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To cite this article: A I L Abd El Fatah 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **975** 012022

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Commercial approach for highly pure thorium from Egyptian monazite mineral acid process

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Abstract. Thorium has a special interest in the future nuclear energy as a fuel especially the breeder reactors. The present research has been fulfilled throughout successive research schedule manner on separation and purification of thorium from Egyptian beach monazite mineral after its acid digestion. Monazite mineral was digested with sulfuric acid 96% at 220°C for 2.5h and dissolved with ice water (1:15), the clear solution precipitated with ammonia solution 16.5% at pH 1 to produce thorium pyrophosphate with 45% thorium content in case of ideal optimized whole process. The purification was carried out after the caustification and leaching with hydrochloric acid followed by the addition of oxalic acid at pH 0.3-0.4 to produce thorium oxalate with 91.68 % purity. Thorium oxalate was transformed to oxide by caustification then washed and separated and dissolved by hydrochloric acid. Highly pure thorium salt was attained with the addition of thiosulphate salt on the produced faint chloride solution under 0.1 to maximum 0.5 phosphate content to produce 99% purity.

Keywords: monazite mineral, thorium, separation, purification.

1. Introduction

Among contentious commercial nuclear power issues are the questions of what to do with long-lived radioactive waste and how to minimize weapon proliferation dangers. The substitution of thorium for uranium as fuel in nuclear reactors has significant potential for minimizing both problems. Thorium is three times more abundant in nature than uranium. Whereas uranium has to be imported in some countries (e.g. Egypt), there is enough thorium in such countries (e.g. USA, Egypt...) alone to provide adequate grid power for many centuries. A well-designed thorium reactor could produce electricity less expensively than an existing generation coal-fired plant or a current-generation uranium-fueled nuclear reactor. Importantly, thorium reactors produce substantially less long-lived radioactive waste than uranium reactors [1].

Thorium is the most abundant natural radioactive element and was discovered in 1828 by J.J. Berzelius and it exists in earth's crust with concentration of 8 ppm and has half-life of about 14.05 billion years with alpha decay. With respect to Thorium geological origin, in typical igneous rocks, thorium is mainly present in the accessory mineral, particularly thorite, monazite, allanite, zircon, titanite, anatase, rutile and perovskite. The same is true for sedimentary and metamorphic rocks but in some sedimentary rocks the resistates such as monazite, zircon and titanite may be quite abundant. Thorium is the largest of the tetravalent cations with an ionic radius comparable to that of U^{4+} and Ce^{4+} . The similarities in ionic size, outer electron configuration and bond character are the main reasons for the close relationship between the crystal chemistry of Th, Ce,



U and Zr. The large highly charged Th^{4+} ion has a marked tendency to form complex ions with others in solutions [2].

After mining, concentration and mineral physical beneficiation (separation), the monazite then undergoes attacking either by acid (without further mineral pretreatment) or alkali (necessitate mineral content >97% & grinding to -325 mesh size) to prepare aqueous solution containing all the mineral elemental contents. Starting from solutions produced from mineral solubilization, many schemes may be applied to attain a proper regime to produce ThO_2 powder as final target with highest possible purity and recovery to be ready for fuel fabrication.

During a previous work in the same context to separate and purify the uranium from the Egyptian monazite by applying oxalic- nitrate- TBP extraction method. One of the most important results of this separation was the acquisition of pure thorium. This work required the purification by an organic solvent (TBP), which represent economic burdens on the separation process, which would be avoided in this paper [3].

In another attempt in the same context to reach the highest concentration of thorium by conventional chemical methods (economical, available and easy to scale up), thorium was obtained with 93.88% recovery and 90.2% purity without further treatment with resin or solvent [4].

The present work is to provide an improved commercial method for the recovery of thorium values as an extremely pure product from an acidic aqueous solution containing said values together with rare earth values without further complicated, tedious and economically burdens solvent extraction and ion exchange processes.

