

Preliminary Study for Separation of Heavy Rare Earth Concentrates from Egyptian Crude Monazite

Sherien H. Ahmed, Osama S. Helaly, Mohamed S. Abd El-Ghany

Abstract—Heavy rare earth (HRE) oxalate concentrates were prepared from the Egyptian crude monazite sand (graded about 47%). The concentrates were specified quantitatively for their constituents of individual rare earth elements using ion chromatograph (IC) and qualitatively by scanning electron microscope (SEM) for the other major constituents. The 1st concentrate was composed of 10.5% HREE where 7.25% of them represented yttrium. The 2nd concentrate contained about 41.7% LREE, 17.5% HREE and 13.6% Th. The LREE involved 18.3% Ce, 10.5% La and 8% Nd while the HREE were 8.7% Y, 3.5% Gd and 2.9% Dy. The 3rd concentrate was containing about 8.0% LREE (3.7% Ce, 2.0% La and 1.5% Nd), 10.2% HREE (6.4% yttrium and 2.0% Dy) and 2.1% uranium. The final concentrate comprised 0.84% uranium beside iron, chromium and traces of REE.

Keywords—Oxalic Acid Precipitation, Rare Earth Concentrates, Thorium, Uranium.

I. INTRODUCTION

THE rare earth minerals that represent the chief commercial interest resources are monazite, xenotime, gadolinite, allanite, euxenite, and bastnasite. Monazite mineral is rare earth elements, thorium and uranium phosphate; (REE, Th,U)PO₄ also xenotime mineral is yttrium and heavy rare earth elements phosphate. Xenotime is commonly associated with monazite; however, yttrium in the monazite is usually present substituting for cerium. This is indicated in Table I which summarizes the distribution of rare earth elements and yttrium in monazite from different locations [1], [2].

The most important source of monazite is beach placers black sand. It was separated as by-product during the concentration and recovery of the more abundant economic minerals e.g. magnetite, ilmenite, rutile, zircon, etc. [3]. The Egyptian monazite was obtained from the black sands of Rosetta area on the Mediterranean coast. This monazite sand is generally having a size of about - 65 mesh. It worthy to mention that, the high grade Egyptian monazite sand (97% monazite) contains more than 61.0% REE₂O₃, 27.8% P₂O₅, 5.8% ThO₂, 0.5% U₃O₈ and 4.7% of others. However, the light rare earth oxides (La, Ce, Pr, Nd, Sm) assimilate 93.3% of the total rare earths while the heavy rare earth oxides almost 6.7%.

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TABLE I
RARE EARTH DISTRIBUTION IN MONAZITE FROM DIFFERENT LOCATIONS

Country	Rare earth oxide					
	La	Ce	Pr	Nd	Sm	Y
Idaho, U.S.A	26.2	46.1	6.0	17.0	2.0	1.4
Florida, U.S.A	17.5	43.7	5.0	17.5	4.9	3.2
India	23.0	46.0	5.5	20.0	4.0	1.5
China	23.4	42.7	4.1	17.0	3.0	2.4
Brazil	24.0	47.0	4.5	18.5	3.0	1.4
Mount Weld, Australia	26.0	51.0	4.0	15.0	1.8	low
Queensland, Australia	21.5	45.8	5.3	18.6	3.1	2.5
Egypt [2]	23.2	44.7	4.7	17.6	3.1	2.3

Distribution of these heavy rare earth oxides in the Egyptian monazite were illustrated in Table II.

TABLE II
HEAVY RARE EARTH DISTRIBUTION IN THE EGYPTIAN MONAZITE [2], [3]

Heavy Rare Earth Oxide (HREO)	Distribution, %
Dy	0.8
Eu	0.7
Gd	1.8
Tb	0.1
Ho	0.3
Er	0.4
Tm	0.3
Y	2.3
Σ HREO	6.7%

Rare earth elements have special properties, so they have a wide range of applications in several high technologies and industries. However, there are many domains for their uses at present which involve metallurgy, catalysts, ceramics and glass, magnets, electronics, optical and medical devices, space instrument and nuclear technologies [4]. Rare earth oxides in the composition of phosphors emitting wave lengths of red, blue and green, so they are mainly used into Cathode Ray Tubes as in color television screens and color monitors, X-Ray screens and fluorescent lamps [5].

