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Egyptian Monazite Digestion by Sulphuric Acid Process; Separation of Thorium

O. Helaly[1], N. Abdelmonem[2], K. Abd El-Baky[1], M, Nogami[3], I. Ismail[2,4] *

[1]Inorganic Chemistry Department. Nuclear Material Authority, Cairo, Egypt.
[2]Chemical Engineering Department, Cairo University, Giza, Egypt.
[3]Department of Electric and Electronic Engineering, Kindai University, Japan.
[4]Renewable Energy Engineering Program, Zewail City of Science and Technology, 6th of October City, Giza 12578, Egypt.

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Abstract: The major factors that affect the digestion the monazite mineral obtained from the Egyptian black sand deposits on Rosetta area and the along Mediterranean coast using sulfuric acid were investigated experimentally. The results reveal that digestion temperature of 220^{o}C, acid/monazite ratio of 1.6/1, digestion time of 2.5 hrs and acid concentration of 93% verifies the maximum digestion efficiency for the studied monazite sand, which reached to 93.7%. Precipitation of thorium, rare earths and uranium from the filtrate sulfate solution was carried out using ammonium hydroxide, as a neutralizing agent. The precipitation efficiency of thorium at pH 1.1 was 99.1 % with only 1% of the rare earths co-precipitated. Further precipitation of uranium at pH of 6.5 verifies almost complete precipitation.

Keywords: Monazite, Digestion; Sulphuric acid; Thorium; Rare earths; Uranium.

1 Introduction

Recently, the Chinese government has begun imposing strict export quotas on the rare earth, RE, industry thereby driving RE exploration and mine development in many other regions of the world. The three most common RE minerals that can be mined are bastnäsite, monazite and xenotime. Monazite can be found in Egypt within the black sands. The Egyptian black sands deposits occur along the north Mediterranean coast of the Egyptian Nile delta starting from the west of Rosetta to Damietta and extending to Rafah through 400 km and contain up to 15% of its weight valuable materials [1-7]. The monazite mineral was separated as a by-product during the concentration and recovery of the more abundant minerals e.g., magnetite, ilmenite, rutile and zircon. Monazite is generally forming about 0.4 – 0.6 % of the highly concentrated black sands, and is essentially an orthophosphate of rare earth elements and thorium with low content of uranium.

Many processes have been suggested for monazite sand digestion, some of them are based on pure alkali digestion using sodium hydroxide followed by mineral acid and/or solvent extraction [6,8-10], while others adapted the mechanical chemical alkali digestion process using autoclaved ball mill [4,11]. In spite of the fact that the Sulphuric acid process has been introduced long time ago [12], it is still preferable by many researchers. The main advantage of the sulfuric acid process is its ability to digest all types and grades of monazite, bastnasite or xenotime ores without prior fine grinding [13-20]. Besides, it is simple and relatively fast process. This process will reduce the hazardous effects and the cost rose from monazite radioactivity in the concentration or separation plant needed to obtain high grade monazite concentrate (> 99%). In addition, this procedure will raise the overall recovery of the

Corresponding authore-mail: dr_ismail@icem-group.org

crude monazite due to the reduction of the separation steps. The acid solutions obtained from this process contain the valuable elements, while the other gangues left as un-dissolved residue. It allows for the recovery of thorium, rare earths and uranium elements from the acid solutions with minimum co-precipitation of each one with the others through sequential fractional precipitation by gradually increasing the pH.

The main objective of this study is oriented towards the establishment of a simple and inexpensive process for digestion the low-grade Egyptian monazite sand (assaying 48.5% purity), which obtained as a by-product during the physical separation of black sands to separate the more abundant high economic minerals.

2 Experimental

2.1Materials and Reagents

The chemical materials and reagents used during this study are all laboratory grade produced by ADWIC except for Arsenazo III, sodium salt of 2,2-[1,8-dihydroxy-3,6-disulpho-2,7 naphthalene-bis (azo)] dibenzenearsonic acid, and Arsenazo I, Trisodium salt of 2-[4,5- dihydroxy-2,7-disulpho-3-naphthylazo] benzenearsonic acid were obtained from SIGMA.

