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Recovery of Yttrium and Dysprosium from the Rare Earths Concentrate, Southwestern Sinai

Mohamed MF and Saleh ME*

Nuclear Materials Authority, El Maadi, Cairo, Egypt

***Corresponding author:** Saleh M E, Nuclear Materials Authority, El Maadi, Cairo, Egypt, Tel: +20 2 27572499; E-mail: Mail@iaea.org

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Abstract

Separation of ytrrium and dysprosium from the prepared chloride liquor of REEs concentrate (44.1% Y, 9.04% Dy, 5.15% Er, 4.56% Gd, 2.31% Yb, 1.33%Ho and 1.23% Sm) has been studied. The concentrate was obtained by the sulfatizing roasting of the xenotime bearing ferruginous sandstone (from southwestern Sinai) followed by precipitation as oxalates and dissolution in HCl. Treatment of the prepared REEs chloride with Na_2CO_3 was achieved under optimum conditions. By addition of H_2O_2 to carbonate solution, Dy, Gd, Sm and Yb are precipitated while Y and Er left behind in the filtrate. Extraction of 87.3% Dy from the produced precipitate was studied using Cyanex 272. The relevant conditions for the extraction and stripping processes have been optimized. After acidified, Y in the filtrate and Dy in the stripping solution are precipitated as oxalates. Pure products of Y_2O_3 and Dy_2O_3 have been prepared and subjected to different analyses.

Keywords:* *Yttrium; Dysprosium; Leaching; H_2O_2; Extraction; Cyanex272; Xenotime

Introduction

Much attention has been paid to the uses of rare earth elements (REEs) especially Dy and Y in the manufacture of many functional materials. Dy plays an important role in the manufacturing of laser materials, nuclear reactors, hybrid cars, color television tubes and commercial lighting with vanadium and other elements. Dysprosium's main use is in alloys for neodymium-based magnets. This is because it is resistant to demagnetization at high temperatures [1-5]. Yttrium is used in the manufacturing of ceramics, in fluorescent lighting phosphors, computer displays and automotive fuel consumption sensors because Y has the highest thermodynamic affinity for oxygen of any element. Yttria-stabilized zirconium oxide is used in high temperature applications, such as in thermal plasma sprays. Crystals of the yttrium–iron–garnet (YIG) variety are essential to microwave communication equipment [6-9].

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Vijayalakshmi described a process for the recovery of rare earths from xenotime concentrate by digestion with sulfuric acid. A low-grade xenotime concentrates (27% Y_2O_3 and 15.6% heavy rare earth) and a high-grade xenotime (41.8% Y_2O_3 and 20.55% heavy rare earths) are produced in India. Both types of materials have been tested and 98% solubilization of metal values has been achieved. The heavy rare earths have been enriched in the filtrate. Other impurities such as iron, uranium, sulfate and phosphate have been effectively removed by precipitation of rare earths with oxalic acid. The recovery of 99% of HREEs along with Y was achieved [10].

Separation of individual lanthanides from each other is very difficult due to their chemical similarity. Yttrium and dysprosium is separated *via* solvent extraction technique from different acid media using different solvents such as Cyanex 923, bis (2, 4, 4-trimethylpentyl) dithiophosphinic acid, sec-octylphenoxy acetic acid (CA12) synergtic with Bis (2, 4-4-trimethylpentyl) phosphinic acid (Cyanex 272) and trialkyl phosphine oxide [11-15]. Mohammadi et al. studied the separation of Dy, Nd and Y by solvent extraction using D2EHPA and EHEHPA. The results showed that a mixture of D2EHPA and EHEHPA provide a better separation of Y (III) from Dy (III) [15].