Yttrium oxide has high melting point, so it was used in advanced ceramic compounds for special temperature application such as windows for furnaces, microscope lenses (for the study of molten material) and crucibles for vacuum melting of reactive materials like titanium. On the other hand, yttrium oxide is added as sintering agent to Sialon (silicon-nitride based strongest ceramic material). Sialon is used in cutting tool tips, adiabatic and turbo-engines as well as a coating on nozzles for high temperature technology.

Yttrium is also used in the manufacture of superconductors,

in superalloys of nickel and cobalt as well and solid oxide fuel cells. Y-Fe-garnets and Gd-Fe-garnets are used as ferrite materials in microwave devices, while Gd-Ga-garnets (GGG's) are used in substrate and thin film magnetic bubble memory system which are used mostly in communication and computer systems. On the other hand, Gd-oxide has a high neutron absorption cross-section and reduces the consumption of uranium nuclear fuels by improving the efficiency of energy output in boiling water reactors. Also, Eu and Dy are used as neutron absorbers in fast breeder nuclear reactor [6].

Sulphuric acid digestion for crude monazite sand is the classical method which has been used for many years by the processing industry [7]. The higher boiling point provides sufficient support for its choice in addition to the availability, low cost and plant corrosion; also it can be used for great variety and grades of monazite sands. The conditions, at which complete digestion of the monazite sand can be achieved, were sand particle size range 30 - 120 mesh, sulphuric acid concentration of 93%, the acid (calculated as 100%) to monazite weight ratio of 2 - 2.5 : 1, digestion temperature 200 - 230°C and agitation period 2 - 4 hours [8].

The product after digestion was pasty gray and contains anhydrous sulphates of rare earth elements [(REE)₂(SO₄)₃]. Rare earth sulphates having a lower solubility at relatively high temperatures (45°C), so half or more of the rare earth sulphates can be left un-dissolved at the water leaching stage while about 97% of thorium and uranium was dissolved [9]. In this regard the un-dissolved rare earth sulphates part can be dissolved at second water leaching stage.

The next step after leaching involves separation of the constituents from clear pregnant solutions through different precipitation methods in form suitable for further purification. The most common and promising precipitation methods are acidity control (using neutralizing agent), anhydrous sodium or ammonium sulphates and oxalic acid precipitations. These methods considered relatively selective precipitation methods where one or more of them can be used [1].

Precipitation of rare earth elements using oxalic acid was considered as the better method to produce precipitate free from the majority of accompanying and troublesome ions that hinder latter extraction processes, such as sulfate and phosphate, while leaving all uranium in solution. Also, the resultant precipitates are easily filterable and can be readily converted to hydroxide (using caustic soda) or oxides (through calcinations at about 500°C). Completeness of oxalate precipitation was found to be virtually independent of pH between 0.4 to 3.0 and temperature between 20°C to 80°C. However, pH range between 1.1 and 1.5 was preferred. Oxalate precipitation proceeds according to the following equation:



One of the largest expenses involved in oxalate precipitation process is the cost of oxalic acid, so any means of its recovering would result in substantial savings. However, oxalate precipitation for the rare earth elements has the

features of complete separation from iron, aluminum, nickel, chromium, manganese, titanium, zirconium, hafnium and uranium [10], [11].

II. EXPERIMENTAL

A. Instruments

Rare earth elements (REE) were determined individually using Dionex Ion Chromatograph DX-500 (Dionex Corporation, Sunnyvale, California, USA) equipped with AD20 UV-Visible wavelength detector and GP40 gradient pump. The REE cations were separated using an IonPac CS5A analytical column and IonPac CG5A guard column.

Scanning Electron Microscope (EDAX) was used for qualitative analysis of the rare earth and the other major constituents. Operating conditions were low vacuum, 30 KV, Take-off: 34.89, AMPT: 51.2, Detector Type: SUTW-SAPPHIRE, Resolution: 132.14.

UV-Visible spectrophotometer, multi positions, single beam, model SP-8001, Metretech Inc. version 1.02, 2000/10/01, with glass cell of 10 mm. was used for determination of thorium. Thorium was determined using Thoron [12] and uranium was determined by titration with ammonium meta vanadate [13].