2.2 Instruments

1) Laser-Fluorometer "UA-3" Uranium Analyzer (Scintrex, Canada) is used for uranium determination. An intense excitation source, N_2-Laser, at 337 nm is applied for exciting uranium. All measurements are carried out in nitrate solutions.

2) UV-Double Beam Spectrophotometer (UNICAM) with 1 cm cells. The optical system is checked automatically and the instrument is periodically calibrated.

3) pH-meter (SCHOTT GERATE, Germany), is used for all experiments in the present work. Calibration of the pH-meter is carried out before each experiment by using two successive buffer solutions (pH 4 and 7, or pH 7 and 10).

2.3 Monazite Sand Digestion

The experimental work was conducted upon low-grade monazite sand (about 48.5 % monazite) produced during physical beneficiation of Rashid black sand, Egypt. The bench scale experimental work involves mainly two steps, the first involves studying the digestion of monazite sand, while the second step involves studying precipitation of thorium, rare earths and uranium from the produced solutions. However, large sample weighing 2 kilograms was also tested to verify the bench scale results.

Sulfuric acid process was applied in this work, in this regards the conditions of maximum digestion of thorium and rare earths were investigated. These conditions involve mainly acid to ore weight ratio, the digestion temperature, agitation time and acid concentration. During digestion conditions study, one factor is varied while the others were kept constant as was mentioned at each case. At all tests the concentrated acid, proportional with initial monazite sand weight, was firstly heated to about 100°C in 250 ml Pyrex beaker before beginning the digestion test. At each experiment 50 gram of monazite sand, of -100 mesh, was added gradually to the hot concentrated acid with continuous stirring at 450 r.p.m using mechanical stirrer, then the temperature was thoroughly increased to the required tested temperature or as mentioned. At the end of each experiment, the reactants paste were cooled to 70°C then transferred to a beaker of one liter using ice water to prevent the temperature increases above 17°C during leaching for 4 hours, where the quantity of ice water added equivalent to ten times of monazite sand weight except when the optimum dilution ratio was studied. The leach slurry was then decanted, filtered using filter paper then the residual was washed three times using dilute sulfuric acid. The filtrate and wash were up to a total volume of one liter.

2.3.1Effect of Digestion Temperature

Effect of temperature on monazite sand digestion was studied at temperature ranges from 160°C to 300°C at intervals 20°C between each test, while the acid (100%) to ore weight ratio was kept constant at 1.6/1. The required tested temperature was controlled during further heating using adjustable hot plate and external temperature sensor measurement. The agitation was continued for 2.5 hours from beginning the monazite sand addition and through the controlled temperature tested.

2.3.2 Effect of Acid to Monazite Sand Ratio on the Digestion

The effect of the acid to monazite sand ratio on the digestion efficiency was studied using ratios from 0.6/1 to 2/1. The required ratios of sulfuric acid were firstly heated to 100°C then the monazite sand gradually added as previously mentioned then the temperature was increased to 220°C and kept constant during agitation each test for 2.5 hours.

2.3.3 Effect of the Digestion Time

To determine the effective digestion time required for reaction completion, several experiments were conducted at constant temperature of 220°C and acid to monazite sand ratio of 1.6/1. The digestion time varies between 0.5-4 hrs.

2.4 Sequential precipitation

The precipitation tests were carried out upon 25 ml sample of clear solution, where pH value was adjusted using 17.5% ammonia solution. The effect of initial dilution ratio on the precipitation efficiency was tested using dilution ratios ranging from 1:5 to 1:20 through 2.5 incremental increases. The quantities of consumed ammonia were determined during the test to know the effective final dilution for accurate concentration calculations. After precipitation, the slurry was left to settle and samples of clear solutions were withdrawn for analysis against rare earths and uranium to calculate their precipitation efficiency.