Vasconcellos et al. studied the solubility of REEs in Na_2CO_3. The used concentrate contains (%) 2.4 Y_2O_3, 0.6 Dy_2O_3, 2.7 Gd_2O_3, 2.5 CeO_2, 33.2 Nd_2O_3, 40.3 La_2O_3, 4.1 Sm_2O_3 and 7.5 Pr_6O_{11}. The ability of carbonate for the dissolution of REEs and an easy separation of yttrium was achieved. The experiments indicated that a single leaching operation was sufficient to get a rich yttrium solution with about 60.3% Y_2O_3. In a second step, this yttrium solution was treated with an excess of hydrogen peroxide, the other REEs peroxides being completely precipitated and separated from yttrium. Yttrium was recovered from the carbonate solution as the oxalate and finally as oxide. The final product is an 81% Y_2O_3 [16,17].

The present work is oriented to study the recovery of Y and Dy from rare earths concentrate prepared by chemical processing of xenotime bearing ferruginous sandstone, Southwestern Sinai. Treatment and precipitation of the REEs chloride (prepared from the concentrate) with Na_2CO_3 and H_2O_2 respectively were investigated. Y was left behind in the filtrate while the other REEs were precipitated. Separation of Dy has been studied *via* solvent extraction technique using Cyanex 272 modified in kerosene. Y and Dy were precipitated by addition of oxalic acid from their corresponding solutions after being acidified with HCl.

Experimental

Materials preparation

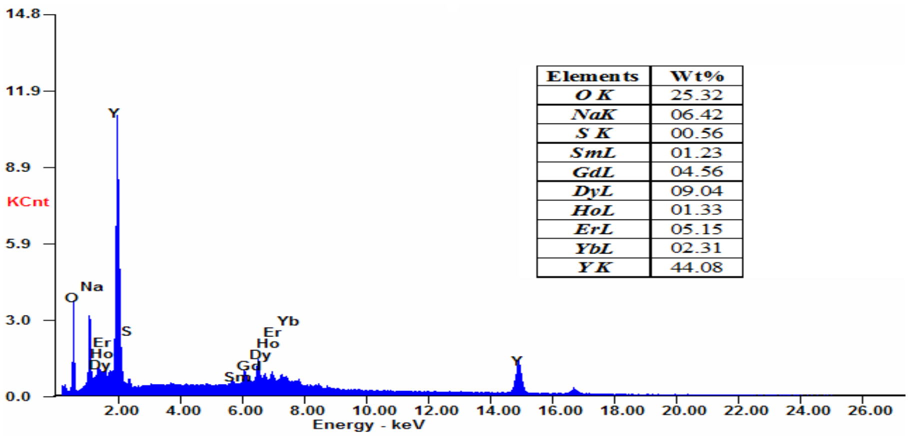
The working rare earths (REEs) concentrate has been prepared from the xenotime bearing ferruginous sandstone of Wadi El Sahu, Southwestern Sinai. The latter is chemically processed with concentrated H_2SO_4 (in 1/1.5 S/L ratio at 250°C for 2 h) where about >90% of the REEs are solubilized. The REEs sulfate was precipitated as oxalates and calcined at 850°C [18]. A known weight of the obtained rare earths oxides is dissolved by a calculated volume of HCl in the beaker with continuous heating followed by addition of de-ionized water to obtain on the rare earths chloride solution. Bis (2, 4-4-trimethylpentyl) phosphinic acid (Cyanex 272) was provided by Loba Chemie Pvt. Ltd., as well as kerosene, methanol, HCl and Na_2CO_3 were provided by El-Nasr Chemicals Company, Egypt.

Separation investigations

Several experiments were performed by the reaction of a known volume of rare earths chloride solution with the same one of Na_2CO_3 solution at room temperature under different conditions. The precipitation of heavy rare earths (except Y) from carbonate solution was carried out by the addition of different volumes of H_2O_2. Yttrium was left behind in the filtrate (which can be precipitated with oxalic acid), while the peroxy precipitate was acidified with HCl and reacted with Cyanex 272 in kerosene under optimum conditions. The stripping of Dy from Cyanex 272 has been carried out using carbonate solution under desired conditions. The recovered dysprosium is precipitated with oxalic acid.