2. Experimental methods

2.1. Chemicals and reagents

All chemicals used in the preoperative work were included the following: Sodium hydroxide, oxalic acid, sodium thiosulfate, hydrochloric acid, sulfuric acid, ammonia solution. The reagents were prepared by distilled water only for analysis and the final purification, while the separation and concentration processes tap water was used for commercial concepts during up-scaling proposal. The pH of the solutions was readjusted using 0.1M HCl and 0.1M NaOH.

2.2. Analytical techniques (instrumentation and methods)

The most common analytical techniques used to determine thorium in its various media (mineral, processes solution and solid products) were:-

X-ray fluorescence (EDXRF) using Rigaku spectrometer NEX CG with polarized optics [5], energy dispersive X-ray fluorescence [6, 7] and gravimetric [8].

Nuclear Materials Authority labs, Cairo, Egypt, were used to monitor the analysis through the processing of monazite.

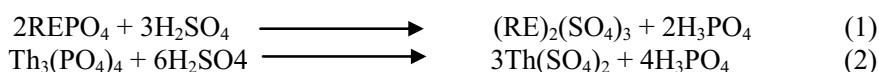
2.3. Hydrometallurgical procedures

A process for separating Th(IV) from the sulfuric acid solution of monazite mineral was carried out as the following process.

Monazite mineral digestion and dissolution:-

The mineral was digested in concentrated sulphuric acid after addition of 0.05% of BaCl_2 at 220°C for about 2.5 hours and the reaction products were leached by ice water by the ratio (1:15) and reduction of acidity to pH 1 to precipitate thorium pyrophosphate by ammonia solution (16.5%).

There are three main reactions occurring in the mineral digestion reaction beaker as follows:





2.3.1. Caustafication of thorium pyrophosphate cake.

About 1 Kg of wet thorium precipitate was reacted with sodium hydroxide in stiochiometric ratio applying external heat (90°C – 1h). The obtained thorium hydroxide was filtered of and washed thoroaly then dissolved in concentrated hydrochloric acid to produce thorium chloride solution. The produced solution will be the starting liquor for the different thorium purification regimes.

2.3.2. Oxalate precipitation

Thorium oxalate precipitate was produced with the addition of different amounts of oxalic acid (12.5, 6.25, 3.125, 2.5, 1.67, 1.25, 0.83 and 0.625 g) to thorium chloride solution (200 ml for each experiment) at different pH (0.3-0.4, 0.8, 1.2).

2.3.3. Thiosulphate precipitation

Thorium oxalate precipitate was converted to hydroxide by boiling with caustic soda solution, filters, washes thoroaly then dissolved by hydrochloric acid and boil(to reduce Ce(IV) to Ce (III)) to faintly acid solution, sodium thiosulfate was added in different amounts.

3. Results And Discussion

3.1. Monazite sand composition

A sample of monazite mineral after a proper sampling technique (which carried out as the following: making a pile of conical shape of all amount of the sample then spread out into a circular for through mixing. The process may be repeated if necessary. The sample is made again a pile and flattened, then divided into quarters; two quarters diagonally opposite are taken while the other two are rejected. The two quarters are collected together and subjected to coning and quartering until a lot of material of the desired size is obtained). The obtained sample was sent to NMA Analytical Lab for X-ray fluorescence analysis. This to investigate the chemical composition of the main targeted constituents in the high-grade monazite sand sample (about 85% monazite) produced during physical beneficiation of Rashid black sand, Egypt for more abundant Heavy Economic Minerals (HEMs) e.g. zircon, illmenite, rutile [9].The thorium, rare earth elements and uranium concentrations were indicated in Table 1.

Table 1. REEs, Th and U concentration percents in monazite mineral (85% purity) analyzed by XRF.

Metal Oxide	%
(REE) ₂ O ₃	58.7
ThO ₂	4.6
U ₃ O ₈	0.5

3.2. Solubilization of monazite by sulfuric acid

Monazite mineral was digested by concentrated sulfuric acid. About 85 % of the sample was dissolved forming acidic leach liquor via dilution using ice water with about 15 % residue part which was filtered off.

