



Original Article

A novel Procedure for the Recovery of Rosetta Monazite Metal Values through its Acid Treatment

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ABSTRACT

Egyptian monazite is chemically processed after its breakdown using sulfate process for recovering of REEs, thorium and uranium. Beside removal of these elements as radioactive contaminates from REEs products, their recovery would increase to their importance in the field of nuclear energy. In this work Egyptian monazite with 90% concentrate was used. The later has 57.8% of REEs in addition to thorium and uranium assays 5.8% and 0.29% respectively as well as small quantity of ferric oxide, titanium oxide and silica. In this work monazite is digested in 2M sulfuric acid where Th^{4+} ion combine with sulfate ions to form anion complex and uranyl complex whose passes through strong cation resin Amberlite IR120 where thorium precipitated using oxalic acid leaving behind uranium which precipitated at 5.5 pH as uranyl phosphate. On the other hand REEs adsorbed on resin completely by excess addition of hydrazine sulfate to reduce Ce (IV) to Ce (III) followed by elution with 4N HCl to form pure REEs.

Key words: Egyptian monazite, REEs, Thorium and Uranium.

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INTRODUCTION

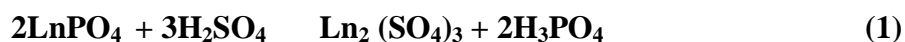
Monazite is one of the three most important source minerals of lanthanides while the other two minerals are xenotime and bastnasite. Monazite and xenotime are phosphates of the light and heavy lanthanides respectively whereas bastnasite is a fluorocarbonate of the light lanthanides. Thorium and to much less extent uranium are generally associated with the lanthanides and their assay in monazite attain 5 to 6% and <1 respectively. In other words the mineral monazite is composed of rare earth phosphates (Ce, La, Nd) PO_4 (Harlov *et al.*, 2002; El-Nadi, 2007; Kim *et al.*, 2009; Clavier *et al.*, 2011) in addition to thorium and uranium to a much less extent. According to Cuthbert (1958) monazite is essentially a phosphate of Ce and La in which Th and minor Y substitute for Ce, Its general chemical formula is (Ce, La, Y, and Th) PO_4 , in which Th and U constitutes are about 5-10% and 0.1-0.4%, respectively besides a few to moderate concentrations of Fe, Al, Ca, Si, Ti and Zr while Large commercial detrital

deposits of the former are found in Australia, USA, India, Brazil and Egypt (Abdel-Rehim, 2002).

In Egypt monazite occurs as large reserves in the heavy black sands that extend along the beaches of the northern parts of the Nile Delta from Rosetta to Damietta (Anwar and Abdel-Rehim, 1970; Rittman and Nakhla, 1958; Higazy and Naguib, 1958; Elshazly, 1965; Hellal *et al.*, 1986) have reported that the RE₂O₃ attain 62-64%, together with 5-6% ThO₂, 0.4-0.48% of U₃O₈ and 26.74-27.84% of P₂O₅. As a matter of fact uranium, thorium and rare earth elements are actually considered as important industrial metal value that are also required in several environmental and applications (Borai and Mady, 2002).

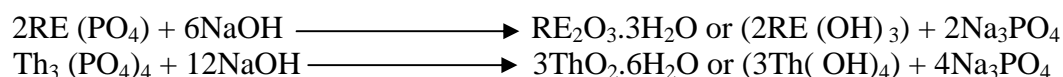
El-Shazly (1965), has estimated the reserves of heavy economic minerals in million metric tons as about 30 in the top meter and about 615 in the top 20 m. Besides the REEs, the Egyptian black sand beach deposits are considered as the chief thorium ore in Egypt due to the presence of monazite (Farrag, 1979; El-Nadi *et al.*, 2005).

In the field of processing, there are actually two main processes for the breakdown of monazite concentrate, namely the sulfuric acid treatment and the alkali caustic soda method. The former method produces a monazite sulfate solution of U, Th and REEs while silica, zircon or other admixed gangue minerals are left insoluble.



