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Preparation of Thorium-Magnesium Alloys and Pure Thorium by Magnesium Reduction of Thorium Tetrachloride

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Preparation of Thorium-Magnesium Alloys and Pure Thorium by Magnesium Reduction of Thorium Tetrachloride

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PREPARATION OF THORIUM-MAGNESIUM ALLOYS AND PURE THORIUM BY MAGNESIUM REDUCTION OF THORIUM TETRACHLORIDE

by

T. T. Campbell,[1] G. B. Robidart,[2] and F. E. Block[3]

ABSTRACT

Studies were conducted by the Bureau of Mines to develop a process for preparing thorium-magnesium master alloys or pure thorium metal by magnesium reduction of thorium tetrachloride in a semicontinuous reactor. Thorium tetrachloride was prepared in a fluidized-bed reactor by chlorination of thorium oxide or thorium oxalate. Conditions were established for producing a suitable thorium oxide feed for a fluidized-bed reactor. Thorium tetrachloride was purified by vacuum sublimation and subsequently reduced by magnesium in a semicontinuous reactor to form thorium-magnesium alloys. Relatively pure thorium was produced by removing magnesium from the alloys by vacuum sublimation. Close to 100 percent of the thorium fed into the reactor was recovered either as metal (~93 percent) or as thorium oxide (~7 percent). The oxide can be recycled directly into the process.

INTRODUCTION

Interest in thorium metal is largely due to its potential use as a source of fuel for nuclear power reactors. When naturally occurring thorium-232 is subjected to neutron bombardment, it captures a neutron, emits a beta particle, and is converted to fissionable uranium-233. It is estimated that there is almost three times as much thorium in the earth's crust as there is uranium (1, 3).[4]

In addition to its potential use as a nuclear fuel, the introduction of small amounts of thorium into magnesium produces magnesium-base alloys that possess superior high-temperature strength and creep resistance properties as well as stiffness. The reader is referred to an excellent review of the properties of magnesium-thorium alloys by Leontis (4). At present, one of the major uses of thorium is its use as an alloying additive to magnesium. Magnesium-thorium alloys are prepared by introducing elemental thorium or

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[1] Supervisory chemical research engineer.

[2] Chemical engineer.

[3] Chemical research engineer.

[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

magnesium-thorium master alloy (30 to 40 percent thorium) into molten magnesium. It is estimated that over 65,000 pounds per year of contained thorium is presently being used in magnesium-thorium alloys (8).

The commercial procedures used to prepare magnesium-thorium master alloys involve the use of a large excess of magnesium to reduce either thorium tetrachloride ($ThCl_4$) or thorium tetrafluoride (ThF_4) in fused salts (NaCl-KCl or $MgCl_2$) (5). Reduction of $ThCl_4$ is essentially a batch process, whereas ThF_4 is reduced by a semicontinuous process, but reaction efficiency, ranging only from 50 to 80 percent, is lower than desirable.

Commercial-grade thorium is prepared by calcium reduction of either thorium oxide (ThO_2) or ThF_4 in bomb reactors (3). More recently, the Bureau of Mines developed techniques by which high-purity thorium metal can be prepared by Kroll process techniques utilizing sodium or magnesium to reduce $ThCl_4$ (2, 6). The method has major disadvantages: It is essentially a batch process, and an excessive amount of time, with concomitant increased cost, is needed to prepare and purify $ThCl_4$.

In this earlier work, $ThCl_4$ was prepared in a three-step process: (1) preparation of active ThO_2 by thermal decomposition of thorium nitrate tetrahydrate [$Th(NO_3)_4 \cdot 4H_2O$] or thorium oxalate [$Th(C_2O_4)_2$], (2) static-bed chlorination of ThO_2 to $ThCl_4$, and (3) purification of $ThCl_4$ by vacuum sublimation.

In view of the foregoing considerations, the Bureau of Mines undertook the present investigation to develop a continuous or semicontinuous process that could be adapted to the production of magnesium-thorium master alloys. A secondary objective was the production of pure elemental thorium metal from master alloy.

EXPERIMENTAL PROCEDURES AND RESULTS

In the present work major efforts were directed toward developing procedures that could be used to produce thorium-magnesium alloys or thorium metal in a semicontinuous reactor. Particular care was made to use methods that could be adapted readily to industrial use. Initial studies were made to develop procedures that would permit production of $ThCl_4$ in a fluidized bed reactor.

This was done because fluidized-bed reactors used industrially lend themselves to continuous operation. Usually, feed is introduced into the fluid bed, and the product is removed by downcomers or is removed by entrainment in the exit gas stream. A small, laboratory-scale, fluidized-bed reactor similar to that described by Rossmassler (7) was designed and constructed for this purpose (fig. 1). Initial work with this reactor quickly indicated that techniques previously used to prepare ThO_2 gave a feed material that was not suitable for use in a fluidized-bed reactor because the feed tended to cause either gas channeling or freeze up of the bed. Accordingly, extensive studies were undertaken to prepare a ThO_2 feed which would be suitable for use in a fluidized-bed chlorinator.

