

ISSN 2249-8540

Original Article

Evaluation of Rare Earth Double Sulphate Precipitation From Monazite Leach Solutions

Ahmed, S.H.*, Helaly, O.S., Abd El-Ghany, M.S.

Nuclear Materials Authority, P.O.Box 530 El-Maadi, Cairo, Egypt

*Corresponding Author: boutey@yahoo.com

Received 12 December 2014; accepted 15 January 2015

Abstract

Egyptian crude monazite sand was digested using sulphuric acid and the produced gray past was cooled to ambient temperature then leached through two successive stages using normal water. The two leach solutions contain 16.77, 59.29 g/l light rare earth (LREE) and 1.81, 3.67 g/l heavy rare earth (HREE) respectively. Rare earth double sulphate precipitation was carried out upon the leach solutions using 4.5% anhydrous Na_2SO_4 for the first and 7.0% for the second. The precipitate from each solution was classified during the washing step into three fractions according to the specific gravity then converted separately into hydroxide; washed and dried at 180°C . Specification of the six precipitate fractions against their constituents reveals that there is no appreciable concentration for any of the rare earth elements; on the other hand, thorium was substantial co-precipitated.

The hydrous cakes were then subjected to cerium IV and trivalent rare earth separation in two concentrates through dissolving REE^{3+} using 1.0 M nitric acid at control pH of 3.0 where most of Ce^{4+} was lifted un-dissolved with thorium and uranium. The dissolved REE^{3+} were precipitated at pH 8.5 using 10% sodium hydroxide, while the remained clear solution was thoroughly precipitated at pH 12. Cerium concentrate was containing more than 48% Ce with about 3% La, 4% Nd and 6% Th. The trivalent rare earth concentrate containing more than 65% LREE and about 5% HREE where the LREE composed of about 25% La, 23% Nd, 6% Ce, 5% Pr and 4% Sm. The precipitate at pH 12 composed mainly of calcium and magnesium with trace amounts of light rare earth

© 2015 Universal Research Publications. All rights reserved

Key words : *Crude monazite; Leaching; Light rare earth; Thorium; Double sulphate precipitation; Cerium; Trivalent rare earth; Concentrates.*

1. Introduction

Monazite mineral is considered as a source of the world supply of both rare earth elements and thorium. Rare earth elements have special properties, so they have a wide range of applications in several high technologies and industrial products. However, there are many domains for their uses at present these involve metallurgy, catalysts, ceramics and glass, magnets, electronics, optical, medical and nuclear technologies⁽¹⁾.

The most important source of monazite is beach placers black sand. The Egyptian black sand was obtained from the deposits at Rosetta area on the Mediterranean coast and the mineral, monazite, was separated as by-product during the concentration and recovery of the most abundant economic minerals e.g. magnetite, ilmenite, rutile, zircon, etc⁽²⁾.

Digestion of crude monazite sand by sulphuric acid is the classical method which has been used for many years by the processing industry. The higher boiling point provides sufficient support for the choice in addition to the

availability, low cost and plant corrosion also it can be used for great variety of monazite sands size and grades^(3,4).

The gray past product after monazite digestion contains anhydrous sulphates of rare earth elements, thorium, uranium as well as phosphoric acid and the excess sulphuric acid. Depending upon the fact that rare earth sulphates having lower solubility at relatively high temperatures, so that more than half of the rare earth sulphates can be left un-dissolved at the water leaching stage while about 97% of thorium and uranium was dissolved. In this regard the un-leached rare earth sulphates part can be dissolved at second water leaching stage⁽⁵⁾.

The next step follow leaching is separation of rare earth constituents from the clear pregnant solutions in a suitable form using different precipitation methods for further purification. The most common and promising precipitation methods are acidity control using neutralizing agent, anhydrous sodium or ammonium sulphates and oxalic acid. These methods considered relatively selective precipitation where one or more of them can be used⁽⁶⁾.

Precipitation of rare earth elements with anhydrous sodium sulphate is interesting direct precipitation from sulphuric acid solutions (or after thorium removal through acidity control). The resultant rare earth double sulphate precipitate is composed mainly of the majority of light rare earth elements in the form $(\text{REE})_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ while most of yttrium and the other heavy rare earth elements in addition to 50 – 60% of gadolinium remain unprecipitated. The precipitate is easily filterable and washing also convenient to store as starting material for the manufacture of rare earth materials in addition it can be converted to hydroxides by caustic soda. The precipitation method permits recycling the acids (sulphuric and phosphoric) for a subsequent monazite breakdown which are more efficient^(7,8,9).

