Arab Journal of Nuclear Sciences and Applications

Web site: ajnsa.journals.ekb.eg



# Individual Separation of Yttrium and Dysprosium Oxides from the Rare Earths Product obtained from Xenotime Mineral Concentrate

# Saleh M. El Hady

**ISSN 1110-0451** 

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

### ARTICLE INFO

Received: 18th Nov. 2023

Accepted: 15th Dec. 2023

Available online: 31st Dec. 2023

Article history:

Keywords:

Dysprosium.

Extraction,

Lactic Acid.

Rare earths.

PC88A.

Yttrium,

### ABSTRACT

The separation of ytrrium and dysprosium from the REEs product (48.15%  $Y_2O_3$ , 11.05%  $Dy_2O_3$ ) obtained from a xenotime mineral concentrate was studied. The REEs chloride liquor is prepared followed by precipitation of yttrium using lactic acid. The optimum conditions of the yttrium precipitation included 2 M lactic acid concentration, lactic acid pH 5 with  $L_{(REEs solution)}/L_{(lactic acid)}$  1/0.75 at contact time of 168 h at 25 °C. The extraction of dysprosium from Y-free REE chloride solution was investigated using PC88A (2-Ethylhexyl 2-ethylhexy phosphonic acid). The optimal conditions of the dysprosium extraction were an extractant concentration of 2.2 M, 1/1 O/A ratio in a chloride solution at pH 3, and 9 min., as contact time. While the optimal conditions of its stripping considered 1.5 M H<sub>2</sub>SO<sub>4</sub> in 1/1 O/A ratio for 20 min., as stripping time. Ultrapure products of Y and Dy were prepared and analyzed using ICP-MS.

# INTRODUCTION

Both of yttrium and dysprosium are never found in nature as free elements, though, like other lanthanides which are found in various minerals such as xenotime [1-3]. These two elements are among the most expensive rare earth elements due to the high demand and the low supply which have high-tech applications in the nuclear and elsewhere [4, 5]. In the non-nuclear sector, Y and Dy are used in the manufacture of super conductor, fluorescent color television. ceramics, lighting phosphors and computer displays [6-10]. In the nuclear sector, these two elements are used as control rods in nuclear reactors due to their relatively large neutron absorption cross section [11-14].

Different processes for the separation of individual rare earths from natural mixtures of rare earth elements rely primarily on small differences in alkalinity resulting from a reduction in ionic radius from lanthanum to lutetium [15]. Differences in alkalinity also affect salt solubility, ionic hydrolysis, and the formation of complex species, and these properties form the basis for separation methods using fractional precipitation, solvent extraction and ion exchange [16-19].

Over the past years, efforts have been made to separate yttrium and dysprosium individually from the solutions of rare earths product which obtained from xenotime mineral using three different techniques as mentioned above [20-27]. One of these techniques is the solvent extraction technique (SX) which depends on transfer rare earth element from organic phase into aqueous phase and its stripping by acid or base. Examples of the used solvents are Cyanex 923, diisooctyldithiophosphinic acid, trialkyl phosphine oxide, CA12 and D2EHPA [28-44]. One such attempt is to separate yttrium and dysprosium from REEs concentrate using two types of techniques: direct precipitation and solvent extraction. first Direct precipitation is used to separate Y using a carbonate and hydrogen peroxide system, followed by a solvent extraction technique to separate Dy using Cyanex 272 [45].

The main objective of this work is to investigate the individual separation of Y and Dy oxides from rare earths product prepared by chemical treatment of xenotime mineral concentrate, southwestern Sinai using ferric sulfate salts. The REEs product is dissolved with HCl to prepare RECl<sub>3</sub> solution. From the previous solution, yttrium is precipitated using lactic acid and the optimum conditions

have been obtained. Separation of Dy was investigated by a solvent extraction technique using PC88A (2-Ethylhexyl 2-ethylhexy phosphonic acid) in modified kerosene.

# EXPERIMENTAL

#### 2.1. Material Characterization

A working sample of rare earths elements is obtained from a xenotime mineral concentrate, which is separated from xenotime - bearing ferruginous sandstone, Sarabit El Khadem area, SW Sinai. The latter is chemically treated with ferric sulfate salt in a ratio of 1/20 concentrate/ferric ion and at a dissolution temperature of 65 °C for 30 hours using 10 g/L ferric sulfate where about >95% of the REEs are solubilized followed by its precipitation as oxalates and calcined at 850°C to obtain on REEs product [**25**]. The obtained rare earths product is subjected to extensive chemical analyzes by the XRF technique withinside the Egyptian National Research Center (NRC) using Axios Advanced, Panalytical, Holland.

#### 2.2. Experimental procedures

# 2.2.1. Preparation of the Rare Earths Chloride Solution

A sample of a known weight of the REEs product is dissolved with a known volume of HCl in a beaker with heating, after which distilled water is added to produce a rare earth chloride solution. The latter represented the required liquor of the present work for the preparation of Y and Dy products. For all analysis of individual heavy rare earths elements, ICP-MS spectrometry in the Egyptian Chemical Warefare was used.

#### **2.3. Recovery Procedures**

#### 2.3.1. Recovery of Yttrium

Several experiments have been achieved for precipitation of yttrium by mixing a known amount

(20 ml) of REEs chloride solution with an equal amount of a prepared organic acid solution such as tartaric acid, citric acid, lactic acid, succinic acid and maleic acid at room temperature. Various conditions were investigated to determine the optimal values of the relevant precipitation factors for yttrium. These included organic acid concentration, pH of organic acid, Liquid (REEs solution) /Liquid (organic acid) ratios and contact time.