The thorium precipitation was investigated in the pH range of 0.5-1.9, rare earths precipitation was investigated in the pH range of 2.1 to 4.1 while uranium precipitation was investigated in the pH range of 4.3 to 6.5.

2.5 Analytical Determination Procedures

Analytical determination procedures for thorium and rare earths were carried out utilizing two main procedures; gravimetric in case of high concentration samples or spectrophotometrically using UV-Double Beam Spectrophotometer (UNICAM) in case of low concentration samples. In the gravimetric case, thorium was analyzed by oxalic acid hexamine precipitation method, while rear earths were analyzed by oxalate precipitation method [21]. The lower concentration samples of thorium and rare earths were analyzed spectrophotometrically using arsenazo III.
Uranium concentration was always analyzed by UB – 3 uranium analyzers utilizing arsenazo I [21-22].

3 Results and Discussion

3.1Digestion of Monazite Sand

The raw monazite sand utilized in this research has an effective monazite mineral of 48.5 %. Besides it has other economic minerals such as zircon, rutile and ilmenite, which in total, represent about 33.5%. The latter minerals cannot be attacked during processing of the raw monazite with sulfuric acid and remain as residue, which could be further treated. The composition of the raw monazite sand that was used in this work is indicated in Table 1:

Table 1: The composition of the raw monazite sand.

Constituent	Monazite	Zircon	Rutile	Ilmenite	Silicates and others
%	48.5	21.5	6.5	5.5	18

Moreover, the results of the chemical analysis of the main constituents as oxides, in the 48.5 % monazite are illustrated in the following table:

Table 2: The chemical analysis of the main constituents as oxides, in the 48.5 % monazite.

Metal Oxide	$(REE)_2O_3$	ThO_2	U_3O_8	P_2O_5
%	30.5	2.97	0.22	13.37

The liquor produced through digestion of monazite with sulfuric acid contains different useful elements such as rare earths, U, Th and Fe. The high commercial value of rare earth elements depends on their purity and the quality of their compounds. In order to purify the liquor, the rare elements are usually precipitated either in the form of rare earth and sodium double sulfate through added amounts of NaOH and sodium sulfate [17] or simply by the addition of ammonia solution [1,19]. The rare earth recovery could be approximately > 98% when stoichiometric amount of the reagent was two times as high.

3.1.1 *Effect of Temperature on Digestion Efficiency of Monazite Sand*

The effect of temperature on digestion efficiency of monazite sand was investigated in the temperature range of 160°C to 300°C. The digestion efficiency was calculated as percentage of weight loss of the residuals as compared with the original sample weight. The results of these investigations were illustrated on Fig. 1. It is noticeable that the digestion efficiency of monazite sand increased from 63.1% at 160°C to a maximum value of 93.7 at 220°C before it was reduced to 77.9 % at 300ºC respectively. Finally, we can conclude that the optimum digestion operating temperature is 220ºC, which verifies 93.7% digestion efficiency for the monazite sand. This optimum temperature is close to the case of xenotime digestion by sulfuric, which was reported by Vijayalakshmi et.al to be 250°C [15].