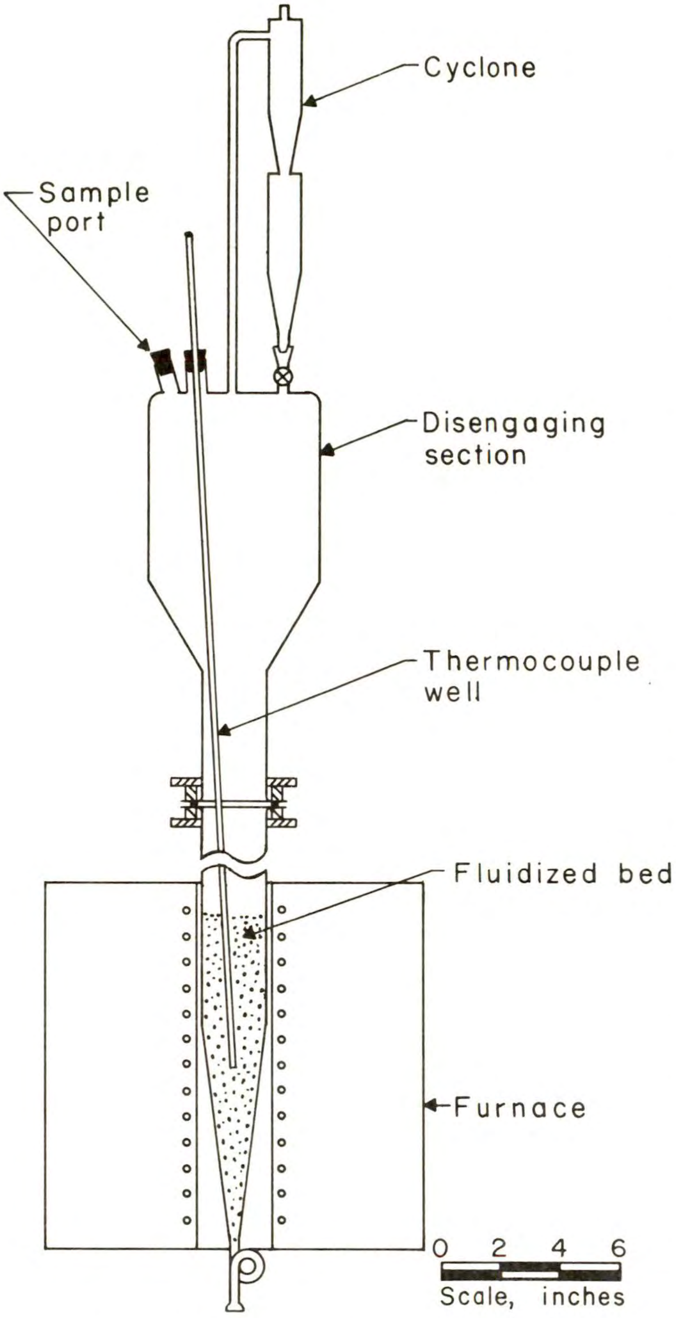

FIGURE 1. - Fluidized-Bed Chlorinator.

Conversion of Thorium Nitrate Tetrahydrate to Thorium Oxide

The initial tests involved the thermal decomposition of $Th(NO_3)_4 \cdot 4H_2O$ at temperatures ranging from 100° to 700° C. The $Th(NO_3)_4 \cdot 4H_2O$ used in this study was purchased from a commercial supplier. Analysis showed that the material contained 40.7 percent thorium, 8.3 percent nitrogen, and 40 parts per million iron, which was the major metallic impurity, and only trace amounts of other impurities. Denitration of $Th(NO_3)_4 \cdot 4H_2O$ was conducted either in an air atmosphere or under vacuum. Vacuum denitration was performed by introducing $Th(NO_3)_4 \cdot 4H_2O$ into a 5-inch-diameter quartz tube (both ends sealed), which was heated by a 5-inch clam-shell resistance furnace. A water aspirator, constructed of zirconium, was used to provide a vacuum of about 25 inches of mercury.

Although vacuum denitration was much faster than oven denitration in an air atmosphere, the ThO_2 prepared by vacuum denitration was generally not suitable for use in the fluidized-bed reactor. The ThO_2 prepared by vacuum denitration usually contained a relatively high nitrogen content (2.5 to 3.5 weight-percent), and this type of feed tended to cause channeling or to agglomerate in the fluidized-bed chlorinator. For this reason, the ThO_2 used in this study was usually prepared by denitration in an air atmosphere.

Denitration was effected by heating up to 4.6 kilograms of $Th(NO_3)_4 \cdot 4H_2O$ in evaporating dishes for varying periods of time at temperatures from 220° to 700° C. The results of these tests are given in table 1.

TABLE 1. - Thermal denitration of thorium nitrate tetrahydrate to crude thorium oxide at atmospheric pressure

Temperature, ° C	Time, hr	Charge weight, g	Product				Conversion:
			Weight,[1] g	N, pct	Th,[2] pct	Crystallite size,[3] A	$Th(NO_3)_4 \cdot 4H_2O$ to ThO_2, pct
220	336	2,188	1,137	1.87	81.7	30	92.9
220	384	4,604	2,406	3.22	75.0	30	85.3
250	48	2,406	2,372	1.94	79.3	35	90.2
250	216	3,014	1,535	2.0	78.1	30	88.9
275	360	3,802	1,923	1.64	80.4	45	91.5
[4]150	2	26.3	12.9	.64	84.5	40	96.1
300	4						
[4]150	2	29.5	14.0	.168	87.1	40	99.1
350	4						
[4]150	2	31.5	14.8	.040	87.3	50	99.3
400	4						
500	2	30	25.3	.023	87.9	70	100
500	8	31.2	26.3	.0180	87.9	140	100
500	16	30.1	25.1	.0090	87.7	160	99.8
600	2	62.4	52.6	<.0010	87.9	170	100
700	2	31.1	25.7	<.0010	87.9	240	100

[1] Includes ThO_2 and undecomposed $Th(NO_3)_4 \cdot 4H_2O$.
[2] Theoretical Th in ThO_2 is 87.9 pct.
[3] Values given are apparent mean crystallite size as determined by X-ray diffraction.
[4] Charge heated 2 hours at 150° and 4 hours at higher temperature.

Inspection of table 1 shows that over 92 percent of the $Th(NO_3)_4 \cdot 4H_2O$ feed was converted to ThO_2 at temperatures as low as 220° C. Although conversions of 99.1 to 99.9 percent could be effected at 350° to 700° C, the ThO_2 prepared at these temperatures was not suitable as a feed material in a fluidized-bed chlorinator.

The procedure used most often to prepare a suitable ThO_2 feed for chlorination involved heating 2 to 4.6 kilograms of $Th(NO_3)_4 \cdot 4H_2O$ for 48 hours at 150° C in air, after which the temperature was raised to from 225° to 275° C for periods up to 384 hours, depending on the amount being processed.

Conversions of nitrate to oxide could be effected in a relatively short period (26 to 48 hours) when small quantities were processed. This is attributed to the fact that heat transfer and diffusion through deep beds inhibited the rate of denitration. One would expect that denitration could be effected much more rapidly in a rotary kiln than was the case in this study. After denitration, the ThO_2 product was ground and separated into minus 70- plus 100-mesh and minus 100-mesh screen fractions. The bulk of the ThO_2 (over 90 percent) was readily ground to minus 100-mesh size.