### 2.3.2. Recovery of Dysprosium

A solvent extraction technique is used to extract Dy from Y-free chloride liquor using the synergistic PC88A/Octanol system in kerosene as a diluent to prepare it at various concentrations. Octanol ( $C_8H_{18}O$ ) was used as a modifier (0.06 M) to eliminate the formation of the third phase during Dy stripping. The solvent PC88A is also known as purified 2-ethylhexy I-2-ethylhexphosphonic acid (HEHEHP) and has the chemical and physical properties listed in Table (1).

In each extraction experiment, the organic phase and the aqueous phase of dysprosium chloride were stirred together in a separatory funnel for a specific time. The two phases were then allowed to settle, separated, and the residual metal content of the aqueous phase was analyzed to estimate the extraction efficiency. In this way, appropriate factors of solvent extraction were investigated, i.e. the concentration of solvent, the contact time, the pH value of the liquor and the ratio of aqueous phase to organic phase (A/O). On the other hand, a solvent-loaded sample was prepared to study the stripping behavior of metallic dysprosium extracted with sulfuric acid. Relevant factors were also examined namely; Contact time and concentration of acid.

Property	Value
Chemical Name	2-Ethylhexyl 2-ethylhexy phosphonic acid (HEHEHP)
Molecular Weight	306.4
Molecular Formula	$C_{16}H_{35}O_{3}P$
Structural Formula	C <sub>8</sub> H <sub>17</sub> O=P-O-C <sub>8</sub> H <sub>17</sub> OH
Appearance	Colorless to light yellowish liquid
Purity	95%
Density	0.95 g/cm <sup>3</sup>
Boiling point	390 °C at 760 mmHg
Flash point	190 °C
Enthalpy of vaporization	73 Kj/mol

#### 2.4. Control Analysis

As a control analysis for all extraction experiments used, all the individual heavy rare earth elements in different workflow solutions were analyzed with ICP-MS. Also, both Y and Dy products were also analyzed by ICP-MS spectrometric analysis in addition the identification of the yttria product using ESEM in Egyptian Nuclear Materials Authority.

### **RESULTS AND DISCUSSION**

#### **3.1.** Characterization of Rare earths Concentrate

The obtained XRF analysis of the working rare earth product resulting from the above-mentioned chemical treatment of the xenotime mineral concentrate is analyzed in National Research Center (NRC) (Table 2).

# **3.2.** Preparation of the chloride liquor of REEs product

25 ml of concentrated HCl is used to dissolve 20 g of a sample of the rare earths product by heating and stirring until the rare earth elements are completely dissolved. Distilled water is then added to a volume of 1 litre. The chloride solution is analyzed as presented in Table 3 and shows that concentrations of the REE elements reached values of 7.58, 1.45, 1.04, 0,98, 0,86, 0,68, 0,48, 0.28 and 0.03 g/l for Y, Dy, Gd, Sm, Tb, Yb, Er, Ho and Lu respectively.

#### 3.3. Results of Y Recovery

# 3.3.1. Optimization of the Relevant Factors of Yttrium Precipitation

Several Factors are studied for precipitation of yttrium from the prepared REEs chloride solution namely; reagent type, reagent concentration, pH of the reagent, Liquid (REEs solution) /Liquid (lactic acid) ratio and contact time.

### 3.3.1.1. Effect of reagent type

The effect of some organic acids such as citric acid, tartaric acid, succinic acid, lactic acid and maleic acid upon precipitation of individual rare earth elements from the prepared REEs chloride solution was investigated. In these experiments, 0.05M of citric acid, tartaric acid, succinic acid, lactic acid and maleic acid concentrations were used. The other parameters precipitation factors are fixed as contact time 24 h., pH of organic acid 3 and 1/1 L (organic acid) /L (REEs solution) ratio at ambient room temperature (25 °C).

From these results, lactic acid was observed to precipitate yttrium at precipitation efficiency 15.2% without the associated rare earth elements. But the rest of organic acids did not affect the precipitation of individual rare earth elements. So, it is decided that lactic acid is the best organic acid for direct precipitation of yttrium only.

### 3.3.1.2. Effect of lactic acid concentration

The concentration of lactic acid effect upon precipitation of individual rare earth elements was examined via series of various concentrations of acid from 0.1 to 0.3. Conventional controlling parameters were used as 24 h. contact time, L (lactic acid) /L (REEs solution) ratio of 1:1 and pH of lactic acid 3 at room temperature of 25°C. The observation results are demonstrated in Fig. 1.

The yttrium precipitation efficiency progressed from 18.1% to 28.2% when the lactic acid concentration was gradually increased from 0.5 M to 2 M without precipitation the associated rare earth elements. Increasing the lactic acid concentration from 2 M to 2.5 M did not move forward the precipitation efficiency of Y and its associated REEs. In this manner, a lactic acid concentration of 2 M is the best concentration for yttrium precipitation without the associated rare earth elements (Dy, Gd, Sm, Tb, Yb, Ho, Er and Lu). This depends on the coordination chemistry between the yttrium atom and the ligand mode (O-H in lactic acid) as well as the size of the yttrium atom.

Component	Wt, %	Component	Wt, %
<b>Y</b> <sub>2</sub> <b>O</b> <sub>3</sub>	48.15	H02O3	1.60
$Dy_2O_3$	8.32	$Lu_2O_3$	0.17
$Gd_2O_3$	5.99	$SO_3$	0.76
Sm2O3	5.68	Na <sub>2</sub> O	9.66
<b>Tb</b> <sub>2</sub> <b>O</b> <sub>3</sub>	4.95	<i>K</i> <sub>2</sub> <i>O</i>	2.39
<b>Yb</b> <sub>2</sub> <b>O</b> <sub>3</sub>	3.87	CaO	1.77
$Er_2O_3$	2.74	<i>Al</i> <sub>2</sub> <i>O</i> <sub>3</sub>	3.53
	Total	99.58	

Table (2): XRF analysis of the working REEs concentrate sample (Wt, %).

