.)	Yield of Soluble Th (%)	Insolubles as Carbon (gms.)	Loss of Carbon (gms.)	Comments
271-1	160	19.0	19.1	28.8					7 gms of CCl_4 recovered from tubing
271-4	60	19.0	23.9	9.5	2.0	8.6			
271-8	60	19.0	8.2	61.0					
271-10	60	19.0	22.8	13.7					
271-12	60	19.0	0.13	99.5			6.44	3.16	
271-14	60	19.0	0.22	99.3			8.44	1.16	
271-20	60	19.0	0.22	99.3			9.17	0.43	
271-6	60	19.0	5.6	78.8					
271-16	60	19.0	12.7	51.7	12.7	55.0			
271-22	60	19.0	1.0	96.3	22.2	95.7			
271-26	60	19.0	23.8	9.5	2.9	12.5			Below melting point
271-28	60	19.0	8.4	61.0	15.5	66.8			
271-32	60	19.0	2.39	90.5	21.12	91.0			Using vycor sparger
271-24	60	19.0			4.95	21.3			
271-34	60	19.0	0.40	98.5	21.84	94.3	5.75	3.85	Using vycor sparger
271-36	60	19.0	0.25	99.1	21.66	93.3	0.79	4.21	
271-38	60	19.0	run lost						
271-39	60	19.0	22.61	14.35	2.91	12.6	0	2.5	
271-40	60	19.0	22.16	16.1	2.99	12.8	0	1.0	
271-45	60	19.0	20.87	20.8	4.49	19.4	0.54	3.46	
271-47	60	19.0	20.21	23.5	3.22	13.9	0.16		
271-49	120	19.0	2.58	90	18.82	81.0	0.13		
271-57	120	19.0	1.93	93	22.53	97.1	1.49		

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Table 1. (cont'd)

Run No.	Wt. of $Th(NO_3)_4 \cdot H_2O$ (gms.)	Wt. of $NaCl \cdot KCl$ (gms.)	Wt. of NaCl (gms.)	Wt. of Carbon (gms.)	Wt. of NH_4Cl (gms.)	Chlorinating Agent	Wt. or Flow of Agent (ft^3/h)	Ratio of Wt. or Vol. to Theory	Temp. Range °C
271-64	55	85		5.0		Cl_2	3.54	20: 1	700-750
271-55	55		85	9.6		Cl_2	3.54	20: 1	939-968
271-59	55		85	porous car.rods		Cl_2	1.77	20: 1	850-900
271-30	110	170				$COCl_2$	4.0	10: 1	600-650
271-51	55		85			$COCl_2$	4.0	3.3: 1	800-850
271-66	55		85			$COCl_2$	4.0	20: 1	870-900
271-68	110	85							
275-11	55	85		9.6		Cl_2	3.54	20: 1	700-750
275-12	55	85		4.0		Cl_2	3.54	20: 1	700-750
271-72	110	85				$COCl_2$	4.0	20: 1	600-650
275-13	110	85				$COCl_2$	4.0	20: 1	600-650
275-19	55					$COCl_2$	4.0		600-650
275-23	55	85				$COCl_2$	4.0	20: 1	700-750
275-9	110	85				$COCl_2$	4.0	20: 1	600-650
275-17	110	85				$COCl_2$	4.0	20: 1	600-650
275-21	55	85				$COCl_2$	4.0	20: 1	600-650
	55					$COCl_2$	4.0	20: 1	600-650
271-70	110	85				$COCl_2$	4.0	20: 1	600-650
275-15	82.7	85				$COCl_2$	4.0	20: 1	600-650
275-25	55	85			21.5	$COCl_2$	4.0	20: 1	600-650
275-27	55	85			21.5	$COCl_2$	4.0	20: 1	600-650
275-29	82.8	85				$COCl_2$	4.0	20: 1	600-650
275-31	55	85				$COCl_2$	4.0	10: 1	600-650
275-33	55	85		2		Cl_2	3.54	10: 1	600-650
275-37	55	85		2		Cl_2	3.54	10: 1	600-650
						$COCl_2$	4.0	10: 1	600-650

