

# Solvent Extraction of Rare Earth Elements from the Mineralized Calcareous Shale of Wadi Nasib Area, Sinai, Egypt

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**Abstract**– Aprocess for recovering a total REEs using di-2-ethylhexyl phosphoric acid(D2EHPA)in kerosene from the sulfate solution of calcareous shale ore material of Wadi Nasib area was performed. Chemical composition of the ore material revealed the presence of 0.2% of U, 0.18% of REEs as well as 2.7% of Cu as the elements of interest. The pregnant sulfate solution has been already prepared by agitation leaching of 250g of the fine ground ore sample using 200g/L of H<sub>2</sub>SO<sub>4</sub> solution at S/L ratio of 1/4 and string for 4 h at 80°C. The latter was found assaying 400 mg/L of REEs with achieved leaching efficiency of 96%. REEs extraction efficiency was achieved using 1M of D2EHPA. The stripping process of REEs from the loaded organic phase was conducted using 0.5M H<sub>2</sub>SO<sub>4</sub> solution.

**Keywords**, REEs, D2EHPA, H<sub>2</sub>SO<sub>4</sub>, Calcareous shale ore material.

## 1. INTRODUCTION

Some rare earth oxides (RE<sub>2</sub>O<sub>3</sub>)e.g. Gd<sub>2</sub>O<sub>3</sub>have nuclear applications when mixed with U to achieve a uniform neutron flux during the life time of a fuel element in the boiling water reactors of "General Electric's". Beside Gd, Eu, Sm and Dy have high capture cross section for thermal neutron and are thus used as control rods besides using of Ce and Y hydrides as useful neutron moderators due to their high hydrogen atom density and high temperature stability. They are used to produce or reduce energy consumption, increase energy efficiency and advance lifestyle consumer and medical products [1].

The recovery of mixed REEs is generally accomplished by a variety of methods including the mineral acids or sodiumhydroxide at high temperature including proper fusion or else roasting with sodium carbonate [2-4]. The choice of leaching agent depends mainly on the selectivity in the separation of REEs, type of gangue minerals in the ore and the type of the reagents to be used in the further extraction procedures[5-11]. Also, usingdilute H<sub>2</sub>SO<sub>4</sub>leaching of total RE from deep sea nodule were has been studied [12].Separation processes namely; solvent extraction, ion exchange, supported liquid membrane, adsorption and precipitation methods are very

familiar for extracting REEs from numerous aqueous solutions [13–17].With respect to direct precipitation of REEs from aqueous solutions containing U as strong oxalate compounds was performed by several authors [18-20].

Solvent extraction (SX) method has wide applications in hydrometallurgical extraction process due to its great potential on high selectivity, effective separation and high metal enrichment [15]. The organic extractantse.g.di-2-ethylhexyl phosphoric acid, D2EHPA has a wide range of applications and becomes more causative for effective and efficient extraction of REEs from the various aqueous complex mixture solutions [21]. Also D2EHPA is considered the best in most investigations for extraction of REEs. It is also found as a cost effective reagents as compared to any other organo-phosphorous reagents e.g. tri-butyl phosphate, (TBP) and thereby, it is being considered as one of the best suitable commercial organic extractant in solvent extraction processes [22].

Exploration program of the Nuclear Materials Authority (NMA) is mainly concerned with the uranium and other nuclear materials as well as possible interesting associated metals(REEs,Cu.Etc). During these works, the potentiality of proper processing of these resources especially the low grade ores would be needed. Among the latter, calcareous shale ore sample of Wadi Nasib areaof Um Bogma formation, Sinai, Egypt, was found to be variably mineralized. This calcareous shale ore sample was chosen for the present work due to its added values of REEs in relatively reasonable grade.

## II.EXPERIMENTAL

### II.1. Materials

The working sample, calcareous shale ore material,variably mineralized has actually been collected from Wadi Nasib area, Um Bogma Formation, Sinai, Egypt. a representative portion of this sample was properly prepared by crushing, grinding to – 200 mesh size before quartering.The later

subjected to both mineralogical and chemical analysis involving the major oxides besides the tenor of the economic metal values. Solvent extraction experiments were carried out with AR grade of D2EHPA in kerosene. Distilled kerosene (boiling point 160–200 °C) and AR grade isodecanol (Merck) were used as diluents and modifier, respectively. and H<sub>2</sub>SO<sub>4</sub> (Merck) was used as stripping agent.

## II.2. Control analysis

Chemical analysis of the present ore sample ground to a mesh size of -200 has been performed. However the trace elements e.g. Zn, Cu, Pb, Ni, Co, etc. were analyzed using flame atomic absorption spectroscopy FAAS Unicam969. The major elements as oxides such as: Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO and CaO are classically estimated by wet chemistry [23]. An oxidimetric titration method against ammonium metavanadate was used for U analysis in the presence of diphenylamine sulfonate indicator. Prior to titration, proper reduction of U was performed using ammonium ferrous sulfate [24].

Total REEs were estimated by using UV-Vis spectrophotometer Shimadzu model 160A using 0.015% Arsenazo III at λ<sub>654</sub> nm using Ce as reference [25]. The pH values of all solutions are measured by using pH meter (DigimedDM-21). Finally, the prepared product of REEs is identified by using SEM-EDAX technique.