Arab J. Nucl. Sci. Appl., Vol. 57, 1, (2024)

Metal ion	Conc., g/l	Metal ion	Conc., g/l
Y	7.58	Yb	0.68
Dy	1.45	Er	0.48
Gd	1.04	Но	0.28
Sm	0.98	Lu	0.03
Tb	0.86	pH	1.9

 Table (3): Chemical composition of the prepared REEs solution.

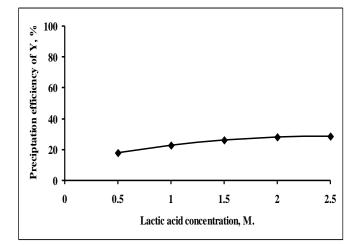


Fig. (1): Effect of lactic acid concentration on the precipitation efficiency of yttrium.

#### 3.3.1.3. Effect of pH of lactic acid

To study the effect of Lactic acid pH on the precipitation efficiency of individual rare earth elements, pH of lactic acid is adjusted at different values from 3 to 5.5 using ammonia solution. The supplementary precipitation conditions were stable, include; 2 M lactic acid with L (REEs solution) /L (lactic acid) ratio of 1:1 and 24 h. contact time at ambient temperature (25 °C). The obtained results are plotted in Fig.2.

The results indicated that, when pH values of lactic acid increased from 3 to 5, the precipitation efficiency of yttrium increased from 28.2% to 52.1% without precipitation the associated rare earth elements. At 5.5 pH of lactic acid, the yttrium precipitation efficiency decreased at 50.2% and also without precipitation the associated rare earth elements. So, it is concluded that 5 pH is the best value of lactic acid for precipitation of yttrium without the associated rare earth elements.

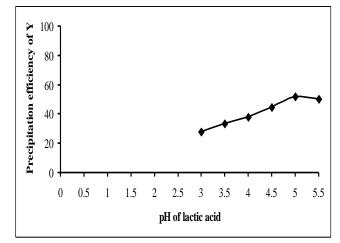


Fig. (2): Effect of pH of lactic acid on the precipitation efficiency of yttrium.

### 3.3.1.4. Effect of Liquid (REEs solution) /Liquid (lactic acid) ratio

Liquid (REEs solution) /Liquid (lactic acid) ratio effect upon precipitation of individual rare earth elements was studied using Liquid (REEs solution) /Liquid (lactic acid) ratios from 1:0.25 to 1:1.50, with other testing parameters involving 2 M lactic acid conc.; 24 h contact time; 25°C temperature; and lactic acid pH 5. Figure (3), shows that the liquid volume of the prepared rare earth chloride solution was saved constantly while the liquid volume of lactic acid was various to attain the optimum L (REEs solution) /L (lactic acid) ratios.

Based on these results, it was found that a 1/0.75 L (REEs solution) /L (lactic acid) ratio, only a good improvement in yttrium precipitation efficiencies than 1/1 L (REEs solution) /L (lactic acid) ratio was achieved. Whereas there's no any uniquely expand by increasing L (REEs solution) /L (lactic acid) ratio to 1/1.25 and 1/1.50 with Y and the rest of REE elements. As a result, a Liquid (REEs solution) /Liquid (lactic acid) ratio of 1/0.75 will be concluded the ideal ratio for accomplishing a 51.9% yttrium precipitation without precipitation the associated rare earth elements

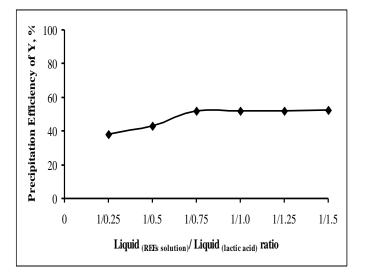


Fig. (3): Effect of Liquid (REEs solution) /Liquid (lactic acid) ratio on the precipitation efficiency of yttrium.

#### 3.3.1.5. Effect of contact time

A Grouping of contact times test from 24 (one day) to 168 h (7 days) has been done. The supplementary precipitation conditions were steady, incorporate; lactic acid pH 5, 2M lactic acid with L (REEs solution) /L (lactic acid) ratio of 1/0.75 at 25°C. The results in Fig. 4 demonstrated that, when the contact time increased from 24 to 168 h, the precipitation efficiency of yttrium increased from 51.9% to 100%. In this way, it can be chosen that 168 h of contact time beneath the favoured factors achieved complete precipitation of yttrium without precipitation the associated rare earth elements.

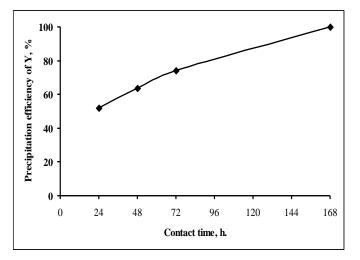


Fig. (4): Effect of contact time on the precipitation efficiency of yttrium.

At last, it may be concluded that lactic acid is successful in complete precipitation of yttrium without the associated REEs elements (Dy, Gd, Sm, Tb, Yb, Er, Ho and Lu) from rare earth product produced from xenotime mineral, southwestern Sinai under the following experimental conditions:

- Lactic acid concentration : 2 M
- Lactic acid pH : 5
- L<sub>(REEs solution)</sub> /L<sub>(lactic acid)</sub> ratio: 1/0.75
- Time : 168 hrs.
- Temperature : 25 °C

#### 3.3.2. Y<sub>2</sub>O<sub>3</sub> Production

It is appropriate to present the synthesis and crystal structure of the primary molecular complex of yttrium-lactate,  $Y(Lac)_3(H_2O)_2$ , in which the yttrium coordination sphere is immersed with lactate ligands and water particles, coming about within the formation a unbiased linkage [46, 47]. The reaction of yttrium chloride with lactic acid produces a white precipitate of yttrium lactate and represented in the Eq. (1). Yttrium lactate is filtrated and touched off at 850 °C to create yttrium oxide as appeared within the Eq. (2). The latter is analyzed using ICP-MS and SEM analyses as shown in Table 4 and Fig. 5 respectively.

