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Preparation of highly pure thorium nitrate via thorium sulfate and thorium peroxide

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Abstract

A simple alternative and selective method has been proposed for the preparation of thorium nitrate using as raw material a hydrated crystalline technical grade thorium sulfate. This salt was produced industrially [1] from the alkaline chemical processing of monazite sand in S. Paulo. From a crude thorium hydroxide as the raw material containing uranium and rare earth elements was prepared a technical grade thorium sulfate [$Th(SO_4)_2.9H_2O$]. A typical analysis of this salt had shown the following composition: ThO_2 47–53%, R_2O_3 (rare earth oxides) 0.5–0.9%, and UO_3 0.01% and minor amounts of iron, titanium, phosphorus, and silicon oxides. The thorium sulfate is dissolved into water and the thorium peroxide is precipitated from acidic medium by addition of hydrogen peroxide. The thorium peroxide is filtered, washed and finally dissolved with nitric acid. Samples of the thorium peroxide were dried and fired to ThO_2 and aliquot of the thorium nitrate solution was evaporated to dryness and calcined to obtain the ThO_2. Both ThO_2 have high purity ($>$99.5%). The content of total rare earth elements is very low (0.23% as oxide). Uranium was not detected. The great majority of the RE is precipitated and recovered from the filtrate by oxalic acid. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

An alternative process is described in this paper for the separation of thorium from rare earths and for the production of highly pure thorium nitrate by controlled preferential precipitation of thorium peroxide. The initial raw material is a technical grade thorium sulfate produced industrially from the Brazilian monazite. The monazite sand is attacked with sodium hydroxide transforming the mineral into water-soluble trisodium phosphate and mixed hydroxides of the rare earth elements and of thorium. This process has been in practice as an industrial scale (2000 tons of monazite per year) since 1949 until 1992.

Some technically pure thorium compounds have been obtained from a crude thorium hydroxide prepared from the alkaline decomposition of monazite [1]. From this thorium hydroxide the correspondent thorium sulfate was produced by the addition of ethanol to a supersaturated thorium sulfate solution.

Addition of hydrogen peroxide to Th^{4+} salts gives a highly insoluble white precipitate of variable composition. The older literature [2] gives thorium peroxide variously as Th_2O_7 and ThO_3 when it is precipitated by hydrogen peroxide from mildly acidic solutions in the presence of ammonium salts. This technique was used in the past only as an analytical separation purpose.

Although for uranyl peroxide there are considerable number of publications in the scientific literature, information for thorium peroxide is very scarce. A reexamination of the literature was undertaken and most of the results reported are for uranium peroxide. A patent has been applied for the conversion of uranium tetrafluoride hydrate into an uranium(VI) peroxide hydrate [3]. A proprietary process is described for the production of sintered nuclear fuel pellets from precipitated solutions with the aid of hydrogen peroxide in an acid medium [4].

Uranium concentrates obtained from leach solutions are known as uranium yellow cakes and represent an intermediate step in the processing of uranium ores. In the nuclear industry the main types of yellow cakes are uranyl hydroxide hydrate, sodium diuranate and ammonium diuranate. Uranyl peroxide hydrate is also included in the group. This is an intermediate compound, whose use is increasing in the nuclear cycle. On the other hand, thorium peroxide is not an usual compound in the production of large scale thorium.

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In this paper the precipitation of thorium peroxide as a technology is considered very convenient, allowing the production of a highly pure thorium compound free from the rare earth elements. The raw material is a crystallized thorium sulfate produced in relatively large scales and stocked for several years. The dissolution of the thorium peroxide with nitric acid leads to a very pure thorium nitrate, still demanded by the local gas mantle industry. IPEN, S. Paulo, is the unique supplier of this material to the local industry.

2. Thorium sulfate as raw material

Thorium sulfate crystallizes in the form of several hydrates with 4, 6, 8 and 9 H_2O [5].