Several conclusions were derived from the denitration studies. If the oven temperature was raised too rapidly, the $Th(NO_3)_4 \cdot 4H_2O$ melted, and the

ThO_2 formed a hard, ceramic material that was difficult to grind and did not fluidize properly during chlorination. Thorium oxide prepared by denitration below 300° C is a collection of smooth particles, whereas oxide prepared above 300° C forms irregular, dendritic particles that tend to interlock. The dendritic material almost always caused channeling in the fluidized-bed reactor. Thorium oxide prepared above 300° C usually contained less than 0.5 weight-percent nitrogen, whereas ThO_2 prepared below 300° C contained 1 to 4 weight-percent nitrogen. Thorium oxide feed containing less than 0.5 weight-percent or more than 2.5 weight-percent nitrogen was not suitable for use in the fluidized-bed chlorinator because it resulted in gas-channeling and bed-plugging. This work indicated that the amount of nitrogen present in the ThO_2 feed can be used as a criterion to determine whether a given lot is suitable for chlorination feed.

The chlorination rate of ThO_2 prepared above 300° C was much slower than that of oxide prepared below this temperature. The decreased reactivity of ThO_2 prepared above 300° C was presumed to be associated with the increase in crystal size of the oxide, that is, a decrease in surface area. As expected, the crystal growth of ThO_2 was dependent on both time and temperature, as can be seen by inspection of table 1.

Chlorination of Thorium Oxide

Chlorination studies were conducted in a small, 2-inch-diameter, fluidized-bed reactor. Phosgene ($COCl_2$) was used both as a reactant and as a fluidizing agent.

Phosgene was preferred as a chlorinating agent because previous work (6) had demonstrated that higher yields and reaction rates were obtained with this reactant than could be realized with chlorine and carbon or with carbon tetrachloride. Small-scale chlorination tests were performed in the fluidized-bed reactor shown in figure 1. The reactor was made of Vycor[5] so that the bed could be observed during operation and also because Vycor is unreactive with the chlorinating agent used and with the reaction products. No provision was made for removing $ThCl_4$ from this reactor during operation. When test runs were completed, the $ThCl_4$ product was removed from the top of the reactor by simply inverting it.

The chlorination reaction was initiated by introducing approximately 150 grams of ThO_2 (8- to 10-inch bed depth) into the reactor and heating to 250° to 300° C. The ThO_2 bed was fluidized and conditioned by passing 25 liters per hour each of phosgene and argon at a bed temperature of 300° C. In 1 to 2 minutes the offtake gases from the reactor turned dark red because of decomposition of small residual amounts of $Th(NO_3)_4$. After nitric oxide fuming ceased (about 20 minutes), the bed was heated to the operating temperatures, which ranged from 500° to 650° C. Typical data on chlorination tests conducted at these temperatures are given in table 2.

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[5] Reference to specific materials is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 2. - Fluid-bed chlorinations of thorium oxide by phosgene

Charge[1]		Temperature, ° C	Time, hr	Product[2]			Conversion,[3] pct
N, pct	Th, pct			Th, pct	Cl, pct	N, ppm	
[4]2.3	75	250 - 300	0.5	81.8	9.8	780	19.6
2.3	75	500	1	75.6	18.9	10	40.8
2.3	76.4	500	2	70.1	22.8	40	53.1
1.94	79.3	500	6	63.9	32.5	50	83.1
1.94	79	550	1	75.6	18.9	280	40.8
			1.5	74.6	20.4	20	44.7
			2	73.5	21.7	<10	48.7
			2.5	73.0	22.7	<10	50.8
			3	71.7	24.4	<10	55.6
			3.5	71.9	24.5	<10	55.7
			4	70.8	25.8	<10	59.5
			5	68.6	26.8	<10	63.8
			6	68.6	28.8	<10	68.6
1.94	79	650	1	73.5	21.6	30	48.0
			1.5	72.0	23.5	70	53.3
			2	70.5	25.5	<10	59.1
			2.5	69.7	27.3	<10	64.0
			3	69.0	29.2	<10	69.1
			3.5	67.1	30.0	<10	73.0
			4	65.9	32.3	<10	80.1
			5	64.7	34.5	<10	87.1
			5.5	63.5	36.1	<10	92.9

[1] Feed consisted of 150 ThO_2; bed depth, 8 to 10 inches.

[2] Theoretical (100-pct) conversion would yield 62 pct Th and 38 pct Cl.

[3] Calculated by Th (as $ThCl_4$)/total Th.

[4] All runs conditioned for 0.5 hr at 250° to 300° C to remove oxides of nitrogen.

It is particularly interesting to note the low conversion (68.6 percent) that was effected when ThO_2 was chlorinated at 550° C as compared to the conversions obtained at 500° (83.1 percent) and 650° C (92.9 percent). This is not an isolated instance, but was typical of results obtained during this study.

Several observations were derived from the chlorination studies discussed above. Evidence indicates that the conversion of ThO_2 to $ThCl_4$ proceeds stepwise in accordance with the following equations:

$$ThO_2 + COCl_2 \longrightarrow ThOCl_2 + CO_2 \qquad (1)$$

$$ThOCl_2 + COCl_2 \longrightarrow ThCl_4 + CO_2. \qquad (2)$$

At 500° C the first reaction predominates until about 80 percent of the oxide is converted to $ThOCl_2$. This was established by determining the weight differences between the water-insoluble fraction in the bed (ThO_2) and the fractions insoluble in ethyl alcohol ($ThO_2 + ThOCl_2$). It was observed that higher argon flow rates were required to maintain the bed in a fluidized state when chlorinations were conducted above 550° C. Usually, 25 liters per hour each of $COCl_2$ and argon were used to maintain fluidization; however, when the bed was operated at 600° to 650° C, the argon flow had to be increased to 40 liters per hour or the bed tended to solidify. The tendency of the bed to solidify was probably associated with a change in the fluidization character of the bed caused by formation of $ThOCl_2$ and $ThCl_4$ as shown in equations 1 and 2 above.

Experience also showed that if the bed was heated above 300° C too rapidly or if phosgene was not added to the fluidizing gas, a central gas channel formed which was surrounded by a static shell of ThO_2. The most important result of the chlorination study was the fact that ThO_2 can be successfully chlorinated in a fluidized-bed reactor.

