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ON THE RECOVERY OF RARE EARTH ELEMENTS FROM LOW GRADE EGYPTIAN MONAZITE BY SULPHURIC ACID PROCESS

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Abstract

The sulphuric acid process has the ability of treatment all types and grades of monazite sand economically in industrial scale, so it was chosen for this study to digest the Egyptian monazite sand concentrate of assaying 48.5% purity and grain size of -100 mesh. The results of digestion experiments that verify the maximum digestion efficiency of monazite sand which reaches (93.7%) were obtained at temperature of 220°C, acid/monazite ratio of 1.6/1, digestion time of 2.5 hrs and acid concentration of 93%. The related extraction efficiency of rare earths was 93.3%.

Separation of rare earths by precipitation from the resultant clear sulfate solution after leaching, decantation and filtration was carried out using ammonium hydroxide (17.5%). The results of these experiments reveal that the dilution ratio of 17.5/1 (parts of water to one part of the original digested monazite sand weight) verifies efficient separation. At this dilution ratio the precipitation efficiency of rare earths was 98.2% at pH 3.3.

Keywords: Monazite, Rare Earths, Sulphuric acid digestion and Precipitation.

Introduction:

The Egyptian black sand is found to occur along the Mediterranean coastal from Abu-Qir in the west to Rafah in the east. Rosetta area contains the greatest and the most accessible concentrations of valuable and economic minerals such as ilmenite, zircon, magnetite, monazite etc. During physical upgrading and concentration of these minerals, monazite sand was separated as a by-product of assay 48.5 %. This monazite concentrate has 30.5% rare earth oxides $(RE)_2O_3$ so it was considered actually as an important source of the rare earths [1,2]. Because of special properties of rare earth elements, they have a wide range of applications in several high technology and industrial products [3].

The mineral monazite is a source of the world supply for rare earth elements. Chemically the mineral is an orthophosphate of the rare earth elements [4]; $REPO_4$.

The rare earth oxides represent 60% of the mineral and consist mainly from the elements which have low atomic numbers (e.g. Lanthanum, Cerium, Praseodymium, and Neodymium) and known as light rare earths group [5].

Monazite processing is of a great importance as a production source of rare earth elements. Many processes have been devised for monazite sand digestion [6]. These methods include sulphuric acid leaching, alkaline leaching with sodium hydroxide solutions, sintering with sodium carbonate at 900°C, sintering with sodium hydroxide at 400-500°C, chlorination of a mixture with coal at 700-800°C, and smelting with coke, lime and flux (calcium fluoride) in an electric arc furnace at 1750°C [7].

Commercially, two methods continue to be used in large-scale industrial plants; the sulphuric acid and the caustic soda methods.

In the case of sodium hydroxide process, the rare earth values are obtained in the form of an un-dissolved residue, mainly hydroxides, which have to be dissolved in appropriate acid for further processing. This method has some defects in its output concentrates qualitl[8,9]. These defects are related to difficulties in continuously obtaining a high grade (97-99%) and fine grain size (-325 mesh) requirements of the input monazite quality.

The sulfuric acid process is alternatively proposed for economic processing of Egyptian monazite[10]. The process is able to use all types and grades of monazite ores [11,12] and is relatively quick. This process will reduce the hazardous effects raised from thorium radioactivity in the concentration-separation plant. Also it will reduce the cost of further physical concentration processing to obtain high-grade monazite concentrate (>97%). In addition, this procedure will raise the overall recovery of the crude monazite due to the reduction of the separation steps. The acid solutions obtained from this process contain the metal values while the other gangues left as undissolved residue. The metal values can be recovered from the acid solutions by fractional precipitation from these solutions by gradually increasing the pH to values of 3.3 to obtain precipitates of the rare earths after get ride of thorium at, pH 1.1. The precipitation pH should not exceed 4.0 to avoid contamination with uranium.

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

Experimental

Reagents and Solutions

Unless otherwise stated, all reagents were of analytical reagent grade and all solutions were prepared in calibrated flasks with doubly distilled water. The experimental work was conducted upon low-grade monazite sand (about 48.5% monazite) produced during physical beneficiation of Rashid black sand, Egypt.

Digestion, Dissolution and Precipitation Procedures

The experimental work involves mainly two steps, the first involves studying the factors affecting digestion of monazite sand, while the second step involves studying the factors affecting precipitation of rare earths from the produced solution.

