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THORIUM METAL PRODUCTION

by

G. G. Briggs and J. H. Cavendish

National Lead Company
of Ohio
Cincinnati, Ohio 45239

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THORIUM METAL PRODUCTION

G. G. Briggs and J. H. Cavendish

ABSTRACT

Modifications to the Ames ThF_4 reduction process for the production of thorium metal were developed to make the operation safer and capable of providing higher quality metal.

The improvements developed included:

1. A precipitation process for production of dense crystalline ThF_4 amenable to rapid filtration and efficient washing.
2. Use of nonhygroscopic ZnF_2 instead of ZnCl_2 as a source of zinc in the reduction charge. This greatly reduced the potential for hydrogen generation by reaction between moisture and the calcium metal in the charge, thereby reducing the explosion hazard (especially in the charge blending operation).
3. Use of ZnF_2 in the reduction process also made it feasible to use CaF_2 slag from the reaction as liner material for the reduction vessels. This development significantly improved the purity of the metal produced.

The process developed has been in routine production at National Lead Company of Ohio (NLO) for several months.

INTRODUCTION

Recently, several tons of thorium metal sponge suitable for arc-melting to finished ingots were produced at NLO. The process was basically the same as that developed near the end of World War II at the Ames Laboratory on the campus of Iowa State College.^{1,2} However, a number of features were incorporated to reduce costs, improve the metal purity, and eliminate certain safety hazards.

In the planning stage, serious consideration was given to the alternate route of preparing the metal by the direct reduction of thorium oxide with calcium. This process was piloted in the mid-1950's by the Sylvania-Corning Nuclear Corporation³ and has been used in production by Nuclear Fuel Services at Erwin, Tennessee. The process was attractive from the standpoint that fewer chemical intermediates must be prepared, and a process already was in existence at National Lead of Ohio for preparing thorium oxide feed.⁴ Eventually, the process was rejected primarily because of concern over the hazards involved in preparing the thorium metal in powder form and the cost of providing the necessary equipment to minimize these hazards. The Ames process produces the metal in a relatively safe, massive, form and also appears capable of achieving a much higher direct recovery yield of metal from the reduction process. Another promising feature of the modified Ames route was the preparation of metal with a lower oxide content. Finally, many of the high-cost equipment items required for the Ames process were available on site and needed little modification.

HISTORICAL BACKGROUND

The development of the thorium metal process at Ames followed closely on the heels of the work done at that site which resulted in the first economical method of preparing large amounts of uranium metal of high purity for nuclear use. Both processes were similar, and the equipment assembled for uranium production was readily adapted for making thorium. The essentially unchanged Ames process was also used at NLO in a production campaign in the years 1953 to 1956.⁵

The following paragraphs present a brief review of the Ames process. Since the literature contains a fully adequate description, only those features are touched upon which relate to the NLO process innovations.

Reduction Process

In the original Ames process, a blended mixture of thorium tetrafluoride, zinc chloride, and calcium metal granules was heated in a refractory-lined, closed, steel pot (or "bomb") until autoignition occurred. The ensuing reaction was highly exothermic and was completed within a few seconds. Under the essentially adiabatic conditions, the reaction products were obtained in a completely molten state and these separated into two phases. The heavy thorium-zinc alloy phase settled to the bottom of the vessel with the slag phase forming over it. The consolidation of the reaction products resulted

in the formation of a large cavity above the slag phase. The overall reaction is:

The reduction of thorium tetrafluoride with calcium posed a considerably more difficult thermochemical problem than that encountered in the analogous reduction of uranium tetrafluoride with either calcium or magnesium. In the uranium reduction, the heat of reaction with calcium is sufficient to yield the completely molten condition required for clean phase separation even when the charge is ignited at room temperature. With magnesium as the reductant, sufficient heat is supplied if the reactants are preheated a few hundred degrees before autoignition occurs. In the thorium system, however, the heat of reaction of the fluoride with calcium is approximately 25 pct less than that in the uranium system. Moreover, the high melting point of thorium (1755°C) in comparison with that of uranium (1133°C) greatly increases the thermal requirement. The difficulty was resolved by incorporating zinc chloride in the charge. The heat of reaction of zinc chloride with calcium is sufficient to raise the peak temperature significantly when approximately 0.25 mole of zinc chloride is added per mole of thorium tetrafluoride. At the same time, the zinc greatly reduces the melting point of the metal phase by alloying with the thorium. The phase diagram for the thorium zinc system published by Chiotti

and Gill⁶ shows a eutectic at 1040°C at 11 wt pct zinc containing the equilibrium phases Th and Th₂Zn. With 0.25 mole of zinc per mole of thorium present in the charge, the data indicate an initial separation of primary thorium crystals from the melt at approximately 1250°C.

In the subsequent dezincing step, the zinc was vaporized from the alloy in vacuum equipment. The rate of zinc removal is rapid at or somewhat above the melting point of the eutectic. The thorium metal sponge from the dezincing operation was melted and cast into ingots in vacuum induction furnaces. In more recent practice, purer ingot metal is produced by pressing the sponge into electrodes and arc-melting.⁷

Reduction Pot Lining

The high temperature and molten condition of the reaction products produced during reduction require that the interior of the steel pot be protected by an insulating layer of refractory material. The liner material must not melt or react excessively with the reaction phases nor introduce undesirable impurities into the thorium-zinc alloy. During the early years of uranium and thorium production in this country, the lining material was dolomitic lime (CaO.MgO). It was quite expensive since it had to be prepared from carefully selected dolomite of unusually high purity. Furthermore, the lime was arc-melted to densify it and render it less susceptible to hydration on exposure to humidity. The fist-sized lumps were milled to powder, and the liner was formed

by jolt-packing the powder around a mandrel inserted into the pot. Usually, approximately 3 wt pct calcium fines were added to the liner before use to react with the adsorbed moisture.

The charged pot was also capped with dolomitic oxide and a graphite disk. The heavy steel lid was bolted to the pot flange without gasketing.

Although the liner material was expensive, it was not feasible to recover it for reuse.

Preparation of Zinc Chloride

The zinc chloride was purchased from commercial suppliers, but it required a special dehydration treatment before use. The material is very hygroscopic and will deliquesce if exposed to air of normal humidity. If the wet material is inadvertently mixed with calcium during the blending of the reduction charge, the released hydrogen will pose a serious fire and explosion hazard. At Ames, the zinc chloride was dehydrated prior to use by heating to a temperature just below its melting point while maintaining a protective atmosphere of anhydrous hydrogen chloride to prevent hydrolysis. At NLO, the drying was done in vacuo at about 350°F.

Preparation of Thorium Tetrafluoride

The thorium tetrafluoride was prepared in several unit operations involving the use of rather expensive chemical reagents and complex alloy equipment operating at elevated temperatures. First, thorium

nitrate solution was acidified with nitric acid, and oxalic acid dihydrate crystals were added to precipitate thorium oxalate hexahydrate:

The reaction was carried out in stainless steel vessels equipped with agitation. The initial concentration of free nitric acid aids in the formation of a more crystalline precipitate which is less thixotropic and thus more easily filtered and washed.

The bulky thorium oxalate was dried to the dihydrate at about 110°C. At Ames the dried cake was then decomposed to the oxide in a gas-fired rotary kiln. At NLO the oxalate was decomposed in an electrically heated, stainless steel, tubular "screw" reactor:

Finally, the thorium oxide was converted to thorium tetrafluoride by passing the powder countercurrent to a flow of anhydrous hydrogen fluoride gas in an electrically heated tubular reactor constructed of Inconel:

The temperature along the length of the reactor in the direction of powder flow was increased from about 250° to 550°C. Careful control of the gas and solids flows as well as temperature was

necessary to achieve essentially complete conversion and to minimize sintering. If sintering occurred, the ThF_4 was contaminated with unreacted thorium oxide. At Ames some of the product ThF_4 was recycled and mixed with the incoming ThO_2 to prevent overheating the powder during the initial phases of the highly exothermic reaction.