In order to facilitate the subsequent rare earth separation and purification steps, it would be preferable to remove the bulk of trivalent rare earth elements from cerium. In this regard, the mixture of rare earth hydroxides was dried at 150 - 180°C for 10 hours to oxidize Ce^{3+} to Ce^{4+} . The oxidized cake is then treated with hydrochloric (or nitric) acid up to a pH of 3.0 - 4.0 whereby about 99% of the cerium remained un-dissolved together with thorium and uranium, if present, and about 10% of the other trivalent rare earth elements. It is worthy to mention that

heating the mixture at 70 - 80°C for ten minutes after pH adjustment has the advantage of enhancing the dissolution process, re-precipitating the less basic elements as well as improvement the filtration properties^(6,9).

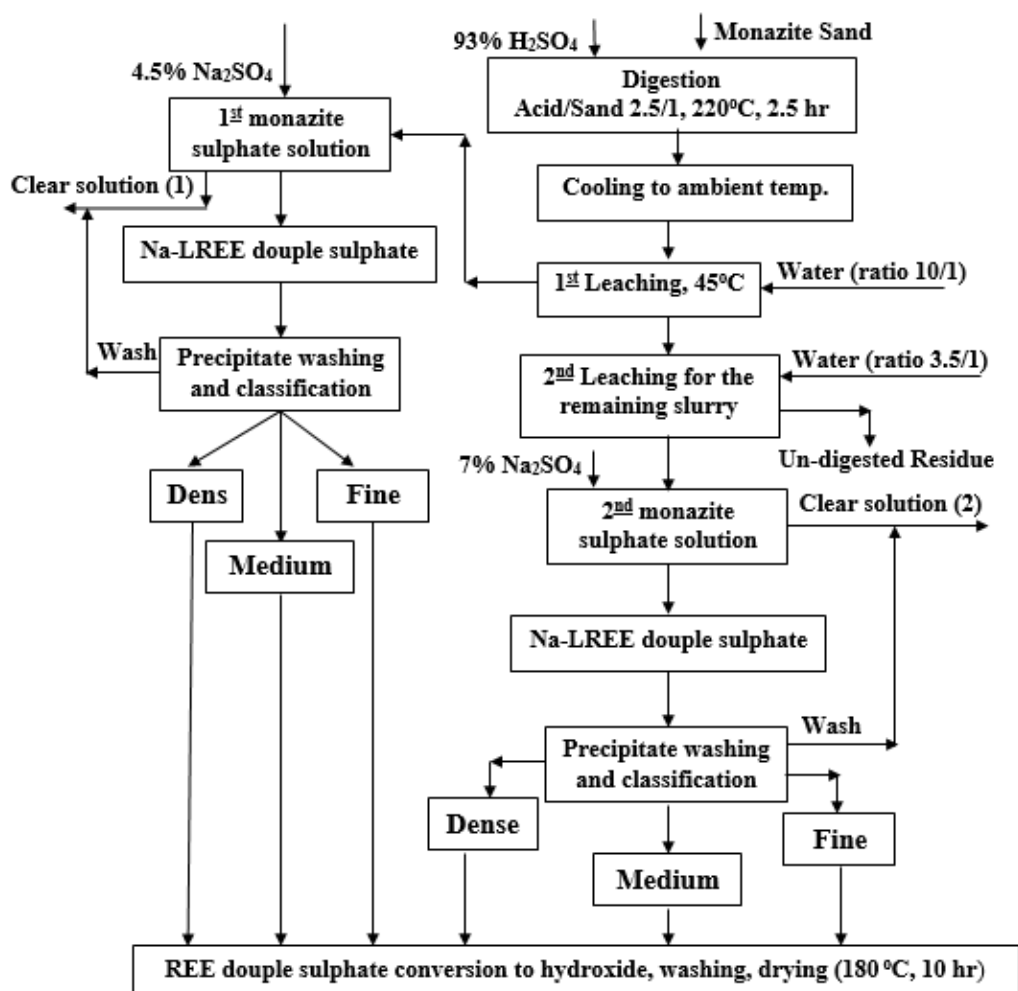
2. Experimental

2.1. Instruments

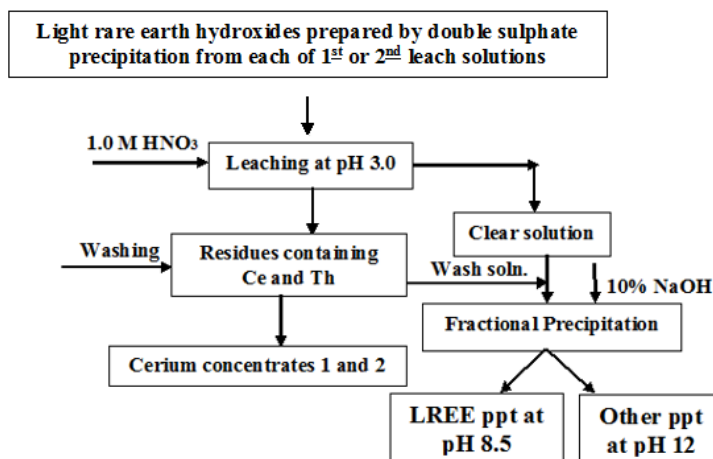
Temperature and pH measurements were done using pH-mv-temp. meter from HAANA instruments. Rare earth elements were determined individually using Dionex Ion Chromatograph DX-500 (Dionex Corporation, Sunnyvale, California, USA) equipped with AD20 UV-Visible wavelength detector and GP40 gradient pump. The REE cations were separated using an IonPac CS5A analytical column and IonPac CG5A guard column. Scanning Electron Microscope (ESEM), model Philips XL 30, was used for qualitative analysis of the rare earth elements and the other major constituents. UV-spectrophotometer, multi positions, single beam model SP-8001, Metretech Inc. was used for determination of thorium. Thorium was determined using Thoron⁽¹⁰⁾ while uranium was determined by reduction-oxidation titration method using ammonium meta vanadate as titrant⁽¹¹⁾.

2.2. Preparation Procedures

Sequence of the present work was shown in flow sheets (1, 2) and includes the following preparation steps:



Flow Sheet 1: Schematic flow diagram showing preparation steps for light rare earth concentrates via double sulphate precipitation



Flow Sheet 2: Flow diagram showing steps of cerium IV and rare earth III concentrates preparation

2.2.1. Preparation of Monazite Sulphate Solutions

The conditions that verify maximum digestion using sulphuric acid of 93% concentration were applied upon 50 kg of the Egyptian crude un-ground monazite sand (- 65 mesh) of grade about 47%. Sulphuric acid (calculated as 100%) in weight ratio to monazite sand of 2.5:1, was preheated to 180°C followed by gradually addition of the sand with stirring. Barium sulphate is added in amount of 0.5 g / kg monazite to keep the associated radium as insoluble radium-barium sulphate. The temperature is 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^(4,12,13).