The sulphuric acid of different concentrations (50-93%) at different acid to ore weight ratio (0.6/1 to 2/1) was firstly heated to different temperatures ranges (160-300) then monazite sand (- 100 mesh size) was added with continuous stirring at 450 r.p.m using mechanical stirrer. The agitation time was varied form 0.5 to 4 hours.

At the end of each test, the digested sample was cooled to 70°C then transferred to a beaker of one liter volume using ice water, and stirred for 4 hours employing different dilution ratios from 5 to 20 with interval dilution increases of 2.5. The leach slurry was treated for analysis to determine rare earths digestion efficiency.

The rare earths digestion efficiencies can be calculated as follows:

$$\% \text{ Extraction efficiency of REEs} = \frac{\text{Extracted REEs}}{\text{original REEs}} \times 100$$

For rare earths precipitation experiments, pH value from 2.1 to 4.1 was investigated through 0.2 increments between each value.

$$\text{Precipitation efficiency of REEs, \%} = \frac{\text{Initial REEs Conc.} - \text{Final REEs}}{\text{Initial REEs}} \times 100$$

Analytical procedures

In the present work, the received concentrate has been subjected to complete chemical analysis[9], a typical analysis for Egyptian monazite concentrate is given in table (1)

Table (1): Percent composition of Egyptian monazite concentrate

Constituent	RE_2O_3	ThO_2	U_3O_8	TiO_2	Fe_2O_3	P_2O_5	SiO_2	ZrO_2
Percent %	62.41	6.04	0.42	0.38	0.46	28.61	1.26	0.40

The total rare earths was determined spectrophotometrically by Arzenazo(III) method[13] using the absorption band at 650 nm on a UNICAM-UV double beam spectrophotometer of high-resolution power.

Results And Discussion

Theoretical aspects

The sulphuric acid process involves the digestion of monazite sands using hot sulfuric acid to form a monazite sulfate paste of rare earths and remaining a residue consisting of silica, zircon and other present gangue materials according to the following reaction (equation 1):

$$2REPO_4 + 3H_2SO_4 \longrightarrow (RE)_2(SO_4)_3 + 2H_3PO_4 \quad (1)$$

The digestion reaction produces a thick grey paste, which after cooling is cautiously diluted with water for about ten times the weight of the mineral and the stirring is continued for at least 1 hour. By this treatment, rare earths go into solution which is decanted out of the silica, rutile, zircon, and the un-reacted monazite.

Because the undigested monazite sands are denser than the gangue, they settle out in a few minutes where they can be recycled. The remaining slurry is then decanted to another vessel, where the gangue (which contains most of the radioactive daughter products of thorium and uranium) is allowed to settle. The gangue either leaves the process as waste or is reprocessed, depending upon evaluation of its composition.

Precipitation of rare earths from the clear monazite sulfate solution is the next step it should be mentioned here that, precipitation from sulphuric acid leach solutions through acidity control using a neutralizing agent, is the most common and promising procedure to separate rare earth elements. Ammonium hydroxide is preferred as a neutralizing agent. In this regard the clear monazite sulfate solution is treated with ammonium hydroxide under pH control. Another procedure precipitate rare earths as ammonium double Sulphate[10] according to the following equations (2-5):

$$NH_4OH \longleftrightarrow NH_4^+ + OH^- \quad (2)$$

$$H_2SO_4 \longleftrightarrow 2H^+ + SO_4^{--} \quad (3)$$

$$2\,NH_4^+ + SO_4^{--} \longrightarrow (NH_4)SO_4 \quad (4)$$

$$(RE)_2(SO_4)_3 + (NH_4)_2SO_4 \longrightarrow (RE)_2(SO_4)_3(NH_4)_2SO_4 2H_2O \quad (5)$$

Effect of Temperature on Digestion Efficiency of Monazite Sand

As previously mentioned in the experimental work, sulphuric acid concentration of 93 % was firstly heated to about 100°C before adding the monazite sand (50gm sample), the temperature was gradually increased to the required studied temperatures (160-300°C) and kept constant during the reaction time of 2.5 hrs. Acid to monazite sand weight ratio is kept at 1.6/1 during studying this factor. The results of these tests were illustrated in figs (1, 2). From these data we can show that; rare earths extraction efficiency was 63.1 % at 160°C while increasing the applied digestion temperature to 220°C increases this efficiency to reach 93.7 %.