Several processes have previously been studied for the recovery of pure mixed REEs as well as Th and U products from the sulfuric acid breakdown method (Audsey *et al.*, 1958; Baddery *et al.*, 1959; Gupta and Krishnamurthy, 1992). However, complete separation of such pure products by these methods is generally difficult and would require another excessive manipulation and in turn relatively high costs. In this regard, Moustafa and Abdelfattah (2009) have suggested separation of the REEs by direct application of anion exchange resin upon the monazite sulfate liquor after adding hydrazine sulfate reagent to insure the presence of Ce (IV) in its trivalent state. This stage would thus separate the REEs from both U and Th which could exist in their anionic complex forms to be later properly separated.

The second method for monazite breakdown is the alkali caustic soda which according to George *et al.*, (1958) and Grainger (1958), the ratio of caustic soda depends on the source, purity and particle size of the monazite ore concentrate. The temperature of the sodium hydroxide treatment should be maintained at 140°C to avoid the formation of a proportion of hard refractory oxide and at the same time to maintain high breakdown efficiency. This relatively low temperature necessitates grinding of the ore to less than 300 mesh, and then adding gradually over a period of 30 minutes. The reaction time is limited to 3 hours and can be represented as follows:



In the alkali treatment of monazite, both thorium and uranium would accompany rare earth elements. The result out hydrous oxide cake. While the excess caustic soda could be recovered for recycling, a tri sodium phosphate results as a byproduct. In the meantime some silica would react with the caustic soda forming a soluble sodium silicate. The result and hydrous oxide cake could then be dissolved in a suitable acid for their separation and recovery as marketable concentrates. In this regard, it can be mentioned that a nitric acid solution of the hydrous oxide cake can first be subjected to solvent extraction using tributyl phosphate for Th and U extraction. However, partial oxidation of Ce (III) to Ce (IV) would result in subsequent extraction of the latter with U and Th. On the other hand, it has also been reported that successful separation of the 3 metal values would start by first precipitating both U and Th

cake from the acid solution by its neutralization to pH 5.8-6.3 followed by its further neutralization to pH 10 to obtain the REEs cake. For Th/U separation and recovery from their cake, different techniques have indeed been used.

According to Janúbia and Carlos (2010) simultaneous solvent extraction of both Th and U could be achieved from the sulfate leach liquor of the hydrous oxide cake by using a mixture of Primene JM-T and Alamine 336. A loaded stripping solution containing 29.3 g/l of ThO₂ and 1.27 g/l of U₃O₈ has thus been obtained. The metals content in the raffinate was below 0.001 g/l, indicating a thorium extraction of over 99.9% and a uranium extraction of 99.4% while the rare earths content in the raffinate has attained 38 g/l as RE₂O₃. On the other hand, Hammad *et al.*, (1986) have separated U from the Egyptian monazite alkaline hydrous oxide cake concentrate being dissolved in concentrated HCl solution by anion exchanger column containing Amberlite IRA400. From the effluent Th effluent was purified by extraction from nitric acid medium by TBP diluted in kerosene.

However, complete separation of such pure products by these methods is generally difficult and would require another excessive manipulation and in turn relatively high costs. In this regard, (Moustafa and Abdel fattah, 2009) have Suggested separation of the REEs by direct application of a cation exchange resin (Dowex 50w) upon the monazite sulfate liquor after adding hydrazine sulfate reductant to insure the presence of Ce (V) in its trivalent state. This step would thus selectively eliminate REEs from both U and Th which are exist in their anionic complex forms namely (Th(SO₄)_n)⁴⁻²ⁿ and (UO₂(SO₄)_n)²⁻²ⁿ) to be later properly separated.

Also, it has to be indicated herein that Amer *et al.*, (2013) have been able through alkali breakdown of Rosetta monazite and subsequent dissolution of the hydrous oxide cake in sulfuric acid to precipitate both REEs and Th as their oxalates for their later separation by selective carbonate leaching of the latter.