## II.3. Preparation of sulfate leach liquor

Sulfate leach liquor was prepared by agitation leaching of a weighted 250g of the fine ground calcareous shale ore material using 200g/L of H<sub>2</sub>SO<sub>4</sub> acid solution at S/L mixing ratio of 1/4 with stirring for 4h at 80°C. It is important to mention herein that, the leaching optimization and recovery of the present interesting metal values namely; U, Cu and elemental sulfur has been treated in a separate work using H<sub>2</sub>SO<sub>4</sub>. After preparation of sulfate leach liquor, the filtered and the residue left behind was thoroughly washed with distilled water and both the filtrate and washings were made up to 2.5 liters and its pH value was found to attain pH 0.5.

## II.4. pretreatment and recovery of Cu and U from sulfate leach liquor

The mentioned prepared sulfate leach liquor was treated with few drops of conc., H<sub>2</sub>SO<sub>4</sub> adjust pH=0.4 and then added 15g of Na<sub>2</sub>S to precipitate almost 99% of Cu metal ion of CuS. The filtered and the residue left behind was thoroughly washed with distilled water and both the filtrate and washings were made up to 2.6 liters and assaying 196 mg/L of reduced U. The latter solution was heated at 70°C in the presence of 30% H<sub>2</sub>O<sub>2</sub> solution to oxidized U<sup>4+</sup> metal ion to U<sup>6+</sup> [26, 27]. The uranium pregnant solution is adjusted to pH =1.7 to be easily loaded upon ion exchange Amberlite IRA<sub>400</sub> from sulfate leach liquor with loaded efficiency of 98%. On the other hand, the raffinate sulfate solution free from both Cu and U metal ions and assaying 180 mg/L of REEs was subjected to recover of REEs metal value. This raffinate solution was then adjusted to pH=3.9 with NaOH solution to remove almost interfering metal

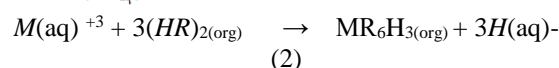
ions of high concentrations such as Fe<sup>3+</sup>, Zn<sup>2+</sup>, Ca<sup>2+</sup>, and Al<sup>3+</sup> to their hydroxides, respectively.

After filtration and well washing, the filtrate assaying 160 mg/L of REEs metal ions was heated at 80°C for reducing its volume to about 1L where REEs concentration raised up to 400mg/L. This solution was then directed to solvent extraction unit for extracting REEs by using D2EHPA. which Selective and quantitative extraction as well as separation of REEs from sulfate leach liquor bearing the other base metals using D2EHPA takes place according to the reported [28,29].

## II.5. Solvent extraction procedures

To optimize the loading of REEs process by using D2EHPA in kerosene, the relevant effective extraction parameters such as: D2EHPA concentration, pH, value, contact time and phases volume ratios aqueous/organic (A/O) were investigated. While, the type concentration of the stripping solution, stripping time and phase's volume ratios (A/O) were studied to optimize the REEs stripping process. All the experiments were performed at an ambient temperature (25±5 °C) using separating funnel (60 mL). The concentration of metal ion in organic phase was calculated from the difference between the metal concentration in the aqueous phase before and after extraction. The distribution coefficient (*D*) and percentage of extraction (% *E*) were calculated using Eq. (1) as described below. The chemical reaction involved on solvent extraction of RE metals with extractant can be expressed as given in Eq. (2)

$$E = \frac{\left( D \cdot \frac{V_{org}}{V_{aq}} \right)}{1 + \left( D \cdot \frac{V_{org}}{V_{aq}} \right)} \times 100\% \quad (1)$$



Where M = ΣREEs and R= organo- phosphorous extractant

## II.6. Preparation of REEs pure product

The strip solution rich in REEs was treated with 10% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution after stirring for 1h at pH1.2 where almost REEs were precipitated as its oxalate RE<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> cake. The latter was washed and ignited at 900 °C for 1h to produce the relevant RE<sub>2</sub>O<sub>3</sub> cake which washed by distilled water, dried. The latter have qualitatively been analyzed using the ESEM-EDX analysis.

## III. RESULTS AND DISCUSSION

### III.1. Characterization of the working sample

XRD mineralogical investigations of the studied sample revealed the presence of minerals such as: gypsum, [CaSO<sub>4</sub>.2H<sub>2</sub>O] [card No., 006-0046]; quartz, (SiO<sub>2</sub>) [card No., 078-2315]; Malachite, Cu<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> [card No., 010-0399]; Dolomite, [Ca Mg(CO<sub>3</sub>)<sub>2</sub>] [card No., 073-2324]; Brochantite, [Cu<sub>4</sub>(SO<sub>4</sub>)OH<sub>6</sub>] [card No., 0454-087]; Azurite [2CuCO<sub>3</sub>.Cu(OH)<sub>2</sub>] [card No., 001-0682] and Sklodowskite, [MgO(UO<sub>3</sub>)<sub>2</sub>(SiO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>7</sub>] [card No., 070-

0497]. While REEs were found adsorbed elements without any recorded mineral, due to presence of gypsum mineral

[30]. Table (1) reflects the complete chemical composition of Wadi Nasieb calcareous shale sample.