However, the extraction efficiency was decreased at temperature above 240°C; it reached 87% at 260°C and only 77.9% at 300°C. This decreasing may be attributed to the formation of the insoluble rare earth pyrophosphate $(RE)_4(P_2O_7)_3$ rather than the soluble rare-earth sulphate.

Finally we can conclude that the optimum digestion operating temperature is 220°C, which verifies 93.7% digestion efficiency for the monazite sand.

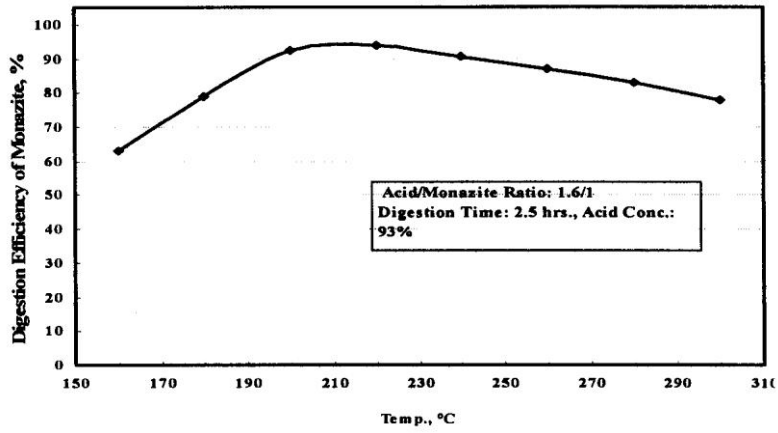

Figure (1): Effect of Temperature on Digestion Efficiency of Monazite

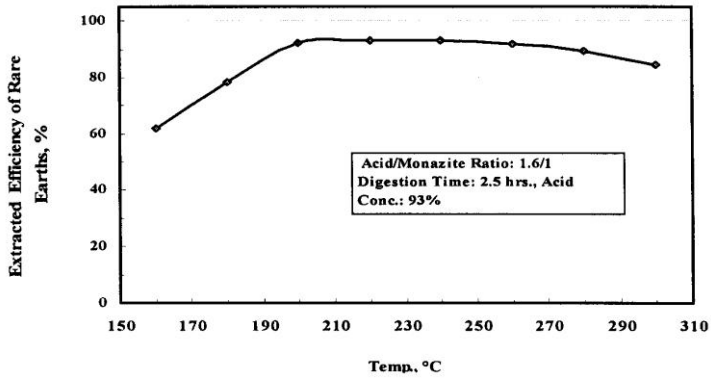

Figure (2): Effect of Temperature on Extracted Efficiency of Rare Earths

Effect of Acid to Monazite Ratio on the Digestion Efficiency

The results of studying acid to monazite sand ratios from 0.6/1 to 2/1 were presented in figs. (3, 4). The reaction temperature applied during these experiments was 220°C while the agitation time was kept at 2.5 hrs. The amount of sulphuric acid (93%) for each experiment was firstly heated to 160°C then the required ratio of monazite sand was added gradually. The reaction temperature was increased and agitated as previously mentioned. From these figures we could show that; increasing the acid/monazite sand ratio will raise the extraction efficiency of rare earths. The extraction 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 at ratio of 2/1 it was 94.4 %.

The overall digestion of monazite sand was 67.8 % at acid to monazite ratio of 0.6/1 while it reached 93.1 % at ratio 1.2/1 & 93.7% at 1.6/1 ratio. The digestion maximum value was 94.7 % at 2/1 ratio.