The gray product after digestion was cooled to ambient temperature then transferred to a polypropylene graduated tank to perform the first leaching step where normal water was added in a ratio to the monazite sand of 10 / 1. The slurry was agitated for one hour, left to decant then the clear solution withdrawn. Five liters of concentrated sulphuric acid was added to the remained un-leached constituents then subjected to second leaching also with normal water in ratio equivalent to 3.5 times of the slurry's volume and agitated for 3.0 hours. Again, the leach slurry was left to decant then the clear solution withdrawn where the remained solids represent the insoluble gangues. Samples from the two leach liquors were analyzed against their constituents.

2.2.2. Preparation of Rare Earth Sodium Double Sulphate Concentrates

Precipitation of the rare earth sodium double sulphate was carried out using 4.5% and 7% anhydrous sodium sulphate for the first and second leach solutions respectively⁽¹⁴⁾. The produced rare earth double sulphate precipitate was left to decant overnight then the clear solutions withdrawn. Samples from the two liquors after precipitation were analyzed against the un-precipitated rare earth elements where the precipitation efficiency was calculated.

Rare earth double sulphate was thoroughly washed through re-pulping with water and decantation several times. During this washing step each precipitate was classified into three fractions depending on the specific gravity. These fractions were then converted individually to

hydroxides by adding sodium hydroxide pellets (equivalent to 20% sodium hydroxide in the solution⁽¹⁵⁾) and good agitated then left over night. The resultant hydroxides slurry was washed efficiently through re-pulping with water and decantation several times, filtered then dried at 180°C for 10 hours for oxidizing the cerium constituents to its tetravalent state. Samples from the produced oxidized hydrous cakes were analyzed against rare earth constituents using ion chromatography (IC) also thorium and uranium were analyzed. Other samples were ignited at 1000°C and qualitatively specified using Scanning Electron Microscope (SEM).