TABLE 1: Complete chemical composition of Wadi Nasieb calcareous shale sample.

Major oxides	Conc., %	Trace elements	Conc., mg/L
SO <sub>3</sub>	17	U	2000
SiO <sub>2</sub>	13	REE	1825
Al <sub>2</sub> O <sub>3</sub>	10.7	Cu	27000
TiO <sub>2</sub>	0.22	Zn	5300
MnO	0.395	Pb	454
Fe <sub>2</sub> O <sub>3</sub>	6.69	Ni	330
CaO	25.7	Co	120
MgO	2.9		
Na <sub>2</sub> O	0.6		
K <sub>2</sub> O	0.465		
P <sub>2</sub> O <sub>5</sub>	0.07		
*LOI	28.5		
Total	98.743		

\* LOI (total loss on ignition)

### III.2. Chemical composition of the prepared sulfate leach liquor

The resulted optimum leaching conditions have been applied upon a sample portion of 250g of the working

sample. The obtained sulfate leach liquor assays 180 mg/L of REEs beside a considerable concentrations of other valuable metal ions, Table (2).

TABLE 2: Chemical composition of the prepared sulfuric acid leach liquor.

Metal ion	Conc., mg/L	Leaching efficiency, %
U	196	98
Cu	2300	85
ΣREEs	180	96
Fe	400	85
Zn	480	90.6

### III.3. Solvent extraction of REEs

The maximum REEs loading on D2EHPA would be attained by studying the following effective parameters where leach liquor was subjected to removing of both U and copper, and also concentrates the REEs to one liter which assays 400 mg /L REEs.

#### III.3.1. D2EHPA CONCENTRATION

Effect of D2EHPA / kerosene concentration on extraction of REEs was investigated using various D2EHPA concentrations ranged from 0.5 to 2M at equilibrium pH 1.87, phase ratio A/O of 1/1 and shaking for 10 min at room

temperature. Based on results presented in Fig (1) increasing of D2EHPA concentration from 0.5 to 1M reflects a progressively improved of REEs extraction efficiency from 21% to 40%, where further increasing in D2EHPA concentration more than 1M only slight steady increase in the REEs extraction efficiencies. Accordingly, 1M of D2EHPA would be considered as the optimum concentration for the solvent extraction of REEs which the extraction efficiency of REEs would attain 40% under the above mentioned extraction conditions.

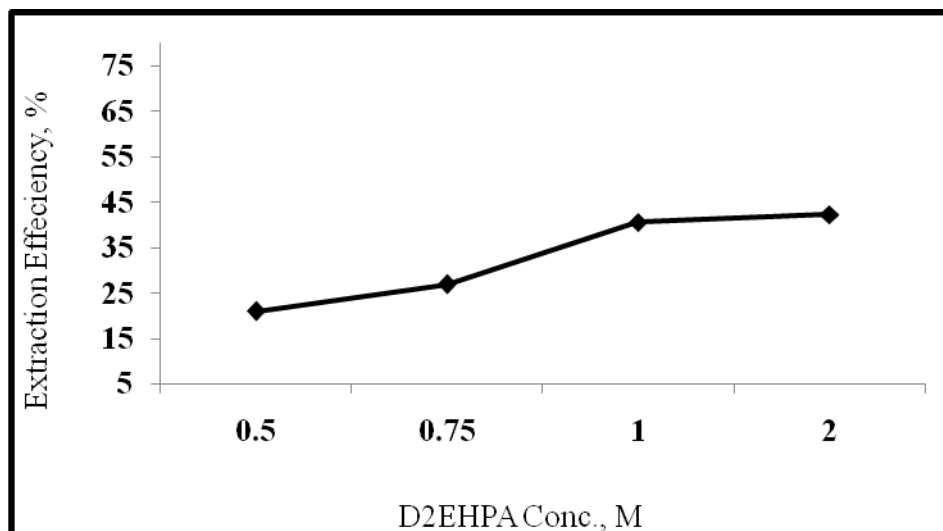


Fig. 1. Effect of D2EHPA concentration upon extraction efficiency of REEs.

### III.3.2. EFFECT OF CONTACT TIME

To study the effect of contact time upon the extraction efficiency of REEs, a set of leaching experiments has been performed at different time periods ranging between 4 to 10 min. at fixed conditions of equilibrium pH 1.87 and A/O ratio of 1/1, the obtained data, Fig. (2) indicates that, REEs extraction efficiency

increased up to 40.7% at a shaking time of 6 min., Extending the time up to 6 min has not any marked effect on the extraction efficiency of REEs. Therefore, the following experiments were performed by shaking time 6 min.