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Table I. (cont'd)

Run No.	Length of Time (min.)	Possible Th Conc. (%)	Insolubles as ThO_2 (gms.)	% Th Converted	Soluble Th (gms.)	Yield of Soluble Th (%)	Insolubles as Carbon (gms.)	Loss of Carbon (gms.)	Comments
271-64	60	19.0	2.5	90.5	19.2	82.8	2.1		Carbon added prior to Cl_2 flow
271-55	60	19.0	0.80	95.5	25.41	100	3.41		
271-59	120	19.0	0.53	98.0	16.9	72.9	0.27		
271-30	60	19.0	26.0	51.0	22.9	49.5			
271-51	10	19.0	27.8	0	0.25	0			ThO_2 settled to bottom
271-66	60	19.0	19.7		0.27	0			
271-68		29.0							Salt mix foamed up & out of tube
275-11	60	19.0	0.1	99.8	25.1	100	6.7	2.9	$Th(NO_3)_4 \cdot 4H_2O$ was predried in oven at 220°C.
275-12	60	19.0	0.01	100	21.6	93.2	2.0	2.0	$Th(NO_3)_4 \cdot 4H_2O$ was predried in oven at 220°C.
271-72	120	29.0	21.9	58	23.4	57.1			"
275-13	120	29.0	6.4	87.6	37.8	81.5			"
275-19		19.0							Predried mat'l acted erratically & was discarded
275-23	60	19.0	11.2	57.5	11.6	50.0			$Th(NO_3)_4 \cdot 4H_2O$ was predried in oven at 220°C
275-9	120	29.0	23.8	55.0	26.6	57.1			$Th(NO_3)_4 \cdot 4H_2O$ was predried in tube at 300°C. without salt
275-17	120	29.0	1.3	97.5	39.3	84.9			
275-21	60	29.0							This was chlorinated in the usual manner
	60		24.5	53.5	22.4	48.3			$Th(NO_3)_4 \cdot 4H_2O$ added at temp. & chlor. cont.
271-70	120	29.0	16.3	69.1	33.0	71.0			82.7 gms TNT concentrted in salt mix at 500°C Add'l 27.3 gms added when temp. was dropped to 300°C.

Table I. (cont'd)

Run No.	Length of Time (min.)	Possible Th Conc. (%)	Insolubles as ThO_2 (gms.)	% Th Converted	Soluble Th (gms.)	Yield of Soluble Th (%)	Insolubles as Carbon (gms.)	Loss of Carbon (gms.)	Comments
275-15	90	24.8	8.6	78.2	22.2	63.7			
275-25	60	19.0	1.2	95.5	20.2	87.1			
275-27	60	19.0	6.9	73.8	15.5	66.8			$Th(NO_3)_4 \cdot 4H_2O$ predried in 220° C oven
275-29	90	24.8	1.2	97.0	31.4	90.2			
275-31	30	19.0	12.5	52.5	10.9	47.0			
275-33	30	19.0	24.7	7.3	0.6	2.58	1.2	0.8	
275-37	1st 30 min.								
	2d 30 min.	19.0	9.6	63.5	14.0	60.1	0.1	1.9	
275-35	60	19.0	0.16	99.0	22.5	97.5			Quartz sparger with 90-120 micron openings
275-39	120	19.0	0.17	99.6	42.2	90.9			Vycor (mace) sparger
A	330		49.3 286			A. 5.42 B. 3.97			A. Upper 1/3 of salt cake B. Lower 2/3 of salt cake Quartz tube
B	360		0			17.8			Quartz tube
C									Frothed over edge of tube Run discontinued
D	360								Quartz tube. Run lost afte measur'g melt'g point
E	330		0			19.1			Carbon crucible
F	360		0			18.9			Carbon crucible
G	375		0			17.5			Downward sparger