The "dry" processing methods outlined above involve intimate rubbing contact of the thorium intermediates against the walls of the stainless steel and Inconel equipment at elevated temperatures in corrosive atmospheres. As a result, it was difficult to prevent pickup of metallic impurities.

PROCESS MODIFICATIONS

Substitution of Zinc Fluoride for Zinc Chloride

In the present NLO process, zinc fluoride is used as the thermal "booster" and source of zinc for alloy formation. The material is easily precipitated by reacting zinc oxide with aqueous hydrofluoric acid. After removing the water of crystallization, the zinc fluoride exhibits no hygroscopicity and does not require special care in storage.

On both a molar and weight basis, ZnF_2 supplies more heat than ZnCl_2 in its reaction with calcium. Whether or not the additional heat available in the reduction is of actual benefit is not known however. (For example, we have not explored the possibility of reducing the ratio of zinc to thorium in the reduction charge.)

Another advantage of zinc fluoride is that the reduction slag will contain only the single halide, calcium fluoride, rather than a mixture of calcium fluoride and calcium chloride. The desirability of a "single component" slag stems from its use as the liner material as discussed more fully in the next few paragraphs.

Use of "Recycle" Liner

One of the most clever advances made in uranium metal technology during the early-1950's was the elimination of electrically fused dolomitic oxide as the liner material when it was realized that the magnesium fluoride reaction product produced in the reduction could be recycled for this purpose.⁸ In the present thorium process, the same scheme is followed except that the liner now consists of calcium fluoride.

To prepare the liner material, the rock-like slag mass and at least half of the liner material from each reduction is recovered and reduced to a powder by crushing and ball-milling.

Besides eliminating the high cost of dolomitic oxide (at least \$150/ton), the recycle liner has the advantage that it need not introduce significant amounts of impurities other than those which are already present in the reactants charged into the reduction pot. However, because the slag and recycled liner do contain as much as 8 wt pct free calcium, special precautions are necessary to minimize the reaction of this calcium with nitrogen, oxygen, and

moisture in the air. The liner material must also be ground in equipment which does not contaminate it with impurities such as iron.

It is probable that the use of zinc chloride as the booster would render the slag unusable as liner material because the calcium chloride formed would lower the melting point of the liner material too much. Excessive sintering of the liner would be expected which would make breakout difficult.

Precipitation of Thorium Tetrafluoride

In the present process, thorium tetrafluoride of high density and excellent purity is prepared by direct precipitation in a semi-continuous manner utilizing special polypropylene equipment:

After recovery of the hydrated salt by filtration, the material is dried at 350°F in air to a moisture content of 1 or 2 pct. The ThF_4 is then thoroughly dehydrated in batch tray retorts of Inconel construction by heating in the range 800° to 1000°F under very small flows of nitrogen and anhydrous HF to prevent oxidation or pyrohydrolysis.

The process is much less costly than the older method starting with the preparation of thorium oxalate. Chemical reagent costs are low since no oxalic acid is required and aqueous by-product HF replaces anhydrous HF. Total equipment requirements are only a fraction of

that needed for the oxalate route. Far less care need be exercised in each step to insure production of a product of the desired quality.

Argon Purging of Reduction Vessels

In the present process, the reduction vessels are gasketed, evacuated, and back-filled with argon before they are furnaced. During the entire heating and cooling cycle, an argon line is connected through the lid of the vessel so that a positive pressure of 2 psig can be maintained within the vessel. These precautions have been found to be absolutely necessary to prevent contamination of the metal, slag, and liner with nitrogen from the air. Although oxygen also will be taken up by the charge if air inleakage is permitted, experience indicates that the metal phase does not retain more than approximately 300 ppm oxygen. The difference in retention of nitrogen and oxygen in the metal phase is explained by the relative solubility of the two gases in the molten metal. The data of Gerds and Mallet⁹ indicate a solubility of nitrogen in pure thorium metal of 0.20 wt pct at 1200°C falling to about 0.07 wt pct at 900°C. On the other hand, oxygen is virtually insoluble in thorium metal even at high temperatures.¹⁰ Any oxygen taken up by the metal phase during reduction results in the formation of thorium oxide inclusions which are largely removed from the molten metal phase by liquation into the slag phase.

DESCRIPTION OF THE NATIONAL LEAD PROCESS

In the following section, the present process is discussed in greater detail. The various unit operations are illustrated in the block diagram of Figure 1.

Preparation of ThF_4 - Feed Materials and Equipment

Initially, the thorium nitrate was prepared at NLO from various feeds by solvent extraction using diamyl amyl phosphonate in Solvesso diluent. Later, the thorium nitrate used for metal production consisted of less pure solutions generated by the reprocessing of irradiated thoria at Savannah River. Before use in the precipitation, the feed is diluted from about 450 g thorium per liter to 300-330 g thorium per liter and is transferred to a 200-gal stainless steel head tank fitted with a sight glass for volume measurement.

The hydrofluoric acid is obtained as a by-product of UF_4 manufacture; it varies in strength between approximately 20 and 35 wt pct HF. Minor impurities include sulfur-bearing compounds and a trace of soluble uranium in the tetravalent state. The acid is transferred to the thorium production area in a rubber-lined tank from which it is blown by air pressure to a smaller calibrated 80-gal polyethylene head tank located near the precipitation equipment. To each 80-gal batch of acid in the head tank, 80 g of potassium chlorate (or an equivalent amount of sodium chlorate) is added to oxidize the U^{+4} to UO_2^{++} . This is done to eliminate coprecipitation of traces of UF_4 with the ThF_4 .

The precipitation is carried out in a cone-bottom, 400-gal, tank constructed of 1/4-in.-thick polypropylene sheets joined by multi-pass welds (Figure 2). Rigidity is provided by circumferential bands of 1/4-in.-thick polypropylene. Four baffles extend inwards 6 in. from the straight-wall section. A loose cover provided with a removable hatch encloses the top of the tank. The tank is drained at the base of the cone through a flanged nozzle reinforced by ribbing. A similar nozzle near the top of the straight-wall section connects to an overflow pipe.

The tank is mounted on an elevated platform and rests on a sheet steel cone. Vertical steel supports joined by circumferential bands enclose the tank snugly to provide additional rigidity.

An identical polypropylene tank is mounted below the precipitation tank (Figure 3). It serves as both a decanter and hold tank for the precipitated slurry before it is filtered.

Filtration is accomplished on two vacuum box filters constructed of rubber-coated steel (Figure 4). Each contains 20 sq ft of filtration area. The filter medium consists of a layer of polypropylene felt over which is laid polypropylene cloth. The latter is sealed at the edges with Okum caulking and cotton rope. Because the cloth will become blinded after a few days' use with an encrustation of hydrated thorium tetrafluoride, a second loose layer of the same cloth is placed over the first. After each filtration, the upper cloth is removed and washed free of solids. The underlying cloth remains clean.

Filtrate and decant liquors are drawn off to a 1000-gal rubber-lined steel tank. Vacuum is provided on this tank with a single-stage steam ejector of Haveg construction.

Both the precipitation tank and hold tank are provided with special "home-made" agitators constructed of polypropylene (Figure 5). The blades or impellers are built entirely of polypropylene while the shafts consist of 7/8-in.-diameter stainless steel shafting encased in 1 $\frac{1}{4}$ -in. OD polypropylene pipe.