 $YCl_3 + 3C_3H_6O_3 + 2H_2O \rightarrow Y(C_3H_5O_3)_3(H_2O)_2 + 3HCl$  (1)

Yttrium chloride	Lactic acid	Yttrium lactate	
2Y(C <sub>3</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub>		$+18 \text{ CO} + \text{H}_2\text{O} + 18 \text{H}_2$ (2)	
Yttrium lactate	Yttri	um oxide	

# Table (4): ICP-MS analysis of the final yttrium precipitate and its impurities

Element	Y	Si	Al	Na	K
Content,%	81.23	0.0013	0.0340	0.0124	0.0090

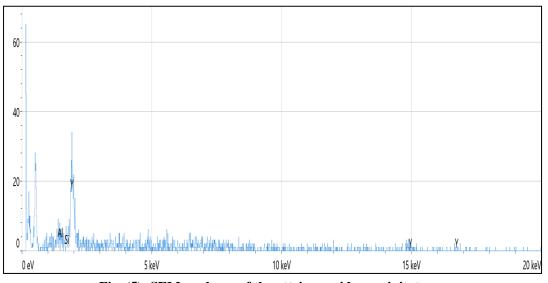


Fig. (5): SEM analyzer of the yttrium oxide precipitate.

#### 3.4. Results of Dy Recovery

# 3.4.1. Optimization of the Relevant Factors of PC88A Extraction of Dysprosium

After separation of the yttrium lactate, the remaining chloride solution was first re-evaporated to 500 mL and found to have a pH of 1.9. The latter was then subjected to dysprosium extraction with PC88A-kerosene in the presence of octanol as a modifier.

The expected reaction of PC88A in kerosene (organic phase) with dysprosium chloride (aqueous phase) would involve an exchange of dysprosium for hydrogen in the O-H bond of 2-ethylhexyl-2-ethylhexphosphonic acid (PC88A) and is represented by the reaction shown in **Eq. (3)**; viz:

 $3R_1R_2PO_3H + DyCl_3 \rightarrow (R_1R_2O_2PO)_3Dy + 3HCl$  (3) Where  $R_1 = R_2 = C_8H_{17}$ 

The important factors affecting solvent extraction of the studied dysprosium involved the solvent concentration, the contact time, the pH of the chloride liquor and the aqueous/ organic ratio (A/O).

# 3.4.1.1. Effect of pH of the Prepared Chloride Liquor

To investigate the influence of the pH of the prepared chloride liquor on the extraction efficiency of Dy and achieve the optimum condition, six experiments were conducted at various pH values ranging from 1.5 to 3.5 in ambient conditions of A/O 1:1 and using 0.6 M PC88A in kerosene and determining 0.06 M octanol within a contact time of 3 min. Extraction of Dy using cationic extractant PC88A occurred depending on the exchange of hydrogen ions [48]. From the results presented in Table 5, it is decided that the

maximum Dy extraction efficiency (26.93 %) was attained at pH 3.0. Further increase the pH value to 3.5 shows no significant increase in Dy extraction because  $H^+$  ions may not be available in the organic phase to exchange the  $Dy^{+3}$  ions.

Table (5): Effect of pH of the chloride leach liquor onthe extraction efficiency of Dy & Gd.

nU	Extraction efficiency,%		
рН	Dy	Gd	
1.5	11.31	5.61	
1.9	13.79	4.85	
2.3	17.24	3.12	
2.5	21.38	1.83	
3	26.93	0.05	
3.5	26.99	0.06	

### 3.4.1.2. Effect of PC88A Concentration

The influence of PC88A concentration on the Dy extraction efficiency was investigated by mixing equal volumes of a chloride leach solution with PC88A solvent of various concentrations ranging from 0.6 to 2.4 M in kerosene and determining 0.06 M octanol with contact time 3 min., at pH 3.0. From the data illustrated in Table 6, it is noticed that the Dy extraction efficiency increased from 26.93 to 84.14 % when the concentration of PC88A increased from 0.6 to 2.2 M respectively. When increased the concentration of extractant to 2.4, the dysprosium extraction efficiency decreased to 77.24 % because of the solvent viscosity and very difficult movement of the solute from the aqueous phase into the organic phase. Therefore, a PC88A concentration of 2.2 M was considered the optimum concentration for dysprosium extraction from the prepared chloride liquor of the rare earths product.

Extraction efficiency,%		
Dy	Gd	
26.93	0.05	
44.13	0.001	
59.31	0.000	
71.03	0.000	
84.14	0.000	
77.24	0.000	
	Dy 26.93 44.13 59.31 71.03 84.14	

 Table (6):Effect of PC88A concentration on Dy and Gd extraction efficiency from the prepared chloride liquor.

Contact Time,	Extraction efficiency,%	
min.	Dy	Gd
3	84.14	0.000
5	88.97	0.000
7	93.79	0.000
9	99.17	0.000
11	99.20	0.000

Table (7): Effect of contact time on Dy and Gd extraction

efficiency from the prepared chloride liquor.

#### 3.4.1.3. Effect of Contact Time

To investigate the influence of contact time on the Dy extraction efficiency of PC88A, several tests were examined at various contact times from 3 to 11 min., with other extraction factors set to O/A 1:1 and using 2.2 M PC88A in kerosene and specifying 0.06 M octanol as modifier at pH 3.0. From the results presented in Table 7, it is observed that increasing the contact time from 3 to 9 min., increased the Dy extraction efficiency from 84.14 to 99.17% respectively. By increasing the contact time to 11 min., the extraction efficiency of dysprosium showed negligible effect to 99.2 %. This may be due to the fact that the transfer of dysprosium ion from the aqueous phase to the organic phase is saturated to form a complex at equilibrium [46]. Therefore, a contact time of 9 min., was considered the optimal value for the extraction of Dy from the leach liquor.