Material analysis

The rare earths contents in the solid concentrate are analyzed using scanning electron microscopy SEM, JSM-84OA, JEOL, Tokyo, Japan, with the possibility of enlargement by 180.000 times and the resolution of 10 nm and represented in FIG. 1. For analysis of individual heavy rare earths elements, ICP-MS spectrometry model Philips PV 8490, China was used [19]. The capability of (ICP-MS) for simultaneous multi-element determination makes it very attractive for the analysis of geological and chemical materials. Morphologically, the solid REEs concentrate is yellowish white color and relatively soft grains [18]. Chemically, the obtained concentrate mainly contains % of 44.08 Y, 9.04 Dy, 5.15 Er, 4.56 Gd, 2.31 Yb, 1.33 Ho and 1.23 Sm, with minor amounts of some impurities.



Elements	Wt%
O K	25.32
NaK	06.42
S K	00.56
SmL	01.23
GdL	04.56
DyL	09.04
HoL	01.33
ErL	05.15
YbL	02.31
Y K	44.08

FIG. 1: **SEM analysis of REEs in the xenotime concentrate.**

For the analysis of heavy rare earths, the concentration of initial sample was measured (C_o) before treatment or extraction step. After each process, the aqueous solution was separated and analyzed for rare earths contents. The experimental (E) % can be calculated as follow:

$$\text{Experimental efficiency (E) \%} = [(C_o - C_f)/C_o] \text{ X } 100$$

Where, C_o is the concentration of the initial sample and C_f is the concentration of treated one. The experimental efficiency (E) was expressed as enrichment percent (%) of studied materials.

Results and Discussion

Preparation procedure

The sample of 40 g working rare earth concentrate (produced *via* the chemical processing of xenotime bearing ferruginous sandstone as mentioned above) is dissolved in 50 ml concentrated HCl with continuous heating until evaporated to half volume. REEs are completely dissolved followed by addition of distilled water to attain up to volume 1000 ml. The analysis of the chloride liquor was reported in TABLE 1. The analysis indicate that the concentrations of rare earths have attained value of 19.8 g/l, 4.78 g/l, 2.74 g/l, 2.05 g/l, 1.24 g/l, 0.14 g/l and 0.08 g/l for Y, Dy, Er, Gd, Yb, Ho and Sm respectively.

TABLE 1. **Analysis of the REEs chloride liquor.**

Elements	**Y**	**Dy**	**Er**	**Gd**	**Yb**	**Ho**	**Sm**
Conc. (g/l)	19.8	4.78	2.74	2.05	1.24	0.14	0.08

Sodium carbonate treatment

The carbonate chemistry is very important for precipitation of the rare earths [17]. Rare earths carbonates system is of utmost importance from both the analytical and industrial aspects and the leaching efficiency of rare earth elements depends on many factors such as reaction time and Na_2CO_3 concentration.

Effect of reaction time

A series of experiments was performed at room temperature by the reaction of 10 ml prepared $RECl_3$ sample with the same volume of 1% Na_2CO_3 (10 ml) under different periods of time ranging from 10 min-30 min. The results of the solubility efficiency for individual rare earth elements have been plotted in FIG. 2.

