

## Extraction of yttrium from ferruginous sandstone, southwestern sinai, Egypt

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### ABSTRACT

The Ferruginous sandstone ore was obtained from Ramlet Hemeyir area, Southwestern Sinai, Egypt, which contains 10 % (REE) rare earth elements. A representative sample has been subjected to acid agitation leaching using  $H_2SO_4$  where 93% of the REE content was released by mixing the ground sample to (-100 mesh) with concentrated  $H_2SO_4$  at solid/liquid (S/L) ratio of 1/2 for 5h at a temperature ranged from (250 - 300°C).

The REE was precipitated in the oxalate form from the prepared sulfate leach liquor. Next selective extraction of 98% Y was achieved by contacting Y was extracted by di-(2-ethylhexyl)phosphoric acid (D2EHPA) with the aqueous solution of nitric acid leaching of the REE cake. Stripping was done by hot  $H_2O$  (80 °C). Finally, a precipitation with oxalic acid was done followed by ignition at 950°C. A yield of 95% Y oxide was produced.

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### KEYWORDS

Yttrium;  
Rare Earth Elements;  
Separation;  
D2EHPA;  
Precipitation.

### INTRODUCTION

The studied sample of Ramlet Hemeyir area consists of white to pale brownish pebbly and ferruginous sandstones from the topmost of El Adedia Formation which is up to 72m thickness. The uppermost beds of this formation are highly ferruginous and usually stained by manganese and iron oxyhydroxides<sup>[12]</sup>.

Yttrium and REE are finding increasing application in the field of high technology, such as nuclear reactor, laser, super conductors, batteries and transport of hydrogen in the post-hydrocarbon economy<sup>[6]</sup>.

Several methods have been industrially applied for the breakdown of the most common rare earth minerals (monazite, bastnasite and xenotime). The economic treatment upon high grade concentrates of these minerals should be achieved by physical beneficiation meth-

ods such as: (gravimetric, magnetic, flotation and electrostatic). Extraction of rare earths from xenotime can be achieved using sulfuric acid digestion at temperature range of (250-300°C) for 1to2h followed by water leaching; such leaching is uneconomic for concentrates containing less than 10% xenotime<sup>[13]</sup>.

Depending upon the nature of the pregnant solution and the element concentration several techniques could be used to recover REE from its ores by different leaching processes followed by some separation techniques among which are direct precipitation, ion-exchange and solvent extraction.

Different solvents, such as di-(2-ethylhexyl) phosphoric acid (D2EHPA)<sup>[3]</sup>, Tributylphosphate (TBP) and tri-n-octylphosphine oxide<sup>[8]</sup>, carboxylic acid derivatives<sup>[15]</sup>, amines<sup>[10]</sup> and ketones<sup>[1]</sup>, were used to extract REE from aqueous solutions.

The extract REE ions are usually stripped by mixing the loaded solvent with aqueous mineral acids. In this article yttrium was stripped by hot water.

## EXPERIMENTAL WORK

### Mineralogical Identification

To investigate the mineralogical composition of feruginous sandstone ore; heavy liquid separation was performed upon a representative bulk sample. About 1 Kg of the ore sample was washed with excess amount of tap water to get rid of the slimes. The slimes-free sample was dried, properly sieved by a set of sieves ranging from 500  $\mu\text{m}$  down to 100 $\mu\text{m}$  (35 to 140 mesh grain size) and the obtained size fractions were subjected to heavy liquid separation using bromoform (sp.gr. 2.84). The obtained heavy fractions were isodynamically separated at (0.2, 0.5, 0.8, 1.0 and 1.5 Amp.) using Frantz isodynamic separator where the separated fractions were picked under the binocular microscope. On the other hand, identification of the mineralogical composition of the ore sample and analysis of the prepared products were detected by the X-ray diffraction (XRD) model Phillips X-ray (PW3710) with a generator (PW1830) and Cu target tube (PW223/20). It was operated at 40 kV and 30 mA.

### Methods of Analysis

A number of analytical methods have been used during the present work. Beside the analysis of leaching and separation experiments, the host rock was first analyzed for its major and some trace elements' contents.