# 3.4.1.4. Constrution of McCabe-Thiele Extraction Diagram

From the Y-free prepared chloride liquor, the influence of the aqueous phase / organic phase ratio (v/v) on the Dy extraction was conducted from 3:1 to 1:3, while the other extraction factors were fixed at their assaying optimum values (2.2 M PC88A, contact time 9 min., at 25 °C and the aqueous phase pH value 3.0). The resulting equilibrium data were used to create a McCabe-Thiele extraction diagram (Fig. 6). From this diagram, it is possible to determine the necessary theoretical number of extraction stages by drawing a specific operating line. Depending on the slope of the selected operating line reaching a value 3 (A/O), 3 theoretical stages would be needed to almost complete extraction of Dy from the Y-free chloride solution prepared from the REEs product.

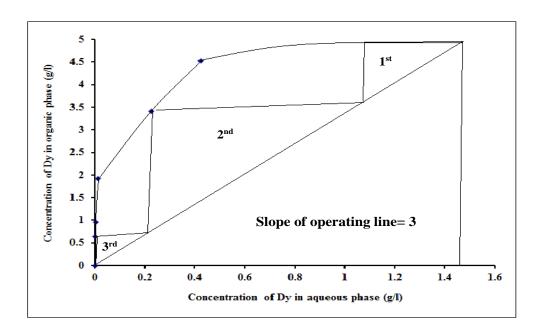


Fig. (6): McCabe-Thiele diagram for Dy extraction.

Arab J. Nucl. Sci. Appl., Vol. 57, 1, (2024)

# 3.4.2. Optimization of the Relevant Stripping Factors of Dysprosium

To strip dysprosium, liquor containing PC88A/kerosene with a content of 1.44g Dy/L prepared and processed with  $H_2SO_4$  solution under different tests conditions. These included the concentration of acid, the contact time and various A/O ratios. The acid stripping reaction can be illustrated in **Eq.(4)** as follows:

 $2 (R_1 R_2 O_2 PO)_3 Dy + 3 H_2 SO_4 \rightarrow 6 R_1 R_2 O_2 POH + Dy_2 (SO_4)_3$  (4) Where  $R_1 = R_2 = C_8 H_{17}$ 

#### 3.4.2.1. Effect of Acid Concentration

To strip Dy, a series of stripping experiments were performed using  $H_2SO_4$  solution of various concentrations from 0.5 to 2 M with contact time of 5 min., and using 1/1 O/A ratio at 25 °C. The results obtained are summarized in Table 8, which it is evident that 1.5 M  $H_2SO_4$  gave a Dy stripping efficiency of 93.7% and remained constant.

Table (8): Effect of H2SO4 concentration on stripping<br/>efficiency (%) of Dy.

H2SO4 Conc., M	Dy Stripping efficiency %
0.5	44.20
1.0	79.60
1.5	93.70
2.0	93.80

#### 3.4.2.2. Effect of Stripping Time

The influence of the stripping time on the stripping efficiency of Dy was investigated from 5 to 20 min., at 1.5 M sulfuric acid and 1/1 O/A ratio. From the results presented in Table 9, it was observed that 20 min., is sufficient stripping time in which the stripping efficiency exceeds 99%.

Contact Time, min.	Dy Stripping efficiency %
5	93.70
10	96.60
15	98.10
20	99.37

# 3.4.2.3. Construction of McCabe-Thiele Stripping Diagram

From the equilibrium stripping data at various A/O ratios and using  $1.5 \text{ M H}_2\text{SO}_4$  solution for a contact time 20 min, the corresponding McCabe-Thiele diagram (Figure 7) was generated. From the latter, the theoretical number of stripping stages can be derived after adjusting the working line to the isotherm, whose slope reaches 0.43 (A/O ratio). Therefore, theoretically three stripping stages would be required for nearly complete stripping of dysprosium.

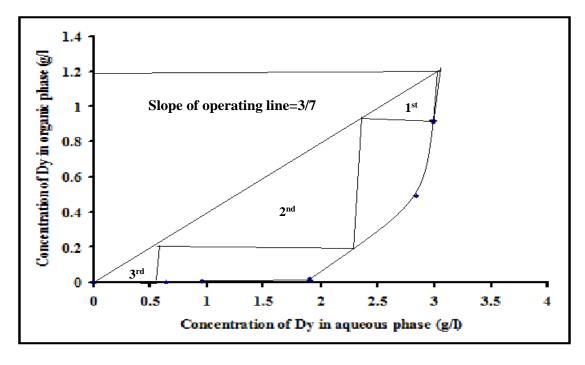


Fig. (7): McCabe-Thiele diagram for Dy stripping.

#### 3.4.3. Dy<sub>2</sub>O<sub>3</sub> Production

From the dysprosium strip solution, Dy is completely precipitated with 10% oxalic acid at pH 0.7 as dysprosium oxalate  $[Dy_2(C_2O_4)_3]$  according to the represented reaction in **Eq. (5)**.

$$Dy_2(SO_4)_3 + 3 C_2O_4H_2 \rightarrow Dy_2(C_2O_4)_3 + 3 H_2SO_4$$
 (5)

After ignition at 850 °C, very pure  $Dy_2O_3$  was produced as represented in **Eq. 6** and subjected to analysis using ICP-MS as shown in Table 10.

$$\begin{array}{cccc} 850^{\circ}\mathrm{C} \\ \mathrm{Dy}_2(\mathrm{C}_2\mathrm{O}_4)_3 \ \to \ \mathrm{Dy}_2\mathrm{O}_3 \ + \ 3\ \mathrm{CO}_2 \ + \ 3\ \mathrm{CO} \end{array} \tag{6}$$

 Table (10): ICP-MS analysis of the final Dy precipitate and its impurities.