The thorium nitrate solution is pumped to the precipitation tank with a Milton Roy, single-piston, constant-volume, pump. The hydrofluoric acid is fed with a Monel diaphragm pump (Lapp Pulsafeeder). In general, polypropylene-lined steel pipe is used in all lines which handle fluoride-containing liquids or slurries. Where flexibility is required, as in decant lines or filter feed lines, short lengths of Teflon Flexhose are used. Most of the valves are Teflon-lined plug cocks, but a few neoprene diaphragm valves also are used.

Precipitation Procedure

The thorium metal process is operated on a three-shift, five-day per week schedule. The precipitation work, however, is limited to the daytime shift. A semicontinuous technique is employed in which the thorium nitrate and hydrofluoric acid are pumped continuously into a body of the slurry in such a manner that the slurry always contains an HF excess in the range of 5 to 20 pct. To start the process, a heel of 3 N nitric acid is added to the precipitation

tank to cover the impeller of the agitator. Steam is introduced through a submerged Kynar sparging pipe to bring the temperature up to $205 \pm 5^{\circ}\text{F}$. The precipitation is started slowly by adding intermittently approximately two-gallon increments of the hydrofluoric acid followed by five-gallon increments of the thorium nitrate. After each thorium nitrate addition, the newly formed precipitate is permitted to digest briefly (2 min) before adding more of the reactants. This intermittent method of addition is continued over the first half hour of the precipitation or until 25 gallons of the thorium nitrate have been fed. Then the two feeds are introduced simultaneously and continuously at controlled rates until the volume of slurry reaches the working capacity of the tank.

Starting the reaction out in a heel of nitric acid is important, since the acid promotes the formation of an initial dense crystalline precipitate. The intermittent method of startup insures that an initial small excess of HF is established in the slurry.

At all times during the precipitation, an HF excess must be maintained if a product of maximum density is to be produced. If the mother liquor is permitted to become deficient in HF for even a brief period, the physical characteristics of the precipitate will deteriorate. A bulky precipitate characterized by slow settling, slow filtration, and extreme thixotropy will be produced. The effect cannot be reversed satisfactorily by reestablishing an excess HF concentration in the precipitation mother liquor.

Both the thorium nitrate and HF are introduced through submerged polypropylene pipes at controlled pumping rates. Periodic checks of the individual feed rates and of their ratio are made by monitoring the levels of the feeds in the head tanks. As the precipitator fills, occasional samples of the slurry are dipped out into glass bottles to observe the settling characteristics of the solids. The rate of settling and the degree to which the settled precipitate packs after a period of several minutes is diagnostic of the final density of the thorium tetrafluoride. If it is observed that the precipitate becomes appreciably bulkier as the precipitation proceeds, the rates of feed may be reduced. The HF feed rate may be adjusted to increase the excess to as high as 20 pct; but, as the volume of slurry approaches the working capacity of the precipitation tank, the HF feed can be reduced to bring the overall excess of HF down to about 5 pct.

The temperature of the agitated slurry is maintained slightly above 200°F and may be permitted to rise to 210°F. However, boiling is avoided because fuming becomes excessive. The temperature is held nearly constant by automatic control of the rate of introducing sparging steam. The temperature-sensing element is a stainless steel gas expansion bulb inserted into a U-shaped length of water-filled polyethylene tubing which is partially submerged in the slurry.

When the precipitator is full, the feed pumps, steam flow, and agitator are stopped. The slurry is permitted to settle briefly concentrating the solids in the bottom of the tank and is then

dropped to the hold tank until the level in the precipitator falls to about five inches above the impeller of the agitator. The two head tanks are refilled, and the precipitation is restarted with both feeds entering continuously until the precipitation tank is again filled. After dropping slurry to the hold tank, the cycle is repeated. At the end of the day's precipitation run, the precipitator is drained completely to the hold tank. Any settled solids are flushed from the precipitator with deionized water.

As each batch of slurry is delivered to the hold tank, it is agitated briefly and then permitted to settle. The clear supernatant HNO_3 -HF liquor is drained off through a Teflon Flexhose to the evacuated rubber-lined tank. These steps are repeated after one or two more batches of slurry have been dropped from the precipitator. Then deionized water is added with agitation to resuspend the solids and to cool the slurry to a temperature below 150°F .

Filtration

The slurry is fed by gravity onto one of the two box filters until approximately half the day's production of ThF_4 is collected on the one filter. When the remainder of the day's production has been precipitated, decanted, and reslurried, it is processed on the second filter box. The initial filtration is rapid, but slows down as the solids settle and compact on the filter cloth. When the supernatant liquor above the settled cake becomes clear, it may be drawn off rapidly to the filtrate receiver through a length of polyethylene tubing.

The filter cake which covers the filter cloth to a depth of five or six inches is washed with several additions of deionized water. The cake is somewhat thixotropic and requires vigorous and frequent tamping during the final stages of water removal. Shrinkage cracks must be sealed shut to maintain the full pressure drop across the cake. The washing and final dewatering normally extends over one eight-hour shift.

The decant, filtrate, and wash liquors collected in the vacuum receiver are periodically transferred by air pressurization to an agitated rubber-lined tank. Caustic solution is added to neutralize the acids. After filtration in a plate-and-frame press to remove insoluble residues, the liquors are sent to the General Sump for ultimate disposal.

Capacity of the Precipitation Process

A satisfactory dense thorium tetrafluoride hydrate can be precipitated in the 400-gal tank at a rate of at least 200 lb thorium per hour. Normally, about 1200 lbs of thorium are precipitated in a eight-hour shift. Considerably greater precipitation rates are possible, but productivity is limited by the capacity of the present filtration equipment.

Drying

The filter cake is broken up and hand-scooped into stainless steel pans, the bottoms of which are protected with a loose sheet of 1/32 or 1/16-in.-thick Teflon. To hasten the pan loading, large chunks

of cake are broken into smaller pieces by dropping them through a divelling machine. Drying is accomplished in six Despatch shelf dryers, each rated at 12 kw and equipped with internal air circulation across the shelves (Figure 6). The vapors are drawn off to a wet scrubber in which caustic solution is recirculated to scrub out small amounts of nitric acid and HF vapors evaporated from the wet cake. A day's production of ThF_4 normally fills four of the dryers. The temperature controls are set to bring the air up to 350°F , and usually the material is dry after 18 hours. However, it is standard practice to maintain heat in the ovens for 24 hours to insure that all material in every tray is thoroughly dried.

Dehydration

Drying of the thorium tetrafluoride in air at 350°F leaves a small hydrate moisture content which must be removed by heating at higher temperatures under conditions which do not permit loss of fluorine by oxidation or pyrohydrolysis. The dehydration is accomplished batchwise in three tray-filled retorts constructed of Inconel (Figure 7). Each retort holds 22 trays, $15\frac{1}{2}$ in. in diameter, 2 in. deep, spun from $1/4$ -in. plate. Each tray has a central sleeve so that it can be slipped over and stacked around a perforated pipe which serves as an internal gas distributor. The top tray is not filled. The entire tray assembly can be suspended from the retort cover by a tie-rod which passes down through the perforated pipe. The stack is lowered into the retort shell and the cover is bolted to the flange. The cover and flange are tongue-and-grooved to

accommodate a Monel-asbestos envelope gasket. Additional fittings attached to the retort cover provide for admitting either nitrogen or anhydrous HF into the central perforated pipe and removing the off-gases. A thermocouple is inserted down through the retort cover and top tray so that its tip rests in the powder on the second tray.