This work is actually concerned with studying in detail the proper conditions required for quantitative separation of the 3 metal values through sulfuric acid digestion and applying the cation exchange resin Amberlite IR120. To realize this objective a representative monazite concentrate sample was digested in 2M sulfuric acid where Th⁴⁺ ion would combine with sulfate ions to form anion complex which together with the uranyl sulfate complex would passes through the cation resin bed. From the resin effluent thorium would be precipitated using oxalic acid leaving behind uranium to be later precipitated at pH 5.5 as uranyl phosphate. On the other hand the REEs adsorbed on the resin have almost been completely by eluted with 4N HCl to form pure RE chlorides.

EXPERIMENTAL

Materials

The monazite used in this study was obtained from the black sand deposited of the Rosetta area on the Mediterranean coast, using appropriate upgrading techniques (Mustafa, 2003).

Preparation of monazite sulfate leach liquor

About 100 g sample portion of Rosetta monazite concentrate 90-97% and ground to a mesh size 100-200 mesh was treatment with concentrated sulfuric acid at a ratio of S/L 1:2 at 250°C for 4 hours. After digestion, the digested cake was properly water diluted to an acidity of acid 2N.

Preparation of Amberlite IR120 resin column

A resin bed of about 500 ml volume of Amberlit IR 120 resin (-100 mesh size) was properly paked in a glass column of 100cm length and 5cm diameter. To ensure the resin to be in its H⁺ form 10% H₂SO₄ acid solution was passed through the resin bed. The saturation capacity of the working resin is given as 1.7 meq / ml.

Experimental procedure

A series of factors have been studied such as the normality of sulfuric acid of sulfate leach liquor. The quantity of hydrazine sulfate added for convert Ce (IV) to Ce(III).

Analytical procedures

REEs and Th analysis

Analysis of the REEs and Th in the prepared monazite sulfate leach liquor as well as in different stream solution was performed spectrophotometrically achieved using Arsenazo III (Marzenko, 1986). On the other hand, uranium in the monazite sulfate leach liquor as well as in the different stream solution was titrimetrically achieved using ammonium Meta vanadate.

Laser-Fluorimetric Determination of Uranium

Uranium was determined in sulfuric acid solution without prior extraction using N₂-Laser Fluorimetric Technique (UA-3) as follow:

A suitable sample volume (10-50) μ l was mixed with the prepared buffer solution by the ratio buffer to sample = 2:3 (Tikoo and Murty, 1980), completed up to 7 ml with distilled water in the cuvette cell and mixed well.

The fluorescence of the measured standard uranyl solution in the cell was compared with the sample and internal standard measurements (Robbins, 1978).

RESULTS AND DISCUSSION

Characterization of Rosetta monazite Concentrate

The chemical composition of the representative working sample of Rosetta monazite concentrate (90 % purity) is summarized in the table (1) after Bakry (2011).

Table 1: The chemical composition of the representative Rosetta Monazite concentrates (90 % purity)

Component	Wt., %	Component	Wt., %
RE ₂ O ₃	57.80	TiO ₂	2.80
ThO ₂	5.80	P ₂ O ₅	27.35
U ₃ O ₈	0.29	SiO ₂	2.07
Fe ₂ O ₃	3.00	Total	99.11

This table indicates that Rosetta monazite is the main source for REEs is 57.80%, Th is 5.8 % and U is 0.29 %, for that we trials for the separation of REEs, Th and U as follow:

Description of the Process

About 500ml of monazite sulfate leach liquor were enough for saturated 500ml of cation resin. The fraction takes every 100ml of sulfate liquor for analysis of REEs, Th and U, after prior hydrazine sulfate add to sulfate leach liquor in different quantity 0.5 g/L and 2 g/L for liquor to reaches complete reduction of Ce (IV) to Ce(III). The cerium (IV) compound present in the sulfuric acid is reduced with a reducing agent and then an ion exchange is affected. According to (Sherief and Almasy, 1968) the concentration of sulfuric acid used is adjusted to a value of about 2M free acid content.