2.2.3. Cerium IV / Rare Earths III Separation:

The oxidized hydroxide cake was slurred with water then treated with 1.0 M nitric acid to pH 3.0 for leaching major of the trivalent rare earth elements and leaving the tetravalent cerium as concentrate. Cerium concentrate was filtered, washed with acidified water of the same pH then dried where sample was specified quantitatively using IC and qualitatively using SEM. The leach solution, containing major of light and other trivalent rare earths, was subjected to precipitation at pH 8.5 using 10% sodium hydroxide.

The clear solution after solids decantation was withdrawn and the light rare earths concentrate was filtered, washed then dried. The pH of clear solution was thoroughly increased to 12 for precipitation any of the other constituents. Samples from the two produced precipitants were specified quantitatively using IC and qualitatively using SEM.

3. Results and Discussion

3.1. Leaching of the Digested Monazite

Concentration of rare earth and some elements in the prepared two leach solutions are illustrated in Table 1. It is clear that the second leach liquor contains high concentration of the rare earth elements (59.29 g/l light rare earth and 3.67 g/l heavy rare earth) and their amounts represent 2/3 of the total. On the other hand, most of thorium and uranium goes into the first leach solution, however, presence of thorium and uranium in the second leach liquor was due to un-washing the slurry before conducting the second leaching step. So, if the slurry was filtered then washing the residue with minimum amount of hot water to avoid dissolution of the rare earth, thorium and

Table 1: Concentration of rare earth and some elements in the obtained two leach solutions

Constituent	Concentration of rare earth elements and some other metals in monazite sulphate solution, g/l	
	1 st leach	2 nd leach
La	4.61	15.17
Ce	7.29	28.71
Pr	0.90	2.5
Nd	3.27	10.3
Sm	0.70	2.61
Σ LREE	16.77	59.29
Eu	0.04	0.06
Gd	0.46	1.17
Tb	0.05	0.07
Dy	0.27	0.58
Ho	N.D.	0.05
Er	0.09	0.07
Tm	0.32	0.44
Y	0.58	1.23
Σ HREE	1.81	3.67
Th	4.66	1.33
U	0.41	0.12
Fe	5.80	1.66
Ti	0.43	0.10

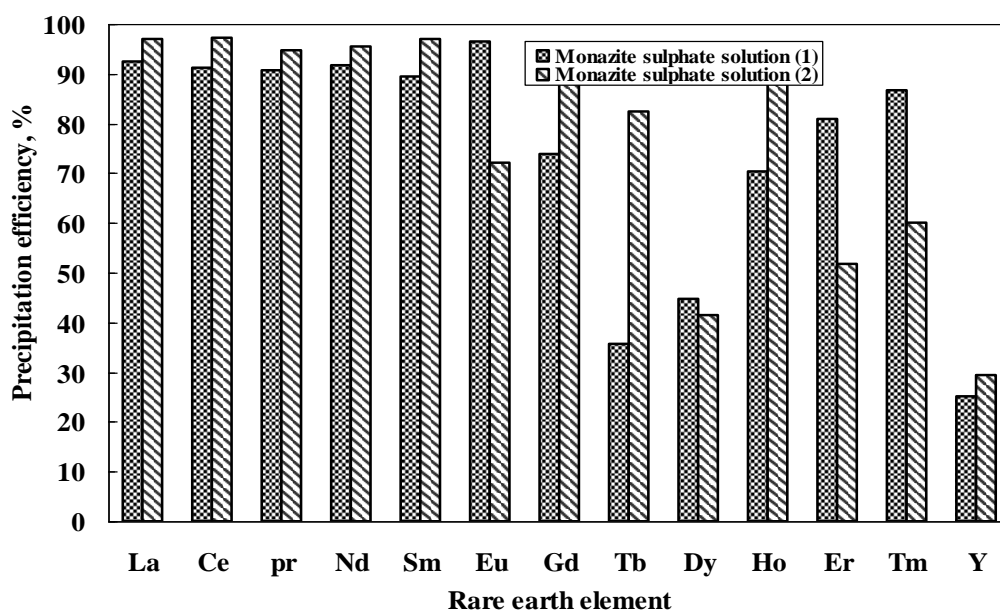


Fig. 1: Individual rare earth double sulphate precipitation efficiency

uranium can be sharply decreased.