Adjustment of pH for solution samples was done using pH-mv-temp. meter from HAANA instruments provided with H1 1270 combination electrode. The pH-meter was calibrated by HAANA Hi kit buffer solutions of values 4.01 and 7.01.

B. Historical of Monazite Sand Digestion, Leaching and Light Rare Earth Precipitation [14]

Egyptian crude monazite sand of 50 kg (assaying 47%) was digested using sulphuric acid under the conditions that verify maximum digestion of rare earth elements and thorium. Sulphuric acid concentration of 93% was preheated to 180°C followed by gradually addition of monazite (and barium sulphate) with stirring using mechanical stirrer. The acid to monazite sand weight ratio was equivalent to 2.5: 1.0. The temperature was increased due to the exothermic reaction, so further heating was controlled using an external temperature sensor measurement to maintain the temperature at about 220°C where the reactants digested for a period of 2.5 hour and the agitation was 2000 r.p.m.

Gray product from the digestion was cooled to room temperature then transferred to a polypropylene tank which keeps the heat of sulphuric acid dilution during the first leaching step. Tap water was added to the slurry in ratio equivalent to 10 parts / part of monazite sand then leached for one hour. The leach slurry was left to decant over night then the clear solution was withdrawn. The un-leached rare earth elements were subjected to second leaching stage where tap water was also added to the remained slurry with a ratio equivalent to 3.5 times of the slurry volume then agitated for 4.0 hours. Again, the leach slurry was left to decant over night then the clear solution was withdrawn from the remained insoluble gangues such as zircon, ilmenite and the others.

Anhydrous sodium sulphate was used to precipitate major

of the light rare earth elements from the two monazite sulphate solutions (4.5% and 7.0% Na_2SO_4 for the first and the second leach liquors respectively) then well agitated for 1.0 hr. The slurry was left to decant over night then the clear solutions were collected to conduct this experimental work.

C. Steps of Heavy Rare Earth Concentrates Preparation

1. Thorium Precipitation and Other Treatments

Thorium precipitation and the other treatments from clear solutions after double sulphate precipitation were illustrated in the flowsheet Fig. 1. Thorium was firstly precipitated from the collected solutions at pH 1.1 using 32% ammonia solution. After settling, the clear solution was withdrawn then neutralized to pH 6.5 using also ammonia solution to precipitate the remained light and heavy rare earth elements, uranium and the other constituents. The slurry of precipitate, containing rare earth as phosphate, were converted into hydroxides using sodium hydroxide pellets (equivalent to 20% w/v) in a polypropylene tank which kept the released heat due to sodium hydroxide dissolution and raise the temperature of the slurry. The converted precipitates were left over night then good washed several times through re-pulping with water to free the slurry from the alkali. The produced hydroxide precipitates in slurry were leached with hydrochloric acid at control pH of 3.0. After settling, the clear solution was withdrawn leaving the residue for further leaching.

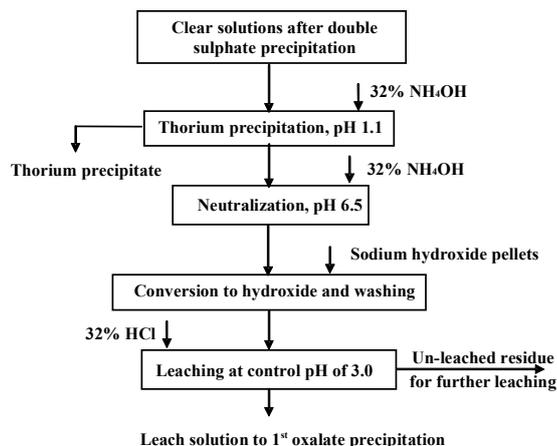


Fig. 1 Flowsheet showing different treatments for the clear solutions after double sulphate precipitation

2 Heavy and Other Rare Earth Oxalate Precipitation

Heavy and other rare earth oxalate precipitation from the hydrochloric acid leach solution was illustrated in the flowsheet Fig. 2.