Chlorination of Thorium Oxalate

In addition to studies on the chlorination of ThO_2, work was also performed in which $Th(C_2O_4)_2$ was used as feed. The $Th(C_2O_4)_2$ was prepared by precipitation from 2.25 to 4.3 molar thorium nitrate solutions at room temperature by reaction with a solution of 4 to 6 normal oxalic acid. The $Th(C_2O_4)_2$ precipitate was washed, filtered, oven-dried at 120° C, and then ground and separated into minus 40- plus 70-mesh, minus 70- plus 100-mesh, and minus 100-mesh screen fractions. The dried oxalate contained 51 to 52 percent thorium and 10.6 to 10.8 percent carbon, which corresponds to the composition of $Th(C_2O_4)_2 \cdot 2H_2O$. Analyses also showed the presence (in parts per million) of 10 aluminum, 80 calcium, 60 iron, and 40 silicon. Chlorination tests were made on all size fractions with no apparent difference in the fluidization behavior of the various fractions; however, if the $Th(C_2O_4)_2$ was not ground and separated into screen fractions, the bed acted as a classifier and tended to solidify.

When ThO_2, prepared from $Th(NO_3)_2 \cdot 4H_2O$, was chlorinated it was necessary to condition the bed for approximately ½ hour at 250° to 300° C to remove oxides of nitrogen; however, $Th(C_2O_4)_2$ did not require a conditioning step, but could be chlorinated directly. The procedure used was to load approximately 100 grams of $Th(C_2O_4)_2$ into the fluidized-bed reactor, which had been preheated to 100° C. The furnace was set to the desired operating temperature (350° to 600° C), and a flow of argon gas was started immediately. As soon as the bed was fluidized, $COCl_2$ was added to the gas stream. The bed required about 75 liters of argon per hour to effect fluidization.

It was much more difficult to separate $Th(C_2O_4)_2$ into screen fractions than it was to separate ThO_2, and higher gas flow rates were required to fluidize oxalate. This was due to the fact that $Th(C_2O_4)_2$ tended to agglomerate readily. After the bed was fluidized, 25 liters of phosgene per hour was introduced into the reactor to effect conversion of $Th(C_2O_4)_2$ to $ThCl_4$.

Operating data and yields effected during chlorination of Th(C_2O_4) are given in table 3.

TABLE 3. - Fluid-bed chlorinations of thorium oxalate by phosgene[1]

Time, hr	Temperature, ° C	Product[2]			
		Th, pct	Cl, pct	Conversion,[3] pct	C, ppm
1	350	68.7	19.5	46.4	6,000
2	350	67.1	22.4	54.5	4,700
4	350	64.7	26.2	66.2	1,700
1	450	70.7	23.3	54.0	860
2	450	67.1	28.5	69.4	1,300
4	450	63.9	33.4	85.4	510
1	550	71.9	23.3	52.9	1,070
2	550	68.2	26.9	64.4	670
4	550	64.6	34.7	87.8	480
1	600	68.6	27.6	65.7	690
2	600	65.1	34.3	86.1	250
4	600	62.8	36.7	95.5	180

[1] Feed consisted of 100 g Th(C_2O_4)$_2$ containing 51.6 pct Th and 10.8 pct C. Bed depth, 8 to 10 inches.

[2] Theoretical (100-pct) conversion would yield 62 pct Th and 38 pct Cl.

[3] Conversion calculated by Th(in $ThCl_4$)/total Th.

Inspection of table 3 indicates that conversions in excess of 95 percent can be effected by chlorination of Th(C_2O_4)$_2$ with $COCl_2$. In general, somewhat higher conversions to $ThCl_4$ were effected than when ThO_2 was chlorinated (table 2). Thorium chloride prepared from oxalate at temperatures from 350° to 600° C contained from 180 to 1,700 parts per million carbon, which transfers to the metal during reduction of the chloride.

At this time it is not possible to state definitely whether ThO_2 or Th(C_2O_4)$_2$ is the better feed for a fluidized-bed chlorinator. Thorium oxide prepared from nitrate has a bulk density of 1 gram per cubic centimeter and contains about 80 percent thorium, whereas the bulk density of Th(C_2O_4)$_2$ is only 0.65 gram per cubic centimeter, and it contains only 52 percent thorium. As a result, higher throughputs of thorium would be expected for a given size of reactor when oxide is used as a feed instead of oxalate. Also, ThO_2 is much cheaper than thorium oxalate. On the other hand, somewhat higher conversions are effected when oxalate is chlorinated, and reaction rates are faster. Further work specifically directed toward determining reactor throughputs is required to resolve this question.

A more serious problem pertaining to the use of Th(C_2O_4)$_2$ is the fact that the carbon impurity in chloride prepared directly from oxalate is much higher, from 180 to 1,700 parts per million, than chloride prepared from ThO_2, which usually contained less than 100 parts per million carbon.