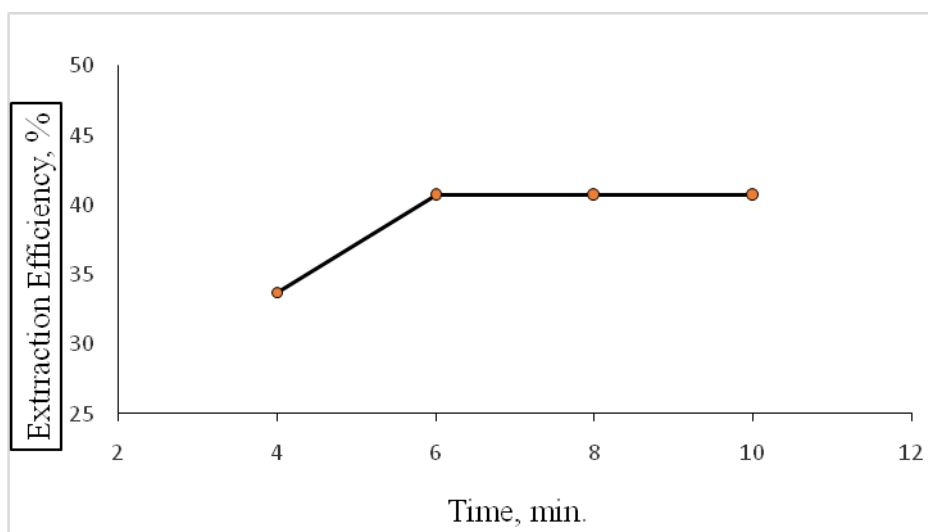


Fig. 2. Effect of shaking time upon extraction efficiency of REEs

### III.3.3. Effect of equilibrium pH

The effect of pH values of the prepared sulfate leach liquor upon REEs extraction efficiency was studied in the range from 0.3 to 2.2. The fixed extraction conditions involved an 1M D2EHPA, A/O of 1/1 and contact time of 6 min. Data in Fig.(3) revealed that, the percentage of REEs extraction efficiency increased from 59.2 to 76% with

increasing the pH value of the sulfate leach liquor from 0.3 to 1. While further increase in the pH values to 1.8 and 2.2 has an opposite effect, where REEs extraction efficiency decreased up to 39.7%. This due to the decreasing in the acidity of the working sulfate liquor lead to formation of hydroxides of some trace elements [31].

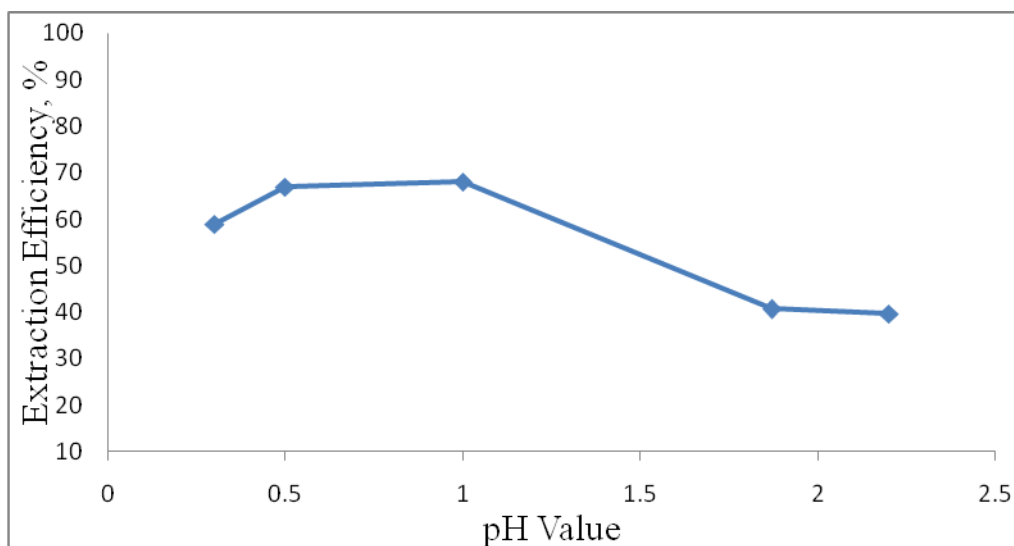


Fig. 3. Effect of pH value upon extraction efficiency of REEs .

### III.3.4. EFFECT OF A/O, (MCCABE THIELE DIAGRAM)

McCabe-Thiele diagram is properly constructed by plotting of the equilibrium concentration data of REEs extraction in the organic and aqueous phases, followed by fitting a suitable operating line. In these experiments, the other working fixed conditions involved; 1M D2EHPA, shaking time of 6 min and pH1. The obtained results, Table (3), clearly evident that both (the extraction distribution coefficient)  $D_A^O$  and the extraction efficiency of REEs are directly proportional to the increase in the A/O ratio. Increasing A/O to 1/4 where a  $D_A^O$  reached 5 and an

extraction efficiency achieved of 95.2%. This is due to the increased input [Extractant]/[REEs] ratio; a matter which would however be at the expense of a decrease in the REEs concentration in the organic phase that has decreased down to only 95 mg/L. In the meantime, it would be possible at this A/O ratio of 1/4 to decrease the REEs concentration in the raffinate to 19 mg/L. On the contrary, at A/O ratios of 2/1, 3/1 and 4/1 the extraction efficiencies of REEs decreased to 39, 26.8 and 20.3%, respectively. Although almost complete REEs extraction has been achieved at the A/O ratio of 1/4, 1/3 and 1/2 but these ratios are not applied because they give a diluted loaded REEs in the organic phase. Indeed, A/O ratio of 1/1 saves the used solvent.