3.2. Precipitation of Rare Earth Double Sulphate:

Precipitation efficiency of rare earth double sulphate from the 1st and 2nd monazite sulphate leach solutions was illustrated in Fig. (1). It is clear that precipitation efficiency of light rare earth (La – Sm) was about 91% from the 1st leach solution while it was reached to about 97% from the 2nd leach solution. However, about 80% of Gd was precipitated, while precipitation efficiency of yttrium, which represents the major constituent of the heavy rare earth, was about 41.5% and 29% from the two leach solutions respectively. Precipitation efficiency of the heavy

rare earth elements Tb were about 35.8%, 82.5% from the 1st and the 2nd leach solutions respectively.

3.3. Qualification of the rare earth concentrates prepared from double sulphate precipitation:

Quantitative analysis of rare earth elements using the ion chromatography for the prepared three double sulphate fractions (dense, medium and the fine particulates) from the two monazite sulphate leach solutions are shown in Table 2. The results reveal that there is no appreciable concentration for any of the rare earth elements in these fractions. However, the sum of light rare earth elements in all fractions ranged from 61% to 73% while the sum of

Table 2: Quantitative analysis of the classified double sulphate precipitate fractions from the 1st and 2nd monazite sulphate solutions using ion chromatography

Element, wt. %	Double sulphate precipitate produced from					
	1 st Monazite sulphate solution			2 nd Monazite sulphate solution		
	Particulates			Particulates		
	Dense	Medium	Fine	Dense	Medium	Fine
La	18.74	20.22	19.8	20.12	20.53	18.63
Ce	23.42	30.94	31.74	27.05	32.52	27.54
Pr	3.81	3.33	3.25	4.53	3.55	2.63
Nd	12.86	16.17	14.62	14.63	15.10	13.00
Sm	2.58	2.93	2.49	3.33	3.28	2.7
∑ LREE	61.41	73.59	71.9	69.66	64.98	64.5
Eu	N.D.	0.15	0.07	N.D.	N.D.	0.13
Gd	1.10	1.57	1.38	1.40	1.98	1.10
Tb	N.D.	0.14	0.04	N.D.	N.D.	N.D.
Dy	0.24	0.31	0.27	0.34	0.25	0.21
Tm	1.05	0.86	1.5	1.53	1.46	0.78
Y	0.71	0.80	0.68	0.90	0.97	0.65
∑ HREE	3.1	3.83	3.94	4.17	4.66	2.87
Th	6.72	6.46	8.1	1.44	1.41	1.30
U	0.61	0.67	0.82	0.05	0.05	0.03

* N.D.: Not detected

* Ho, Er, Yb and Lu not detected

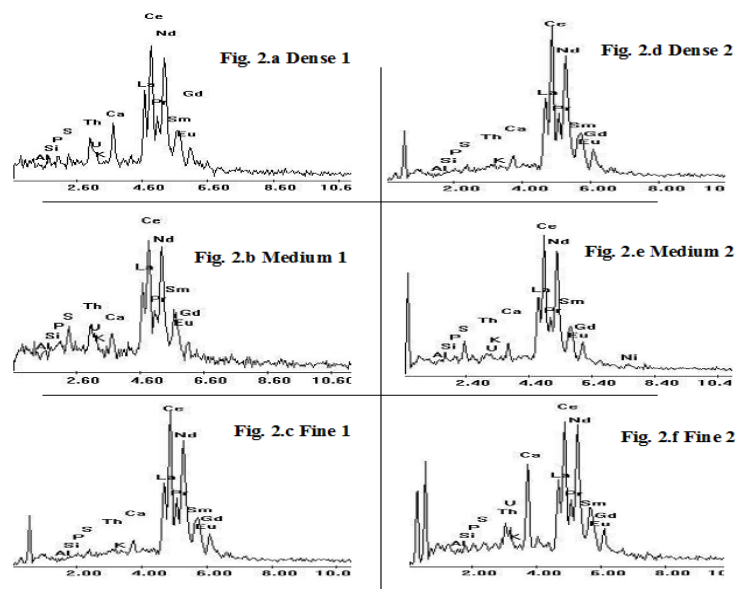


Fig. 2: SEM specification for the prepared rare earth double sulphate precipitates fractions (ignition at 1000°C)

heavy rare earth elements was in the range of 3% - 4%.

The results of qualitative analysis for the studied ignited fractions using Scanning Electron Microscope (SEM) were shown in Table 3 and Fig. 2. a – f. Taking in consideration these results, it is clear that the three fractions prepared from the 1st monazite sulphate solution containing high thorium content about 5.0 - 10.0% while that prepared from the 2nd leach solution contain low thorium 1.5 - 3.0%. It is worthy to mention that appreciable amount of uranium (1.0 – 1.6%) was also co-precipitated with the precipitates prepared from 1st monazite sulphate solution. Again, there is no concentration for any of the major elements La, Ce or Nd in these fractions where this result appeared from

comparing the ratios of Ce / La, Ce / Nd and La / Nd in these fractions (Table 4) with that originally present in the treated monazite sample.