### Major and Trace Elements Analyses

The major and minor oxides were analyzed as reported by Shapiro and Brannock (1962) for rapid silicate analytical procedure. This procedure includes the preparation of two main solutions; namely an alkaline solution for  $\text{SiO}_2$  determination and an acid solution for determination of other oxides like  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , total iron oxides, etc.

Concerning the total REE, a UV-VIS spectrophotometer (Shimadzu UV-160) was used for its quantitative analysis using 0.015 % arsenazo(III) at 654 nm taking Y as reference<sup>[7]</sup>.

The economic metal values namely; Zn, Ni, Mn, Pb and Cu were measured using a Unicam atomic absorption spectrophotometer model-969 (AAS) flame type at  $\lambda$  213.9, 232, 279.5, 217 and 324.8 nm respectively.

The final products of REE concentrates and Y were analyzed by X-ray microanalyzer (Module Oxford 6587 INCA X-sight) attached to JEOL JSM-5500 LV scanning electron microscope at 20kV after gold coating using SPI-Module sputter coater.

### Procedures for Metal Values Separation

The hydrometallurgical processing of the ore material is represented by two main stages, leaching then separation of the studied metal values.

### Preparation of Sulfate Leach Liquor

Acid digestion was performed by mixing different concentrations of  $\text{H}_2\text{SO}_4$  with 100g ore sample and agitating at various S/L ratio, temperature and agitation time. The optimum conditions were applied to prepare a pregnant leach liquor of about 1.5 liters.

### Separation Procedures

#### Separation of Total REE

The prepared leach liquor was subjected to the precipitation of the total REE as their oxalates. For this purpose, different experiments were carried out to determine the optimum oxalic acid concentration, as well as the pH and the temperature required for achieving the highest precipitation efficiency.

#### Separation of Yttrium from REE Concentrate

For Y recovery by di-(2-ethylhexyl) phosphoric acid (D2EHPA), the extraction and stripping experiment were performed in separating funnels where the organic and the aqueous phases were shaken for the proper time. The two phases were then allowed to separate and an aliquot sample of the aqueous phase was analyzed for its metal content while the metal content in the organic phase was calculated by subtraction from the total element's concentration in the leach liquor. On the other hand, the aqueous strip solution was analyzed for Y transfer from the loaded solvent.