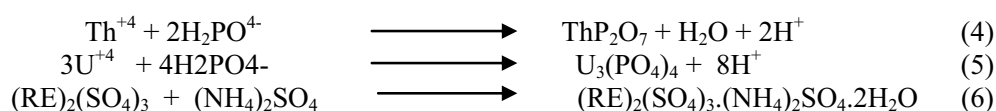
This process consists essentially of heating the ore with concentrated acid to convert thorium and lanthanon to a hydrous sulfates and extracting the reaction product with water. This product consists of hydrous sulfates in a mixture of phosphoric and sulfuric acids, excess sulfuric acid being need to give complete reaction. When it is extracted with water, the results obtained depend on the acidity of the final solution, which is controlled by the amounts of excess sulfuric acid and of water. If the acidity is low, thorium phosphate is precipitated but lanthanon remains in solution, lanthanon phosphate being soluble at much lower acidities than thorium phosphate. At higher acidities, both thorium and lanthanon remains in solution (monazite sulfate solution). At very high acidities, lanthanon sulphate is precipitated by the high sulfate concentration, although thorium sulphate can also be “salted out” of solution by increase in sulfuric acid concentration, its precipitation is inhibited by phosphoric acid. After the initial reaction product has been extracted with water, there for, a solution of both thorium and lanthanon was targeted and prepared. This process is a temperature, acid/ore ratio and dilution ratio dependent to control the percent dissolution of each main element of mineral component.

3.3. Separation of crude thorium concentrate

Separation of thorium, rare earths and uranium from the clear monazite sulfate solution obtained after mineral solubilization, via precipitation is a highly sensitive pH control process affected by the neutralizing agent used to control the pH [10]. The clear monazite sulfate solution is treated with ammonium hydroxide under acidity control. The acidity of the solution is gradually decreased with precipitant spray over all solution surface area while stirring until substantially all of the thorium is precipitated and most of the rare earths remain in the solution. There is no sharp pH value to precipitate each constituent individually but rather a range of acidities through which each content can be precipitated. Therefore, instead of sharp separation of each constituent, the bulk of thorium separates from the bulk of the rare earths.

The clear monazite sulfate solution was precipitated at three stages with ammonium hydroxide solution; first at pH 1.0 precipitation of thorium then at 2.5-3.0 to produce rare earth elements precipitate then finally at pH 5.5-6 to precipitate uranium.

Thorium and uranium are most probably precipitated as thorium-pyrophosphate and uranium-phosphate respectively while rare earths are precipitated as rare earths ammonium double sulphate as shown in the following equations



The most usual starting point for thorium purification is a crude hydroxide or phosphate material in which phosphate will range from 5 - 40% $\text{P}_2\text{O}_5/\text{ThO}_2$ and lanthanon from 25-100 % $\text{Ln}_2\text{O}_3/\text{ThO}_2$. The sequence of precipitation intended mainly to remove lanthanon and phosphate, and the principal impurities (iron, titanium...).

3.4. Purification of thorium

Many processes of purification were carried out on the first crude cake of thorium phosphate which precipitated at pH 1-1.5 from the mother acid leach solution derived after mineral digestion and dissolution as stated below.

3.4.1. Caustafication-hydrochloric acid leaching process.

Thorium and total rare earth content in the crude thorium pyrophosphate concentrate is given in table 2. From the table it's clear that, the crude cake contains 49.96% thorium and 43.13% total rare earth elements. The precipitate was reacted with sodium hydroxide in stiochiometric ratio to

produce the hydrated oxides of the elements of the cake (Th and REEs) as in the following equation:



Table 2. Thorium and total rare earth percents in the crude thorium pyrophosphate cake precipitated at 1.5 after mineral digestion and solubilization.

Elements	%
Th	49.96
ΣREEs	43.13

Thorium hydrated oxide precipitate was washed thoroughly with water till neutralization. The wet precipitate was leached with hydrochloric acid to produce thorium chloride as the following equation:



The produced residue after filtration was analyzed and its composition with respect to Th and REEs is given in table 3., which contains 18.74% thorium and 78.72 % rare earth elements. EDXRF analysis provides that the most of 78.72% REEs consists of light group.