The leach solutions were precipitated using oxalic acid (equivalent to 10%) where the first rare earth oxalate concentrate (denoted oxalate 1) was produced at low pH value. The precipitate was separated after decantation and good washed with 1% oxalic acid solution then dried. The clear solution from the 1st oxalate precipitation was mixed with the residue from HCl leaching stage where almost complete

dissolution for the slurry was occurred and inconsequent another rare earth oxalate concentrate (denoted oxalate 2) was produced also at low pH value. The precipitate was separated after decantation, filtration and washing with 1% oxalic acid solution then dried. The latter clear solution was successively adjusted to pH 3.6 where another rare earth oxalate concentrate (denoted oxalate 3) was produced which decanted, filtered and washed with 1% oxalic acid solution then dried. Finally, the last clear solution of pH 3.6 was neutralized to pH 7.5 where the final concentrate was produced which will contain uranium and any other constituents.

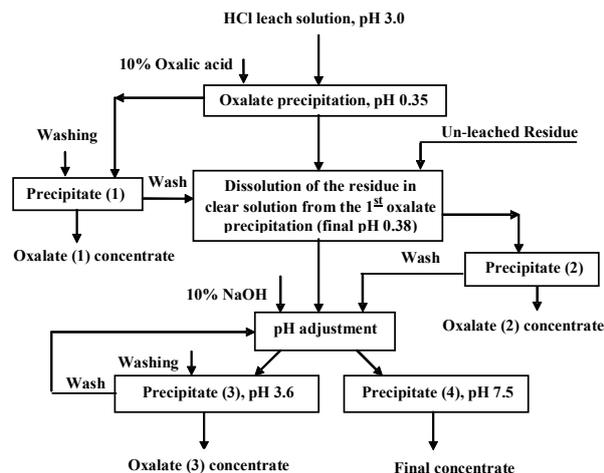


Fig. 2 Flowsheet showing steps for preparation heavy rare earth concentrates

III. RESULTS AND DISCUSSION

A. Monazite Sand Digestion and Leaching

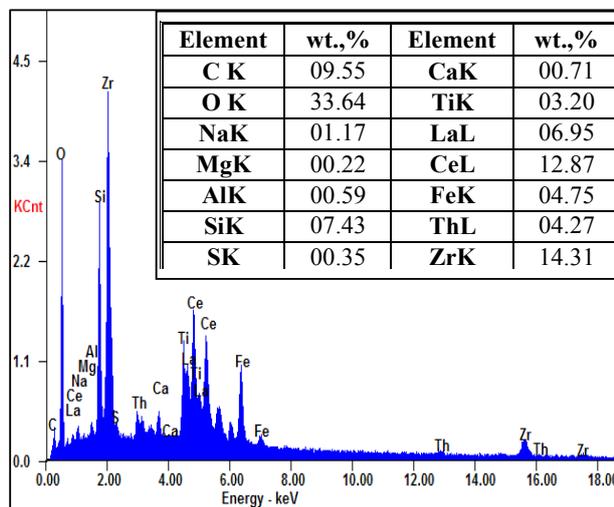


Fig. 3 Specification of the Egyptian crude monazite sand using the scanning electron microscope (SEM)

Egyptian crude monazite sand sample was specified by the scanning electron microscope (SEM), where the results indicated in Fig. 3. The sample composed of monazite in

addition to ilmenite (3.2% Ti, 4.75% Fe) and zircon (14.3% Zr, 7.3% Si). The digestion efficiency for this sample was 91.2%, 96.6% and 92.1% for cerium, thorium and overall monazite sand respectively. After leaching the grey past produced from monazite sand digestion into two stages, the precipitation efficiency of light rare earth as double sulphate was more than 90% and 96% from the two leach solutions respectively [14].

B. Concentration of Rare Earth Elements in the Hydrochloric Acid Leach Solution

The hydroxide precipitate, prepared from the solutions after light rare earth double sulphate and thorium precipitations, was leached with hydrochloric acid at control pH of 3.0. Concentration of rare earth elements in the HCl clear leach solution was shown in Table III.