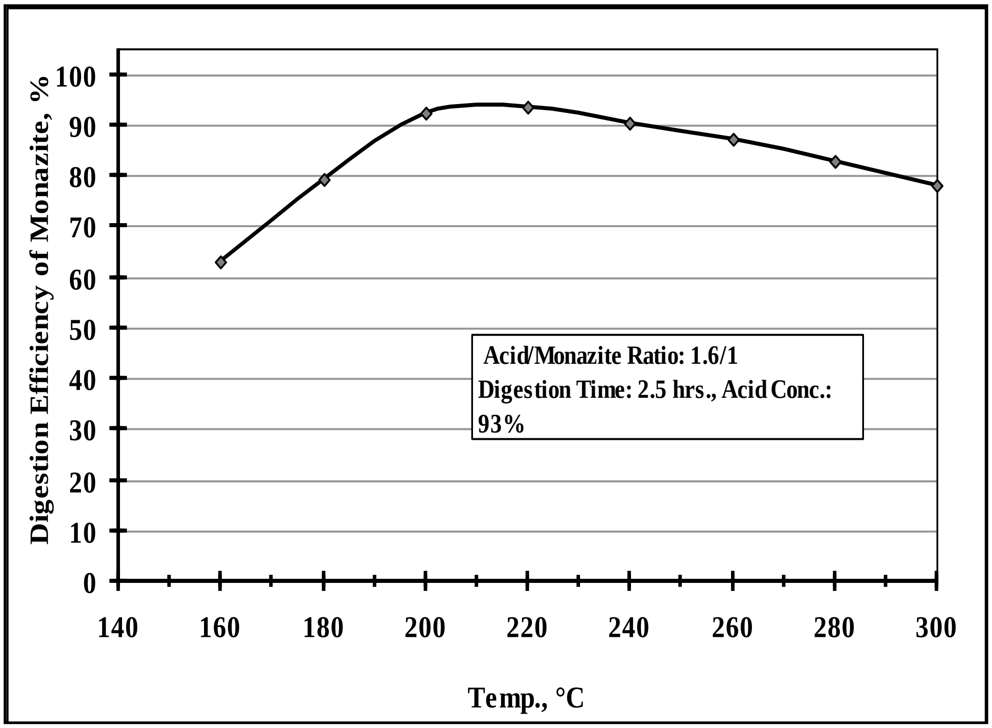

Fig. 1: Effect of temperature on the digestion efficiency of monazite.

3.1.2 Effect of Acid to Monazite Ratio on the Digestion Efficiency

The results of studying the effect of acid to monazite sand ratio, in the range of 0.6/1 to 2/1, on digestion efficiency are presented in Fig.2. It can be noticed that increasing the acid/monazite sand ratio increased the extraction efficiency of rare earths. This efficiency increased from 66.6 % at ratio of 0.6/1 to 92.5% at ratio 1.2/1 while there is a slightly increase at the higher ratios where at ratio of 1.6/1 it was 93.3% and 94.4 % at ratio of 2/1. The slight increase in the digestion efficiency after a ratio of 1.6, does not justify the extra huge amount of acid and neutralizing chemicals needed at higher acid to monazite ratios.