Table 3. Thorium and total rare earth percents in the residue after hydrochloric acid leaching of thorium hydrated oxide.

Elements	%
Th	18.74
REEs	78.72

At low pH values hydrous thorium (IV) oxides are quite soluble, but at pH values higher than 3-4 solubilities decrease significantly. Ryan & Rai (1987) [11] found the solubility values of amorphous ThO_2 to decrease steeply from 10^{-3} - 10^{-2} M to 10^{-9} - 10^{-10} M between pH 3.6 and pH 4.7. The solubility of crystalline thorium oxide, ThO_2 , is extremely low, Baes & Mesmer (1986) [12] report the calculated minimum value above pH 6 to be $10^{-9.6}$ M. ThO_2 is also known to equilibrate very slowly with the aqueous phase. Thus, in this work it was regarded reasonable to use amorphous hydrous Th(IV) oxide, which is the primary solid phase precipitated under oversaturation conditions, and which equilibrates more rapidly with the aqueous phase.

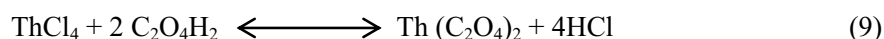
Complexing agents, such as Cl^- ions, affect solubility properties according to Felmy et al. [13], who found solubility values of hydrous Th(IV) oxide in chloride media to be higher when compared to those of Ryan & Rai (1987), who had a pure Th(IV)- H_2O system. The solubility values obtained by Felmy et al. (1991) increased with increasing chloride concentration ($[\text{Cl}^-]$ = from 0.6 M up to 3 M).

As a result of the previous work, most of thorium content was dissolved after addition of hot hydrochloric acid in stoichiometric ratio 1 (precipitate):4 (acid) with 15 minutes of stirring. The un-dissolved part contains mainly light rare earth elements may be attributed to the oxidized part of cerium which may resist reduction and dissolution by hydrochloric acid. The weight percent

of un-dissolved part was calculated in relation to the mother cake amounted to 0.1g which represents 0.23% of the mother cake.

3.4.2. Oxalic acid purification

The produced filtrate after hydrochloric acid leaching was precipitated with oxalic acid as solid particles to produce thorium oxalate according to the following equation:



During oxalic acid addition, a thorium solid phase precipitated under acidic conditions at below pH 3 was attributed to the formation of $\text{Th}(\text{C}_2\text{O}_4)_2$ as revealed from thermal analysis of the solid phase [14-18].

Oxalic acid concentration (g/experiment) the effect was inspected and tabulated in table 4. The results in table 4 represent the effect of oxalic acid variation, added in grams, per 200 ml of thorium chloride solution (eight experiments labeled from A to H). The produced oxalate precipitate was ignited and analyzed for thorium and total REEs contents in each one.

Table 4. Thorium and rare earth concentration after oxalic acid addition to thorium chloride solution which analyzed by EDXRF.

oxalic acid addition in grams	% Th	% REEs
12.5	(A) 45.37	54.63
6.25	(B) 47.04	52.96
3.125	(C) 51.08	48.92
2.5	(D) 70.28	22.35
1.67	(E) 62.86	30.88
1.25	(F) 65.25	26.01
0.83	(G) 63.62	29.26
0.625	(H) 64.61	28.71

From table 4., it was found that, in the first three oxalic acid addition which equals 12.5, 6.25 and 3.125 there is there is a slight increase in thorium concentration(A, B and C) which equal 45.37, 47.04 and 51.08 % respectively, on other hand rare earth's concentration decrease from 54.63 to 48.92 %. At 2.5g oxalic acid addition (D), the high concentration of thorium reaches to 70.28% with 22.35% of REEs. The last four additions (E, F, G and H), thorium concentration decreases again in the presence of different amounts of REEs. So, the best addition of oxalic acid for pure thorium precipitation was 2.5g which equal 70.28% with small amounts of REEs.