3.4. Qualification of the Concentrates from Cerium IV / Rare Earths III Separation:

3.4.1. Specification of Cerium Concentrate:

Results of cerium concentrates analysis produced after rare earth III separations using IC was shown in Table 5 while that specified using SEM was shown in Fig. 3. The data was revealed that cerium concentrate containing more than 48% Ce but also containing appreciable amount of the other main light rare earth (more than 3% of each La and Nd).

Table 3: Qualitative analysis of the classified double sulphate precipitate fractions from the 1st and 2nd monazite sulphate solutions using the SEM

Element, wt. %	Double sulphate precipitate produced from						
	1 st Monazite sulphate solution				2 nd Monazite sulphate solution		
	Particulates				Particulates		
		Dense	Medium	Fine	Dense	Medium	Fine
	Wt., %	8.54	37.46	54.00	17.16	17.61	65.23
LOI, %	20.0	20.0	21.0	18.0	20.0	23.0	
AlK	0.26	0.77	0.48	0.34	0.43	0.31	
SiK	1.16	0.39	0.98	0.40	0.98	1.42	
P K	1.42	1.62	0.78	0.44	0.69	0.88	
S K	0.67	2.76	0.30	0.59	2.45	2.37	
ThM	4.73	7.84	10.25	1.50	1.95	2.96	
UM	1.05	1.61	1.09	0.12	0.32	0.22	
CaK	1.45	1.85	6.86	1.21	1.36	3.83	
LaL	22.2	22.5	19.86	23.56	21.98	21.12	
CeL	42.66	41.86	37.39	47.79	44.51	42.19	
PrL	4.14	2.51	3.41	4.98	3.88	3.94	
NdL	17.75	16.14	15.70	16.92	16.76	17.55	
SmL	1.92	0.55	1.96	1.70	3.03	2.35	
EuL	0.00	0.00	0.00	0.00	0.59	0.63	
GdL	0.59	0.41	0.49	0.45	1.07	1.16	
Σ REE	89.26	83.97	78.81	95.4	91.82	88.94	

Table 4: Ratio of the major light rare earth elements in classified double sulphate precipitate fractions and the original monazite

Elements ratio	Monazite sand (grade 97%)	Rare earth concentrates prepared from the 1 st leaching			Rare earth concentrates prepared from the 2 nd leaching		
		Dense	Medium	Fine	Dense	Medium	Fine
Ce / La	1.93	1.92	1.82	1.88	2.03	2.03	2.00
Ce / Nd	2.54	2.40	2.60	2.38	2.80	2.66	2.40
La / Nd	1.32	1.25	1.40	1.30	1.40	1.30	1.20

Table 5: Composition of cerium concentrate produced after rare earth III separations

Element	La	Ce	Nd	Pr	Th	U
wt., %	03.43	48.61	3.96	0.76	6.10	0.60

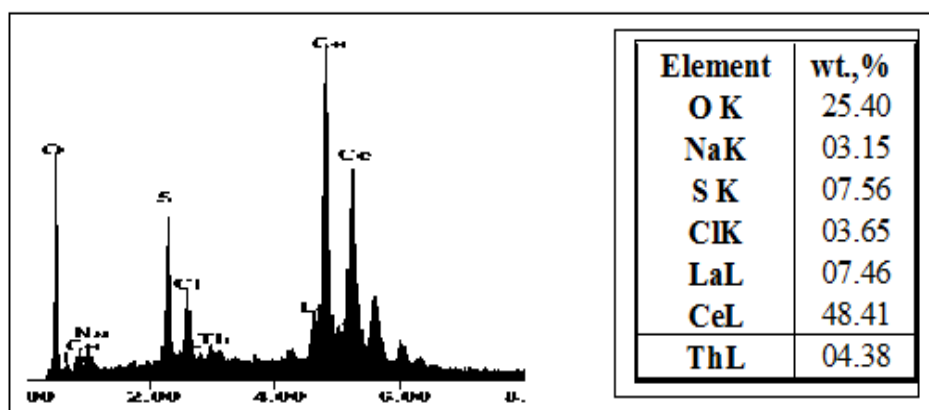


Fig. 3: Scanning Electron Microscope specification for cerium 1 and 2 concentrates produced after rare earth III separations

3.4.2. Light Rare Earths Specification:

The concentrate containing most of light rare earth elements was prepared after precipitation at pH 8.5 from the leach solutions. Results of analysis this concentrate using IC was shown in Table 6 and its specification using SEM was shown in Fig. 4. The data was indicated that the concentrate containing about 66% of light rare earth (about 6% of them cerium) and containing about 5% of heavy rare earth elements.