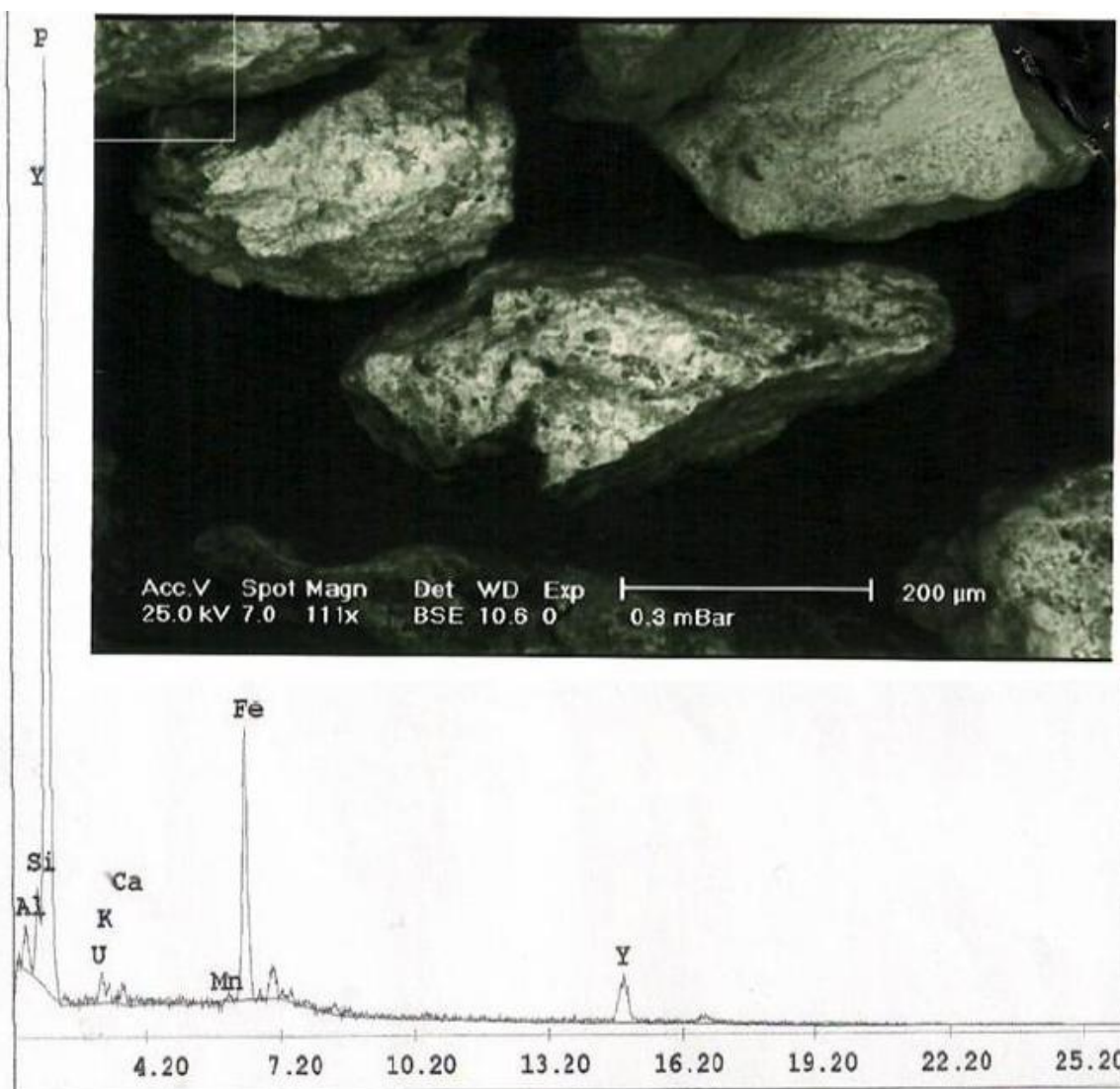
For performing yttrium extraction stage; first, the obtained REE cake was solubilized in 15ml of 31.5% nitric acid. Secondly, the nitrate leach liquor was ad-

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justed to pH 7.5-8.0 then 120g/L ethylene-diamine-tetracetic acid (EDTA) was added to aqueous solution then it was contacted with 2M D2EHPA in kerosene at organic/aqueous (O/A) : 3/1. Finally stripping

was done by using different stripping agents: (1-4) M  $\text{HNO}_3$ , (1-4) M  $\text{HCl}$ ,  $\text{H}_2\text{O}$  and hot  $\text{H}_2\text{O}$  (80°C).

Yttrium was pre cipitated from the strip solution by means of 10% oxalic acid. The obtained Y-oxalate was



Element	Wt %	At %
$\text{Al}_2\text{O}_3$	1.73	2.81
$\text{SiO}_2$	3.13	8.60
$\text{P}_2\text{O}_5$	26.81	31.22
$\text{UO}_2$	2.66	1.63
$\text{K}_2\text{O}$	0.13	0.23
$\text{CaO}$	0.71	2.10
$\text{MnO}$	0.00	0.00
$\text{Fe}_2\text{O}_3$	19.75	20.44
$\text{Y}_2\text{O}_3$	45.08	32.99
Total	100.00	100.00

Figure 1: ESEM photomicrographs and EDAX analysis of xenotime separated after Isodynam separation at 0.2 Amp



filtered and properly washed with distilled water to get rid of any impurities. After dryness, the precipitate was ignited at 950°C for 3hr.