Element	Dy	Gd	Al	Na	Κ
Content,%	86.131	0.0250	0.0125	0.0025	0.0008

# 3.5. Proposal Flowsheet

A successful extraction procedure of yttrium and dysprosium from rare earths product (48.15% Y<sub>2</sub>O<sub>3</sub> & 11.05% Dy<sub>2</sub>O<sub>3</sub>) obtained from the xenotime concentrate is achieved. The rare earths product is completely dissolved with hydrochloric acid to obtain on rare earths chloride

leach liquor. From the latter, yttrium and dysprosium were subjected to a detailed study for their extraction using direct precipitation and solvent extraction techniques respectively. Firstly, yttrium is precipitated as yttrium lactate using lactic acid and the studied optimum conditions for precipitation involved 2 M lactic acid concentration, lactic acid pH 5, 1/0.75 L<sub>(REEs solution)</sub> /L<sub>(lactic acid)</sub> ratio and contact time of 168 hrs at 25 °C. After filtration of the yttrium precipitate, Dy is s extracted using 2-Ethylhexyl 2-ethylhexy phosphonic acid (PC88A) in modified kerosene. The decided optimum extraction conditions involved an extractant concentration of 2.2 M, 1/1 O/A ratio at 9 min contact time with the chloride liquor at pH 3. The extracted dysprosium was stripped with a 1.5 M sulfuric acid in a ratio of 1/1 O/A for 20 min. According to the relevant McCabe Thiele diagrams, three theoretical stages are required for extraction and stripping. Dysprosium was precipitated from the stripped solution as dysprosium oxalate at pH of 0.7 using 10% oxalic acid solution. The Y lactate and the dysprosium oxalates obtained were then each ignited at 850 °C for one hour. The obtained oxides were analyzed by ICP-MS. Finally, all the obtained data were formulated in a proposal flowsheet (Figure 8).

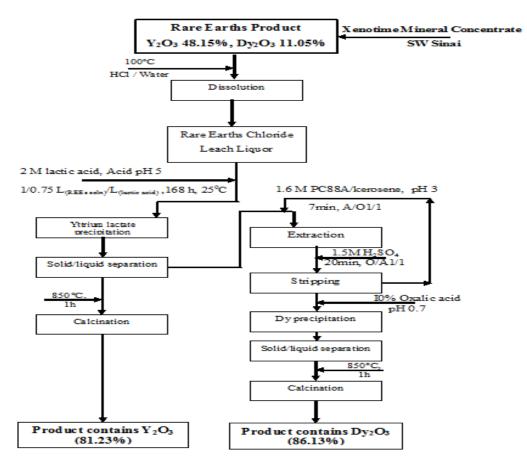


Fig. (8): Proposal flowsheet for extraction of yttrium and dysprosium oxides from the rare earths product obtained from xenotime mineral concentrate.

Arab J. Nucl. Sci. Appl., Vol. 57, 1, (2024)

# CONCLUSION

Yttrium and dysprosium are recovered from the rare earths product which produced from the xenotime mineral concentrate. Yttrium is firstly extracted using direct precipitation technique by lactic acid to produce yttrium lactate after preparation of the rare earths chloride solution. This is followed by extraction of dysprosium using solvent extraction technique (PC88A), while its stripping was performed by sulfuric acid then precipitated from the stripped solution by oxalic acid as dysprosium oxalate. Yttrium lactate and dysprosium oxalate were calcined to obtain on yttrium oxide and dysprosium oxide respectively.

# REFERENCES

[1] Wall, F. (2021) Rare Earth Elements, Encyclopedia of Geology (Second Edition), United Kingdom, 5, 680-693.

Doi: 10.1016/B978-0-08-102908-4.00101-6.

- [2] Balaram, V. (2019) Rare earth elements: A review of applications, occurrence, exploration analysis, recycling, and environmental impact, Geoscience Froniters, India, 10 (4), 1285-1303.
   <u>Doi: 10.1016/j.gsf.2018.12.005.</u>
- [3] Gupta, C.K. and Krishnamurthy, N. (2005) Extractive metallurgy of rare earths, CRC Press, NY, USA, 77.
- [4] Filho, W.L., Kotter, R., Özuyar, P.G., Abubakar, I.R., Eustachio, J.H. and Matandiortya, N.R. (2023) Understanding rare earth elements as critical raw materials, Sustainability Journal, MDPI, 15, 1-18. <u>Doi:10.3390/su15031919.</u>
- [5] Perwira, N.K., Basuki, K.T., Biyantoro, D., and Effendy, N. (2018) IOP Conference Series: Materials Science and Engineering, Yogyakarta, Indonesia, 1-8. <u>Doi:10.1088/1757-899X/349/1/012044.</u>
- [6] El-Hefny, N. E., Gasser, M. S., Emam, Sh. Sh., Mahmoud, W. H., Aly, H. F. (2018) Comparative studies on Y(III) and Dy(III) extraction from hydrochloric and nitric acids by cyanex 572 as a novel extractant, Journal of Rare Earths, 36 (12), 1342-1350.

Doi:10.1016/j.jre.2018.04.012.

[7] Kumar, V., Jha, M. K., Kumari, A., Panda, R., Kumar, J.R. and Lee, J.Y. (2014) Recovery of rare earh metals (REMs) from primary and secondary resources: A review, Rare Metal Technology 2014, Edited by: Neale R. Neelameggham, Shafiq Alam, Harald Oosterhof, Animesh Jha, and Shijie Wang. TMS (The Minerals, Metals & Materials Society), 81-88.

Doi:10.1002/9781118888551.ch16.