The loaded retort, which normally holds about 400 lb ThF_4 , is lowered into one of two electrically heated Rockwell furnaces (Figure 8). Tubing and pipe connections are made to the nitrogen and HF supply lines and the off-gas line. Insulation panels are placed around the top of the retort, and the furnace is turned on to bring the temperature up to 1100°F as measured by a thermocouple inserted against the outside of the retort. During the first hour of heating, the retort is purged with a small flow of nitrogen; but, as the temperature continues to rise, the nitrogen atmosphere is replaced with anhydrous HF delivered from a cylinder mounted on a weigh scale. The HF gas flow rate is adjusted to admit approximately $1/2$ lb HF per hr. Heating is continued for four hours, after which the furnace is turned off. The retort remains in the furnace an additional hour. The HF flow is then discontinued, nitrogen is admitted to sweep out the HF, and the retort is removed to the floor where it cools under a low nitrogen flow.

The internal temperature, as measured by the thermocouple inserted in the topmost loaded tray, is followed on a strip-chart recorder. The peak temperature reached at this point is approximately 850°F , but the temperature on lower trays is known to reach 1000°F .

When the retorts have cooled, they are disassembled, and the ThF_4 is hand-fed through a disk mill to reduce lumps to powder. The material from each retort, which comprises a lot, is blended in a double-cone blender and packaged out into 5-gal cans. A sample is analyzed for pct thorium, fluoride, water, and ppm Fe and Ni. Tapped density is also measured.

Preparation of Zinc Fluoride

The zinc fluoride is also produced in an aqueous system by reacting Technical-Grade zinc oxide with aqueous-byproduct hydrofluoric acid. Since zinc fluoride is somewhat soluble, the reaction is carried out under rather concentrated conditions to give an overall recovery yield of about 85 pct. Extensive washing of the precipitate is avoided to minimize ZnF_2 loss. No attempt is made to recover the soluble zinc fluoride contained in the mother liquor and wash water.

The reaction is carried out batchwise in the 400-gal polypropylene hold tank described above. Aqueous HF is added to the tank in sufficient quantity to provide a 10 pct excess for reaction with 800 lb of zinc oxide. The agitator is started, and the zinc oxide is added rapidly until the heat produced by the exothermic neutralization reaction raises the temperature of the slurry to the boiling point. The rate of addition of the zinc oxide is then slowed to avoid excessive spattering. After all the zinc oxide has been added, the slurry is simply permitted to cool over a period of five or six hours while maintaining agitation. (Heat dissipation is slow since the hold tank is not provided with a means of cooling.)

Zinc fluoride undergoes a phase transition on cooling at 162°F which involves an increase in the water of crystallization. A definite temperature arrest occurs, and the slurry tends to thicken until the agitator cannot maintain the crystals completely suspended in the mother liquor. Deionized water is added as necessary to thin the slurry, since the crystals will set to a rock-like mass if they are permitted to settle out before the phase transition is complete.

As soon as the transition has been completed, the thick slurry of relatively coarse crystals is filtered on the two box filters. The material filters very rapidly. The crystals are washed with just sufficient deionized water to remove most of the residual mother liquor.

Essentially the same procedures are followed in drying and dehydrating the zinc fluoride as are used for the thorium tetrafluoride. A much greater weight loss occurs in drying the zinc fluoride, and corrosion of the stainless steel trays and interior of the dryers is more severe. The dehydration of the material follows a similar heating program, but the material is processed in a smaller tray retort which served as the prototype for construction of the three larger retorts used for ThF₄ dehydration. The dehydrated zinc fluoride is disk-milled, blended, and packaged in 5-gal steel cans. It is analyzed for wt pct Zn, F⁻, H₂O, and ppm Fe and Ni.

Liner Preparation

At breakout of the reduction products, the rock-like slag mass weighing about 120 lb and approximately 200 lb of partially sintered liner material are recovered. The slag mass is broken up with an air hammer until the pieces drop through a steel grating into a drum. Further size reduction is accomplished by jaw-crushing until all the material passes through 1-in.-diameter holes in a sieve. Final size reduction takes place in a Hardinge ball mill equipped with a Whizzer air classifier for control of the particle size distribution. The mill is capable of producing at least 200 lb of liner per hour.

During development of the procedures for liner preparation, it was found that as much as 2000 ppm Fe was picked up from steel grinding balls and that this level of contamination led to excessive Fe pickup in the Th-Zn alloy produced in pots lined with the material. Tests showed that the Fe could be removed by a suitable magnetic device, but the problem was actually resolved by replacing the steel grinding balls with pieces of thorium metal cut from scrap rods.

The product liner issuing from the cyclone separator of the mill is noticeably warm, indicating that the free calcium content of the slag undergoes appreciable oxidation and hydration during the grinding process. The drums of finished liner are kept closed to minimize the exposure of the material to humid air. A sample of liner from each drum is analyzed for ppm N and C. Samples composited weekly are also analyzed for wt pct H₂O and ppm Fe. A particle size analysis is also made.

Reduction - Charge Preparation

The reduction pot is illustrated in Figures 9 and 10. It is constructed of Cor-Ten steel and is tapered to facilitate breakout. The heavy 1-in.-thick lid is bolted to the pot flange with eleven $3/4$ -in.-diameter steel bolts. One bolt hole is left empty to facilitate attachment of a thermocouple to the sidewall of the pot for detection of the reaction.

As stated previously, the liner is formed by jolt-packing the calcium fluoride powder in the annulus between the pot wall and a hollow, tapered, stainless steel mandrel which is held centered in the pot (Figure 11). The liner thickness varies from $3/4$ in. at the top of the pot sidewall to $1\frac{1}{4}$ in. at the bottom sidewall. Liner thickness on the bottom of the pot is $1\frac{1}{2}$ in. The mandrel is usually left in the pot until just before the pot is to be filled with the reduction charge. This precaution is observed because of the tendency of the liner surface to spall when exposed to humid air.

Charging of the lined pot is accomplished within a ventilated enclosure in which the major piece of equipment is a 5 cu ft blender fitted with a rupture disk and a dial thermometer for safety. The blender may also be purged with argon, and a pneumatic vibrator is mounted on one side of the blender to help remove the charge.

The standard reduction charge contains 192 lb of thorium tetrafluoride, 16.1 lb of zinc fluoride, and 64.6 lb of calcium. These quantities are calculated on the basis of $1/4$ mole zinc per mole of thorium, and sufficient calcium to provide a 15 pct excess over the

stoichiometric amount needed to react with the fluorides. The calcium is the double-distilled, 6-mesh grade supplied by the Charles Pfizer Company.

With the blender positioned so that its Gemco valve is at the top, argon is admitted to displace the air. Then the thorium tetrafluoride and zinc fluoride are dumped in from an overhead bin. The valve is closed, and the blender is rotated for 5 min. At the end of this period and after a second purge with argon, the calcium is added. Blending is continued for a second 5-min period after which the blender is stopped with the Gemco valve positioned at the bottom. While the blending is in progress, the mandrel is pulled from the lined reduction pot, and the liner is inspected for flaws. The reduction pot, resting in a wheeled dolly mounted on rails, is positioned under the blender. The charge is emptied into the reduction pot in three or four increments. After each increment is added, the pot is rolled out of the charging enclosure and the loose charge is packed down by rodding and tamping. After all the charge has been tamped into place, the pot is filled to the top with worked and tamped liner material. The cap thickness will normally be at least 4 in. A steel disk, $10\frac{1}{2}$ in. in diameter and $1\frac{1}{2}$ in. thick, is then centered in place on top of the capping liner and worked down until it protrudes about $1/8$ in. above the pot flange. The disk has a number of spacer strips welded to its upper surface so that a gap of at least $1/8$ in. will exist between it and the pot lid. (During evacuation of the vessel, this gap is deemed necessary to provide a sufficiently open path for the flow of gas to the outlet

located in the center of the lid.) A wad of glass wool is placed at the center of the steel disk to serve as a filter preventing excessive carry-over of liner material into the evacuation system. A gasket, consisting of a length of 1/4-in. copper tubing formed into a circle and joined by silver solder, is placed onto the pot flange. The lid is lowered into place and bolted tightly with an air wrench. Compression of the simple tubing gasket consistently forms a good, vacuum-tight, seal—despite the fact that the surfaces of the pot flanges and lids become nicked and scratched after usage.