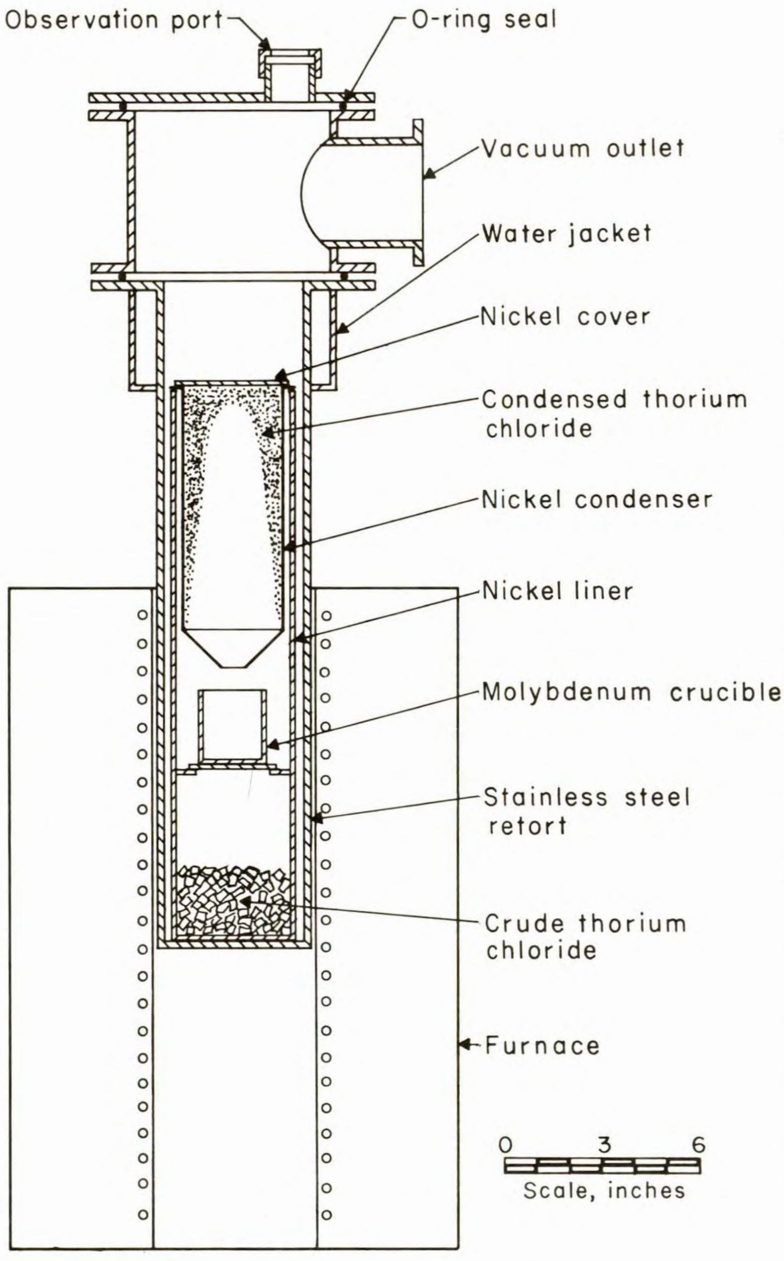

FIGURE 2. - Thorium Chloride Purification Apparatus.

Purification of Thorium Tetrachloride

Most of the $ThCl_4$ used in purification and subsequent reduction studies was prepared by chlorination of ThO_2 in a static-bed chlorinator, as described by Poppleton (6) in a previous paper. This was done for convenience and because of the availability of two static-bed chlorinators.

The crude $ThCl_4$ product from the static-bed reactors was purified by vacuum distillation in the apparatus shown in figure 2. Up to 1,000 grams of $ThCl_4$ was loaded into the 5-inch-diameter, nickel-lined retort. The chloride was then heated and distilled for 16 to 20 hours at 750° to 800° C under a dynamic vacuum of less than 0.5 micron. Generally, double distillation was necessary to produce high-purity chloride. After the first distillation the furnace was raised so that the condenser could be heated; the retort was backfilled with argon gas to 1 atmosphere pressure; and the condenser was heated slightly above 765° C, the melting point of $ThCl_4$.

The molten $ThCl_4$ ran from the nickel condenser into a collection crucible. Collection crucibles were constructed from either tantalum, molybdenum, or titanium. After distillation the condenser and retort were cleaned, and the chloride was redistilled from the crucible onto the condenser. After redistillation was completed, the retort was cooled to room temperature and backfilled with argon to 1 atmosphere pressure, and the condenser was removed from the retort. Because $ThCl_4$ is very hygroscopic, the condenser was transferred as rapidly as possible into a handling chamber with an inert atmosphere, where the $ThCl_4$ was removed from the retort. When larger quantities of $ThCl_4$ were required, a 13-inch-outside-diameter retort was used. This retort had the same basic design shown in figure 2. Approximately 20 kilograms of $ThCl_4$ was prepared in a single batch in this unit. The chloride was recovered as a dense cake, which was crushed, ground to minus 4-mesh size, and stored in 1-quart Mason jars under an argon gas cover. Typical analyses of both singly and doubly distilled chloride are given in table 4.

TABLE 4. - Typical analyses of thorium tetrachloride feed materials

Condition	Percent				Parts per million						
	C_2H_5OH insol.	H_2O insol.	Th	Cl	Al	Ca	Cr	Fe	Mg	Ni	Si
Crude chloride...	3.2	0.25	63.4	35.0	10	300	<40	40	40	30	150
Singly distilled.	1.2	.07	62.4	37.4	40	20	40	200	100	800	50
Doubly distilled.	.5	$<.03$	62.2	37.7	40	<10	20	100	60	40	20

Reduction of Thorium Tetrachloride

In previous studies (2), Kroll process procedures were used to prepare high-purity thorium by sodium or magnesium reduction. In this batch operation, sodium was preferred over magnesium as a reductant for several reasons, including the following: (1) Thorium sponge prepared by magnesium reduction was extremely dense and difficult to remove from the reduction crucible; (2) with magnesium the exothermic reaction was very rapid, difficult to control, and the heat evolved became increasingly more troublesome as the reduction scale was increased; and (3) because thorium forms stable compounds with magnesium ($ThMg_2$ and $ThMg_3$), a large excess of magnesium was needed to complete the reaction.

Since the primary purpose of this study was to produce magnesium-thorium alloy in a semicontinuous reactor, most of these objections were not applicable. It was anticipated that the problem of controlling the reaction and the related problem of handling the heat evolved could be avoided by controlling the rate at which $ThCl_4$ was fed into the reactor.

Initial reduction studies were performed in a U-tube reactor on the assumption that $ThCl_4$ and magnesium could be fed into one arm of the reactor and that byproduct $MgCl_2$ could be removed via an overflow weir in the other arm. It was also assumed that mixing and equilibration of thorium-magnesium alloy would take place in the right arm of the reactor. In practice, mixing and equilibration did not occur, and the composition of ingots cast from this type of reactor varied widely. Also, the tendency of $MgCl_2$ to freeze prevented its removal.

Because of operational problems associated with this design, a new and simpler reactor was constructed. This reactor, shown in figure 3, provided increased capacity, simplified operation, and gave better control of the composition of cast ingots.