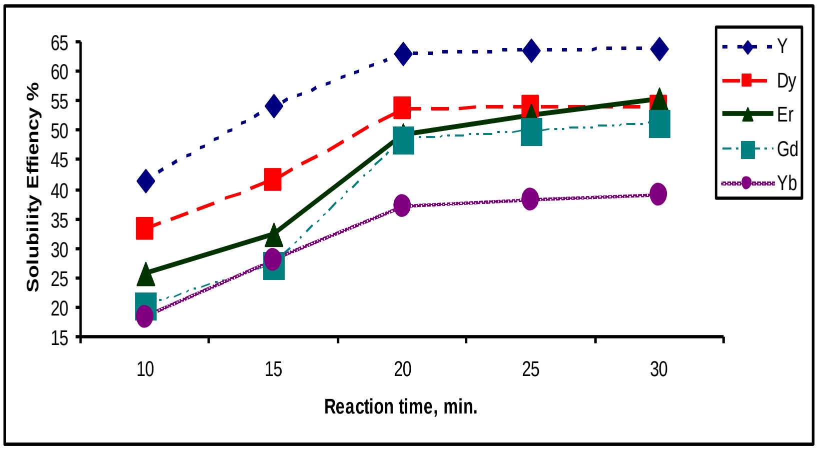


FIG. 2: **Effect of reaction time on the treatment process.**

The results show that, at 20 min the solubility efficiency has been increased and reached the values of 63.1%, 53.7%, 49.2%, 48.4% and 37.2% for Y, Dy, Er, Gd and Yb respectively, with trace concentration of Sm and Ho. Further, increase in the time at 20 min has not improved the solubility efficiency of individual rare earth elements.

Effect of Na_2CO_3 concentration

At room temperature, different concentrations of Na_2CO_3 ranging from 1%-7% have been studied during 20 min using the same volume of the prepared HREEs sample and Na_2CO_3. The results of the solubility efficiency of individual rare earth elements versus Na_2CO_3 concentrations have been plotted in FIG. 3.

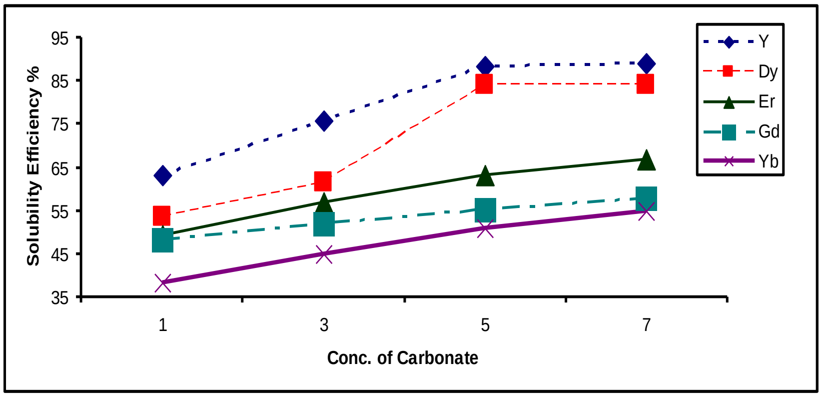


FIG. 3. **Effect of carbonate concentration on the dissolution process.**

The data in the FIG. 3 indicate that, under the applied experimental conditions, the dissolution of individual rare earth elements in (5%) Na_2CO_3 has increased to become 88.3, 84.2, 64.6, 57.3 and 46.2 for Y, Dy, Er, Gd and Yb respectively. After 5% of Na_2CO_3, the solubility of yttrium and dysprosium has slightly increased. This indicates that the rare earths solution has saturated with carbonate [17-19]. Therefore, it can be concluded that 5% Na_2CO_3 would be considered as an optimum concentration for reach the maximum dissolution of individual rare earth elements in the carbonate system.

Recovery of Y_2O_3

At room temperature a series of precipitation experiments were performed by adding different volumes of hydrogen peroxide (H_2O_2) ranged from 20 ml-100 ml to (50 ml) rare earths carbonate solution (containing 17.45 g/l Y, 4.02 g/l Dy, 1.77 g/l Er, 1.17 g/l Gd and 0.57 g/l Yb). The resulted data is shown in TABLE 2.