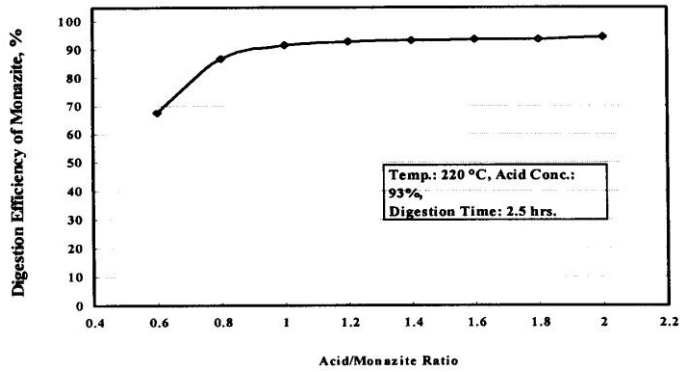

Figure (3): Effect of Acid Monazite Ratio on the digestion Efficiency

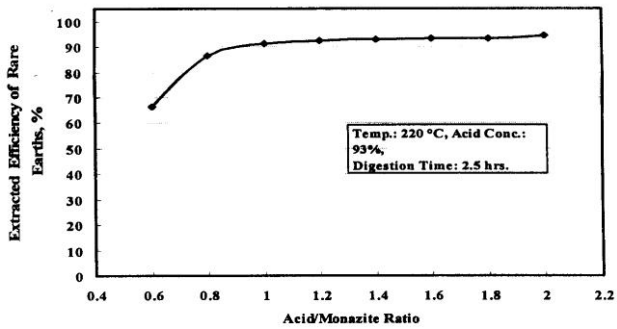

Figure (4): Effect of Acid Monazite Ratio on the Extracted Efficiency of Rare Earths

Effect of Reaction Time on the Digestion Efficiency of Monazite Sand

The results of studying the digestion times from 0.5 hr to 4 hrs were represented in figs (5, 6). As previously mentioned, the reaction temperature applied during these tests was 220°C, while the acid to monazite sand ratio was 1.6/1. The sulphuric acid concentration of 93% was firstly heated to 160°C then the monazite sand gradually added. The reaction temperature was then increased to 220°C and the reactants agitated for the required tested time. From these figures we can demonstrate that; the extraction efficiency of rare earths increases with the increase in reaction time from 60.7% after 0.5 hr to 93.1% after 2.0 hr. However, after 2.5 hr, there is a slight increase where it was 93.3%. The extraction efficiency begins to slightly decrease when the time increased more than 2.5 hr, where it reached 93%, 92.3%, 92% after 3hr, 3.5hr and 4 hr respectively.

The over all digestion of monazite sand was 60 % at time 0.5 hr and reached its maximum value of 93.7% after 2.5 hr. The monazite digestion efficiency decreased above this range of reaction time to reach about 90.5% after of 4hrs. From these results, it was found that the reaction time of 2.5 hrs is the suitable digestion time because the monazite digestion efficiency decreases above this time.

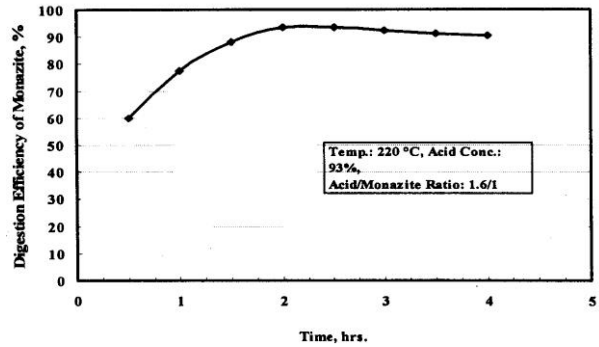

Figure (5): Effect of Reaction time on the digestion Efficiency of Monazite

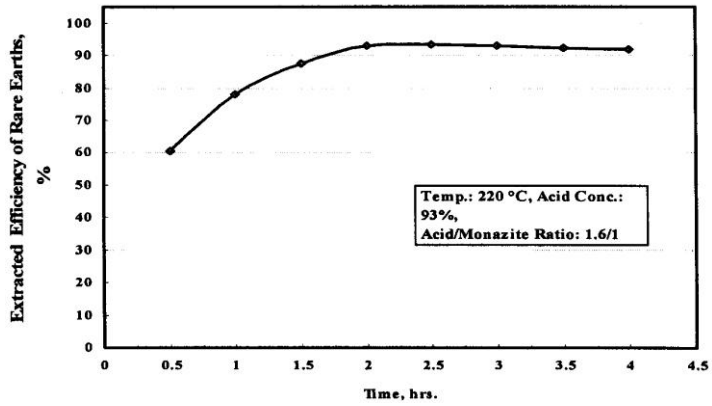

Figure (6): Effect of Reaction Time on the Extracted Efficiency of Rare Earths

Effect of Acid Concentration on the Digestion Efficiency of Monazite Sand

The tested acid concentrations were 50%, 75%, 90% 93% and 97%. The reaction temperature applied during these tests was 220°C, while the acid (100%) to monazite sand ratio was 2/1 and the digestion was continued for 2.5hrs. The results of studying the acid concentration effect on the digestion efficiency of monazite sand are represented in figs (7,8). From these figures we can show that; the extraction efficiency of rare earths was only 47.2% at acid concentration of 50%. This efficiency was increased to reach 80.3% when acid concentration increased to 75%.