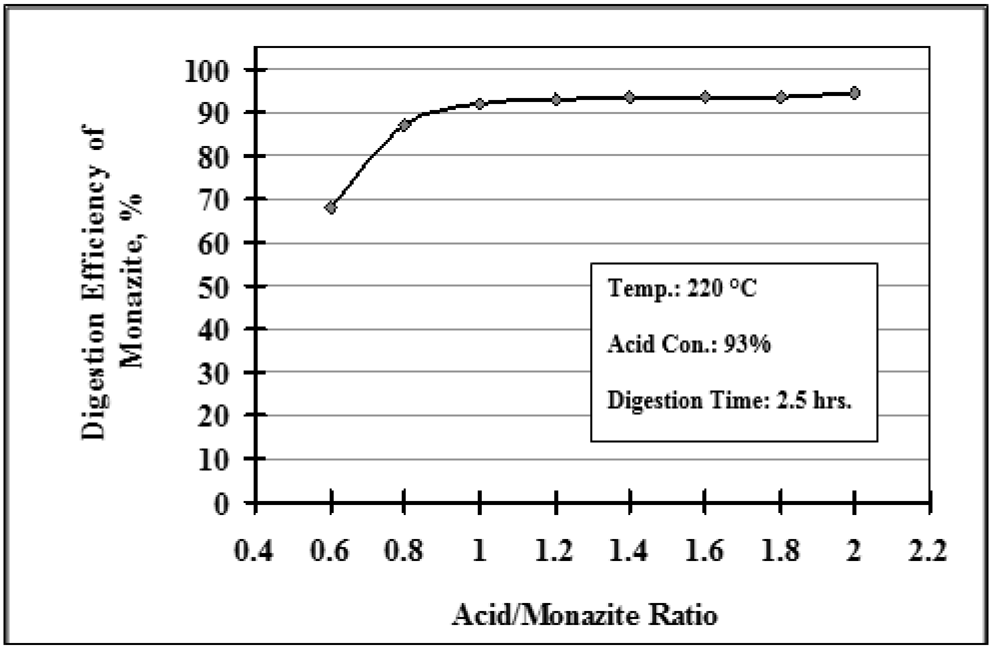

Fig. 2: Effect of acid/monazite ratio on the digestion efficiency of monazite.

3.1.3 *Effect of Reaction Time on the Digestion Efficiency of Monazite Sand*

Fig. 3 shows the effect of reaction time on the digestion efficiency in the reaction time range of 0.5 hr to 4 hrs. From this figure it can concluded that the best reaction time is 2.5 hrs. The reduction in digestion efficiency after 2.5 hrs may be attributed to the deposition of some sulfate products on the residual solid particle surface.

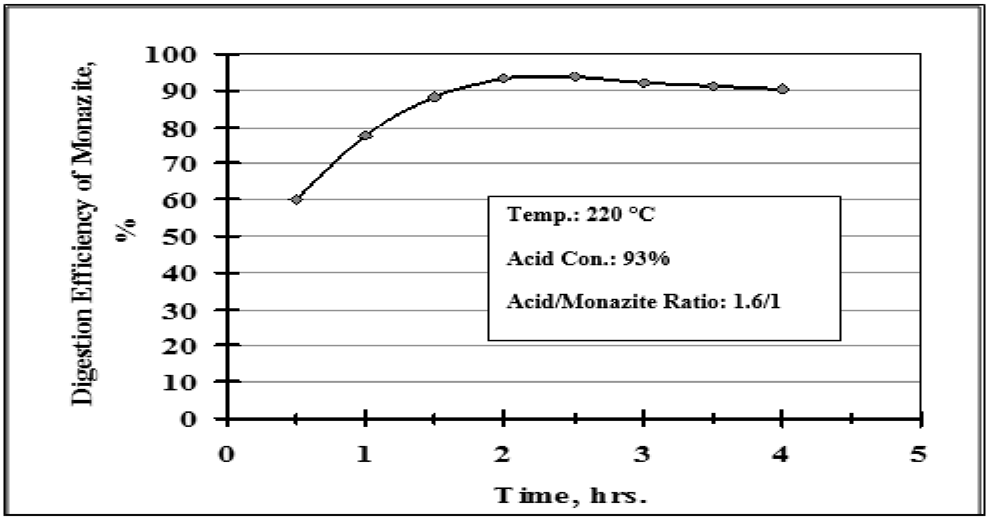

Fig. 3: Effect of time on the digestion efficiency of monazite.

3.2 *Sequential Precipitation*

The different main constituents of the clear liquor, obtained after digestion, dilution and filtration, namely thorium, rare earths and uranium, were sequentially precipitated by increasing the pH using NH_4OH. The detailed results of rare earths were published elsewhere [3], while those of uranium will be published later on. We shall mainly discuss the detailed study results for thorium in this article.

The precipitation efficiency of thorium from the clear liquor was calculated according to following equation:

$$\text{Precipitation Efficiency of Th} = \frac{[\text{Initial Th Conc. - Final Th Conc.}]}{\text{Initial Th Conc.}} X\,100 \quad (1)$$

While the extraction efficiency of Th was calculated according to Eq. 2:

$$\%\ \text{Extraction efficiency of Th} = \frac{Extracted\,Wt.Th}{Original\,Wt.Th} X\,100 \quad (2)$$