TABLE III
CONCENTRATION OF RARE EARTH ELEMENTS IN HYDROCHLORIC ACID LEACH SOLUTION

Element	Gd	Tb	Dy	Er	Tm	Y
Conc., ppm	380	72	1485	253	1353	7788

The results indicated that the heavy rare earth elements, Y, Dy and Tm were leached selectively at the control pH of 3.0 while the others (Gd, Tb and Er) were partially leached leaving almost whole of the light rare earth elements un-leached.

C. Composition of the Prepared First Rare Earth Oxalate Concentrate

The prepared first rare earth oxalate concentrate weighing 2.44 Kg and the loss on ignition was 62.2%. Results of quantitative analysis for the concentrate using Ion Chromatograph (IC) were indicated in Table IV. The results revealed that the concentrate composed mainly of Y, Dy and Tm (about 7.3, 1.4 and 1.3% respectively) and almost free from light rare earth elements.

TABLE IV
CONCENTRATION OF INDIVIDUAL RARE EARTH ELEMENTS IN THE 1ST OXALATE CONCENTRATE (IC ANALYSIS)

Rare Earth Element	wt., %
Gd	0.35
Tb	0.07
Dy	1.38
Er	0.23
Tm	1.26
Y	7.25
Σ HREE	10.54

Results of SEM qualitative analysis were indicated in Fig. 4. The major constituent, other than yttrium, was sodium (36%) while calcium was only 1%. It is worthy to mention that the solution after 1st oxalate precipitation was almost free from heavy rare earth elements which indicate that complete precipitation was occurred.

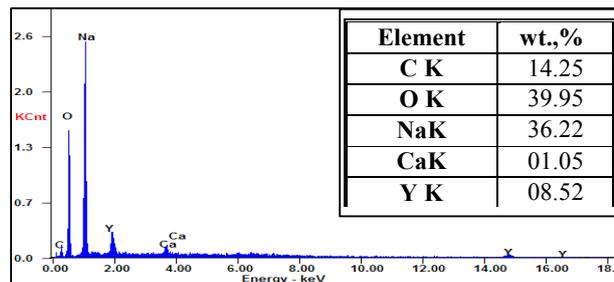


Fig. 4 SEM qualitative analysis for the 1st oxalate concentrate

D. Composition of the Prepared Second Rare Earth Oxalate Concentrate

The clear solution from the 1st oxalate precipitation having high concentration of the oxalic acid which lowering also the pH value of the solution from 3.0 to 0.35. Accordingly, it was decided to its re-use for dissolution of the remained un-leached slurry from the HCl leaching stage where almost complete dissolution was occurred and in the same time another rare earth oxalate concentrate was precipitated also at low pH value which reached to 0.38.

The prepared second rare earth oxalate concentrate weighing 1.46 Kg and the loss on ignition was 46%. Results of quantitative analysis for the concentrate using Ion Chromatograph (IC) were indicated in Table V. The results revealed that the concentrate composed mainly of light rare earth elements (about 41%) while the heavy rare earth elements was about 17%. The results also assure that the light rare earth elements were almost un-leached with hydrochloric acid during the first leaching step at pH 3.0.

TABLE V
CONCENTRATION OF INDIVIDUAL RARE EARTH ELEMENTS IN THE 2ND OXALATE CONCENTRATE (IC ANALYSIS)

Element	wt., %	Element	wt., %
La	10.53	Eu	0.05
Ce	18.27	Gd	3.51
Pr	2.54	Tb	0.47
Nd	8.13	Dy	2.90
Sm	2.27	Er	0.45
Σ LREE	40.74	Tm	1.18
		Y	8.70
Th	13.6	Σ HREE	17.26

On the other hand, the high percent of heavy rare earth content could be sharply decreased from the second rare earth oxalate concentrate if the slurry was pre-filtered and good washed with acidified water (pH 3.0 or less) and the filtrate was added to the original HCl leach solution. In this case most of Y, Dy and Tm can be separated in the first rare earth oxalate concentrate. The results show also presence high percent of thorium (13.6%), however, due to the flocculent nature of thorium phosphate precipitate, it can be withdrawn with the clear solutions. Accordingly, it would be polish the solutions through filtration stage before conducting neutralization step during the pre-treatment stage. Also, it must be assured that almost complete precipitation of thorium was achieved to prevent its appearance in the second rare earth oxalate concentrate as soon as possible.