Evacuation and Backfilling with Argon

Each new reduction pot and those returned from breakout are routinely pressure-checked to insure that they are gas-tight. Leaking pots are usually repaired by welding.

The charged pots are connected to a vacuum and argon backfilling system through a 1/2-in. pipe fitting in the center of the lid. In standard practice, the pot is evacuated for 1/2 hour and then backfilled with argon. The process is then repeated. Checks are made to see that the gasket and tube fittings permit no more than a very slight leakage. The pot is then disconnected from the vacuum-argon purging system and is ready for furnacing.

Reduction Heating and Cooling Cycle

Just before the pot is placed into the electrically heated Rockwell furnace, a Chromel-Alumel thermocouple enclosed in a stainless steel protection tube is inserted down through the one empty set of bolt holes in the lid and flange and is strapped to the outside of the pot. The tip is located opposite the center of slag formation at the point of maximum heat flux through the sidewall after the reaction takes place. The thermocouple is connected to a strip-chart temperature recorder. Although the main function of the temperature measurement is to detect the reduction reaction, it also serves during the rest of the heating cycle to detect malfunction of the furnace heating controls.

The charged pot is placed in the furnace, and a tubing connection is made to an argon purging system. The furnace control thermocouple is inserted through the side of the furnace to contact the pot wall, and the furnace power is turned on. The following heating program is followed:

<u>Furnace Set Point, °F</u>	<u>Total Elapsed Time, Hr</u>
1300	1.5
1400	2.5
1450	4.5 (or until ignition)

If the reduction reaction does not take place, or if there has been no positive indication of ignition, the pot is cooled in the furnace for 8 hr before removal. In recent practice the charges have fired in $3\frac{1}{2}$ to $4\frac{1}{2}$ hours.

During the entire time that the reduction pot is in the furnace, a pressure of 2 psig is maintained on the argon purging system so that air inleakage cannot occur. However, during the initial period of heating, the pressure within the sealed vessel will rise above 2 psig because of the expulsion of expanded argon. More important, a significant volume of hydrogen is formed as moisture from the liner and charge reacts with the calcium. Analysis of the gas evolved from the reduction vessel (where the vessel is permitted to vent freely) indicates that the gas consists almost entirely of hydrogen after the charge has heated for about half an hour.

A special two-way flow control valve is incorporated in the argon purging system. As long as a gas pressure greater than 2 psig exists within the reduction charge, gas flows out of the vessel. When gas evolution ceases and the pressure within the charge tends to drop below 2 psig, argon will flow into the vessel.

During the development stage, several of the reductions yielded thorium-zinc alloy "derbies" which were grossly contaminated with nitrogen. The reason was not immediately apparent, since, although the vessels were ungasketed, a continuous metered flow of argon (approximately 15 cc per sec) was admitted through the lid, and the flow certainly seemed sufficient to buffer against inleakage of air at the pot flange. Subsequent investigation revealed the mechanism by which air does enter an ungasketed pot. As stated previously, the argon atmosphere in the heated charge soon is

replaced by hydrogen. After a heating time of approximately one hour and when the thermocouple on the surface of the reduction pot indicates approximately 1050°F, a sudden reaction takes place within the charge between the hydrogen and calcium to form the condensed phase, calcium hydride. As a result, an actual vacuum is produced within the charge. Since the small argon purge flow is insufficient to return the internal pressure to a value above atmospheric, air is drawn in at the pot flange for a period of several minutes. Since the incoming air also reacts with the hot calcium to form the condensed phases, calcium nitride and calcium oxide, air will continue to flow into the charge until the incoming argon can slow the reactions and eventually restore a slight positive pressure at the pot flange.

Not all of the reductions performed with ungasketed pots resulted in metal contaminated with nitrogen. Evidently, the onset of the hydriding reaction sometimes takes place more gradually so that the argon purging rate is sufficient to maintain a slight positive pressure within the charge.

With the present argon purging system, the following sequence of events is observed. As the charge begins to heat, the pressure within the vessel rises above the value of 2 psig. The expelled argon and eventually hydrogen are permitted to escape through the two-way pressure control valve and through a water bubbler which gives a rough visual indication of the rate of gas evolution. After

approximately 45 minutes, the evolution of hydrogen suddenly slows down and stops, signaling the onset of the hydriding reaction. Soon after, argon begins to flow into the pot, as indicated by the rise of the ball in the rotameter used to indicate the argon flow. Over a period of several minutes, the argon flow will reach a maximum and then diminish to a very small flow. Hence, up to the time of ignition, only a slight leakage of argon is observed.

At ignition, a pressure rise occurs suddenly and is recorded on a circular-chart recorder. At the same time, a brief but vigorous evolution of gas through the two-way valve and bubbler system is observed. The pressure pulse persists for only a few seconds. A pressure switch is incorporated in the purge system to actuate a buzzer to alert the operator that the reduction charge has fired. The recorded pressure pulses have been as high as 70 psig. (Partial plugging of the purge system lines with ejected liner or condensed calcium vapor may account for a large variation in the pressure pulses observed at ignition.) Within a minute or two, an additional indication that the charge has fired is given by a rise in temperature indicated by the thermocouple strapped to the outside of the pot.

The furnace power is turned off, and the reduction pot is removed from the furnace and placed in a brick-enclosed cooling well. During the transfer, the purging system is disconnected, but a valve is closed in a section of tubing retained on the pot so that air cannot

enter the vessel. When the pot has been placed in the cooling well, a second argon purge line is connected. After the vessel has cooled for a few hours, it is removed to a third argon purging station on the floor of the reduction area (Figure 12). Here, the argon purge is maintained until the pot is cool to the touch.

Breakout and Derby Cleaning

The cooled pots are transferred to a ventilated breakout station. Here, the pot lid, gasket, and steel disk are removed, and the cap liner is perforated to make sure that the charge had actually reacted. The pot is then upended over a jolting table and bounced until the contents drop out. The alloy derby (Figure 13) is given a preliminary cleaning with a pneumatic tool to remove adhering, sintered, liner material. It is then sealed in a 10-gal can under argon.

As stated previously, the slag and liner are also collected and held in a closed drum for processing to liner material.

The derbies are returned to the thorium production area and are carefully cleaned of adhering liner in a grit-blasting machine. Since the slag-metal separation is excellent, the tops of the derbies seldom require any cleaning. The grit used is a blast furnace silicate produced under the trade name "Black Beauty." After weighing, they are resealed in argon-purged 10-gal cans to await dezincing. The thorium-zinc alloy is quite reactive and sparks like Misch metal

when struck. The surface of the derby darkens quite readily on exposure to the air. Because of the reactivity, the alloy is always stored under argon.

The reduction yield computed from the weight of the cleaned derbies has averaged about 96.2 pct. In calculating the yield, the assumption is made that the recoveries of both thorium and zinc in the alloy are in the same ratio.