Separation of pure REEs

The prepared monazite sulfate leach liquor which contains 54.5 g/l RE₂O₃ while ThO₂ assays 5.2 g/l and UO₂ assaying 0.23 g/l after analysis spectrophotometrically using Arsenazo III (Marzenko, 1986) was then passes using a flow rate 5ml/min through 500 ml of Amberlit IR 120 cation exchange resin bed in its hydrogen form. The resin is packed in a100 cm length and 5 cm diameter glass column. The grain size of the resin is -100 mesh and its saturation capacity is (1.7 meq/ml w.s.r) of wet settled resin. The resin saturated after the passage 500

ml of monazite sulfate leach liquor. The adsorbed REEs was eluted by 4N HCl followed by precipitated using NaOH at pH 9-10 to precipitate the total REEs as their hydroxide. The precipitate was ignited at 900°C for one hour to obtain the pure RE₂O₃ in table (2) experimental No.1 about 35g net weight of pure RE₂O₃ which would indicate a recovery efficiency of about 60% while in table (3) the experimental No.2 the net weight of pure RE₂O₃ 48g where the recovery efficiency increasing to about 85.5%. The increasing of recovery efficiency may due to the amount of Ce(IV) in sulfate leach liquor in experimental 2 was reduced completely to Ce(III) by excess adding of reducing agent of hydrazine sulfate.

Table 2: Effect of addition 0.5g/l hydrazine sulfate upon reduction of Ce

Volume, ml	Th, g/l	Ce, g/l	U, g/l
100	5.1	15.2	0.21
100	4.8	13.2	0.20
100	5.1	14.5	0.18
100	4.9	17.6	0.20
100	4.98	25.7	0.19

Thorium and Uranium Separation

The reduced solution after hydrazine sulfate addition in various amount as in table 2 and 3 which indicated that adding the reducing agent in excess is necessary in order to avoid the oxidation of the solution upon contacting air. The reduced solution passing through a strong acidic cation exchange resin column, thorium passes through resin due to it can combine with sulfate ions to form anionic complex compound Th(SO₄)_n⁴⁻²ⁿ.

Table 3: Effect of addition 2g/l hydrazine sulfate upon reduction of Ce

Volume, ml	Th, g/l	Ce, g/l	U, g/l
100	5.10	0	0.20
100	4.92	0	0.19
100	4.79	0	0.17
100	5.10	2.5	0.18
100	5.00	5.4	0.19

In the meantime, the uranyl ion UO₂²⁺ could also form anionic complexes of the type (UO₂(SO₄)_n)²⁻²ⁿ where n could be 1, 2 or 3 (Preuss and Kunnin, 1956). Accordingly, uranium and thorium would be thus pass freely through the resin with thorium to be later separated table (3) in experimental 2 indicated that thorium in fraction 1, 2 and 3 is in a pure form when precipitated using oxalic acid as thorium oxalate leaving behind uranium in solution. After filtration washing and ignition of the precipitate, the oxalates change to oxide. Analysis of the oxide using ESEM reveals a very pure ThO₂ exceeds 95%. The ThO₂ in experimental 1 in all fraction associated with REEs as minor, the mainly of it was Ce(IV) due to incomplete reduction as shown in table (3), while in experimental 2 the pure ThO₂ represent about 80% of the total thorium in leach liquor due to increasing in reducing agent hydrazine sulfate. On the other hand, the filtrate of oxalate which contains uranium which precipitated at pH 5.5 as uranyl phosphate diuranate.