Table I. (cont'd)

Run No.	Wt. of $Th(NO_3)_4.H_2O$ (gms.)	Wt. of NaCl.KCl (gms.)	Wt. of NaCl (gms.)	Wt. of Carbon (gms.)	Wt. of NH_4Cl (gms.)	Chlorinating Agent	Wt. or Flow of Agent (ft^3/h)	Ratio of Wt. or Vol. to Theory	Temp. Range °C
						$COCl_2$	4.0	10:1	600-650
275-35	55	85				$COCl_2$	4.0	20:1	600-650
275-39	11.0	170				$COCl_2$	4.0	20:1	600-650
A	2208	3400				$COCl_2$	4.0		650-700
B	1104	1700				$COCl_2$	4.0		650-700
C	1104	1700		80		Cl_2			
D	1104	1700				$COCl_2$	4.0		650-700
E	1104	1700				$COCl_2$	6.0		650-700
F	1104	1700				$COCl_2$	8.0		650-700
G	1104	1700				$COCl_2$	4.0		650-700

Table II.

Intermediate Scale Laboratory Experiments
(6" diameter unit)

Wt. of $Th(NO_3)_4 \cdot 4H_2O$ (gms)	Wt. of $NaCl \cdot KCl$ (gms)	Wt. of Carbon (gms)	Wt. of NH_4Cl (gms)	Temp. Range (°C)	Time at Temp. (min.)	Soluble Th (gms)	Yield (%)
55		4.8	21.5	600	60	4.0	17.25
55		9.6	21.5	600	60	2.98	12.8
55		4.8	43.0	600	60	10.4	44.8
55		9.6	43.0	600	60	9.75	41.8
55	85	4.8	21.5	700	60	0.65	2.8
55	85	9.6	21.5	700	60	3.91	16.8
55	85	4.8	43.0	700	60	5.6	24.5
55	85	9.6	43.0	700	60	10.19	43.9
55		4.8	21.5	800	60	0.76	3.2
55		9.6	43.0	800	60	2.88	12.4
55		4.8	21.5	800	60	12.4	53.5
55		9.6	43.0	800	60	6.2	26.7

Table III.

Summary of Ammonium Chloride Experimental Runs

	NH_4Cl (moles)	$ThOCO_3$ (mole)	Time (hrs.)	Temp. (°C)	Sol. Th (%)	Cl (%)	NH_3 (%)	Insol. (%)
1. a)	4	1	1	350	58.0	30.2	7.1	0
b)	4	1	1	450	82.6	8.1	0.13	0.62
*c)	4	1	1	550	0.84	2.5	--	94.9
d)	8	1	1	350	42.3	40.0	13.4	0
e)	8	1	1	450	77.2	12.4	0.012	3.3
*f)	8	1	1	550	52.5	3.6	--	45.5
2. a)	4	1	1	450	78.0	13.8	0.15	0.20
b)	4	1	2	450	77.0	8.2	0.014	5.7
3. a)	4	1 (as ThO_2)	1	350	3.8	26.9	8.98	58.0

* Soluble Th was determined in 5% HCl.

Table IV.