As a good results of thorium oxalate precipitation, there was another experiments were done applying controlled different pH values. Taking the filtrate produced after caustification and opening with hydrochloric acid for the first ore and precipitate by oxalic acid higher obtained values at pH 0.3-0.4 and 0.8. Table 5 was shown the results of thorium oxide precipitate after ignition at 750°C.

Table 5. thorium and rare earth content after oxalic acid addition to thorium chloride solution at different pH.

pH	% Th	% REEs
0.3-0.4	90.24	9.76
0.8	41.72	51.45

From this table it was found that thorium oxide produced with good purity equal 90.24% with 9.76% of REEs. At pH 0.8 the purity of thorium decreases to the half which equals 41.72 % due to the precipitation of rare earth elements most properly the heaviest members.

After the aforementioned thorium purification trials, one can conclude that, thorium oxalate is precipitated from acid solutions by addition of either oxalic acid or sodium oxalate. The precipitation gives a good degree of separation from phosphate, this being better the more strongly acid the initial solution. Light REEs oxalates are more soluble in acid solution than thorium oxalate and, if just enough reagents are added to precipitate all the thorium, some HREEs will be left in solution. An initial REEs level of 40% RE₂O₃/ ThO₂ can be reduced in this way to 10% but the technique is of no value in reducing trace contaminations.

3.4.3. Thiosulfate purification

In this part thorium oxalate precipitation which produced after oxalic acid addition to thorium chloride solution was leached with hydrochloric acid according to the following equation:



The un-reacted part which weight 0.1g (0.28% of mother oxalate precipitate) was analyzed as shown in table 6.

Table 6. The analysis of the residue of thorium oxalate precipitate after leached with HCl.

Elements	%
Th	91.68
LREEs	8.32

Thorium was precipitated again with the addition of sodium thiosulfate to the produced filtrate with 99% purity without rare earth elements.

Addition of sodium thiosulfate to a slightly acid thorium solution precipitates thorium thiosulphate. The REEs compounds were decomposed by acid (boil chloride solution before addition of precipitating agent to reducible Ce (IV) to Ce (III)). The presence of phosphate not only reduces the efficiency of REEs separation but also adversely affects the nature of the precipitate.

A maximum phosphate level of 0.5% P₂O₅/ThO₂ can be tolerated; it should preferably be less than 0.1%. The thiosulphate is soluble in HCl, giving a solution of ThCl₄ with a precipitate of sulphur.

So, if these conditions were obtained before oxalic treatment, thiosulfate precipitation process can be carried out directly after washing caustification and dissolution of the precipitate with reasonable purification results with respect to trivalent REEs under lower acidity.

After this satisfies results, the experiments were done again at 2 Kg of thorium pyrophosphate to calculate the recovery percents of thorium. 1 Kg was done with the stoichiometric ratios of each reaction, the other one was done with the double stoichiometric ratios of each reaction. It was found that, the precipitation of thorium with stoichiometric ratio for all the reactions, starting from sodium hydroxide reaction with the first crude cake (thorium pyrophosphate), hydrochloric acid leaching, oxalic acid addition, hydrochloric acid leaching finished with sodium thiosulphate precipitation. The produced thorium precipitate has the following results as shown in table 7.

Table 7. The final thorium precipitate with stoichiometric precipitation results after sodium hydroxide reaction with the first crude thorium cake (thorium pyrophosphate), hydrochloric acid leaching, oxalic acid addition, hydrochloric acid leaching finished with sodium thiosulphate precipitation analyzed by EDXRF.

Elements	%
Th	78.69
LREEs	11.62

From table 7., thorium has 78.69% purity in the presence of rare earth elements. Thorium percent decreases from 99 to 78.69 % due to increase the heat of reaction with the precipitation of rare earth elements.

On other hand, the precipitation of thorium with the double stoichiometric ratio of all precipitants follows the same steps (starting from sodium hydroxide reaction, hydrochloric acid leaching, oxalic acid addition, hydrochloric acid leaching finished with sodium thiosulphate addition).The results of the final product were shown in table 8.