## RESULTS AND DISCUSSIONS

### Mineralogical Composition

The binuclear microscope investigation revealed that most of magnetic fractions are highly mineralized where xenotime which was the dominant mineral had a wide

**TABLE 1: Chemical composition of the ferruginous sandstone ore material**

Major Oxides	Conc., (%)	Trace Elements	Conc. (ppm)
SiO <sub>2</sub>	42.0	U	2600
TiO <sub>2</sub>	0.33	Ni	138
Al <sub>2</sub> O <sub>3</sub>	3.40	Pb	900
Fe <sub>2</sub> O <sub>3</sub>	26.0	B	200
CaO	0.02	Cu	130
MgO	3.20	V	150
MnO	1.80	Zr	180
Na <sub>2</sub> O	0.90	Cr	160
K <sub>2</sub> O	0.70		
P <sub>2</sub> O <sub>5</sub>	3.60		
RE <sub>2</sub> O <sub>3</sub> *	12.60		
L.O.I**	4.06		
Total	98.61		

RE<sub>2</sub>O<sub>3</sub>\*: representing Y<sub>2</sub>O<sub>3</sub><sup>[7]</sup>; L.O.I\*\*: loss of ignitio

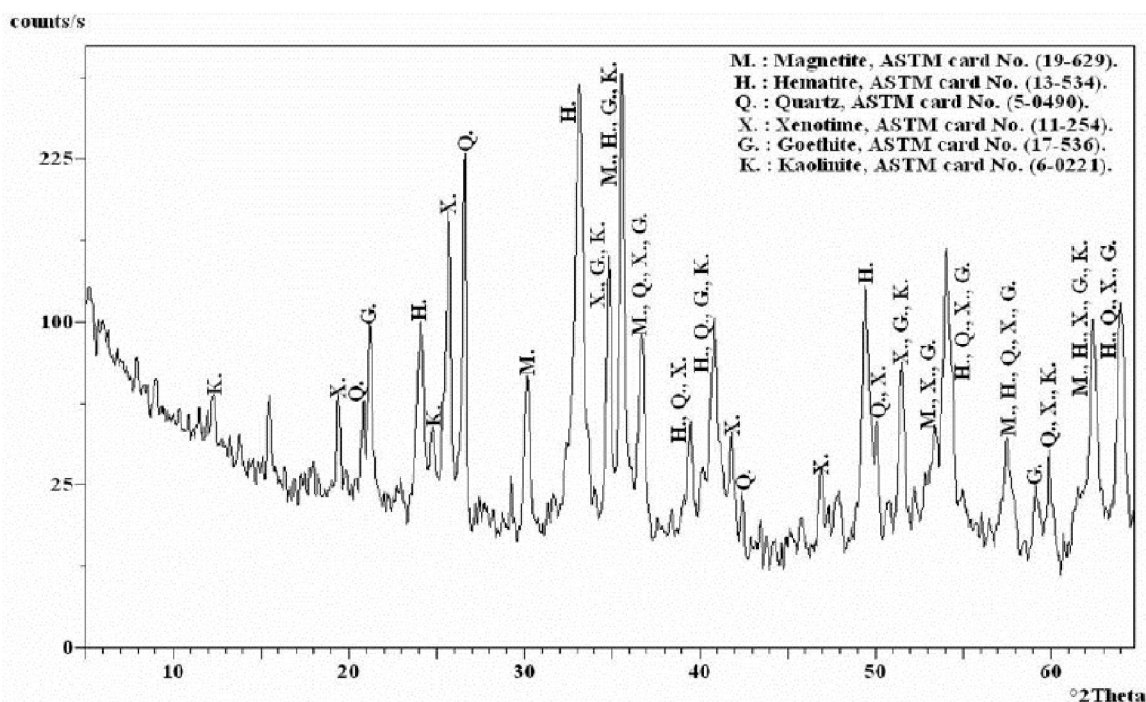
distribution in 0.5 Amp., 1.0 Amp., and 1.5 Amp. magnetic fractions. It represented 32–40 % of these magnetic fractions while zircon was dominant in 1.5 Amp. non-magnetic fraction. Iron oxides (hematite, goethite and rarely magnetite) separated at 0.2 Amp. magnetic fraction were widely dispersed in these heavy magnetic fractions. Figure 1 shows the SEM image of xenotime separated after Isodynam separation at 0.2 Amp. The obtained minerals as analyzed by XRD are shown in Figure 2. These are kaolinite Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, quartz (SiO<sub>2</sub>), goethite FeO(OH), hematite Fe<sub>2</sub>O<sub>3</sub>, magnetite Fe<sub>3</sub>O<sub>4</sub> and xenotime YPO<sub>4</sub>.