Dezincing - Equipment

The Th-Zn derbies are dezincing in two vacuum induction furnaces originally installed for melting and casting uranium metal and its alloys. The smaller and older unit built by National Research Corporation measures about 42 in. in diameter and 70 in. in height. The lower tank section which formerly housed the ingot mold for uranium casting has been removed and blanked off with a heavy steel plate. The newer furnace, built by the F. J. Stokes Machine Company, is much larger; it is approximately 74 in. in diameter and 12 ft high. The unused mold tank was not removed. Both furnaces are fitted with flanged dished lids with neoprene gaskets. The tanks and lids of both furnaces are jacketed for water cooling.

A graphite susceptor sleeve in each furnace is heated with a water-cooled copper tubing induction coil. The coils are encapsulated in a castable mullite insulating refractory which serves to protect the coils from becoming coated with deposits which cause arcing between

the turns. Power for both furnaces is supplied from a single 200 kw motor-generator set at a frequency of 3000 cps. The furnace lids are provided with sight glasses for visual observation and for taking temperature readings with an optical pyrometer. Furnace vacuums are measured continuously with Alphatron vacuum gauges or intermittently with McLeod gauges. A common vacuum system serves both furnaces. The vacuum is produced by a Stokes Microvac Pump (5 hp, 500 rpm, 150 cfm) in combination with an axial flow booster pump (Ingersoll Rand "Axi-Compressor"). An oil diffusion pump is available for use with the large vacuum furnace, but it is not used at present.

Three derbies are dezincd in each run with the small furnace; four derbies may be accommodated in the large unit. The derbies are contained in graphite pots, 15 in. OD, 13 in. ID, and 8 in. high (Figure 14). These are stacked on top of each other in the susceptor sleeve. The top edge of each pot is scalloped to permit escape of the zinc vapor. New pots are baked out at 700°F, and the interiors are brush-coated with a slurry of ThO_2 powder in chlorethylene before each use. Evaporation of the chlorethylene leaves a loosely adherent ThO_2 coating to serve as a barrier limiting the reaction between the Th-Zn alloy and the graphite to form thorium carbide. The coating also extends the life of the pots by reducing the adhesion of the dezincd metal to the graphite.

Dezincing Procedure

The graphite pots containing the derbies are lowered into the susceptor sleeve using special lifting devices. A graphite lid is placed on the topmost pot, and ceramic insulating covers are positioned above the lid. Slotted holes in the insulation permit viewing of the graphite lid for optical pyrometer temperature measurement (Figure 15). The temperature also may be checked with a W-Re thermocouple in a niobium protection tube which is inserted into a hole drilled down through the sidewall of the topmost pot.

The specifications call for pumping down to less than 100 micron pressure and a leak rate of not more than 20 micron per min. A power-time heating cycle is followed which differs somewhat for the two furnaces:

<u>Small Furnace</u>	<u>Large Furnace</u>
(1) 40 kw for 5 hr.	(1) 45 kw for 5 hr.
(2) 55 kw to 2450°F as measured by the thermocouple in the top pot or for 90 min in the event of thermocouple failure.	(2) 60 kw to 2450°F as measured by the thermocouple in the top pot or for 3 hr in the event of thermocouple failure.
(3) 50 kw to hold 2450° to 2475°F for 3 hr.	(3) 57 kw to hold 2450° to 2475°F for 3 hr.
(4) Power off.	(4) Power off.

The vacuum is maintained one hour after turning off the power. The furnace is then sealed off from the vacuum system and backfilled with argon to a pressure of 15 in. Hg absolute.

In general, if the production schedule permits, the cooling period under reduced argon pressure is extended until the thermocouple in the top pot indicates less than 150°F. In the larger furnace, the furnace may be opened sooner after admitting argon to atmospheric pressure. This is done when the thermocouple measurement indicates that the temperature has dropped below 500°F. The stack of pots is lifted out in an enclosing argon-purged shield and is deposited in an argon-purged cooling drum.

During the heating under vacuum, the rate of zinc evolution from the alloy is rather slow until partial melting begins at approximately 1900°F. At this point, the derby gradually swells until it contacts most of the pot wall and bottom. The power input is carefully regulated through this stage of rapid zinc evolution so that the rate of temperature rise in the temperature interval 1900° to 2100°F is about 1.3°F per min. Too fast a heating rate through this critical period will cause excessive swelling and even explosive splitting open of the derbies as the zinc endeavors to escape from the interior of the alloy. After most of the zinc has been removed, the rate of heating may be increased to bring the sponge up to 2450°F for complete zinc removal.

Most of the zinc evaporated from the derbies deposits on the underside of the furnace lid, although some deposits on the encapsulated coil structure and other furnace parts. In general, the more massive deposits are easily removed from the lid with scraping tools while

the lid is suspended above a special ventilated station. The loose dusty deposits are moved by vacuuming.

When cooled to 150°F or less, the dezincd derbies (Figure 16) are dislodged from the graphite pots in a ventilated enclosure by inverting the pot and rapping. The inverted derbies are exposed to the air for at least 24 hr during which the thin layer of surface carbide hydrolyzes to thorium oxide and spalls off. Most of this thorium oxide is collected for use in coating the graphite pots as described previously. Finally, the derbies are wire-brushed and vacuum-cleaned.

The derbies are sawed in half across a diameter, and a half-slice 3/16-in.-thick is taken for sampling and analysis (Figure 17).

Nibblings from the derby slice are analyzed spectrographically (or by other methods) for the elements, Al, B, Be, Bi, C, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, K, Mg, Mn, Mo, N, Na, Ni, O, Pb, Si, Sn, Sr, U, V, and Zn.

The NLO thorium process terminates with the preparation of the sponge metal. The metal is shipped off-site in argon-filled, sealed, drums to the customer's facilities where it is double arc-melted to form massive ingots. The ductile sponge metal along with recycled scrap is compressed in a die to form primary electrode sections 24 in. long with a 4-in. on edge square cross section.

MATERIALS SPECIFICATIONS - PRODUCT PURITY

Tabulated below are specifications regarding impurities or other properties of the chemical intermediates, liner material, and product thorium sponge metal. Whenever possible, data are presented for the average impurity levels encountered in the chemical intermediates and sponge metal.

I. Calcium Metal; Redistilled, 6-Mesh Nodules

<u>Element</u>	<u>ppm</u>	<u>Element</u>	<u>ppm</u>
Al	10	Fe	10
B	1	Li	1
Be	1	Mg	5000
C	100	Mn	20
Co	2	N	100
Cr	1	Ni	50

Screen Analysis (Typical)

Mesh	+4	+6	+8	+20	-50
Pct	Trace	40.0	50.5	95.0	Trace

II. Zinc Oxide; U.S.P. GradeIII. Anhydrous Hydrogen Fluoride; 30 or 60-lb cylinders.IV. Aqueous Hydrofluoric Acid

<u>Item</u>	<u>Level</u>
HF	20% minimum assay.
U	75 ppm, sample wt basis.
Fe	50 ppm, sample wt basis.

V. Thorium Nitrate Solution*

<u>Item</u>	<u>Al</u>	<u>Be</u>	<u>Ca</u>	<u>Cl</u>	<u>Cr</u>	<u>Cu</u>	<u>F</u>	<u>Fe</u>	<u>K</u>
Max. ppm (Th basis)	20	5	100	100	120	20	200	400	100
Typical ppm (Th basis)	<10	<0.5	<4	5	95	<1	50	310	5
<u>Item</u>	<u>Mg</u>	<u>Na</u>	<u>Ni</u>	<u>PO₄</u>	<u>Si</u>	<u>U</u>	<u>Zr</u>	<u>Other</u>	
Max. ppm (Th basis)	100	100	30	3600	40	100	30	50†	
Typical ppm (Th basis)	5	50	30	2275	12	8	<5		

* These specifications apply to thorium nitrate solution returned from AEC Reactor Sites which is not solvent-extracted before use in the thorium metal process.