The reactor, which was 3½ inches in diameter by 18 inches high, was constructed from type 430 stainless steel tubing, 1/8 inch thick. The top of the

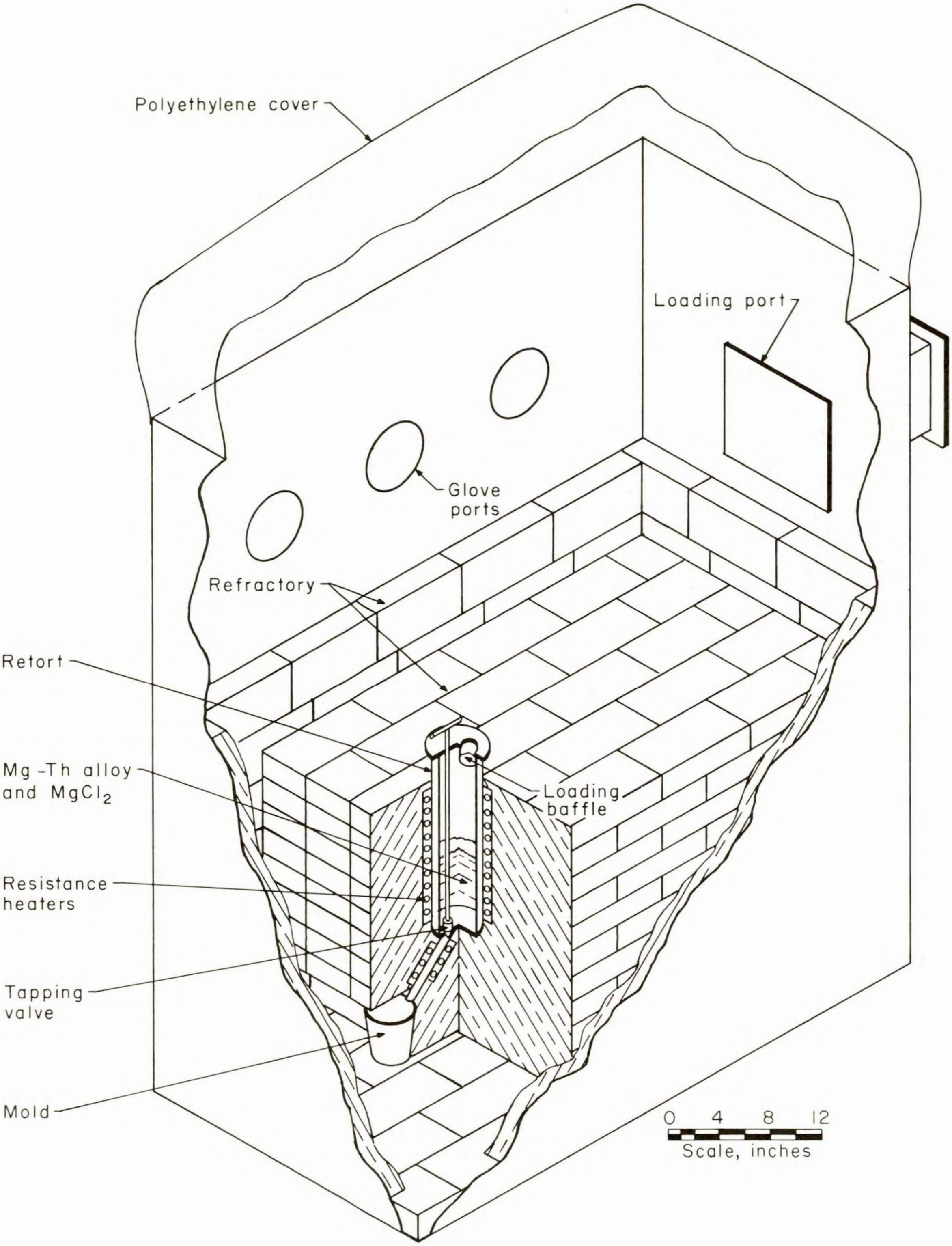

FIGURE 3. - Semicontinuous Reactor.

reactor was constructed of 22-gage stainless steel provided with a 2-inch feed opening and a loading baffle. The bottom of the reactor was 1/2-inch stainless steel plate. A conical surface, varying from 3/4 inch to 1/2 inch, served as a valve seat for a stainless steel (type 430) valve. The valve seat led into a 1/2-inch-diameter tapping hole which fed into a 1-inch-diameter downspout. During operation, alloy was tapped from the reactor by raising the valve stem about 1 inch. The reactor was heated by electrical resistors, and the entire assembly was encased in a refractory brickwork.

Thorium chloride and magnesium were stored in the loading port, which was evacuated and backfilled with argon. Prior to operation the reactor, the associated brickwork, and the polyethylene cover were also evacuated and backfilled with argon. This was done to minimize pickup of moisture or oxygen from the air during reduction of $ThCl_4$ by magnesium. The reactor was heated rapidly to 800° C, which melted the $MgCl_2$ byproduct salt remaining from the previous run. At this time, $ThCl_4$ and magnesium were transferred from the loading port while under the polyethylene cover and charged into the reactor.

The $ThCl_4$, which was stored in 1-quart Mason jars, was fed into the reactor directly from the jars as a free-flowing crystalline solid, whereas the magnesium reductant was introduced as 3/4- by 3/4- by 4-inch sections cut from pure ingot metal. Alternate additions of $ThCl_4$ and magnesium reductant were made periodically. The temperature in the reactor was maintained between 750° and 800° C during reduction. Sufficient magnesium was added to produce thorium-magnesium alloys containing from 20 to 45 weight-percent thorium. Feed rates from 0.25 to 1.5 kilograms of $ThCl_4$ per hour were utilized in this 3-1/2-inch-diameter, semicontinuous reactor. During operation, thorium-magnesium alloy was periodically tapped from the reactor and cast into molds via the tapping valve. The valve was then reseated, and additional feed was introduced into the reactor. This cyclic operation could be repeated as often as desired. Ingots produced in this way generally weighed from 0.5 to 1.5 kilograms. Reaction efficiency in terms of $ThCl_4$ was close to 100 percent.

Because $ThCl_4$ is hygroscopic and readily forms hydrates and also because small amounts of $ThOCl_2$ are formed during chlorination, there is some loss due to the formation of ThO_2 by the following reactions:

$$ThCl_4 \cdot XH_2O \longrightarrow ThO_2 + HCl$$

$$2ThOCl_2 \longrightarrow ThO_2 + ThCl_4$$

Most of this ThO_2 is easily recovered from the $MgCl_2$ byproduct salt since ThO_2 is insoluble in water and can be separated from the salt by simple water leaching.