### Chemical Analysis

The chemical analysis is given in TABLE 1 for major oxides and some trace elements. The chemical composition reflects the previously mentioned mineralogical composition.

### Preparation of Sulfate Leach Liquor

Sulfuric acid digestion was done upon a representative ferruginous sandstone sample by varying different factors till reaching the following optimum conditions: mixing 100g ore sample with concentrated H<sub>2</sub>SO<sub>4</sub> at 1/2 S/L ratio for 5h at temperature range of (250–300°C). A pregnant solution of 1.5 liters was prepared



**Figure 2: XRD analysis of the mineralogical composition**

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by adding the washings to the original filtrate. The pH of the produced sulfate leach liquor was 0.02. This liquor was analyzed mainly for its content of rare earth, iron and uranium, (TABLE 2).

### Separation of REE by Direct Precipitation

The prepared leach liquor was subjected to selective precipitation for the total REE by means of oxalic acid. This is due to the fact that, the REE form stable insoluble oxalates and thus can be used for their separation<sup>[5]</sup>.



For this purpose, pH of the prepared leach liquor was raised from 0.2 to 2.5 by means of ammonia solution. Some factors affecting the REE precipitation using oxalic acid were studied as follows:

#### Effect Of Ph

Effect of pH on REE precipitation efficiency was studied at pH values (2, 1.5, 1, 0.8 and 0.5) by addition of 35% oxalic acid to five prepared leach liquors having pH of 2.5 at 25°C. The obtained data plotted in Figure 3 showed that REE precipitation efficiency increased from 12% to 98% by decreasing pH value from 2.0 to 1.0 then decreased to 10% by further decrease in pH value to 0.5.

It was reported by Woyski and Harris (1963) that the oxalate precipitation of REE was preferred at a pH value between 1.1 and 1.5 where the acidity can be adjusted by ammonia solution.

#### Effect of Oxalic Acid Concentration

This factor was studied by adding different concentrations of oxalic acid (5, 10, 15, 20, 25, 30, 35 and 40 %) to eight prepared sulfate leach liquors each of pH 1.0 with continuous stirring at 25°C. After settling and filtration, REE were analyzed in the filtrates to calculate their precipitation efficiencies. The obtained data plotted in Figure 4 showed that, increasing the acid concentration from 5% to 35% increased REE precipitation efficiency from 26% to 98% where pH value was fixed at pH 1.0. This may be due to common ion effect. This behavior was similar to that found by Chung *et al.*, (1998). Further increasing of oxalic acid concentration led to a slight increase in the precipitation efficiency.