Summary of Experimental Gaseous Chlorination Runs

Heat No.*	Wt.* Matrix (gms)	Wt. Lindsay $ThOCO_3$ (gms)	Wt. Horizons $ThOCO_3$ (gms)	Wt. TNT (gms)	Pretreatment of $ThOCO_3$ Time	°C	Chlor.† Agent	Time of Reaction (hrs)	°C Temp. of Reaction	% Th Converted	Remarks
R-1-C	85	--	--	55	--	--	$COCl_2$	1/3	690	45	St'd run for comparison
R-2-C	85	--	--	55	--	--	$COCl_2$	1/3	690	37.5	Porous graphite rod used
R-3-C	85	--	--	55	--	--	$COCl_2$	1/3	690	39.5	" "
R-1-H	42.5	--	--	55	--	--	$COCl_2$	1	690	44.5	Attempt to increase % Th in product
R-2-H	42.5	--	--	55	--	--	$COCl_2$	1	690	18.6	TNT added to hot furnace
R-1-N	60	40	--	--	--	--	$COCl_2$	1	700	19.3	Incremental additions
R-2-N	46.5	30.8	--	--	--	--	$COCl_2$	2	715	100	Used as molten chg for next run
R-2-N_2	65	37	--	--	--	--	$COCl_2$	1	715	48	Produced a 28% cell feed
R-3-N	50***	49.8	--	--	--	--	$COCl_2$	3	695	100	Produced a 45.5% cell feed
R-4-N	50***	20.5	13	--	none	none	$COCl_2$	4	700	100	Produced a 42% cell feed
R-5-N	51.5	--	40	--	60	110	$COCl_2$	5	700	100	Incremental additions
R-6-N	34	--	40	--	60	220	$COCl_2$	3½	690	100	Pre-mixed and melted
R-7-N	26	--	40	--	60	220	$COCl_2$	3-1/4	710	100	37% cell feed produced
R-8-N	85	30.8	--	--	--	--	HCl	1	700	100	Pre-mixed and melted
R-9-N	26	40	--	--	--	--	HCl	5½	700	100	37% cell feed produced
R-1-T	26	40	--	--	--	--	HCl	5	700	100	Increments added to molten salt
R-2-T	26	--	40	--	60	220	HCl	6-3/4	700	100	Increments added to molten salt
R-3-T	26	40	--	--	--	--	HCl	5	800	98	" "
R-4-T	26	--	40	--	60	110	HCl	6½	700	100	" "
R-5-T	26	--	100	--	--	--	HCl	5½	700	100	Undried filter cake used

* All runs were run with a KCl: NaCl eutectic matrix.

† Flow rates standardized at 4 cfh.

** Losses due to volatilization neglected.

*** Initial charge contained 30% Th as chloride, produced from TNT phosgenation.

Table VI.

Summary of Reaction Times for Basic Thorium Oxycarbonate

Carbonate Source	Drying Temp.	Thickness of Cake	Drying Time (hrs)	1st Increment	2nd Increment	3rd Increment	4th Increment	Total time of reaction
Lindsay	----no treatment ----			9	20	28	60	117
Horizons	110°C	1/4"	8	14	45	70	85	214
Horizons	220°C	1/4"	2	29	52	77	103	261
Horizons	220°C	1/4"	4	29	68	105	220	422
Horizons	250°C	1/4"	1/2	9	20	25	35	89
Horizons	250°C	1/2"	1/2	8	13	12	35	68
Horizons	250°C	1/2"	1	17	19	16	28	80
Horizons	250°C	1	2	11	33	30	45	119

SPECIFICATION ITEM A_1

Thorium Nitrate Dissolver Tank

Performance Data:

Material Handled - - - - - -	Thorium nitrate solution - 10% based on Th content
Quantity	420 gallons
Temperature	80°C
Specific Gravity	1.17 - 1.20

Equipment

Vertical 1,250 gallon welded 3/8" steel cylindrical dished bottom tank; 1-1/2" bottom center outlet, standard 1-1/2" flange. 72" OD x 68" depth, supported on four I-beam legs to give 18" head room. Split border cover, hinged for access to tank interior.

Accessories

Specification Item A-100

Model 117, two propeller type portable Alsop mixers; 1 HP totally enclosed 3 phase, 220V, 60 cycle non-ventilated motor, gear-reduced to 420 RPM, shaft 1" x 60" steel with 2 x 12" perforated propeller; one 16" x 1" coupling to shaft --overall shaft length 64". All parts extending into tank are neoprene covered.

Specification Item A-101

One No. 35 S Palmer 3-1/2" dial reading thermometer, graduated 10 to 120°C. 60" stainless steel stem.