Qualitative analysis for the prepared second rare earth oxalate concentrate using SEM was indicated in Fig. 5 and the corresponding table. The results assure that presence high percent of light rare earth elements (about 36%) and thorium (about 21%).

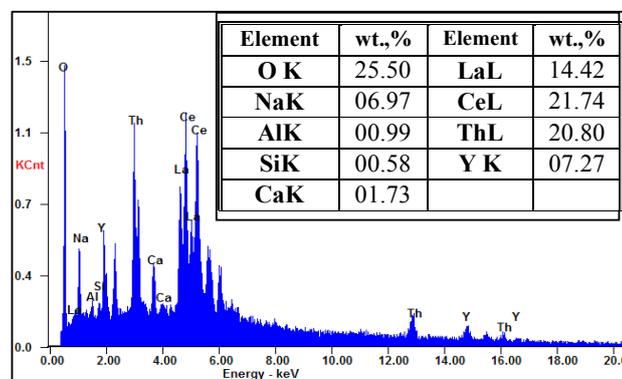


Fig. 5 SEM qualitative analysis for the 2nd oxalate concentrate

F. Concentration of Rare Earth Elements and Uranium in the Solution after the Second Oxalate Precipitation

Concentration of rare earth elements and uranium in the solution after the second oxalate precipitation were indicated in Table VI. The results indicate presence of appreciable concentration of both heavy and light rare earth elements which requires their separation through pH adjustment step.

TABLE VI
CONCENTRATION OF INDIVIDUAL RARE EARTH ELEMENTS AND URANIUM IN THE SOLUTION AFTER 2ND OXALATE PRECIPITATION (IC ANALYSIS)

Element	Conc., ppm	Element	Conc., ppm
La	825	Eu	21
Ce	1560	Gd	1450
Pr	150	Tb	195
Nd	635	Dy	1220
Sm	165	Er	186
U	2450	Tm	505
		Y	3650

G. Composition of the Prepared Third Rare Earth Oxalate Concentrate

The third rare earth oxalate concentrate prepared from the solutions produced after second oxalate precipitation by adjusting its pH to 3.6. This concentrate was weighing about 1.0 Kg and the loss on ignition was about 36%. Results of rare earth elements quantitative analysis using Ion Chromatograph (IC) were indicated in Table VII. The results revealed that the concentrate composed of about 8% light and 10% heavy rare earth elements.

Results of qualitative analysis were indicated in Fig. 6. The data revealed that presence of high percent of iron and uranium. These amounts could be eliminated or sharply decreased if the pH just adjusted to 2.5 or less, in this case the concentrate can be upgraded and its purity increased. On the other hand, precipitation of titanium can be also prevented through addition of hydrogen peroxide.

TABLE VII
CONCENTRATION OF INDIVIDUAL RARE EARTH ELEMENTS IN THE 3RD OXALATE CONCENTRATE (IC ANALYSIS)

Element	wt.,%	Element	wt.,%
La	1.94	Eu	0.03
Ce	3.70	Gd	0.96
Pr	0.36	Tb	0.12
Nd	1.51	Dy	2.12
Sm	0.40	Er	0.22
Σ LREE	7.91	Tm	0.40
		Y	6.36
U	2.1	Σ HREE	10.21

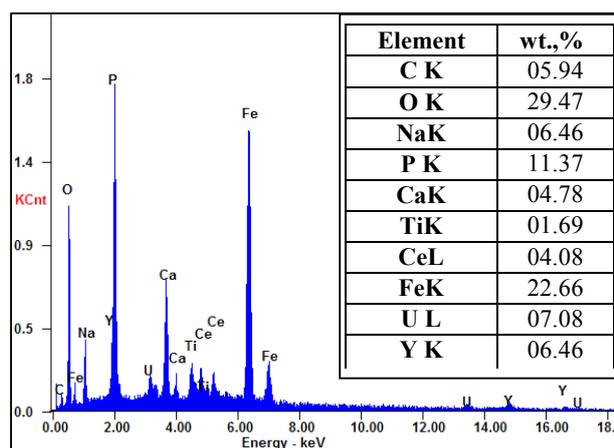


Fig. 6 SEM qualitative analysis for the 3rd oxalate concentrate

H. Concentration of Rare Earth Elements and Uranium in the Final Solution

Concentration of un-precipitated rare earth elements and uranium, in the solution after pH adjustment to 3.6, were illustrated in Table VIII. The results revealed that almost complete precipitation for REE was occurred, but also appreciable amount of uranium was precipitated.