TABLE3. Effect of O/A ratio upon the  $D_A^O$  and extraction efficiency of REEs

A/O ratio	REE conc. at equilibrium, mg/L		$D_A^O$	Extraction efficiency, %
	Organic phase	Aqueous phase		
4/1	325	319	1.03	20.3
3/1	322	293	1.10	26.8
2/1	312	244	1.27	39
1/1	274	126	2.28	68.5
1/2	176	48	3.67	88
1/3	124	28	4.42	93
1/4	95	19	5	95.2

The extraction data obtained at the applied A/O ratios used to construct the corresponding McCabe-Thiele extraction diagram, Fig. (4). It was found that the slope of the operating line which is equivalent to the O/A flow rate in a counter current processing attained about 2.1. Also, there

are three extraction stages would be required for almost extraction of REEs. The maximum REEs extraction efficiency of 68% from the prepared sulfate solution was achieved at D2EHPA concentration of 1M, pH1, contact time of 6 min and A/O ratio of 1/1.

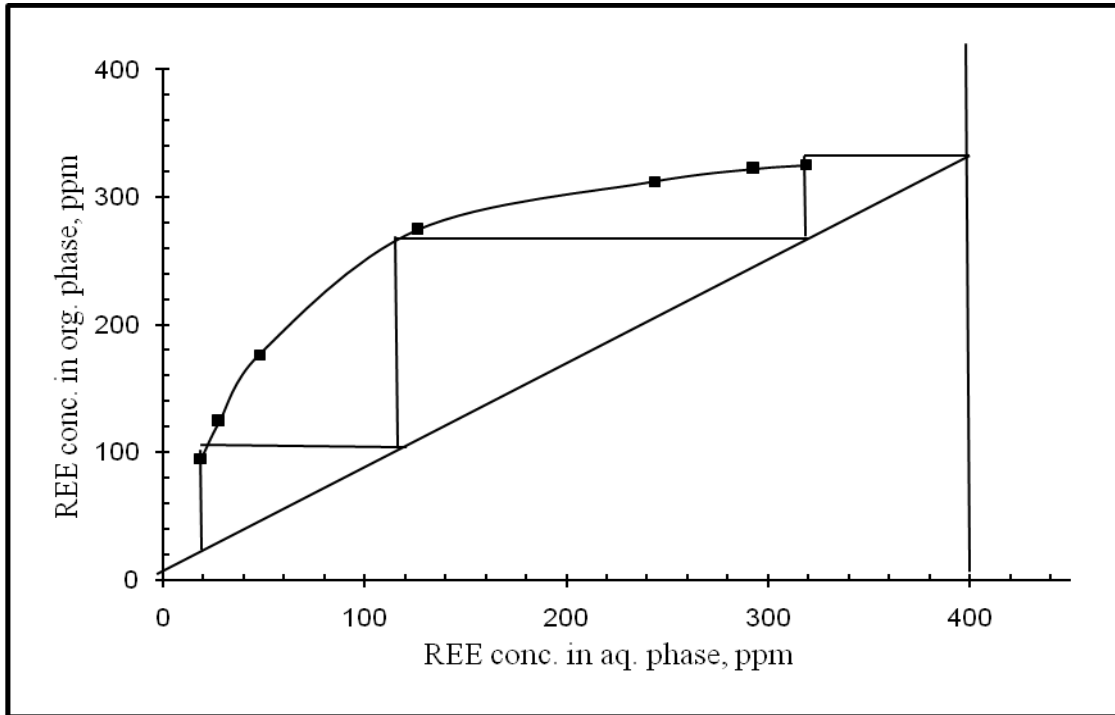


Fig. 4. McCabeThiele loading diagram

III.4. STRIPPING OF REES

Stripping process is not only regenerated the organic phase but also gave concentrated solution required for preparing the products of interest. To optimize the REEs stripping process the following effective parameters were studied.

III.4.1. Effect of stripping reagent types

Stripping of the loaded organic phase was examined at fixed conditions, 10 min shaking time, (A/O) of 1/1 ratio and 0.1 M of different reagents such as: H<sub>2</sub>SO<sub>4</sub>, HCl, and

HNO<sub>3</sub>. The obtained data, Fig (5), indicated that the best REEs stripping efficiency, 74.5 % . was achieved by using both of 0.1M H<sub>2</sub>SO<sub>4</sub> and 0.1M HCl, but H<sub>2</sub>SO<sub>4</sub> was chosen because REEs in sulfate solution yields larger precipitated particles, which is an advantage in filtering and drying the precipitate [32]. Beside H<sub>2</sub>SO<sub>4</sub> is readily available and more economic.

