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PHYSICAL AND INORGANIC SECTION

A METHOD OF RECOVERING THORIUM FROM SLAG MATERIALS

PROBLEM ASSIGNMENT - #16

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ABSTRACT

A method of recovering thorium from slag from the bomb process of producing thorium has been developed. HCl and NaOH are the only chemicals required in quantity. Materials required for a representative slag are given.

Fusion with ammonium oxalate was studied as another possible method. The fusion must be carried out in a nickel or monel crucible at 550°C, and the weight of ammonium oxalate required is four times that of the slag. There is considerable frothing during the fusion. To completely dissolve the melt, it must be removed from the crucible and boiled with aqua-regia in a Pyrex beaker. Although the reagents required are not costly, the process is not readily adaptable to large scale operations.

Digestion with ferric nitrate solution and ferric nitrate-nitric acid mixtures did not dissolve the slag residue.

Experiments using a metathesis reaction with a 50% sodium hydroxide are the most promising of the methods. This process converts the thorium salts to the less soluble thorium hydroxide. After a four-hour boiling, the thick slurry is diluted with water to about four times the volume and filtered. The residue which still contains all the thorium, is extracted with 6 N hydrochloric acid. A second treatment with sodium hydroxide can be carried out on the residue if assay shows it to contain much thorium. From a limited number of experiments it appears that one such treatment will be sufficient. This method is practicable because the sodium hydroxide treatment can be carried out in an iron vessel and the chemicals required are relatively inexpensive.

III. Proposed Process for Recovery of Thorium from Slag

The figures given below are for a representative slag sample weighing one kilogram.

Step 1. Leach with one liter of water. Filter, discard filtrate.

Step 2. Treat the residue from the water leach (1220 grams when dried) with conc. hydrochloric acid. 3300 ml or 7.32# of conc. hydrochloric acid are required. Filter; filtrate contains thorium and is 1-3 normal in HCl. Add 10 ml conc. nitric acid. Add a solution containing 70 grams of oxalic acid (100% excess) and let stand for 12 hours. 81 grams of the oxalate (= 46.2 grams thorium) are produced.

A Method of Recovering Thorium from Slag Materials

I. Introduction

The slag from the reduction of thorium fluoride with calcium and using zinc chloride as a booster contains the following substances: Ca, CaO, ThO₂, Fe, ZnF₂, CaF₂, Zn, Th, and unreduced ThF₄. It is desired to extract the thorium from this slag and precipitate it in a form suitable for reconversion to anhydrous thorium fluoride.

II. Experimental

It has been found that a water leach serves to disintegrate the slag material very well. Since much heat is produced in the reaction, the slag is added to water. There is evolution of hydrogen and acetylene and a thick slurry is formed. All of the thorium remains in the solid phase. The filtrate which is saturated with calcium hydroxide can be discarded.

A treatment of the above residue by concentrated hydrochloric acid dissolves all free thorium metal, thorium hydroxide, iron, calcium oxide and zinc salts. The insoluble material is calcium fluoride, thorium fluoride, and thorium oxide.

The filtrate is made 1-3 normal in hydrochloric acid and thorium is precipitated by adding oxalic acid. Before this precipitation of thorium oxalate, a small amount of nitric acid is added to keep iron in ferric form and prevent co-precipitation of ferrous oxalate. Twelve hours are required for complete precipitation of thorium oxalate.

Several methods have been tested to recover the remaining thorium from the acid insoluble residue. A sample of slag was digested with conc. sulfuric acid for five hours and the resulting slurry poured into cold water. The filtrate contained only about 5% of the total thorium in the residue.

Digestion of the acid insoluble residue in 60% perchloric acid proved to be very effective. Five grams of the residue dissolved in 10 ml conc. perchloric acid in two hours of heating. The cost and unavailability of large quantities of perchloric acid prohibit the use of this method on a recovery process, but it does constitute a convenient method of assaying slag for total thorium content.

Step 3. The acid insoluble residue (230 grams) is mixed well with 200 grams of flake sodium hydroxide and water added to give a volume of approximately 400 ml. It is gently boiled for four hours. It is then diluted to 1-2 liters and filtered. The filtrate is discarded and the residue treated with 6 normal hydrochloric acid. The treatment is repeated on the residue obtained in the above step, using about 50 grams of sodium hydroxide.

The final residue of insoluble material = 37 grams. In the samples to date, solution of this final residue in perchloric acid solution using 12 grams of oxalic acid. This amount of thorium oxalate is equivalent to 8.6 grams of thorium metal.

The amount of hydrochloric acid required after the first hydroxide treatment is about 500 ml and 200 ml after the second cycle. Excess hydroxide must be neutralized and the solution made from 1-3 normal in hydrochloric acid before precipitation of the thorium oxalate.

IV. Quantities of Material Required and Product Obtained (per 1000 grams of slag)

- a) Total thorium recovered: 55 grams (as metal) (This will depend on the efficiency of the reduction process.)
- 1) 83.5% from step 2
 - 2) 16.5% from NaOH treatment
- b) Hydrochloric Acid required:
Step 2	3300 ml or 7.32#
Step 3	<u>700 ml or 1.56#</u>
Total	4000 ml or 8.9 #
- c) Oxalic Acid required:
Step 2	70 grams
Step 3	<u>12 "</u>
Total	82 grams
- d) Sodium Hydroxide required:
Step 3	250 grams

Thorium oxalate has been chosen as the final precipitate of the thorium because it can be conveniently converted to thorium fluoride, the oxalate is easily filtered, and its precipitation offers a convenient separation from iron. The extent of co-precipitation of calcium is small. In an experiment in which 1% of calcium was added to the solution from which thorium oxalate was to be precipitated, there was 100 ppm of calcium in the thorium oxalate.

Oxalic acid is used as the precipitating agent rather than ammonium oxalate since it has been found to give a precipitate which is more easily filtered.