When the reactor was shut down, the two to six ingots resulting from operation were removed from the molds by simple inversion and washed with water to remove $MgCl_2$. The wash water was filtered to recover ThO_2, and the $MgCl_2$ solution was discarded. The ingots were sectioned along the vertical axes, and small, 1/4-inch-thick samples were cut out for chemical and spectrographic analyses. The samples were analyzed chemically for thorium and ThO_2. Metallic impurities were determined by semiquantitative spectrographic analyses.

In most cases, alloys produced in the semicontinuous reactor contained 20 to 45 percent thorium. The nominal, or intended, composition of typical ingots and the results of chemical and spectrographic analyses on ingot samples are given in table 5. Table 5 shows that it was very difficult to maintain close control of alloy composition and that the alloys were not homogeneous; however, in most cases, the average percentage of thorium in the ingots corresponded reasonably well with the nominal compositions.

The lack of homogeneity in the ingots was attributed to two factors, these being inadequate mixing in such a small scale operation and the fact that the alloy was not held molten long enough to reach equilibrium. The authors believe that reasonably close control of alloy composition could be obtained in a commercial-scale reactor and that homogeneous ingots could be produced if a stirrer were used and if the alloys were allowed more time to attain equilibrium.

In most cases only minor amounts of metallic impurities were present in the alloy ingots. Aluminum and silicon impurities originated both from $ThCl_4$ and from the magnesium reductant. Nickel was picked up from the nickel liner used as a condensing surface during purification of $ThCl_4$, and iron, chromium, and manganese originated from minor attack on type 430 stainless steel reactor components.

Analysis of specimens from several ingots indicated that the chlorine content was consistently close to 0.02 percent. Inspection of table 5 shows a rather wide variation in the amount of oxygen in the thorium-magnesium alloys, ranging from none detected to 0.375 percent. In most cases, it was established that approximately 1,000 parts per million of oxygen was introduced into the thorium because of the presence of ThO_2 or $ThOCl_2$ in the $ThCl_4$ feed. Additional oxygen contamination originated from moisture present in the refractory brick and also from leaks in the canopy surrounding the reactor. The authors believe that minor modifications in reactor design and more care in handling $ThCl_4$ to prevent its reaction with moisture in the air would significantly reduce oxygen contamination.

Material-balance data indicated that over 95 percent of the ThO_2 present in the system (including $ThOCl_2$) collected in the byproduct $MgCl_2$ salt and about 5 percent or less collected in the alloy. Thorium oxide or oxychloride present in the $MgCl_2$ was readily recovered by simple water leaching and filtration. The recovered ThO_2 can be recycled to the chlorination step to produce $ThCl_4$.

A total of about 9.7 kilograms of thorium (as $ThCl_4$) was reduced during this study. Approximately 9 kilograms was recovered as thorium metal (elemental thorium or thorium-magnesium alloy) and 0.7 kilogram thorium as ThO_2. In summary, overall recovery of thorium exceeded 99 percent with approximately 93 percent recovered in metallic form and 7 percent recovered as ThO_2.

TABLE 5. - Chemical and spectrographic analyses of thorium-magnesium alloys

Th content, pct			ThO$_2$,[2] pct	O$_2$ in Th,[3] pct	Metallic impurities,[4] ppm					
Intended	Actual[1]	Average			Al	Cr	Fe	Mn	Ni	Si
20	22.1(C)	22.1	0	0	-	-	300-3,000	10- 100	-	-
20	18.1(T)	18.1	.39	.26	-	30- 300	100-1,000	100-1,000	30- 300	10- 100
	18.2(B)	-	0	0	-	30- 300	100-1,000	10- 100	30- 300	10- 100
25	22.6(T)	25.0	.35	.19	-	-	30- 300	10- 100	-	30- 300
	27.5(B)	-	.85	.37	-	100-1,000	300-1,000	10- 100	-	30- 300
30	25.8(T)	30.8	0	0	100-1,000	30- 300	100-1,000	10- 100	100-1,000	30- 300
	35.9(B)	-	.53	.18	100-1,000	30- 300	300-3,000	10- 100	100-1,000	30- 300
30	37.6(T)	39.3	.29	.09	100-1,000	-	100-1,000	10- 100	100-1,000	30- 300
	41.1(B)	-	.43	.13	100-1,000	3- 30	300-3,000	10- 100	100-1,000	100-1,000
35	23.3(T)	24.5	0	0	30- 300	-	30- 300	3- 30	100-1,000	30- 300
	25.7(B)	-	.31	.15	30- 300	-	30- 300	3- 30	100-1,000	30- 300
35	37.7(C)	37.7	.20	.06	30- 300	10- 100	30- 300	100-1,000	30- 300	30- 300
35	30.2(T)	35.8	.15	.06	-	30- 300	0.3-3(pct)	10- 100	30- 300	30- 300
	41.5(B)	-	.04	.01	-	30- 300	.3-3(pct)	10- 100	30- 300	30- 300
40	30.7(T)	40.8	0	0	30- 300	30- 300	10- 100	3- 30	100-1,000	1- 10
	39.2(M)	-	0	0	30- 300	-	30- 300	3- 30	100-1,000	10- 100
	52.4(B)	-	.53	.12	30- 300	-	30- 300	30- 300	100-1,000	10- 100

[1] Letters in parentheses indicate the part of the ingot from which sample was taken. C = composite. T = top. B = bottom. M = middle.

[2] ThO$_2$ determined by HCl-insoluble method.

[3] O$_2$ in Th = Wt insol. (0.121)/Th in alloy.

[4] Other elemental impurities below lower limits of detection; - represents not detected.