TABLE VIII
CONCENTRATION OF INDIVIDUAL RARE EARTH ELEMENTS IN THE SOLUTION AFTER 3RD OXALATE PRECIPITATION (IC ANALYSIS)

Rare Earth Element	Conc., ppm
La	25
Ce	31
Nd	11
Dy	22
Tm	17
Y	55
U	580

Pr, Sm, Eu, Gd, Tb and Er are not detected

Precipitation efficiency of rare earth elements from solutions after pH adjustment to 3.6 was about 98% for La, Ce, Nd, Dy, Tm, Y and almost complete precipitation for the others, while about 76% of uranium was precipitated.

I. Composition of the Final Concentrate Produced after Solution Neutralization

The final concentrate, produced after neutralization at pH 7.5 for the solution from the third oxalate precipitation was weighing 1.73 Kg and the loss on ignition was 14.8%. The

concentrate was specified quantitatively for rare earth elements (Table IX). The results indicate presence of trace amounts of some rare earth elements which was only 0.6% that reveals almost complete precipitation for them at the previous pH adjustment at 3.6, on the other hand, the concentrate was containing 0.84% uranium.

TABLE IX
CONCENTRATION OF INDIVIDUAL RARE EARTH ELEMENTS IN THE FINAL CONCENTRATE AFTER NEUTRALIZATION (IC ANALYSIS)

Rare Earth Element	wt., %
La	0.04
Ce	0.05
Pr	0.01
Nd	0.02
Tm	0.38
Y	0.09
Σ REE	0.59
U	0.84

Sm, Eu, Gd, Tb, Er, Yb and Lu were not detected

However, qualitative analysis for the other constituents in the concentrate using SEM was indicated in Fig. 7. The results indicate presence of iron and chromium with uranium.

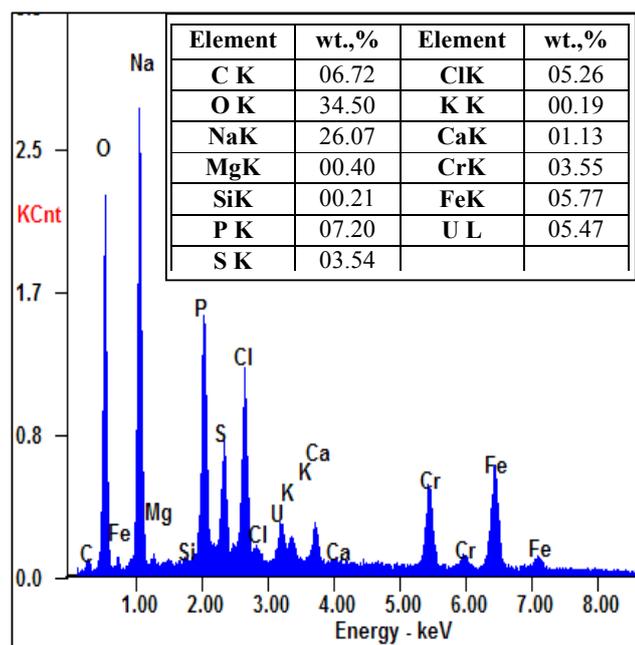


Fig. 7 SEM qualitative analysis for the final concentrate after

neutralization

J. Distribution of Rare Earth Elements in the Prepared Three Oxalate Concentrates

Distribution of rare earth elements in the prepared three oxalate concentrates was illustrated in Table X. The data reveal that about 90% of the light rare earth with 70% of Gd and Tb also 33 – 45% of the other heavy rare earth elements was separated in the second oxalate concentrate.