From table 8. it was found that thorium purity decrease to 71.82 from 78.69 after final precipitation with the double stoichiometric ratio of sodium thiosulphate. This decrease was attributed to the increase of rare earths which equal 17.57%. From all the previous results the precipitation with the stoichiometric results was better than double stoichiometric results but the purity of final product still not satisfied. The good results obtained after addition of small amounts of sodium thiosulphate which give 99% purity of the final product.

Table 8. Analysis of thorium precipitate with double stoichiometric precipitation results after sodium hydroxide reaction, hydrochloric acid leaching, oxalic acid addition, hydrochloric acid leaching finished with sodium thiosulfate addition by EDXRF.

Elements	%
Th	71.82
LREEs	17.57

Figure 1 and 2 show the shape of the precipitate after oxalic acid and thiosulfate purification processes respectively.



Figure 1. Thorium oxalate precipitation after oxalic acid addition.

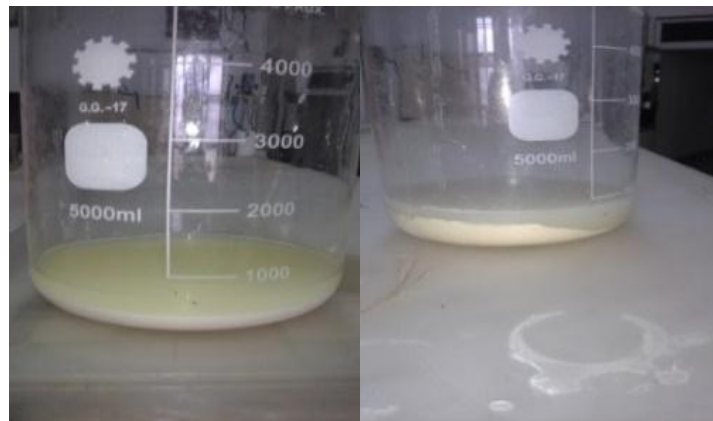


Figure 2. The high pure Thorium after sodium thiosulphate precipitation.

3.5 Up-scaling experiment

After all these experimental work, the procedures were applied at 1Kg monazite mineral with 85% purity. First, monazite was digested with concentrated sulfuric acid at 250°C with stirring for 2.5 h. Dissolution for the paste with 15L of ice water with stirring for 2 hours, decantation then filtration. The filtrate was precipitated with ammonia solution at pH 1 to produce thorium pyrophosphate with 45% purity. The precipitate was reacted with sodium hydroxide to give thorium oxide precipitate which leached with concentrated hydrochloric acid and filtered. Thorium chloride filtrate was precipitated with oxalic acid at pH 0.3-0.4 producing thorium oxalate with 87.3% purity and 82.35% recovery. But the application of thiosulphate precipitation cannot be carried out at the high amounts due to the precipitation of light rare earth elements with thorium precipitate which lead to the decrease the purity and recovery of the final product of thorium and the phosphorous over the tolerate values. The flow chart that summarizes the whole process for obtaining pure thorium oxide after monazite dissolution and thorium precipitation followed by purification can be represented in figure 3. The calculated percent recovery is related to the started Th content in the leach liquor after mineral dissolution.