- [8] Xu, F., Zhang, L., Dong, X., Liu, Q. and Komuro, M. (2011) Effect of DyF<sub>3</sub> additions on the coercivity and grain boundary structure in sintered Nd-Fe-B magnets. Scripta Materialia, 64 (12), 1137-1140. Doi:10.1016/j.scriptamat.2011.03.011
- [9] Seo, Y. and Morimoto, S. (2014) Comparison of dysprosium security strategies in Japan for 2010– 2030. In: Resources Policy, 39, 15-20.
   <u>Doi:10.1016/j.resourpol.2013.10.007</u>
- [10] Zepf, V. (2013) Rare earth elements a new approach to the nexus of supply, demand and use: exemplified along the use of neodymium in permanent magnets, Springer Theses, Berlin, 31-60. <u>Doi:10.1007/978-3-642-35458-8</u>
- [11] Xie, F., Zhang, T.A., Dreisinger, D. and Doyle, F. (2014) A critical review on solvent extraction of rare earths from aqueous solutions. Minerals Engineering, 56, 10–28.
  Doi:10.1016/j.mineng.2013.10.021
- [12] Shi, D. and Zhang, S. (2022) Analysis of the rare earth mineral resources reserve system and model construction based on regional development, Computational Intelligence and Neuroscience, 2022, 1-10.

Doi: 10.1155/2022/9900219.

[13] Zhang, S. (2022) Study on economic significance of the rare earth mineral resources development based on good programming and few-shot learning, Computational Intelligence and Neuroscience, 2022, 1-9.

Doi: 10.1155/2022/7002249.

- [14] Sotnikov, A.V., Bakovets, V.V. and Plyusnin, P.E.
  (2021) Kinetics of Thermal Decomposition of Yttrium and Samarium Hydroxides and Sm(OH)3@Y(OH)3 Compound with a Core–Shell Nanostructure. Russian Journal of General Chemistry, 91, 1368–1378.
  Doi:10.1134/S107036322107015X
- [15] Pathapati, S. V. S. H., Free, M. L. and Sarswat, P. K. (2023) A comparative study on recent developments

for individual rare earth elements separation, Processes Journal, MDPI, 11 (7), 1-28. Doi: 10.3390/pr11072070.

- [16] El Ouardi, Y., Virolainen S., Mouele, E. S. M., Laatikainen, M., Repo, E. and Laatikainen, K. (2023) The recent progress of ion exchange for the separation of rare earths from secondary resources – A review, Hydrometallurgy, 218, 1-20. <u>Doi:1016/j.hydromet.2023.10604.</u>
- [17] Gupta, C. K. and Krishnamurthy, N. (1992) Extractive Metallurgy of Rare Earths, International Materials Reviews, (37) 5, 204-216.
- [18] McNulty, T., Hazen, N. and Park, S. (2022) Processing the ores of rare earth elements, MRS Bulletin, 47, 258-266.
  Doi: 10.1557/s43577-022-00288-4
- [19] Pearse, G., Borduas, J., Gervais, T., Menaral, D., Seddaoui, D. and Ung, B. (2014) Method and system for magnetic separation of rare earths, US2014/0166788 Al, United States.
- [20] Li, D. (2017) A review on yttrium solvent extraction chemistry and separation process. Journal of Rare Earths, 35 (2), 107-119.
   Doi:10.1016/S1002-0721(17)60888-3.
- [21] Pinatti, D. G., Ayres, M. J. G., Ribeiro, S., Silva, G.
  I. J. P., Silva, M. L. C. D. and Martins, A. H. (1988) Yttrium and rare earths separation by ion exchange resin, The 1<sup>st</sup> Conference of State Meeting of New Materials, IAEA, 21 (20), 9.
- [22] Morton, J. R. (1969) Method of separating yttrium from rare earths by ion exchange, US Patent 3,455,646.
- [23] El Hussaini, O., Saalman, H. and Mahmoud, M.
  (2014) Extraction of yttrium from ferruginous sandstone, southwestern Sinai, Egypt, Rare Metal Technology 2014, Editor(s):Neale R. Neelameggham, Shafiq Alam, Harald Oosterhof, Animesh Jha, Shijie Wang. 143-148. Doi:10.1002/9781118888551.ch27.
- [24] Vasconcellos, M. E., Rocha, S., M., Pedreira, W., R., Queiroz, C., A. and Abrao, A. (2006) Enrichment of Y from rare earth concentrate by ammonium carbonate leaching and peroxide precipitation, J. Alloys & compounds, 418, 200-203. <u>Doi:10.1016/j.jallcom.2005.10.076.</u>
- [25] Vasconcellos, M., E., Queiroz, C., A., Abrao, A. (2004) Sequential separation of the yttrium-heavy

rare earths by fractional hydroxide precipitation, J. Alloys & Compounds, 374, 405-407. Doi:10.1016/j.jallcom.2003.11.038

- [26] El Hady, S. M. (2017) A novel procedure for processing of the xenotime mineral concentrate of southwestern Sinai, Korean J. Chem. Eng., 34(7), 2049-2055.
   <u>Doi:10.1007/s11814-017-0095-0</u>
- [27] El Hady, S. M., Bakry, A. R., Al Shami, A. S. and Fawzy, M. M. (2016) Processing of the xenotime concentrate of southwestern Sinai via alkali fusion and solvent extraction, Hydrometallurgy, 163, 115-119.

Doi:10.1016/j.hydromet.2016.03.019

- [28] Ying, H. and Mikiya, T. (2010) Solvent extraction equilibrium of dysprosium (III) from nitric acid solutions with 2-ethylhexylphosphonic acid mono-2ethylhexyl ester, Trans. Nonferrous Met. Soc. China, 20, 707-711. Doi:10.1016/S1003-6326(09)60202-8.
- [29] Singh, D. K., Kotekar, M. K. and Singh, H. (2008). Development of a solvent extraction process for production of nuclear grade dysprosium oxide from a crude concentrate, Desalination Journal, 232, 49-58. <u>Doi: 10.1016/j.desal.2007.10.036</u>
- [30] Gupta, B., Malik, P. and Deep, A. (2003) Solvent extraction and separation of tetravalent lanthanides and yttrium using cyanex 923, Solvent Extraction and Ion Exchange, 21 (2), 239-258. Doi:10.1081/SEI-120018948
- [31] Reddy, M.L.P., Varma, R.L., Ramamohan, T.R., Sahu, S.K. and Chakravortty, V. (1998) Cyanex 923 as an extractant for trivalent lanthanides and yttrium, Solvent Extraction and Ion Exchange, 16 (3), 795– 812.