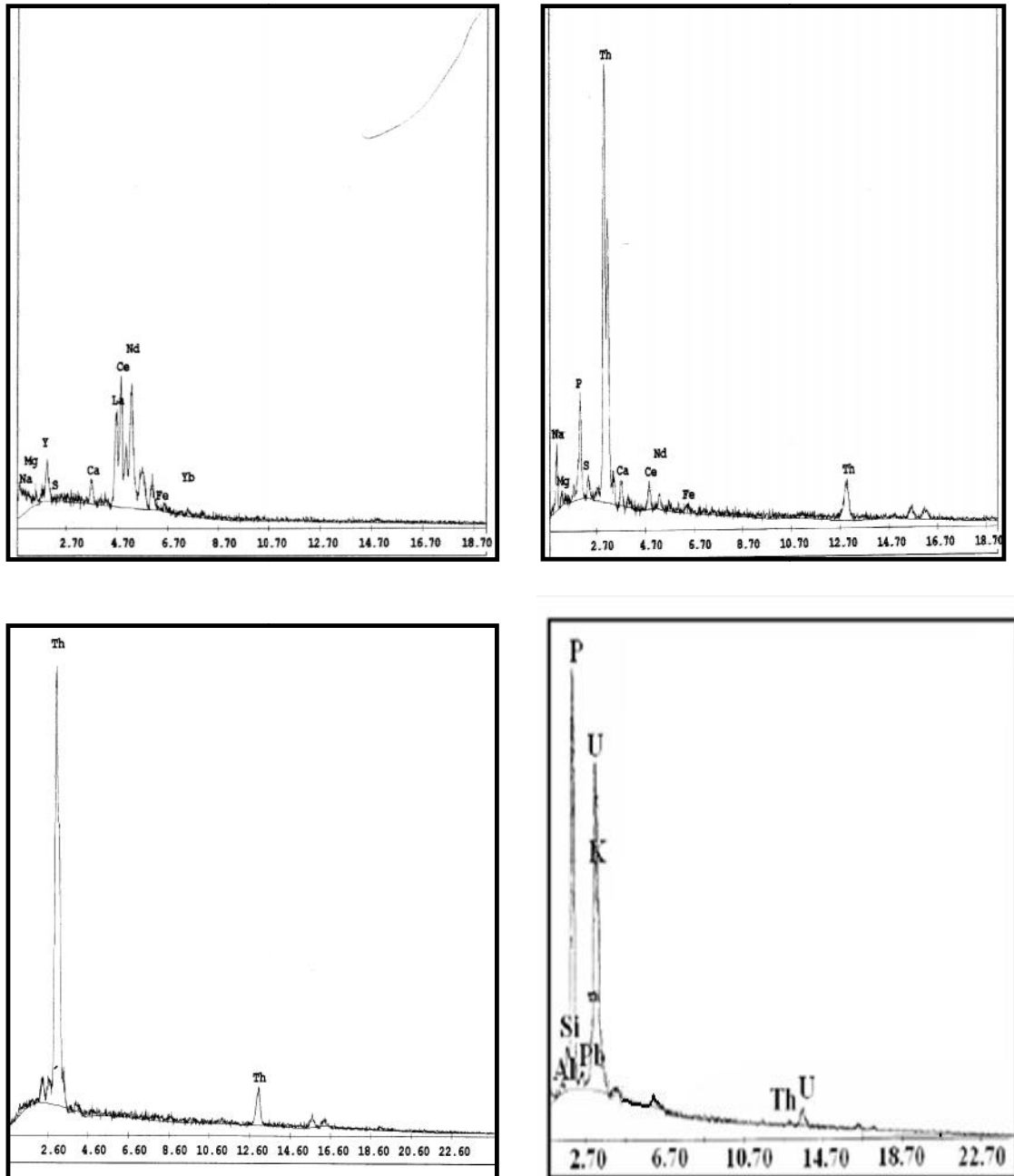


Figure 1: ESEM for Purified REEs, Th and U

CONCLUSION

The proposed chemical treatment of the obtained monazite concentrate has indicated that the separation of thorium, uranium and lanthanides in pure product can successfully be achieved from its sulfuric acid liquor rapidly in one pass. This could be achieved after reduction of the cerium (IV) content, present in monazite sulfate leach liquor with hydrazine sulfate. About of 82% of thorium could be recovered in pure form, while uranium complete precipitate at pH 5.5 as uranyl phosphate. On the other hand the total pure REEs which are adsorbed on resin which eluted by 4N HCl followed by precipitation and ignition to form pure rare earth oxide.