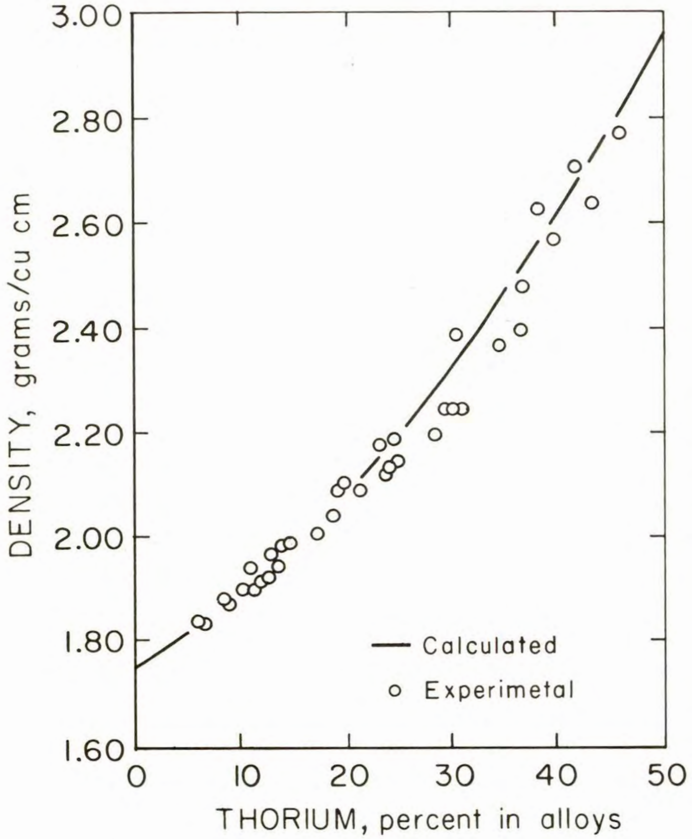

FIGURE 4. - Thorium Content of Thorium-Magnesium Alloys as a Function of Density.

Reactor Control by Density Measurement

Based on the assumption that the volumes of thorium and magnesium were additive, it was felt that the composition of the alloys could be related to their densities. If true, this would provide an excellent means for controlling the composition of alloys produced during operation of a semicontinuous reactor. Accordingly, the densities of the top, middle, and bottom sections of alloy ingots were determined, and the sections were analyzed for thorium content. These data are shown in figure 4, together with the calculated densities of thorium-magnesium alloys. The close agreement between calculated and experimentally determined densities can be seen by inspection of figure 4.

Production of Thorium From Thorium-Magnesium Alloy

It was reasonable to expect that thorium metal could be prepared from thorium-magnesium alloys by subjecting them to a vacuum distillation treatment; however, previous work showed that thorium sponge produced by magnesium reduction of $ThCl_4$ had a pronounced tendency to be pyrophoric. Accordingly, efforts were directed toward establishing distillation conditions which would yield a stable, nonpyrophoric, thorium product.

Sections of thorium-magnesium ingots weighing from 70 to 100 grams were placed in tantalum crucibles and subjected to vacuum distillation at temperatures from 600° to 850° C and absolute pressures from 0.1 to 65 microns. When distillation was conducted for 16 hours at temperatures above 750° C and at absolute pressures of less than 1 micron, excessive bumping and spattering occurred, with subsequent loss of thorium. When distillation was conducted at 600° to 650° C, an excessive amount of time (more than 24 hours) was required, and the thorium products contained from 1 to 10 percent magnesium. These alloys were pyrophoric and tended to burn when exposed to air.

The best results were obtained when distillation was conducted for 16 hours at 700° to 750° C with an absolute pressure of 65 microns. Under these conditions, little or no bumping or spattering occurred, and a nonpyrophoric, relatively dense, thorium product was recovered. Chemical and spectrographic analyses of thorium alloy sections, prepared by vacuum distillation of thorium-magnesium alloy at 700° to 750° C and 65 microns absolute pressure, are given in table 6. The run shown is considered typical.

TABLE 6. - Chemical and spectroscopic analyses of thorium

Element	Ppm	Element	Ppm
Al	40	Ni	200
Cr	400	Si	100
Fe	300-3,000	O_2[1]	1,200
Mg	300-3,000	Th[2] (pct)	99.2-99.75
Mn	200		

[1] Oxygen determined by Leco method.

[2] Determined by difference.

Inspection of table 6 indicates that while only nominal amounts of metallic impurities were present in the thorium product, it contained undesirably high amounts of oxygen. The authors believe that thorium containing less than 500 parts per million of oxygen could be produced if sufficient care were taken to prevent exposure of $ThCl_4$ to atmospheric moisture prior to reduction and if air and moisture were rigorously excluded from the reduction apparatus.

CONCLUSIONS

This work demonstrated that $Th(NO_3)_4 \cdot 4H_2O$ can be decomposed thermally to ThO_2 below 300° C and that this oxide, or alternatively $Th(C_2O_4)_2$, can be converted to $ThCl_4$ in a fluidized-bed reactor. It was further shown that $ThCl_4$ can be reduced by magnesium in a semicontinuous reactor to form thorium-magnesium alloys and that reasonably pure thorium metal can be recovered from the alloys by subjecting them to vacuum distillation to remove magnesium.

The work also demonstrated that almost 100 percent of the thorium fed into the process can be recovered as either thorium-magnesium alloys or thorium metal and that unreacted ThO_2 can be recovered readily and recycled into the process. Over 93 percent of the thorium charged into the reactor was recovered in metallic form, and approximately 7 percent was recovered as ThO_2.

REFERENCES

1. Glasstone, Samuel. Sourcebook on Atomic Energy. Van Nostrand Co., Inc., New York, 1950, pp. 406-408.

2. Good, P. C., and F. E. Block. Metallic Reduction of Thorium Tetrachloride. BuMines Rept. of Inv. 5702, 1960, 12 pp.

3. Hampel, Clifford A. Rare Metals Handbook. Reinhold Publishing Corp., New York, 1961, pp. 536-558.

4. Leontis, T. E. New Magnesium Alloys for High Temperature. Metal Prog., v. 72, No. 8, August 1957, pp. 97-103.

5. Pitts, Frank. Improvements in or Relating to the Extraction of Thorium From Thorium Chloride and to the Production of Magnesium-Thorium Alloys. U.K. Pat. 882311, Nov. 15, 1961, 3 pp.

6. Poppleton, H. O., and F. E. Block. A Process for the Preparation of Thorium by Sodium Reduction of Thorium Tetrachloride. BuMines Rept. of Inv. 6527, 1964, 20 pp.

7. Rossmassler, W. R., and R. L. Harris. Fluidization in Tapered Beds. U.S. AEC Rept. KT-240, 1958, 7 pp.

8. Stevens, Richard F., Jr. Thorium. Ch. in BuMines Minerals Yearbook, 1968, v. 1-2, 1969, pp. 1067-1072.