However, the extraction efficiency reached its maximum value of 94.6% at the acid concentration of 93% while it was slightly decreased to 93.4% at 97% acid concentration.

The over all digestion efficiency of monazite sand was 47.1% at 50% acid concentration and reached its maximum value of 93% at 94.9% acid concentration. The monazite digestion efficiency was slightly decreased when the acid concentration was 97%. From these results, it was found that the acid concentration of 93% considered as the suitable for monazite sand digestion.

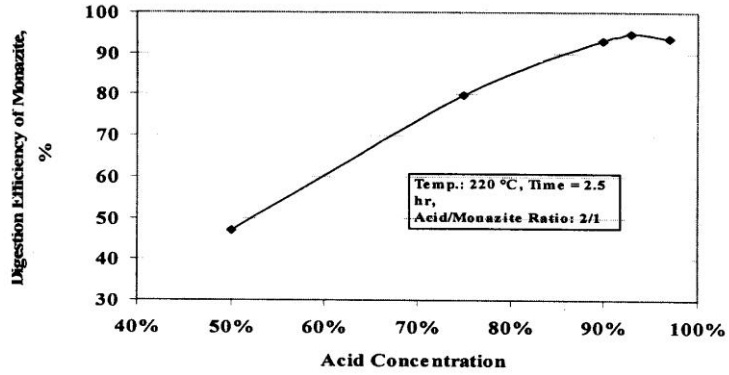

Figure (7): Effect of Acid Concentration on the digestion Efficiency of Monazite Sand

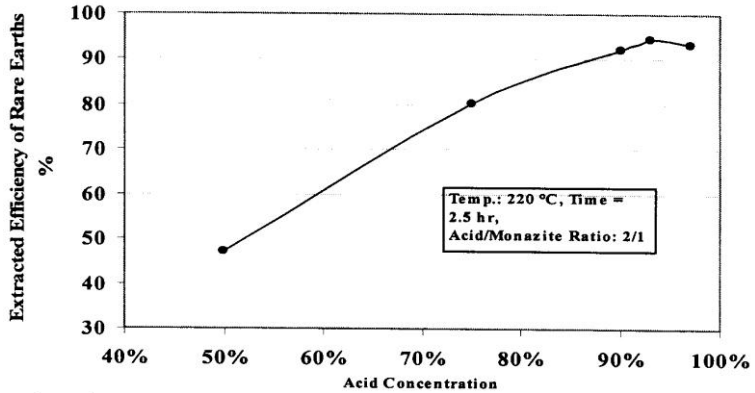

Figure (8): Effect of Acid Concentration on the Extracted Efficiency of Rare Earths

Rare Earths Precipitation Efficiency at Different Dilution Ratios and variable pH

Further tests for studying the precipitation efficiency of rare earths proved also that the efficiency was affected greatly with variation in the initial dilution ratio. This is illustrated in figures (9, 10). These figures show that, at lower dilution values the precipitation efficiency of rare earths is low at ratio 5/1 and pH of value 3.9; the precipitation efficiency of rare earths reached 96.3 %. To precipitate more than 99 % of the rare earths content from pregnant solution, the dilution ratio was 17.5/1 and the pH value was 3.9. At these conditions only 0.04 % of undesired elements were co-precipitated.

From these results we can conclude that the suitable precipitation conditions of rare earths are:

- Dilution ratio of 17.5/1 and
- The pH value of 3.3.

At these conditions the precipitation efficiency of rare earths is 98.2 % while the co-precipitation of undesired elements is only 0.01 %.