Doi:10.1080/07366299808934553

- [32] Reddy, M.L.P., Bharathi, B., Peter, S. and Ramamohan, T. (1999) Synergistic extraction of rare earths with bis(2,4,4-trimethylpentyl) dithiophosphinic acid and trialkyl phosphine oxide, Talanta, 50(1),79-85. Doi:10.1016/S0039-9140(99)00106X
- [33] Wang, Y., Liao, W. and Li, D. (2011) A solvent extraction process with mixture of CA12 and Cyanex272 for the preparation of high purity yttrium oxide from rare earth ores, Separation and Purification Technology, 82, 197-201. Doi:10.1016/j.seppur.2011.09.018

Arab J. Nucl. Sci. Appl., Vol. 57, 1, (2024)

- [34] Jorjani, E. and Shahbazi, M. (2012) The production of rare earth elements group via tributyl phosphate extraction and precipitation stripping using oxalic acid. Arabian J. Chem., in press. <u>Doi:10.1016/j.arabjc.2012.04.002.</u>
- [35] Mohammadi, M., Forsberg, K., Kloo, L., Cruz, J. M. and Rasmuson, Å. (2015) Separation of Nd(III), Dy(III) and Y(III) by solvent extraction using D<sub>2</sub>EHPA and EHEHPA, Hydrometallurgy, 156, 215-224.
  Doi:10.1016/j.hydromet.2015.05.004
- [36] Yoon, H., Kim, C. J., Chung, K. W., Kim, S. D. and Kumar, J. R. (2015) Recovery process development for the rare earths from permanent magnet scraps leach liquors, J. Braz. Chem. Soc., 26 (6), 1143-1151.
  Doi:10.5935/0103-5053.20150077
- [37] Simpson, N. (2000) Solid-phase extraction: principles, techniques, and applications, Varian Associates, Inc., Harbor City, California, USA, 315.
- [38] Preston, J. S., Cole, P. M., Craig, W. M. and Feather, A. M. (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: Leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction, Hydrometallurgy, 41, 1-19. Doi:10.1016/0304-386X(95)00051H
- [39] Basuki, K. T., Arifudin, R., Pusparini, W. R. and Saputra, A. (2020) Dysprosium (Dy) separation from yttrium concentrate in nitric acid solution using Aliquat 336 solvent, Key Engineering Materials, 840, 573-579.
  Doi: 10.4028/www.scientific.net/KEM.840.573
- [40] Thakur, N V. (2000) Separation of dysprosium and yttrium from yttrium concentrate using alkylphosphoric acid (DEHPA) and alkylphosphonic acid (EHEHPA PC88A) as extractants, Solvent Extraction and Ion Exchange, 18 (5) :853-875. Doi: 10.1080/07366290008934711
- [41] Gaudernack, B. (1973) Process for separating yttrium values from the lanthanides, US patent, 3751553.

- [42] Li, J., Huang, X., Zhu, Z., Long, Z., Peng, X. and Cui, D. (2007a) Extracting rare earth from D<sub>2</sub>EHPA-HEHEHP-H<sub>2</sub>SO<sub>4</sub> system. Journal of the Chinese Rare Earth Society 25 (1), 55-58.
  <u>Doi:10.1016/j.mineng.2013.10.021</u>
- [43] Li, W., Wang, X., Meng, S., Li, D. and Xiong, Y. (2007b) Extraction and separation of yttrium from the rare earths with sec-octylphenoxy acetic acid in chloride media. Separation and Purification Technology, 54 (2), 164–169. Doi:10.1016/j.seppur.2006.08.029.
- [44] Li, W., Wang, X., Zhang, H., Meng, S. and Li, D. (2007c) Solvent extraction of lanthanides and yttrium from nitrate medium with CYANEX 925 in heptane. Journal of Chemical Technology and Biotechnology 82, 376–381. Doi:10.1002/JCTB.1680
- [45] Fawzy, M. M. and El Hady, S. M. (2018) Recovery of yttrium and dysprosium from the rare earth concentrate, southwestern Sinai, Egypt, Arab Journal of Nuclear Sciences and Applications, 51 (2), 29-41. <u>Doi:10.21608/ajnsa.2018.6508</u>
- [46] Yapryntsev, A. D., Baranchikov, A. D., Churakov, A. V., Kopitsa, G. P., Silvestrova, A. A., Golikova, M. V., Ivanova, O. S., Gorshkova, Y. E. and Ivanov, V. K. (2021) The first amorphous and crystalline yttrium lactate: synthesis and structural features, Royal Society of Chemistry, 11, 30195-30205. <u>Doi: 10.1039/d1ra05923h</u>
- [47] Golikova, M.V., Yapryntsev, A.D., Jia, Z., Fatyushina, E. V., Baranchikov, A. E. and Ivanov, V. K. (2023) Synthesis and physicochemical properties of yttrium subgroup REE lactates Ln(C<sub>3</sub>H<sub>5</sub>O<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O (Ln = Y, Tb–Lu). Russian Journal of Inorganic Chemistry, 68 (10), 1422-1432. Doi:10.1134/S0036023623601800
- [48] Kumari, A., Panda, R., Jha, M. K. and Pathak, D. D.
   (2018) Extraction of rare earth metals by organometallic complexation using PC88A, Comptes Rendus Chimie, 21, 1029-1034.
   <u>Doi: 10.1016/j.crci.2018.09.005</u>