One No. 540 Union connector, 3/4" thread.

Specification Item A-102

Agilide* valve. 1-1/2". Flange fit Y-type. (See Item B-103)

Agilux* rigid high impact polyvinyl chloride piping, 1-1/2" threaded and flange fit construction.

Specification Item A-103

Vanton Pump - XB-P-120

External bearing. Polyethylene block with neoprene flex liner.

Suction and discharge, 1-1/2".

1200 RPM. 3 phase, 220V, 60 cycle enclosed 1-HP motor with starting compensator.

Delivers from 20 gpm at 0 head to 8.5 gpm at 40 lb. head.
Pressure range 0-60 psi.
Temperature limit 120°F.

* Product of American Agile Co., Maple Heights, Ohio

SPECIFICATION ITEM B_1

Sodium Carbonate Dissolver & Precipitating Tank

Performance Data:

Material Handled - - - - - -	(1) 7.5% sodium carbonate solution (2) Thorium carbonate slurry
Quantity	Approximately 1100 gallons
Temperature	80°C
Viscosity	Medium Slurry
Solids added	395 lbs. light soda ash

Equipment

Vertical 1250-gallon welded 3/8" steel cylindrical dished bottom tank; 1-1/2" bottom center outlet,standard 1-1/2" flange, 72" OD x 68" depth, supported on four I-beam legs, cross-braced at floor and 6 ft. above ground to give 8' 2" head room. Split wooden cover, hinged for access into tank.

Accessories

Specification Item B-100

Model 117, two propeller type portable Alsop mixer; 1 HP totally enclosed, non-ventilated 3 phase, 220V, 60 cycle motor, gear-reduced to 420 RPM, shaft 1" x 60" steel with 2 x 12" perforated propellers; one - 16" x 1" coupling for shaft. All parts extending into tank are neoprene covered.

Specification Item B-101

One No. 35 S Palmer 3-1/2" dial reading thermometer, -10 to +120°C, 60" SS stem.

No. 540 Union connector, 3/4" thread.

Specification Item B-102

(Immersion Heater) "Chromalox"

No. KT LS-315, 230V, 3 phase, 60 cycle, heating element with 24" extension.

Bull's eye indicating light. Thermostatic control for overheating.

Specification Item B-103

Agilide valve. 1-1/2". Flange fit y-type.

Specification Chart

Specific gravity	1.41
Tensile strength, psi at 780°F	8,500
Impact strength, 780°F Izod notched ft-lb/in.	0.9
Thermal conductivity BTU/hr/ft^2/in.	1.3
Thermal expansion/°F	2.9×10^{-5}
Dielectric constant - 1 kc	3.62
Type of material	rigid normal impact polyvinyl chloride

Specification Item B-104

Agilux rigid high impact polyvinyl chloride piping, threaded joints.

Specification Item B-105

Series E11 Burks Super turbine pump, suction and discharge 1", capacity 5 gpm at 23 ft. head. Bronze impeller, self-priming position impeller adjustment. Motor 1/4 HP, 1750 RPM, 110V, 60 cycle, 1 phase.

SPECIFICATION ITEM C_1

Rotary Vacuum Filter (Eimco)

Performance Data:

Material Handled - - - - - - - - - -	$\mathrm{ThOCO_3}$ slurry from B_1 (for information, similar to $\mathrm{MgCO_3}$)
Feed	Heavy slurry - approximately 15% solids. 480 lbs./hr.
Sp. Gr. of feed	Approximately 1.15
Discharge	30% solids, 240 lbs./hr.
Sp. Gravity of filter cake	Approximately 1.4 = 11.5 lbs./gal.
Temperature	To 40°C.
pH of slurry	7.6 to 8.1

Materials of Construction

One - 2 ft. OD x 3 ft. face Eimco rotary drum vacuum filter, combined wash and filtrate discharge; steel, neoprene covered. Eccentric rake type slurry agitator. Variable speed drum 1 to 6 RPM.