TABLE 2: Analysis of the ferruginous sandstone sulfate leach liquor

Metal ion	Conc. (gm/l)
REE	6.20
U	0.154
Fe	10.60
Pb	0.05

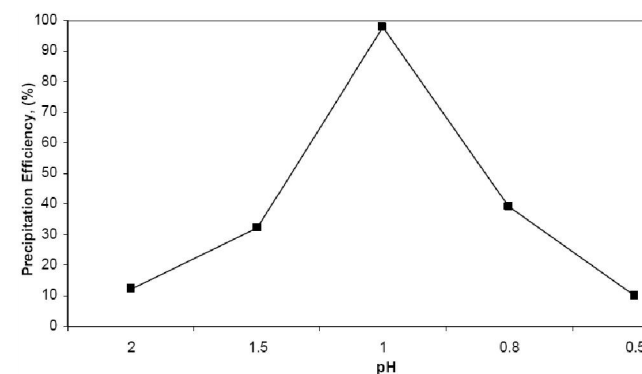


Figure 3: Effect of pH on REE precipitation efficiency

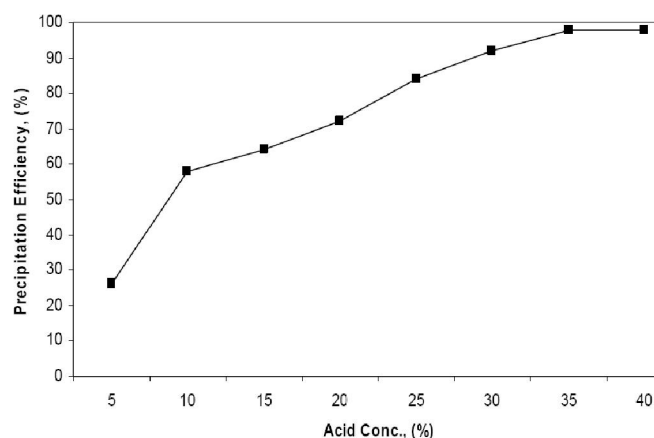


Figure 4: Effect of oxalic acid concentration on REE precipitation efficiency

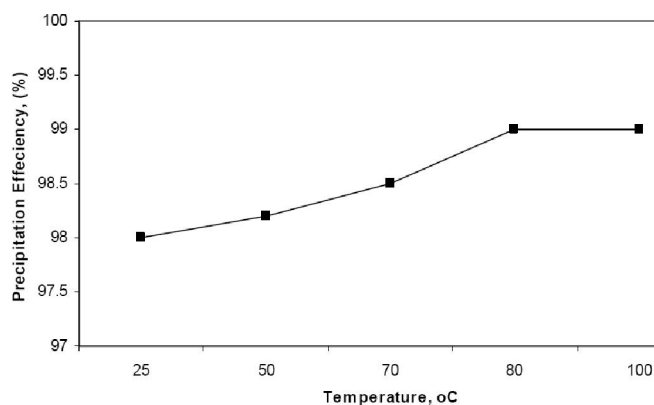


Figure 5: Effect of temperature on REE precipitation efficiency

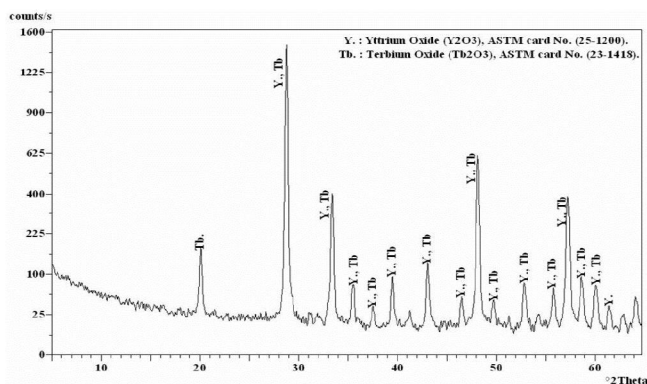


Figure 6: XRD analysis of the produced  $RE_2O_3$  concentrate.

### Effect of Temperature

Effect of temperature upon REE precipitation efficiency was studied at different temperatures 25, 50, 70, 80 and 100°C while the other factors were fixed at 35% oxalic acid and pH of 1.0. The obtained data plotted in Figure 5 showed that, increasing temperature had a slight effect on REE precipitation efficiency.

From the above results, it can be concluded that the optimum conditions for REE precipitation can be summarized as follows: adding 35% oxalic acid to leach liquor of pH 1.0 at 25°C, yielded 98% REE precipitation efficiency.

The obtained REE-oxalate was filtered and washed properly with distilled water to get rid of any impurities. After dryness, the precipitate was ignited at 850°C for 2h. The latter was subjected to XRD analysis to identify its content. It is clearly evident that the obtained rare earth oxide concentrate is mostly composed of heavy rare earth oxides mainly yttrium oxide and terbium oxide Figure 6. The purity was found to be 88% as analyzed by UV-VIS spectrophotometer, while the total recovery of REE from the ore was found to be 75.7%.

### Yttrium Separation from REE Concentrate

Due to the great importance of individual REE, it was decided to use the prepared  $RE_2O_3$  concentrate to separate a pure yttrium product.

According to Gruzensky (1961), more than 120 organic solvents have been tested as possible extractants of yttrium and REE ions from different salt solutions. These tests showed that nitrate salts are more readily extracted than the chlorides.

For Yttrium extraction, a nitrate aqueous feed was

TABLE 3 : Effect of stripping agent type upon Y stripping efficiency (O/A = 2/1, contact time = 20min).