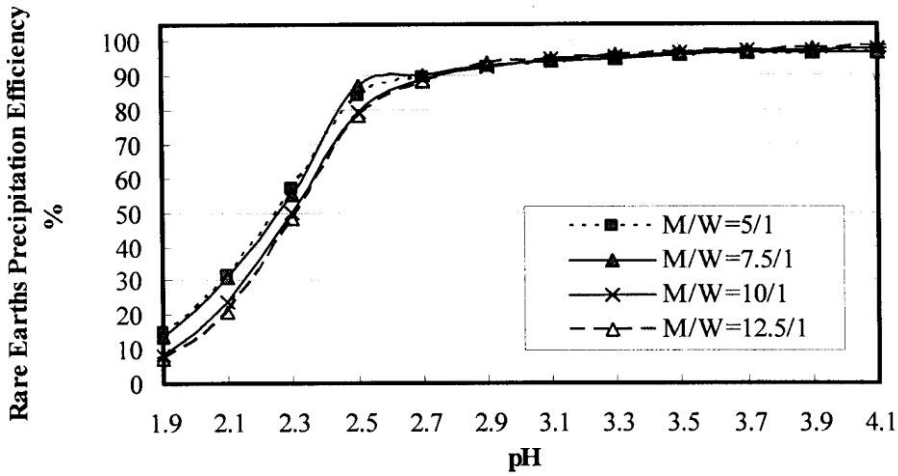

Figure (9): Effect of Dilution Ratios and pH on Rare Earths Precipitation Efficiency.

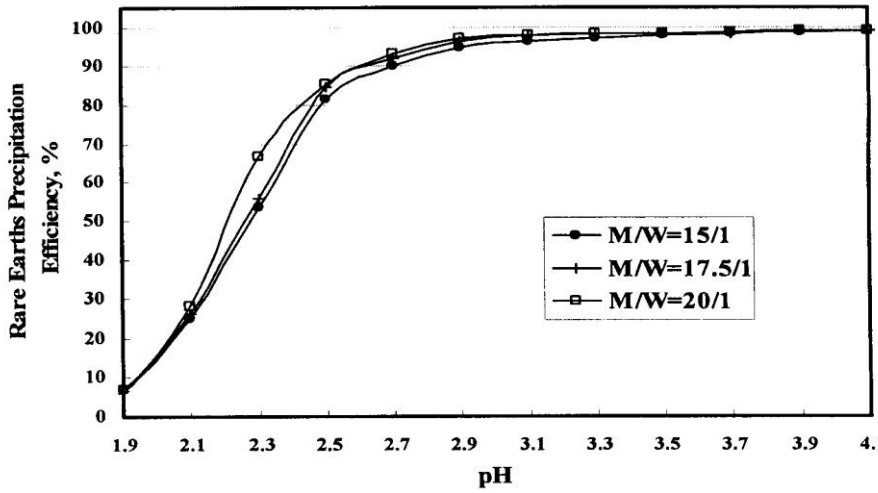

Figure (10): Effect of Dilution Ratios and pH on Rare Earths Precipitation Efficiency.

Suggestion and Application of a Full Separation Process for Rare Earths from monazite sand

From the results of the aforementioned experiments, the optimum conditions for the recovery of rare earth values from monazite employing the sulphuric acid process can be summarized as follow:

- Digestion Operating Temperature: 220De
- Digestion Time: 2.5hrs
- Acid to Monazite Ratio: 1.6/1
- Acid Concentration: 93%
- Dilution ratio: 17.5/1
- The pH value for Rare earths precipitation: 3.3
- Precipitant: Ammonium Hydroxide

Based on the above research results, a process was suggested, developed and applied for the separation of rare earths from Egyptian black sand monazite. Figure (11) gives a schematic flow sheet for the proposed separation process. The hydrous oxide rare earth cake obtained in a typical run had the composition shown in table (2). The result of this working-up is a rare earth concentrate yield of about 98% of the amount employed.

Table (2): Percent composition of the obtained hydrous oxide rare earth product

Constituent	RE_2O_3	ThO_2	U_3O_8	Fe_2O_3	P_2O_5	Moisture Content	Loss at ignition at 1000
Percent %	54.5	N.D.	N.D.	1.55	0.6	27	35.5

N.D. = Not Dtected

Conclusion

The major factors that verify almost complete digestion using sulphuric acid involve the digestion temperature, acid to monazite sand ratio, the digestion time as well as the acid concentration. These factors were studied experimentally on a bench scale in the temperature range of (160 - 300)°C at 20°C intervals between each test, (0.6/1- 2/1) acid/monazite ratio through increasing of 0.2 of acid at each test, (0.5-4) hours at intervals at half an hour intervals between each test and (50% - 97%) acid concentration. The monazite sand grain size was left as it is without prior grinding (-100 mesh). The results of these experiments reveal that digestion temperature of 220oe, acid/monazite ratio of 1.6/1, digestion time of 2.5 hrs and acid concentration of 93% verifies the optimum digestion efficiency for the studied monazite sand, which reached to 93.7% and for rare earths were 93.3%.