Air blower, low pressure, for cake removal. Molded rubber scraper blade. 18 sq. ft. filter area. Dynel filter cloth.

Auxiliary Equipment

Two - 4-1/2" dial face Eimco March vacuum gauges

One - Vacuum receiver - 15" dia. x 48" x 3/16" steel sectionalized, external support ring, flanged connections. Inside and all flange faces 3/16" neoprene-covered, vulcanized to the steel.

One - Roots-Connorsville blower, No. 24AF, low pressure blower, muffler filter and relief valve, base plate and coupling direct to motor.

Motors

Agitator - 1/2 HP drip-proof gear head motor, 220/440V, 60 cycle, 3 phase.

Drum Drive - 1/2 HP Reeves VariSpeed Unit, direct drive drip-proof, 220/440V, 3 phase, 60 cycle flexible shaft coupled to filter worm shaft.

Vacuum Pump - 3 HP, 1750 RPM, drip-proof motor, 220/440V, 3 phase, 60 cycle.

Blower - 1/2 HP, drip -proof, 1200 RPM, 220/440V, 3 phase, 60 cycle.

Filtrate Pump - 1-1/2 HP drip-proof, 1750 RPM, 220/440V, 3 phase, 60 cycle.

Pumps

Filtrate Pump - 1-1/4" Olivite neoprene filtrate pump with check valves, base plate and direct coupling to motor.

Vacuum Pump - size MD-674, Nash rotary wet vacuum rated at 47cfm at 20" high at 1750 RPM.

Blower Pump - No. 24AF Roots-Connorsville, rated at 22 cfm at 2 lbs. head.

SPECIFICATION ITEM D_1

Clarage Scrubber

(Cat. No. 21V2 Capillary Unit Conditioner)

Ser. No. 5580-U, Right hand CCW UBD
Fan Base Dwg. U-4655
Motor frame st'd open type 204
Blower 2200 cfm, 906 RPM
Motor 1-1/2 HP, 1750 RPM, 3 phase, 60 cycle, 220/440V
Adjustable V-belt drive
Recirculating pump 18 gpm, 20 ft. head
Spray nozzles No. 0 Monel (10)
Galvanized suction screen

SPECIFICATION ITEM E_1-E_2

P & H AC Arc Welders
Harnischfeger Corp.
Model TH 403, Ser. No. C-11301
1 phase, 50-60 cycle, 60% duty cycle,
90°C temp. rise.

Primary 220/440V, 152/66 amps.
Secondary 0/70 volts, 0/600 amps.
Low and high ranges.

CHLORINATOR TAPPING PROCEDURES

1. When time to tap:

    (a) bath temperature should be 725 to 750°C;

    (b) one-half hour before tapping shut off all Cl_2 and use argon until all tapping operations are completed.

2. Take blank flange off bottom of side tap and replace it with flange and pipe which extends down into salt receiver. (Be sure to replace graphite cylinder if it falls out.) Make certain bolts are tight so no salt leaks out at gasket.

3. Leave cooling water to side tap electrode and nickel rod on at all times.

4. Turn all (five jackets) cooling water to salt receiver on full.

5. Put 480-500 amps. through side tap--wait 3 to 4 minutes, then back out nickel rod 2-1/4 inches. It may be necessary to increase to 600 amps., but do not maintain this high amperage for long intervals. Salt flow should start within 1 to 10 minutes from start.

6. When salt flow starts:

    (a) cut AC to side tap to 300 amps;

    (b) cut back AC on bayonet heaters so they do not overheat;

    (c) attempt to keep positive pressure of argon in unit (at least prevent vacuum) by increasing argon flow as necessary, watch manometer.

7. When all of salt is in receiver, push nickel rod back into sealing position and cut off AC to tap. As soon as possible replace blank flange on tap bottom.

8. Start next run according to instruction.