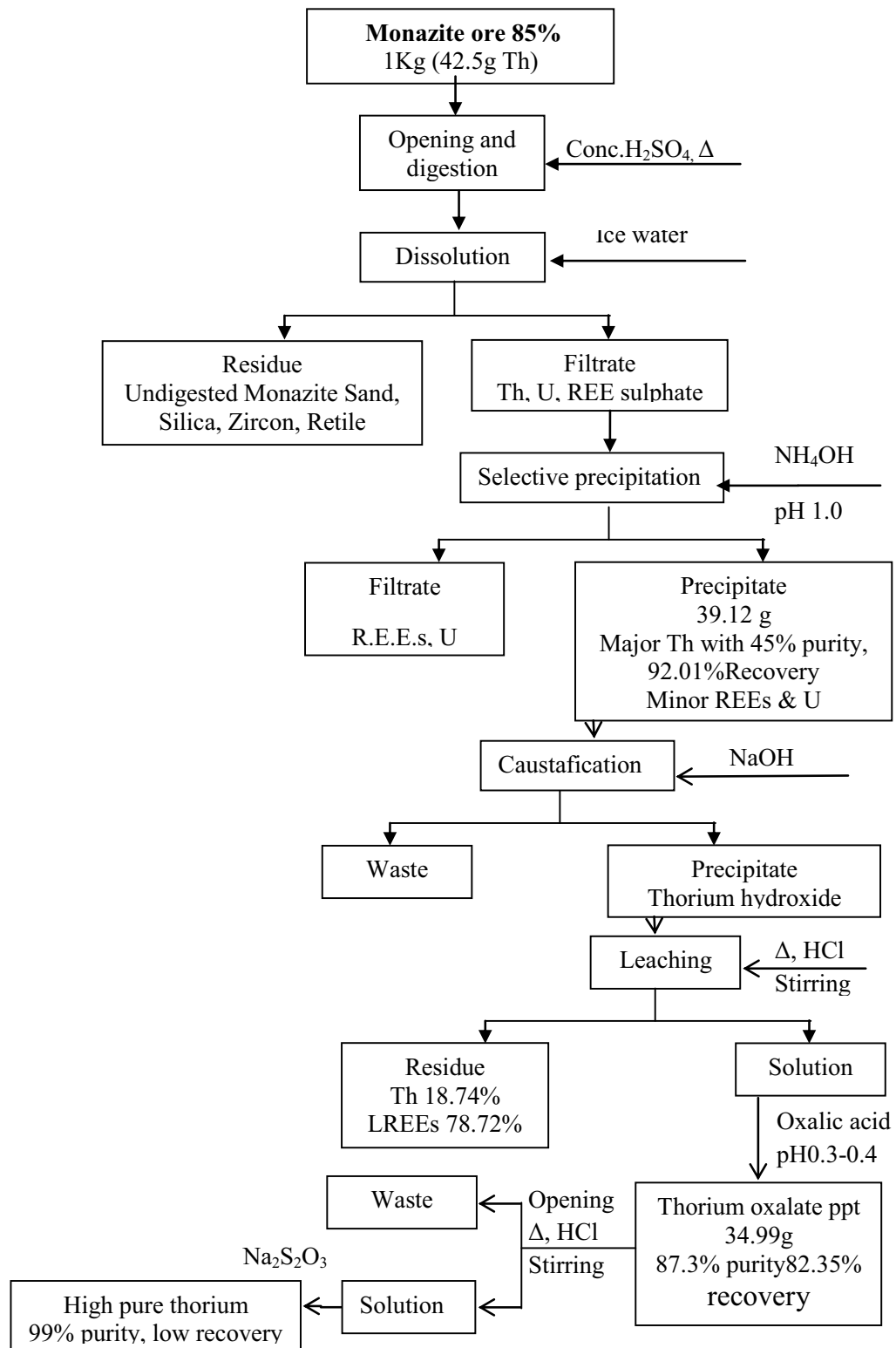


Figure 3. Flow chart of Egyptian monazite processes for thorium separation and high purification.

4. Conclusion

The technical viability of economic process for the purification of thorium from acidified monazite leach liquor was attained and verified to some extent. This process was dependent on the pH, amount of oxalic acid, amount of thiosulfate salt. Thorium undergoes to three stages, first thorium pyrophosphate with 45% purity after mineral digestion, dissolution and filtration then precipitation by ammonia solution. The second stage, 91.68% purity of thorium oxalate was attained after caustification, leaching and oxalic acid addition to thorium pyrophosphate precipitate at pH 0.3-0.4. Finally, the high purification of thorium with 99% purity after leaching by hydrochloric acid and thiosulfate salt addition to thorium oxalate product with low recovery.

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Acknowledgment

The author would like to express her appreciation to the efforts of Prof. **Rabie. K. A.**, for Suggesting the idea of the present work, faithful discussion and critical reading of the manuscript.