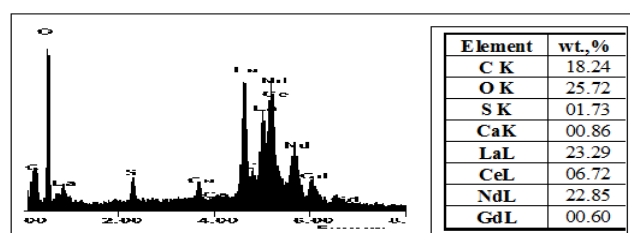


Fig. 4: Scanning Electron Microscope specification for rare earth III concentrate precipitated at pH 8.5

Table 6. Composition of rare earth III concentrate leached from cerium

LREE	wt., %	HREE	wt., %
La	25.38	Eu	0.17
Ce	06.39	Gd	2.34
Pr	05.24	Tb	0.21
Nd	22.95	Dy	0.53
Sm	03.80	Ho	0.08
		Er	0.05
		Tm	0.24
		Y	1.35
	Σ 65.76		Σ 4.97

Table 7: Composition of concentrate precipitated at pH 12

Element	wt., %
La	0.133
Ce	0.079
Pr	0.028
Nd	0.109

On the other hand, composition of the precipitate resultant from further precipitation to pH 12 (Table 6 and Fig. 5) was calcium and magnesium (more than 41%) while the light rare earth was contained in trace amounts that reveals that almost complete precipitation was achieved at pH 8.5.

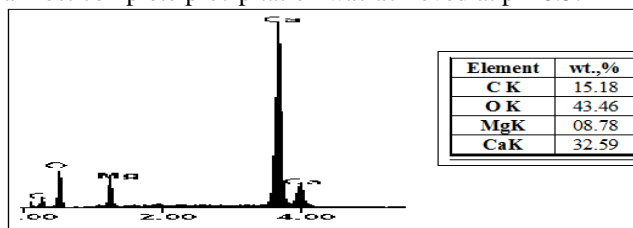
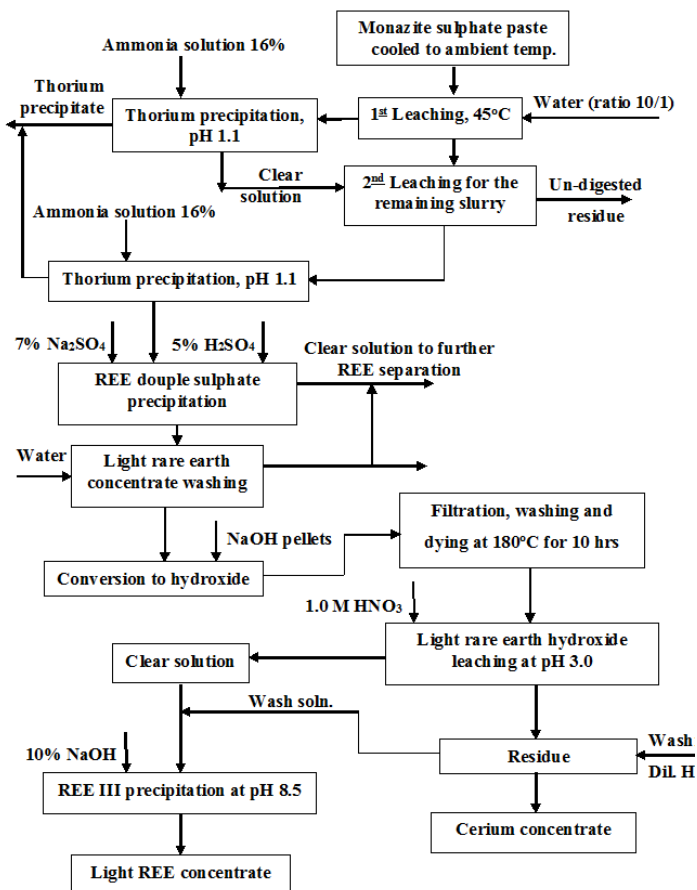