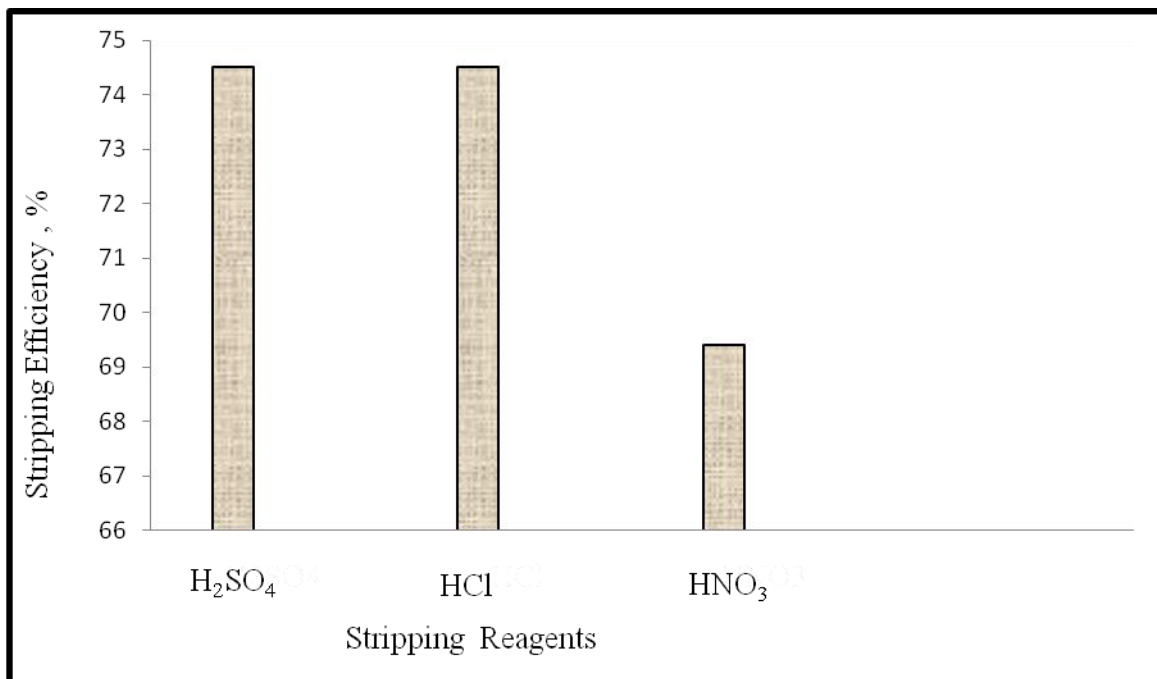


Fig. 5. Effect of stripping reagents type upon stripping efficiency of REEs .



### III.4.2. Effect of H<sub>2</sub>SO<sub>4</sub> concentration

Effect of varying concentrations of H<sub>2</sub>SO<sub>4</sub> in the range of 0.1– 0.7M was examined for stripping of total REEs from loaded organic phase was applied at A/O ratio of 1/1 and contact time of 10min. The results represented in fig (6)

show that the maximum REEs stripping efficiency (78.1%) was attained by using 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. It was noticed that further increasing in acid concentration to 0.7M did not show any noticeable increase in the stripping efficiency.

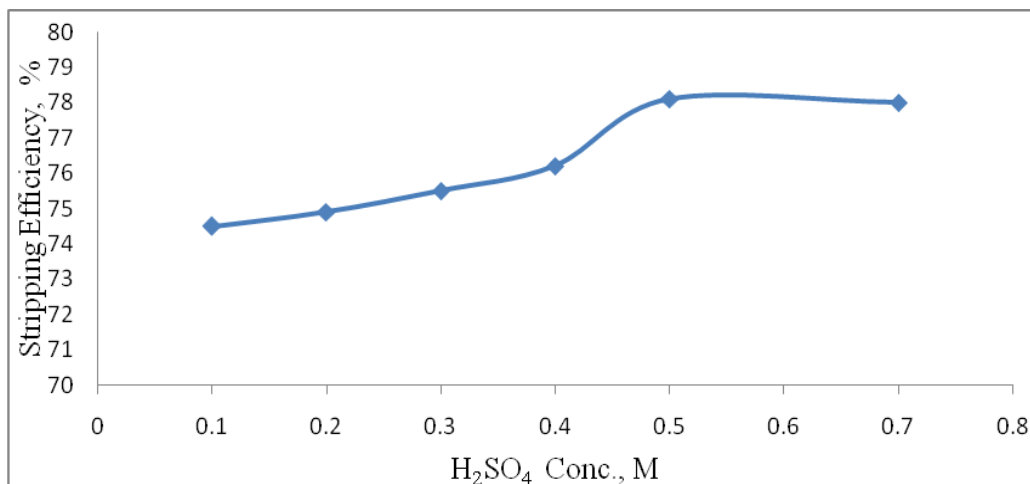


Fig. 6. Effect of H<sub>2</sub>SO<sub>4</sub> concentration upon stripping efficiency of REEs.

### III.4.3. Effect of shaking time.

The effect of the shaking time upon the REEs stripping efficiency by sulfuric acid was studied in the range of 2 to 10 min. The other stripping conditions were fixed 0.5 M H<sub>2</sub>SO<sub>4</sub> at A/O of 1/1. Figure (7) shows the stripping efficiency of REE increased from 64.6% to 78.13% by

increasing the shaking time from 2 to 6 min. Further increase in the shaking time did not show any noticeable increase in the stripping efficiency of REEs therefore, the optimum shaking was chosen at 6 min.