3.2.1 Effect of pH on Precipitation

The effect of pH and dilution ratio on the precipitation of thorium, rare earths and uranium were studied in the pH rang of 0.5 up to 6.5 as can be noticed from Fig. 4. It was found that by increasing the pH of the sulphate clear liquor thorium starts to precipitate at pH of 0.7 and completely precipitated at 1.9, more than 98 % precipitation efficiency, at dilution ration of 5/1. At this relatively high pH value the quantity of rare earths co-precipitated with thorium reaches up to 15 %. By increasing the dilution ratio, the precipitation efficiency of 99 % can be reached at lower pH values which in turn decreasing the co-precipitated rare earths. The rare earths started to precipitate at pH of 1.8 and were completely precipitated at 4.2. The precipitation of uranium started at pH > 4 and was almost completely precipitated (more than 99%) at pH value of 6.5. These pH values were utilized through the rest of experimental work during the study of other parameters effect on the precipitation of different components.

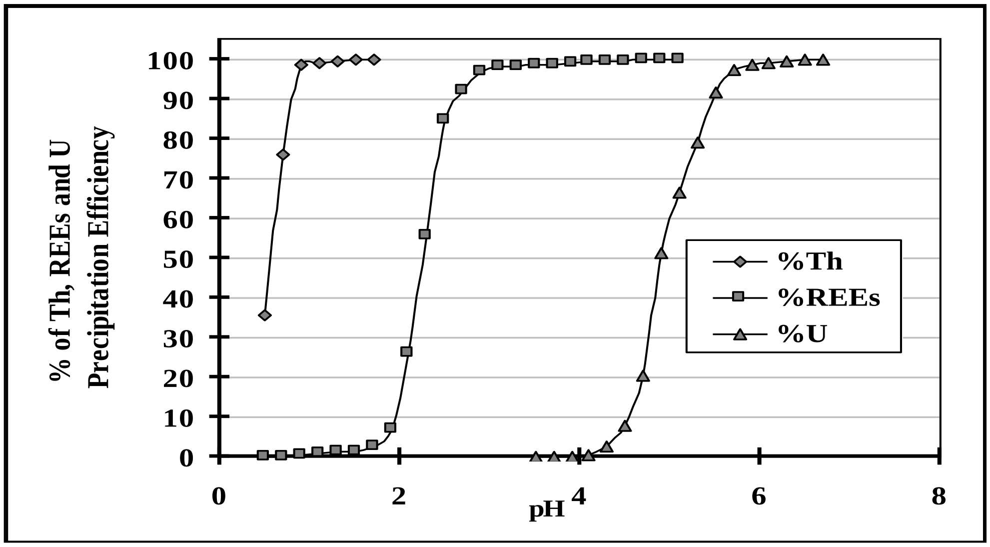

Fig. 4: Effect of pH on the recovery of thorium, rare earths and uranium at dilution ratio of 17.5.

3.2.2 Effect of acid/monazite ratio of thorium precipitation

The thorium precipitation efficiency was found to be equivalent to 80.7 % at ratio of 0.6/1 and increased to its maximum value of 99.2 % at ratio 1.2/1. However, the slight decrease in the extraction efficiency of thorium at the higher ratios as was shown in Fig. 5 is not relevant and can be considered to be within experimental error. From these results, it was found that the ratio of 1.6/1 could be considered as the suitable reactant ratio because this ratio really necessary to maintain the reactants fluidity enough to proceed the reaction. On the other hand, excessive quantities of free sulphuric acid would suppress the fractional precipitation of rare earths and thorium as well as interfere with the later purification step.