The dilution ratio as well as the pH value is considered the effective factors controlling the precipitation efficiency. The results of these experiments reveal that a dilution ratio of 17.5/1 (parts of water to one part of the original digested monazite sand weight) verifies efficient precipitation Le. minimum co-precipitation of each with the other. At this dilution ratio the precipitation efficiency of the rare earths at

pH 3.3 was 98.2%. The process was suggested, developed and applied for the separation of rare earths from Egyptian black sand monazite. The result of this working-up is a rare earth concentrate yield of about 98% of the amount employed.

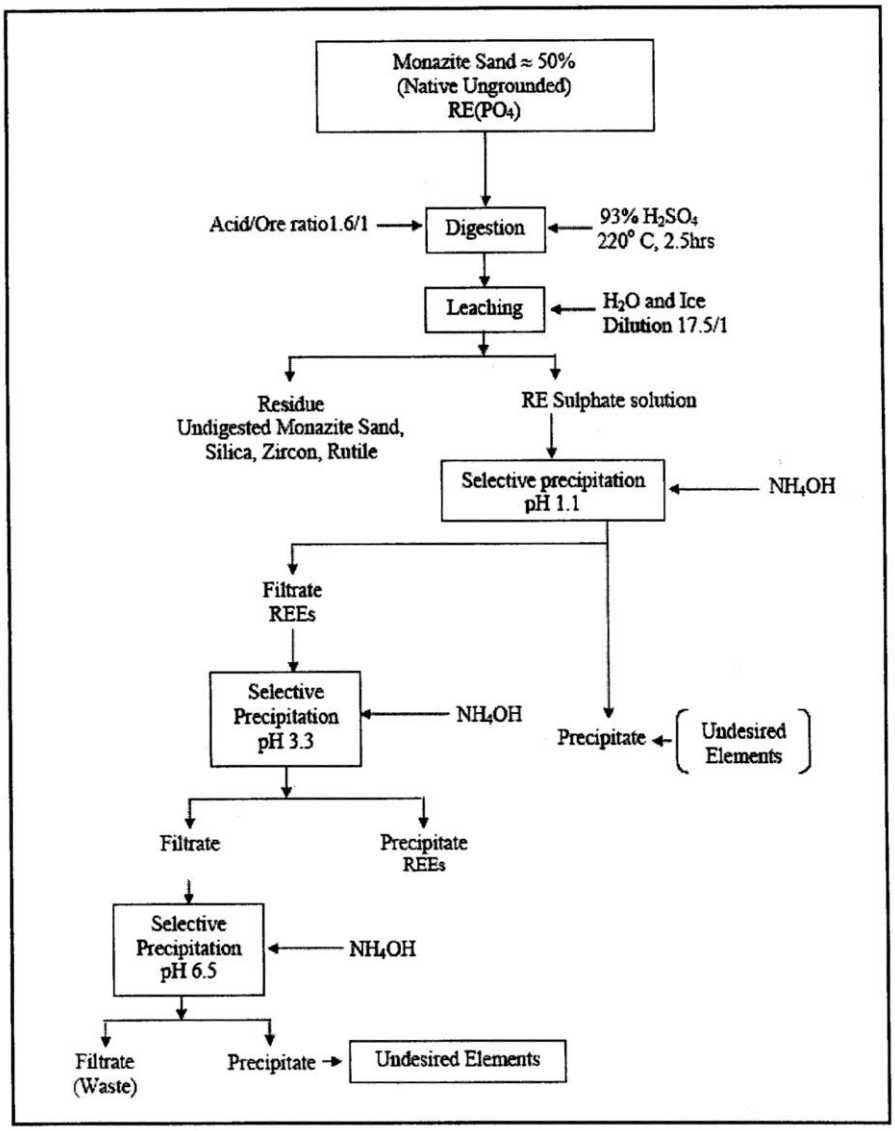

Figure (11): Flowsheet for rare earth elements concentrates separation form commercial native Egyptian monazite applying sulphuric acid process.

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