TABLE 2. **Effect of H_2O_2 addition on the precipitation of REEs.**

Volume of H_2O_2	**Precipitation efficiency %**				
	Y	**Dy**	**Er**	**Gd**	**Yb**
20 ml	Nil	45.9	Nil	39.7	25.4
40 ml	Nil	67.3	Nil	53.8	46.2
60 ml	Nil	81.3	Nil	69.3	56.4
80 ml	Nil	97.8	5.1	83.2	67.1
100 ml	Nil	98.0	5.8	83.7	67.3

From the data, it is clear that the precipitation efficiency of Dy, Gd and Yb elements is increased with increasing the added volume of H_2O_2 to reach 97.8%, 83.2% and 67.1% respectively at 80 ml H_2O_2. On the other hand, Y is not absolute precipitation while Er was suspended and completely precipitated after settling for 24 h. The produced peroxycarbonate HREE precipitate contains 96.8% Dy, 73.0% Gd and 57.0% Yb.

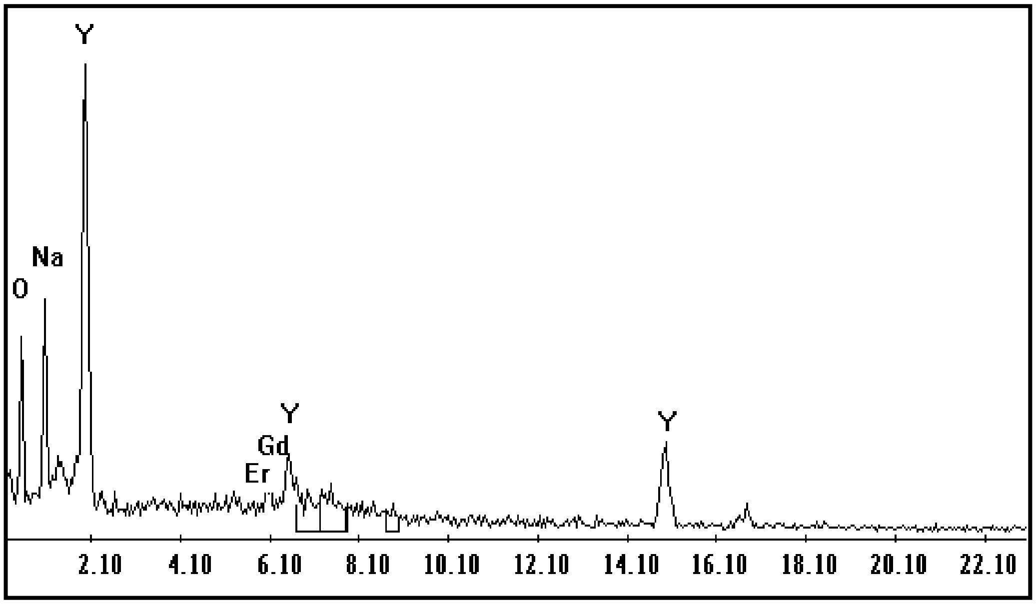


FIG. 4. **Scan electron microscopy (SEM) of the prepared Y product.**

Yttrium was recovered from the filtrate after being washed with 20 ml H_2O_2 (to precipitate the residue of REEs) and acidified with HCl at pH 2 followed by addition of oxalic acid. The light-yellow precipitate oxalate was dried and fired to oxide [20]. The SEM analysis of obtained oxides contains 91.6% Y_2O_3 and 2.7% Er_2O_3 FIG. 4.

Extraction development

In general, liquid-liquid extraction is based on the transfer of a solute substance from one liquid phase to another one according to the solubility. Extraction becomes a very useful tool when choosing a suitable extraction solvent [11-15]. The rare earths solutions were prepared by the dissolution of the peroxycarbonate precipitate of Dy, Gd and traces of Yb with HCl. A series of experiments were carried out using Cyanex 272 in kerosene and the optimum conditions were determined as follows:

Effect of shaking time: It is well known that the shaking time is one of the predominant factors governing extractability. The extraction of rare earths was conducted at different periods of time ranging from 5 min to 25 min. The other fixed operating conditions were 1/1 organic/aqueous (phase ratio) using 0.1 M cyanex concentration at room temperature. The effect of shaking time on extraction of heavy rare earths is represented in FIG. 5.