Fig. 5: SEM specification for the concentrate precipitated at pH

4. Conclusion and Recommendations

Leaching of the digested crude monazite sand recommended to be conduct into two successive stages as illustrated in the proposal flow sheet 3. The first leaching performed after dilution with 10 parts normal water / part of monazite sand and at temperature higher than 45°C to dissolve most of thorium and uranium in the 1st leaching. Thorium in the 1st leach solution can be precipitated using 16% ammonia at pH 1.1 and separated by decantation to prevent its co-precipitation during the double sulphate precipitation of light rare earth elements. The clear solutions withdrawn and used to leach the remaining slurry from the 1st leaching to produce the 2nd leach solution containing most of rare earth elements with minimum thorium.



Flow Sheet 3: Proposal for cerium IV and rare earth III concentrates preparation via double sulphate precipitation

The 2nd leach solution can be subjected also to precipitate its constituent of thorium using 16% ammonia at pH 1.1 and separated by decantation. Rare earth elements contained in the produced clear solution were precipitated selectively using 7% anhydrous sodium sulphate (after addition concentrated sulphuric acid equivalent to 5%) to produce Na-LREE-double sulphate, where more than 97% of the light rare earth (La – Sm) could be achieved. The precipitate was converted into rare earth hydroxides using 18% sodium hydroxide solution with 10% excess and agitation for one hour. Oxidation of cerium contained in the hydrous cake was then conducted during the drying step at 180°C for 10 hours.

The oxidized hydrous cake was slurred in boil water then 1.0 M nitric acid was added under pH control of 3.0 to dissolve the trivalent rare earths. Cerium content in the upgraded product was reached up to 48%, while the concentrate produced after precipitation from the leach solutions at pH 8.5 containing about 66% of light rare earth (about 6% of them cerium) and containing about 5% of heavy rare earth elements.

References

1. Marc Humphries, Rare Earth Elements: The Global Supply Chain, Congressional Research Service 7-5700, R41347 (2012).
2. M.I. Moustafa, Mineralogy and beneficiation of some economic minerals in the Egyptian black sands, Ph. Thesis, Faculty of Science, Mansoura University, Egypt, 1999.
3. P. Kewsuwan, Proceeding of the 6th Conference on Nuclear Science and Technology, 761, 31, (1996).
4. Jamrack W D. Rare metal extraction by chemical engineering techniques. Pergamon Press, London, 1963.
5. L. Stefan and A. Helmut, Recovery of rare earth metals from waste material by leaching in non-oxidizing acid and by precipitating using sulphates Patent EP 2444507 A1, (2012).
6. C.K. Gupta and N. Krishnamurthy, Extractive metallurgy of rare earths. CRC PRESS Boca Raton London New York Washington, D.C. (2005).
7. C.K. Gupta and N. Krishnamurthy, Extractive metallurgy of rare earths. International Materials Reviews, (1992), **37**(5): 197–248.
8. M. Kul, Y. Topkaya and İ. Karakaya, Rare earth double sulfates from pre-concentrated bastnasite. Hydrometallurgy, 2008, **93**: 129.
9. D.A. Renata and A.M. Carlos, Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide. Minerals Engineering, **23**(6): 536 (2010).
10. Z. Marczenko, Rare earths. In: Spectrophotometric determination of elements. John Wiley and Sons Inc. New York, (1986).
11. Jin Hui Yang, Shi Liang Dai, Xiao Kang Pan, Li Liu, Shu Kui Zhou and Jin Song Wang Determination of uranium in ore with volumetry of H₂SO₄-TiCl₃-NH₄VO₃. Applied Mechanics and Materials, Vols. 511 – 512, 12 – 16 (2014)
12. T.N. Tunley and V.W. Nel, Proc. Int. Solvent Extr. Conf., ISEC-74, Lyon, (1974), Soc. Chem. Ind., London, 1519- 1533 (1974).
13. O.S. Helaly Separation of rare earth elements from Egyptian monazite. M. Sc. Thesis, Chemical Eng. Dept., Faculty of Eng., Cairo University, Egypt, (2006).
14. O.S. Helaly Separation of cerium from Egyptian monazite sands using solvent impregnated resin. Ph. D. Thesis, Chemical Eng. Dept., Faculty of Eng., Cairo University, Egypt, (2011).
15. N. E. Topp, The chemistry of the rare earth elements. Elsevier Publishing Co., London, (1965).

Source of support: Nil; Conflict of interest: None declared