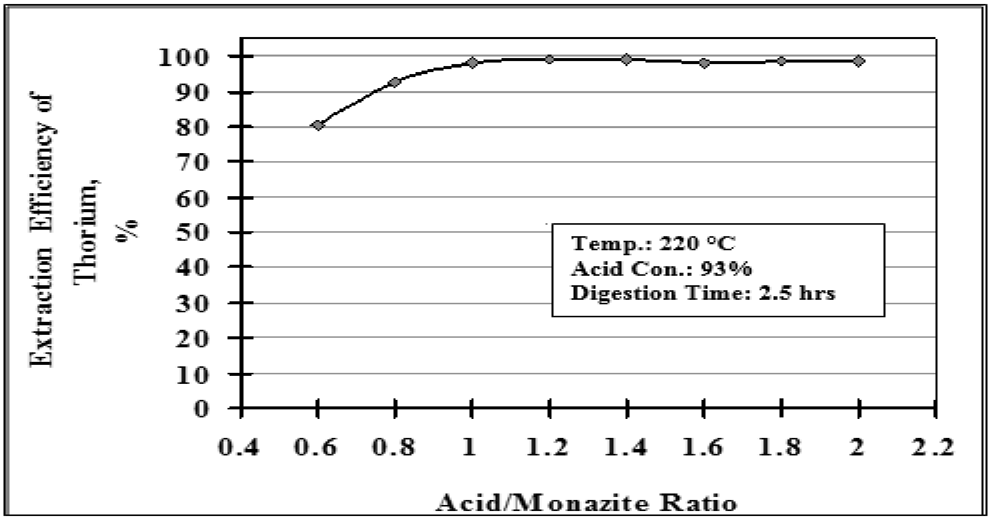

Fig.5: Effect of acid/monazite ratio on the extraction efficiency of thorium.

3.2.3 Effect of temperature of digestion on thorium extraction efficiency

Fig. 6 shows the effect of digestion temperature on the extraction efficiency of thorium. It is obvious that efficiency increases with temperature up to maximum at 220^{o}C. This is in good agreement with the previously discussed results of effect of temperature on monazite digestions. It is expected that the reduction in monazite digestion efficiency at temperature higher than 220^{o}C is due to the decrease in thorium extraction at higher temperature. This decrease may be also attributed to the formation of thorium pyrophosphate at higher temperatures.

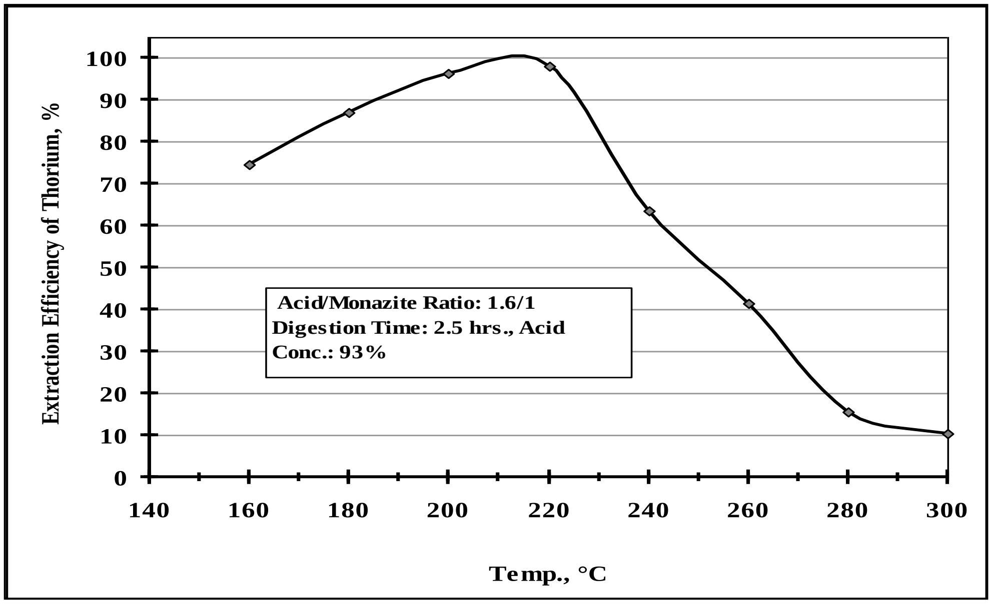

Fig. 6: Effect of temperature on the extraction efficiency of thorium.