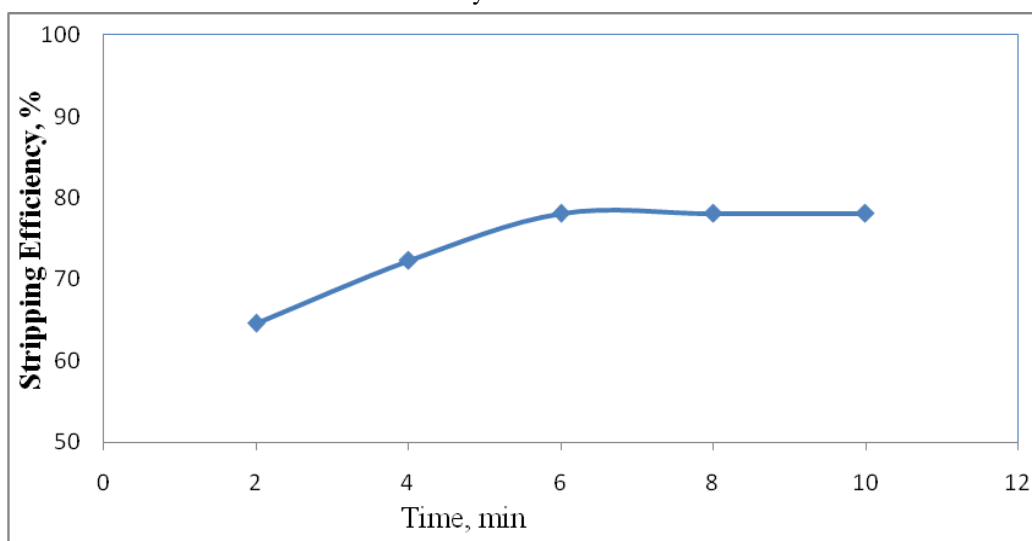


Fig. 7. Effect of shaking time upon stripping efficiency REEs.

### III.4.4. Effect of A/O ratio

Using of 0.5M H<sub>2</sub>SO<sub>4</sub>, several stripping experiments were performed to study the effect of A/O ratio using different A/O ratios upon the stripping efficiency of REEs. These experiments were performed at a shaking time of 6 min. The obtained results, Table (4), indicated that almost loaded REEs from the saturated D2EHPA were stripped with stripping efficiency of 99.29% at A/O ratio of 4/1 and decreased to 96.25% and 90.45% at A/O of 3/1 and 2/1, respectively. While REEs stripping efficiency decreased to 57.78, 43.77 and 34.363% at A/O ratios of 1/4, 1/3 and 1/2,

respectively. From the obtained results, although the REEs stripping efficiency at A/O ratios of 4/1, 3/1 and 2/1 are higher than that of 1/1 (78%), but these ratios are not applied because they give a diluted REEs in the strip aqueous solution. On the other hand, the REEs stripping efficiencies at A/O ratios of 1/4, 1/3 and 1/2 are lower than that of 1/1. Indeed, the ideal applied A/O ratio was 1/1 which is also beneficial during the REEs precipitation stage. McCabe Thiele diagram, Fig (8) shows that there are theoretically three stripping stages were indeed required for almost REEs from the saturated D2EHPA.

TABLE. 4. Effect of A/O ratio on REEs  $D_O^A$  and stripping efficiency.

A/O ratio	REE conc. at equilibrium, mg/L		$D_O^A$	Stripping efficiency, %
	Organic phase	Aqueous phase		
1/4	180.02	375.93	2.08	34.3
1/3	154.07	359.79	2.3	43.77
1/2	115.68	316.63	2.7	57.78
1/1	60.14	213.86	3.5	78.05
2/1	26.17	123.92	4.7	90.45
3/1	10.39	87.87	8.5	96.21
4/1	1.95	68.01	34.88	99.29