† Requires additional analysis for the particular element involved.

VI. Dehydrated, Milled, and Blended ThF₄

<u>Item</u>	<u>Level</u>	<u>Production Average</u>
Th	75.0 pct min.	75.24 pct
F	24.0 pct min.	24.56 pct
H ₂ O	0.10 pct max.	0.06 pct
Fe	100 ppm max. (Th basis)	58 ppm (Th basis)*
Ni	150 ppm max. (Th basis)	35 ppm (Th basis)
Tap Density	1.9 g per cc, min.	2.05 g per cc†

* Several earlier ThF₄ lots were badly contaminated with Fe. After eliminating several sources of contamination, the Fe averaged about 25 ppm.

† The more recent production lots of ThF₄ averaged about 2.4 g per cc in tapped density.

VII. Dehydrated, Milled, and Blended ZnF₂

<u>Item</u>	<u>Level</u>	<u>Production Average</u>
Zn	63.0 pct min.	63.26 pct
F	36.0 pct min.	35.9 pct
H ₂ O	0.20 pct max.	0.12 pct
Fe	75 ppm max. (Zn basis)	145 ppm (Zn basis)*
Ni	25 ppm max. (Zn basis)	22 ppm (Zn basis)
Tap Density		1.45 g per cc

* Several ZnF₂ batches were badly contaminated with Fe primarily because of the use in precipitation of Fe-contaminated aqueous HF. Normally the Fe contamination is expected to average about 60 ppm. The out-of-specification ZnF₂ was utilized in the reduction charges by blending.

VIII. Recycle CaF₂ Liner

<u>Item</u>	<u>Level</u>
N	200 ppm max.
C	300 ppm max.

IX. Thorium Sponge Metal

<u>Item</u>	<u>Al</u>	<u>Be</u>	<u>C</u>	<u>Ca</u>	<u>Cl</u>	<u>Cr</u>	<u>Cu</u>	<u>F</u>	<u>Fe</u>
Max. ppm (Th basis)	50	10	200	1600	300	75	40	1000	100
Average ppm (Th basis)	11	<1	135	162	28	11	<1	34	57

<u>Item</u>	<u>K</u>	<u>Mg</u>	<u>N</u>	<u>Na</u>	<u>Ni</u>	<u>O</u>	<u>Si</u>	<u>U</u>	<u>Zn</u>	<u>Zr</u>
Max. ppm (Th basis)	300	200	200	300	150	1250	75	50	50	40
Average ppm (Th basis)	<1	103	166*	<1	24	287	8	15	‡	8

* Nitrogen values obtained on individual dezincd derbies are broken down as follows:

<u>N, ppm (Th basis)</u>	<u>Pct of Derbies</u>
<100	23
100-200	49
200-300	22
300-400	5
>400	1

‡ Zinc values obtained on individual dezincd derbies are broken down as follows:

<u>Zn, ppm (Th basis)</u>	<u>Pct of Derbies</u>
<25	63
25-100	24
>100	13

DISCUSSION

Thorium Tetrafluoride Preparation

The direct precipitation of ThF_4 from thorium nitrate solution was recognized by a number of earlier investigations as an attractive alternative to the expensive route starting with precipitation of the oxalate. Peterson¹¹ reported on the essential features of batch precipitation of the fluoride. Later, pilot studies of both batch and continuous precipitation were conducted at the Ames Laboratory by Barson and Smutz¹². During the earlier phase of the production campaign at NLO in 1953, ThF_4 was produced by direct precipitation, but the process was abandoned primarily because of corrosion problems associated with the fluoride-bearing nitric acid liquors. Another drawback was the relatively low densities of the thorium tetrafluoride produced. For example, the tapped density of ThF_4 produced by Barson and Smutz ranged from 1.3 to 1.8 g per cc with continuous precipitation methods giving the lower values. Peterson reported densities of 1.9 to 2.1 g per cc from batch precipitation.

In the present work, the precipitation is started in a heel of nitric acid, and the precipitation solution never contains either fluoride or thorium ions in high excess. It is believed that these conditions promote the development of a spectrum of particle sizes which leads to high packing density. Probably of greater importance, however, is the effect of a certain impurity in the by-product HF

used for precipitation. During one period of production, the HF used for precipitation was prepared by dissolving gaseous anhydrous hydrogen fluoride in deionized water. With this relatively pure acid, the precipitated ThF_4 was much lower in density and was only about 1.5 g per cc. The feed rates of the reactants had to be greatly lowered to prevent even further density decrease. During a precipitation run in progress, a dramatic increase in precipitate settling rate and packing density was observed when the aqueous HF was changed from diluted anhydrous HF to the by-product aqueous acid derived from UF_4 manufacture. With the by-product acid, the ThF_4 tapped density (after dehydration) has been as high as 2.9 g per cc, although a value of about 2.4 g per cc is the expected average.

Limited laboratory investigation has suggested that sulfur-bearing impurities in the by-product HF, which includes H_2S , are oxidized to sulfate ion which is adsorbed in the precipitate to affect the crystal morphology..

The density of the ThF_4 produced during the latter stages of the recent campaign was greater than that originally expected. The reduction charge which contained 192 lb ThF_4 could have been increased significantly because the cap thickness often exceeded the required 4 inches by as much as 3 or 4 inches. However, the reduction charge was not increased because the dezincing pots were somewhat undersized and could not always accommodate the swelling of a larger derby.

Another factor which has been observed to result in a lowered ThF_4 density is inordinate delay between the time of precipitation and filtering. The reason for this is not known with certainty, but may be the result of a change in crystal morphology brought about by gradual hydration when the water-slurried material is allowed to cool over a period of several hours before filtration.

Corrosion related to the handling of HNO_3 -HF liquors at temperatures up to almost boiling has not been a serious problem. The use of polypropylene has proved very successful in the construction of the tanks and agitators and as a pipe lining. Rubber linings, as on the box filters, suffer some degradation when contacted with nitric acid; but, if the liquors are diluted and cooled below 150°F , the affect is not serious. The rubber linings in equipment now in use are very old and partially oxidized; new coatings would probably prove more resistant.

During the development of the precipitation process, the reaction was carried out in a 50-gal stainless steel tank fitted with a turbine-type agitator. Surprisingly, the corrosion of the tank was not severe as long as the HF excess was limited in the range 2 to 5 pct. Analyses of the precipitation liquor for Fe, Ni, and Cr indicated that the corrosion rate was not excessive and that long tank life could be expected. The cast impeller of the agitator did fail eventually. Most of the damage may have occurred in one precipitation run made with hydrofluoric acid of much higher concentration than was assumed in the calculation for the volume ratio of the

reactants. The mother liquor in this run was very green in color, indicating rapid corrosion. Although the use of a stainless steel precipitation tank appears feasible, plastic equipment is preferred since the precipitated ThF_4 requires much less washing to remove soluble Fe, Ni, and Cr. Furthermore, the HF excess need not be maintained between the narrow limits required to minimize corrosion in stainless steel equipment.