3.2.4 Effect of digestion time on thorium extraction efficiency

Fig. 7 illustrates the effect of digestion time on the extraction efficiency of thorium, which was found to be equivalent to 54.8 % at reaction time 0.5 hr. and to increase to its maximum value of 99.4 % at reaction time of 2 hr. This efficiency began also slightly decrease to 98.1 % at reaction time 2.5 hr. When the reaction time increases more than 2.5 hr, the Extraction efficiency was sharply decrease from 85 % to 75.7% at times 3 hr and 4 hr respectively. However, this tendency is similar to that of monazite digestion efficiency and may be also attributed to the formation of thorium pyrophosphate. Based on these results, it was suggested that a digestion time of 2.5 hrs is the suitable digestion time.

It is worth noting that an alternative technique to extract U& Th from monazite via alkaline decomposition followed by leaching with alkaline carbonate solutions preferentially extracted by Aliquat-336 from 4 M HNO3 solutions. Hydrochloric acid is considered a good selective stripping agent for Th from U. The extraction efficiency is 80% whereas the stripping efficiency is 82% [9].

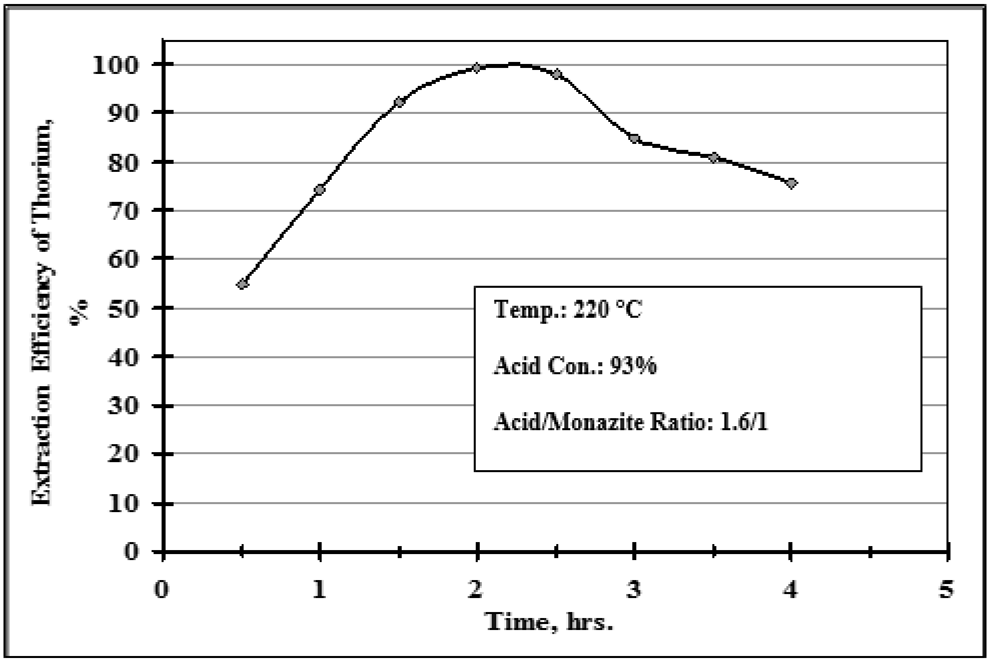

Fig.7: Effect of time on the extraction efficiency of thorium.

4 Conclusions

Egyptian monazite was digested using sulphuric acid process aiming to separate its valuable components. The major factors that affect the digestion using sulphuric acid such as digestion temperature, acid to monazite sand ratio, the digestion time as well as the acid concentration were examined. The results of these experiments reveal that digestion temperature of 220 ^{o}C, acid/monazite ratio of 1.6/1, digestion time of 2.5 hrs and acid concentration of 93% verifies the maximum digestion efficiency for the studied monazite sand which reached to 93.7%. The optimum conditions for precipitation and extraction of thorium, rare earth and uranium were investigated.

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