The thorium sulfate used in this work was obtained industrially [1] as the 9-hydrate species. This material has a solubility in water of 15.7 g/l at 20°C and 67.6 g/l at 55°C. A anhydrous thorium sulfate can be obtained by treating the 9-hydrate at 400°C. The anhydrous thorium sulfate is very soluble in cold water. A typical analysis [1] is given in Table 1.

Table 1
$Th(SO_4)_2.9H_2O$ analysis

Species	(%)
ThO_2	47.0
Rare-earth oxides	0.05
Fe_2O_3	0.1
TiO_2	0.02
P_2O_5	0.045
SiO_2	0.02
UO_3	0.01

3. Production of nuclear grade thorium nitrate via solvent extraction

The alkaline process for breaking up monazite sand has being practiced in Brazil since 1948 in an industrial scale. A thorium concentrate is obtained in a very suitable form for solvent extraction and has been used for the purification of thorium by extraction with TBP-varsol after dissolving with nitric acid.

Supported by several years work at large laboratory scales in the purification of thorium nitrate, a pilot plant was erected based on solvent extraction of thorium nitrate using 50% (v/v) TBP-varsol [6]. The obtained thorium nitrate solution of high purity is designed to be converted into thorium oxide. The thorium pilot plant was equipped to be able to supply crystallized $Th(NO_3)_4.4H_2O$, thorium oxalate and a highly concentrate thorium nitrate solution (about 900 g ThO_2/l).

The purification step is accomplished with a compound extraction–scrubbing pulsed column. The thorium concentrate is a crude thorium hydroxide containing uranium and chloride ions. For this reason the pilot plant is equipped with a section for preparation of a slurry of thorium hydroxide that is further filtered to get rid of chloride ions before the dissolution with nitric acid. The thorium nitrate is extracted with TBP-varsol after addition of sodium nitrate (2.2 M) and free nitric acid (0.8 M). The organic phase rich in thorium nitrate can be scrubbed with 2.2 M $NaNO_3$–0.8M HNO_3 or with pure $Th(NO_3)_4$ solution. Finally thorium nitrate is stripped from the organic phase with demineralized water.

For several years IPEN produced highly pure thorium nitrate starting with a second concentrate, the thorium sulfate. Initially the raw material was converted to thorium hydroxide by treatment of the thorium sulfate with sodium hydroxide–sodium carbonate. The obtained hydroxide is filtered and exhaustively washed with water until nearly complete elimination of the soluble sodium sulfate. Further operation is the dissolution of the hydroxides (thorium and rare earths) with nitric acid and adjustment for the purification by solvent extraction in the $Th(NO_3)_4$–HNO_3–TBP–Kerosene system by pulsed columns. The final product from this installation is a very pure thorium nitrate used internally in the various investigation projects for the fuel cycle at the IPEN.

For several years IPEN has being supplying thorium nitrate to the private gas mantle industry and this business is still active.

Recent experiments were scheduled envisaging the preparation of thorium nitrate from the thorium sulfate via the peroxide, avoiding the solvent extraction process. This process allows the use of stocked thorium sulfate and generates practically no waste.

4. Dissolution of the thorium sulfate for the precipitation of the thorium peroxide

Working out about 30 dissolution experiments using the thorium sulfate as received from the stock the practical figures for the dissolution in demineralized water were confirmed, achieving in media about 10 g l^{-1} at 20–25°C and 59 g l^{-1} at 50°C.

The experiments for the precipitation of the thorium peroxide were performed using 3 l solution. Recently a first experiment of a series was performed using a volume of 300 l of solution (3 kg thorium sulfate).

5. Experimental, reagents and apparatus

Crystallized thorium sulfate (see Table 1) was used as received from the stockpile. Hydrogen peroxide (30%) was purchased in carboy quantities and nitric acid was of analytical grade. Precipitation experiments were performed using a glass 4-l beaker and mechanically stirred.