Stripping agent	Temp., (°C)	Stripping agent conc., (M)	Y stripping efficiency, (%)
HNO <sub>3</sub>	25	1	0.1
	25	2	0.1
	25	3	0.4
	25	4	0.4
	25	1	0.3
HCl	25	2	0.3
	25	3	0.6
	25	4	0.6
H <sub>2</sub> O	25	-	19
	80	-	98

TABLE 4: Effect of stripping time upon Y stripping efficiency (O/A = 2/1, stripping agent hot H<sub>2</sub>O)

Time, (min)	Y stripping efficiency, (%)
5	69
10	82
15	91
20	98

prepared by dissolving the  $RE_2O_3$  concentrate in 31.5% nitric acid with S/L ratio 1/3 for 2h at 70°C. The nitrate solution (10ml) containing about 261g/L  $Y_2O_3$  was then subjected to the yttrium extraction process by D2EHPA and EDTA. The nitrate leach liquor was adjusted to have pH of 7.5-8.0 in presence of 120g/L EDTA was contacted to 2M D2EHPA at O/A of 3/1. The extraction efficiency of Y reached about 99%<sup>[9]</sup>.

Yttrium re-extraction from the loaded organic phase was achieved by using different times and different stripping agents; namely H<sub>2</sub>O at room temperature (25°C) and (80°C), and the acids HCl and HNO<sub>3</sub> with differ-