The Use of Zinc Fluoride

The possible advantages of zinc fluoride as the thermal booster and source of zinc in the reduction charge were not overlooked by early Ames workers. They carried out test reductions using zinc fluoride, but did not get good slag-metal separation. They concluded that zinc chloride provided a necessary fluxing action in the molten system and that phase separation was enhanced by the lowered melting point of the CaF_2 - CaCl_2 slag. In our present work, we have consistently obtained excellent slag-metal separation with zinc fluoride in the reduction charge. We are of the opinion that the poor separation encountered in the Ames tests was caused by introduction of excessive amounts of insoluble oxides into the molten reaction system. The oxides would be derived from the dolomitic oxide liner and probably also from ThF_4 produced via the oxalate route. Standard free energy data indicate that, at the temperatures reached in reduction, thorium metal should react with both CaO and MgO in the liner to yield ThO_2 as the stable phase.

Evidently, the use of zinc fluoride and the use of recycle calcium fluoride as liner are interdependent. Zinc fluoride may be employed if CaF_2 replaces dolomitic oxide as the liner. On the other hand, the use of zinc fluoride eliminates chloride from the reaction slag, making the slag suitable for liner material.

Liner Development - Graphite Liners

At the start of the reduction work, recycle CaF_2 liner was of course not available, since it must be produced by the reduction reaction itself. Therefore, to get the reduction work started and build up an inventory of reaction slag, the initial pot linings were prepared from purchased acid-grade fluorspar which had been preheated to remove moisture. Although the fluorspar performed well as a lining material, its continued use was not practical because of the excessive contamination of the Th-Zn alloy with silicon. Other impurities such as Al, Fe, and $\text{CO}_3^{=}$ in the fluorspar were also objectionable.

A rather extensive effort was made to develop a reusable graphite lining. Several graphite crucibles were machined from electrode stock. These were tapered from top to bottom to facilitate breakout. The taper was increased in the bottom section since the derby often tended to adhere to the graphite quite tenaciously. The graphite lining was centered in the steel pot and fluorspar was packed into the annulus between the graphite lining and steel pot wall. A $1\frac{1}{2}$ -in. layer of fluorspar also separated the bottom of the graphite crucible from the bottom of the steel pot. Several serious difficulties were

encountered in the reductions. Reduction yields were lower because the reaction tended to be quenched near the crucible wall where heat was lost too rapidly into the conductive graphite. Several of the liners cracked. Most troublesome, however, was the reaction of the excess calcium with the graphite in the zone of slag formation. This tended to occur in localized patches and caused undercutting of the liner so that the frozen slag mass could not be removed by gently jolting the inverted reduction pot. Finally, the derby metal was often too contaminated with carbon. None of the graphite liners were serviceable for more than three reductions.

The Nitrogen Problem

Nitrogen contamination of the thorium has been a recurrent problem during the present production campaign. This may be rather surprising since the literature on the Ames process makes little mention of nitrogen as a serious contaminant; whereas, most of the stress has been on contamination with oxygen. However, it has always been recognized that the calcium must be nitride-free. The metal is invariably purified by redistillation to remove the nitrogen and other impurities.

During the earlier phase of the production campaign, nitrogen levels above the specification limit of 200 ppm were associated primarily with the reduction step. After it was discovered that CaH_2 formation during the preheat stage could cause inleakage of air into argon-purged, ungasketed, reduction vessels, the pots were

gasketed. Nitrogen levels then dropped to a range of 40 to 90 ppm in the final dezinced metal. Another period of high nitrogen contamination was then encountered which was finally traced to the use of purchased copper tubing gaskets which had been joined with low-melting soft solder rather than the specified high-temperature melting point silver solder. Still another brief period of nitrogen contamination was tentatively traced to the use of a few drums of nitride-contaminated calcium. More recently, nitrogen levels increased once again to unacceptable levels. Much of this trouble was caused by all too frequent "burnoffs" of the argon purge tubing where it joined to the short section of $\frac{1}{2}$ -in. pipe which is welded to the pot lid. This occurred just after ignition or when the red-hot tubing was twisted when the vessel was lifted out of the furnace. When the tubing is actually broken or fails to seal against inleakage of air, the liner material and at least the upper portion of the slag mass will pick up nitrides. Although the derby metal may not pick up nitrogen since it is protected under the molten slag, the slag and liner material containing the nitrides will contaminate the metal produced in subsequent reductions if it is recycled as liner.

At the present time, the piping and tubing connections which attach to the pot lids are being modified. A longer and stouter section of straight pipe will be welded to the lid and will extend well outside of the furnace before being joined to tubing. The furnace cover and lifting devices must also be modified to accommodate the piping changes. A long reamer tool will also be provided for removing deposits of condensed calcium and sintered slag which will collect in the straight pipe section after a few uses.

During the latter period of production, it also became evident that nitrogen was being picked up during the dezincing operation in both vacuum furnaces. Several small air leaks have been discovered and repaired. In addition, the furnaces have been outgassed periodically. Although improvement is indicated, the problem is still under study.

Possible Process Improvements

No urgent problems of a technical nature remain to be solved in achieving production of thorium sponge metal by the modified Ames route developed at NLO. All purity goals have been met, although the elimination of nitrogen requires constant vigilance. Nevertheless, for sustained production, operating costs could be lowered significantly if more suitable equipment were made available for filtration of the thorium and zinc fluorides, for drying the fluorides, and for high-temperature dehydration of the thorium tetrafluoride. The present batch methods of handling these tasks involve too much manual handling of ThF_4 in a finely divided and dusty form.

An improved method of filtering the thorium tetrafluoride slurry has been investigated. Excellent results were obtained in tests with a small basket centrifuge supplied by a manufacturer of this type of equipment.

CONCLUSIONS

Thorium metal sponge suitable for consumable arc-melting has been produced with enhanced purity and physical properties by a modified

Ames process. Perhaps most significant is the lowering of the oxide content of the sponge metal. This has been made possible by eliminating oxides from the reduction pot lining and from the components of the reduction charge.

Wet precipitation methods for preparing thorium tetrafluoride and zinc fluoride in plastic equipment help to eliminate metallic impurities. The direct precipitation of ThF_4 also results in a large cost saving.

In contrast with the direct reduction of thorium oxide which produces thorium powder, the modified Ames process yields the Th-Zn alloy in a safe massive form. The yield of directly recoverable metal is also much higher. Moreover, the molten state in which the reaction products are formed permits cleaner separation of oxide impurities by liquation.

The safety of the Ames process is also enhanced by the use of non-hygroscopic ZnF_2 .

Besides offering technical benefits, the recycling of the CaF_2 reduction slag as reduction pot lining material results in a significant cost saving.

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$\text{Th}(\text{NO}_3)_4$ Sol'n.
 300 g Th/l
 ~1 N HNO_3
 2000 lb Th

FIGURE 1 - BLOCK FLOW DIAGRAM OF THORIUM METAL PROCESS

FIGURE 2 Polypropylene Tank for ThF_4 Precipitation

FIGURE 3 Polypropylene Hold Tank

FIGURE 4 ThF_4 on Vacuum Filter Box

FIGURE 5 Polypropylene Agitator

FIGURE 6 Shelf Dryers

FIGURE 7 Dehydration Retorts

FIGURE 8 Dehydration Furnace in Foreground.
Reduction Furnace in Background Behind
Shield.

FIGURE 9 - REDUCTION VESSEL SHOWING THE
CONFIGURATION OF THE LINER

FIGURE 10 Reduction Pot with Mandrel for Forming Lining

FIGURE 11 Jolting the Liner

FIGURE 12 Reduction Pot Cooling Under Argon. Copper Tubing Gasket is Shown on Pot Lid.

FIGURE 13 Th-Zn Derby Before Cleaning by Grit Blasting

FIGURE 14 Graphite Dezincing Pot

FIGURE 15 Small Dezincing Furnace. Operator is Taking an Optical Pyrometer Reading.

FIGURE 16 Dezincing Derbies

FIGURE 17 Sawing of Dezincing Derbies