TABLE X
DISTRIBUTION OF RARE EARTH ELEMENTS IN THE PREPARED THREE OXALATE CONCENTRATES

Element	REE Distribution in each Oxalate Concentrate, %		
	1 st	2 nd	3 rd
La	---	88.80	12.20
Ce	---	86.00	14.00
Pr	---	91.20	08.80
Nd	---	88.72	11.28
Sm	---	89.2	10.80
Gd	12.30	73.90	13.80
Tb	17.45	70.00	12.28
Dy	34.60	43.60	21.80
Er	39.12	45.63	15.28
Tm	59.16	33.14	07.70
Y	48.10	34.60	17.30

IV. CONCLUSION AND RECOMMENDATIONS

The conclusion and recommendations for separation of heavy rare earth oxalate concentrates from Egyptian crude monazite were illustrated in the proposal flowsheet Fig. 8. The important recommendations taken in consideration involve filtration the clear solution, withdrawn from the flocculent thorium precipitate, before neutralization in the pre-treatment step to prevent presence of thorium with the second rare earth oxalate concentrate. Also, filtration and washing the residue remained after hydrochloric acid leaching of rare earth – uranium hydroxide at pH 3.0, to reduce the presence of heavy rare earth elements in the second rare earth oxalate concentrate. In this case, each of heavy and light rare earth elements would be up-graded in the first and second oxalate concentrates respectively. Finally, to eliminate or sharply decrease both of iron and uranium in the third rare earth oxalate concentrate, the solution pH just adjusted to 2.5 or less, accordingly the concentrate could be up-graded and its purity increased.

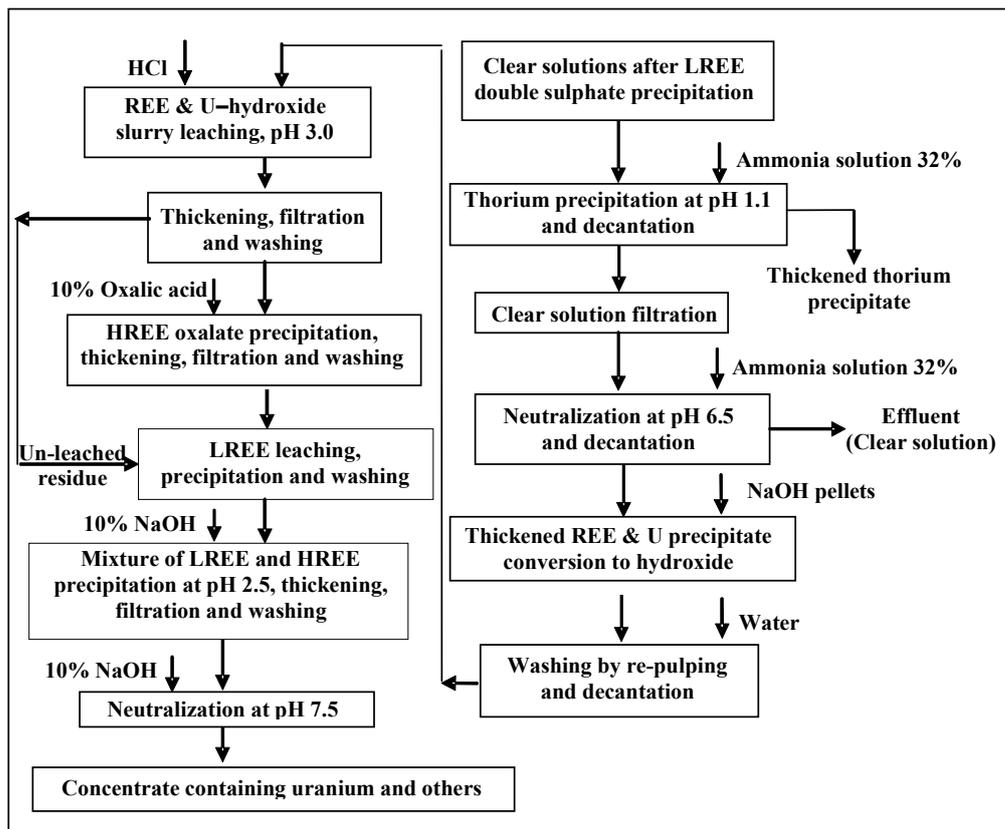


Fig. 8 Proposed flowsheet for separation of heavy rare earth concentrates from Egyptian crude monazite

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