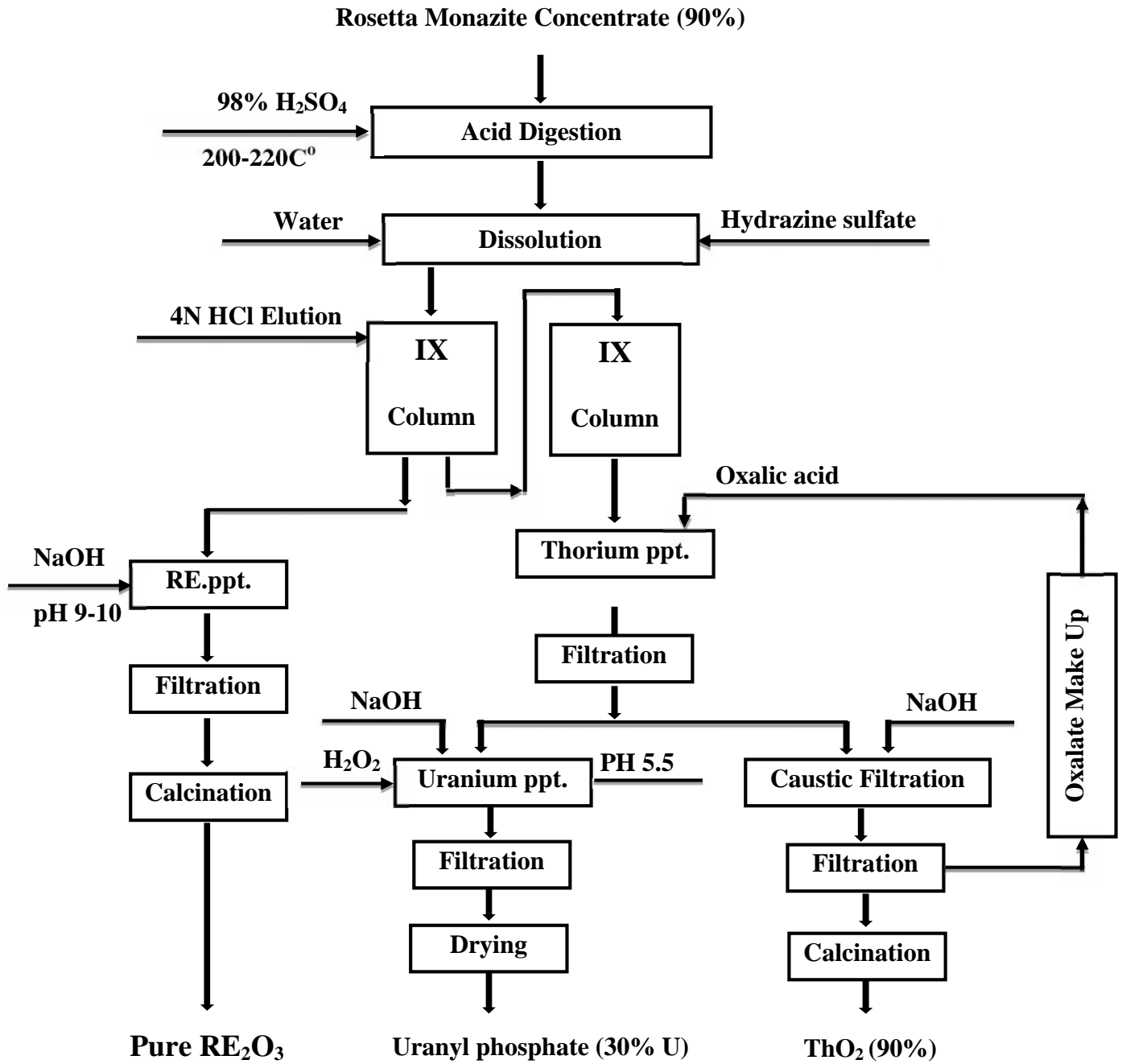


Figure 2: A generalized flow sheet for processing of Rosetta monazite concentrate via acid digestion and ion exchange recovery of the REEs

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