6. Precipitation of the thorium peroxide and rare earth separation

For the dissolution of the thorium sulfate 30 g of the solid was poured slowly into 3 l of demineralized water under agitation at room temperature (20–25°C). Agitation time is about 80 min. The final solution is reasonably clear. At the end of the dissolution the pH of the solution is in the range of 2.57–2.90. Following that is the addition of hydrogen peroxide (30%) over few minutes, under agitation. The amount of hydrogen peroxide is in excess of the stoichiometric value. After the addition of the hydrogen peroxide the agitation is continued for about 90 min. Periodically a small sample was withdrawn from the reactor, filtered and the filtrate checked by addition of hydrogen peroxide to assure the complete thorium precipitation.

The thorium peroxide is vacuum filtered, the precipitate washed with a 0.01 mol l^{-1} HNO_3 and the filtrate tested for sulfate. Washing is finished when sulfate is not detected with Ba^{2+}.

7. Dissolution of the thorium peroxide and preparation of the thorium nitrate

The peroxide is transferred to a beaker and treated with 7.5 mol l^{-1} HNO_3, under agitation. The addition of nitric acid is controlled to avoid large excess. This thorium nitrate solution will be used for the gas mantle fabrication.

8. Recovery of rare earth elements

The rare earth elements are recovered from the thorium peroxide filtrate by addition of oxalic acid. The rare earth oxalate is filtered, washed and calcined in the usual fashion to obtain the rare earth oxides.

9. Results and discussion

Analytical control of the thorium peroxide was made after calcining the peroxide to ThO_2 and analyzing this oxide by spectrographic technique and X-ray fluorescence. The obtained thorium oxide is extremely white, which is an indication of purity. A representative analysis of the thorium oxide prepared via peroxide and directly firing at 800°C is following (Table 2):

Table 2
Typical analysis of ThO_2 produced from the thorium sulfate via peroxide. XR fluorescence analysis

Oxide	$\mu g\ g^{-1}$
Fe_2O_3	841
SiO_2	489
Na_2O	444
Sc_2O_3	315
PbO	245
Nd_2O_3	179
Eu_2O_3	161
MgO	121
Al_2O_3	66
Er_2O_3	53
CaO	52
Sm_2O_3	50
Tb_4O_7	45
Pr_6O_{11}	20
Tm_2O_3	<20
Y_2O_3	<20
La_2O_3	<20
CeO_2	<20
Gd_2O_3	<20
Yb_2O_3	<20
Lu_2O_3	<20

If the precipitation pH is rigorously controlled and maintained at the 2.0–2.5 range, the precipitation of thorium is almost complete. In various experiments, although the test of the filtrate with hydrogen peroxide indicated absence of thorium, the spectrochemical analysis of the rare earth oxides obtained using the peroxide filtrate had shown the presence of some thorium.

The thorium nitrate prepared by the technique here discussed is pure and conforms to the requirement for the gas mantle fabrication.

The biggest drawback found in this process is the relatively large volume of water used for the dissolution of the thorium sulfate. The data collected from various experiments lead to the conclusion that 1 kg of thorium sulfate requires 83 l of water, 5 l of 30% hydrogen peroxide for the precipitation of the peroxide and 4.33 l of 0.75 mol l^{-1} HNO_3 for dissolution of the peroxide.

Although it is stated in the old literature [7] that the thorium peroxide contains in its composition an excess of anions, specially in the case of the precipitate prepared in the presence of sulfuric acid ($ThOOSO_4.3H_2O$, named thorium peroxide sulfate), the product obtained in this work is free of sulfate. Every batch of thorium peroxide prepared was checked for sulfate using the barium sulfate precipitate test, and in no case sulfate was found.

A feature indeed is the ease of separation of rare earth elements from thorium by the precipitation of thorium peroxide at low pH. The raw material used in this work, as mentioned before, is a good quality thorium sulfate, whose main impurity are the rare earth elements. The thorium peroxide is an interesting intermediary product, allowing the preparation of salts by treatment with the correspondent acids or can easily be fired to thorium oxide.

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