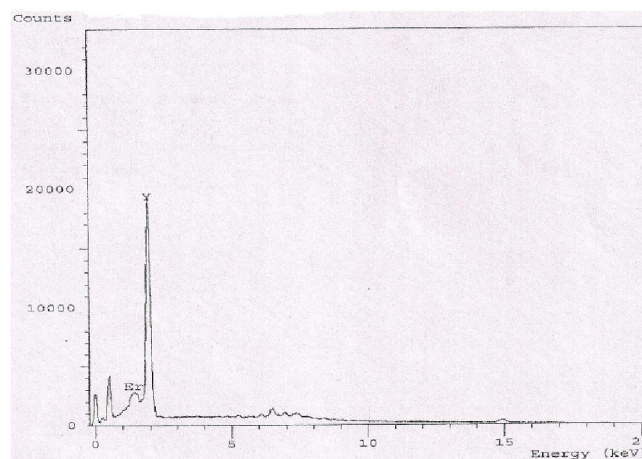


Figure 7: EDAX analysis of Y product

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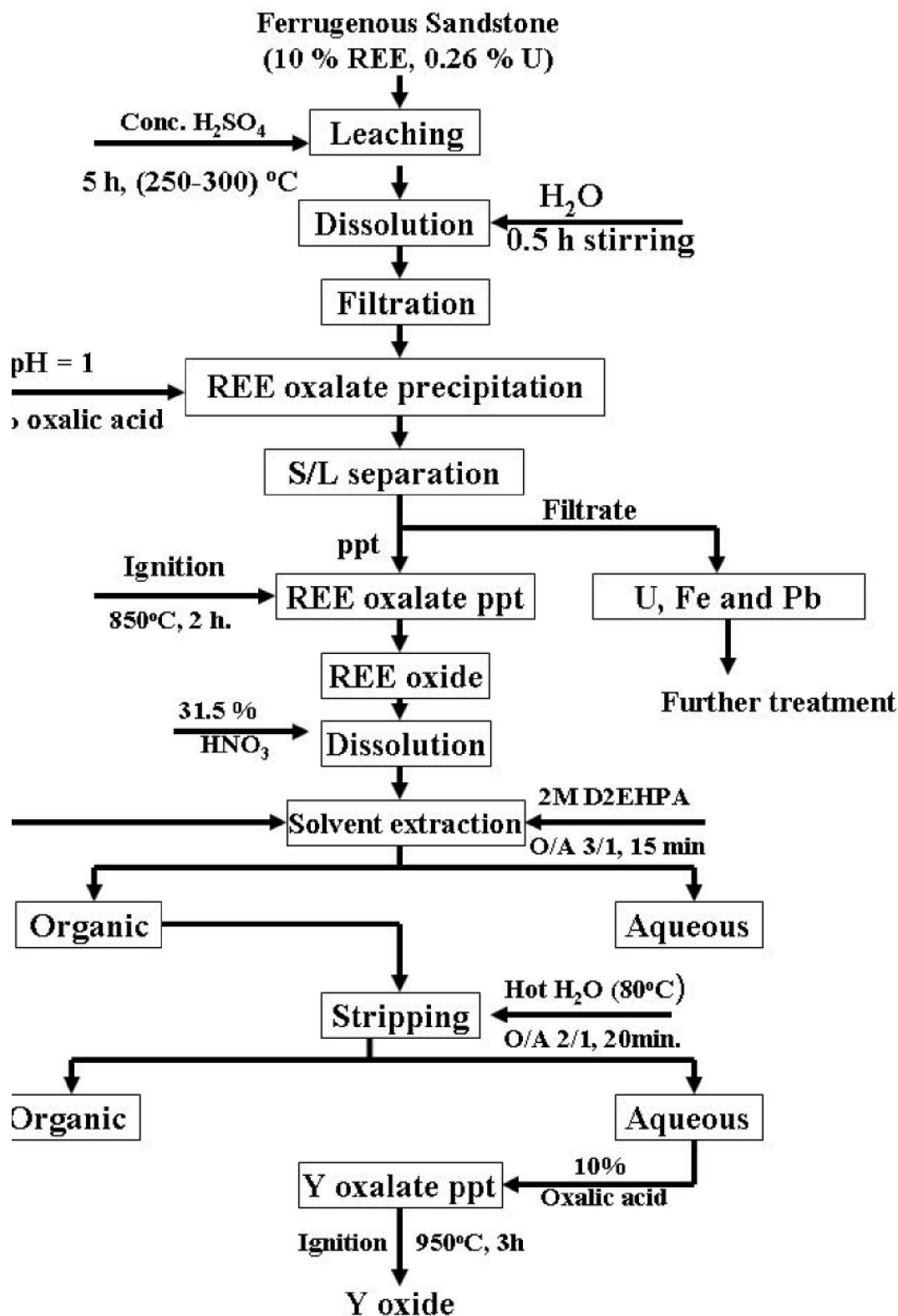


Figure 8: Flowsheet for the separation of REE and Y from Ramlet Hemeyir ferruginous sand stone

ent concentrations. The resulting re-extraction efficiencies were shown in TABLE 3 & TABLE 4. TABLE 3 shows that hot  $H_2O$  (80°C) was the best stripping agent

with respect to others at O/A of 2/1 for 20 minutes contact time.

Yttrium was precipitated from the prepared stripped



solution by addition of 10% oxalic acid gradually to the solution with stirring until almost completion of Y precipitation. The obtained Y oxalate precipitate was filtered, washed, dried then calcined at 950°C for 3h to obtain Y<sub>2</sub>O<sub>3</sub> product. The spot image analysis by EDAX of the product was found to contain 95% Y (Figure 7), this was matched with that obtained by the UV-VIS spectrophotometer. The working flow sheet of the whole process is given in Figure 8.

## CONCLUSIONS

The sulfuric acid digestion of Ferruginous sandstone ore was done and using H<sub>2</sub>SO<sub>4</sub>. Optimum conditions involved: mixing concentrated H<sub>2</sub>SO<sub>4</sub> at solid/liquid (S/L) ratio of 1/2 for 5h stirring time at temperature range of (250 - 300°C). From the prepared sulfate leach liquor REE had first been selectively precipitated at pH of 1 by adding 35% oxalic acid to the sulfate leach liquor to obtain REE of purity 88%.. For Yttrium extraction, a nitrate aqueous feed was prepared by dissolving the RE<sub>2</sub>O<sub>3</sub> concentrate in 31.5% nitric acid with S/L ratio 1/3 for 2h at 70°C. The yttrium extraction process by D2EHPA in presence of EDTA extraction efficiency reached about 99%. Yttrium re-extraction from the loaded organic phase was achieved by using Hot H<sub>2</sub>O at 80°C. Yttrium was precipitated from the prepared stripped solution by addition of 10% oxalic acid gradually to the solution with stirring until almost completion of Y precipitation. The obtained Y oxalate precipitate was filtered, washed, dried and then calcined at 950°C for 3h to obtain Y<sub>2</sub>O<sub>3</sub> product.

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