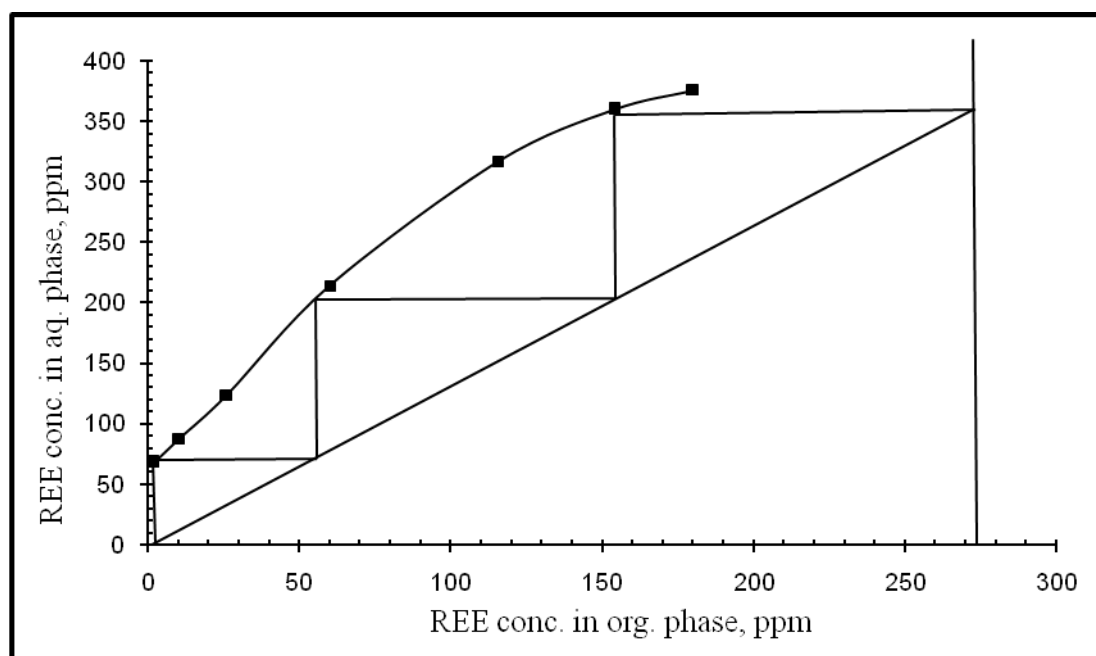


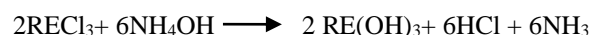
Fig. (8): McCabe–Thiele stripping diagram.

From the forgoing study, it could be concluded that, REEs weretransferred to the aqueous soltion with an achieved stripping efficiency of 57,8% in by using 0.5M  $H_2SO_4$  and stripping time of 6min at A/O ratio of 1/2.

### III.5. PREPARATION OF REES PRODUCT

By applying the overall the organic solvent extraction processes upon the working sulfate solution (900mL) of the working sulfate solution, it was found that 1MD2EHPA in kerosene could be up taken about 548 mg of REE. The strip solution rich in REEs was treated with 10%  $H_2C_2O_4$  solution after stirring for 1h at pH1.2, almost REEs were precipitated as  $RE_2(C_2O_4)_3$  cake. The chemical

analysis of the latter revealed that, it assays 81.5% of REEs beside 14.3% of Ca as the mainly presented interfering metal ion. For further purification, the precipitated REEs-oxalate cake was dissolved in 5% HCl acid solution. The prepared RE chloride solution were treated with  $NH_4OH$  solution to precipitate  $RE(OH)_3$  cake free from Ca ions at pH 9.5[33]. After filtration and washing, the obtained RE-hydroxide cakewas washed and ignited at 650-700 °C for 1h to produce the relevant  $RE_2O_3$  which washed, dried and subjected to SEM-EDAX analysis for identification as shown in Fig (9). The following equations illustrate the purification process:





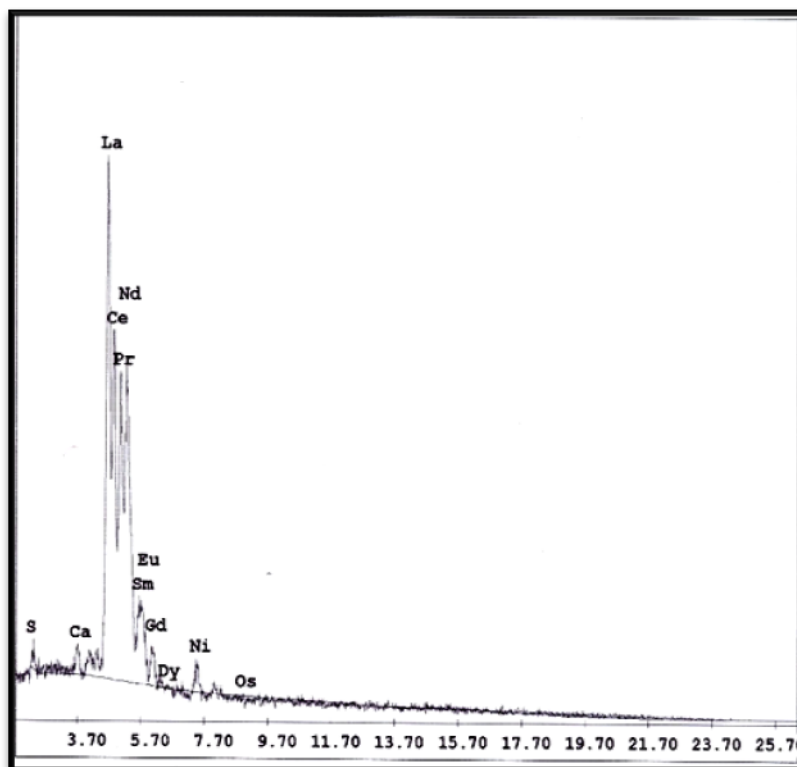


Fig. 9. SEM- EDAX chart for the identification of RE<sub>2</sub>O<sub>3</sub>.

#### IV- CONCLUSIONS

The potentiality of preparing highly pure RE<sub>2</sub>O<sub>3</sub> from sulfate solution of Wadi Naseib mineralized calcareous shale raw material assaying 400 mg/L of REEs has been attained by using 1M of D2EHPA / kerosene for extracting 68.5 % at O/A ratio of 1/1, shaking time of 6 min and pH1. More than 78% of the loaded REEs was already stripped and transferred to the aqueous solution by using 0.5M of H<sub>2</sub>SO<sub>4</sub> solution at A/O ratio of 1/1 and stripping time of 6min. Not less than 99% of REEs in the obtained strip solution was precipitated as RE<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> by using 10% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution at pH1.2, stirring time of 1h at a temperature ranged from 20 to 25°C. The latter was ignited at 900°C to produce RE<sub>2</sub>O<sub>3</sub> of achieved purity of 92.5%.

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