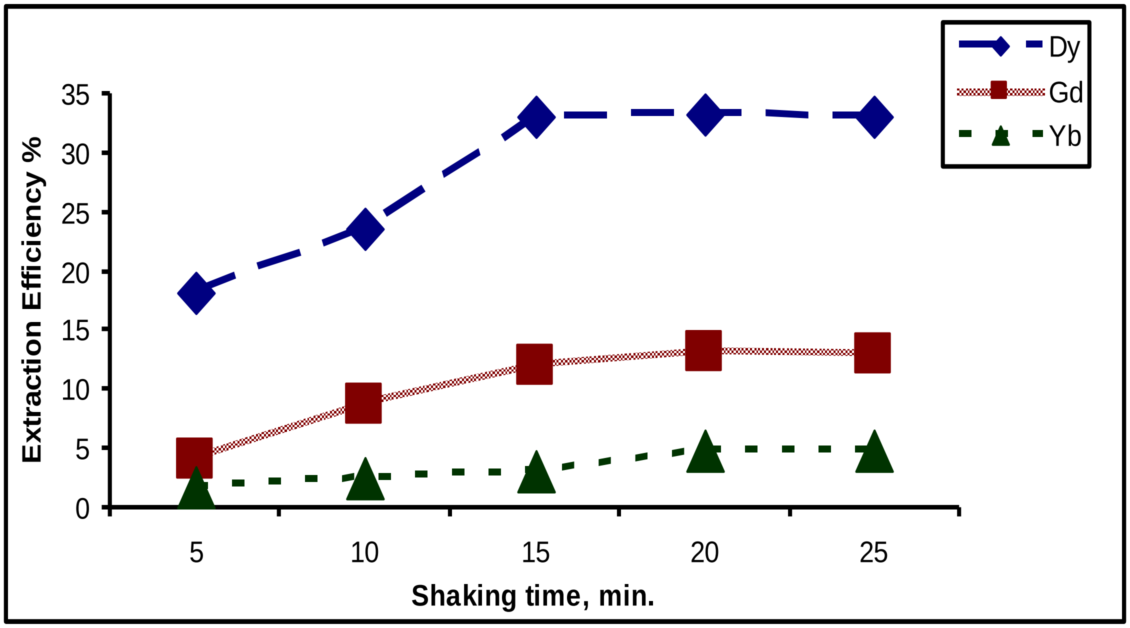


FIG. 5. **Effect of shaking time on the extraction process.**

From the obtained results, the extraction efficiency of Dy, Gd and Yb elements increased as the shaking time increased to reach 33.1%, 11.9% and 3.08% respectively up to 15 min. However, when the contact time exceeded 15 min, the extraction efficiency was constant. The low values of extraction efficiency in 5 min were due to the fact that the feed passed immediately into the solvent without separation. As the contact time increased, the solvent phase became rich in the feed and therefore, the extraction efficiency of heavy rare earth elements increased. The results for the effect of shaking time were in agreement with Buchalova et al. [20] as well as Jorjani and Shahbazi [14]. The period of 15 min is the optimum time which given the highest values for extraction process of Dy.

Effect of phase modifier: During the contact of solvent (cyanex 272) with HREEs chloride solution (free from Y), a "third phase" of an insoluble viscous solution was formed. Several experimental conditions such as aqueous acidity, extracted metal, diluents and extractant structure can affect the formed third phase. This phenomenon is more important for extraction systems containing extractants of amine type and solvents with low polarity and leads to the increase of separation duration simultaneously with the diminution of its efficiency. The formation of the third phase can be avoided by addition of a “phase modifier” in the organic solvent [21,22]. Generally, this compound should be an alcohol with an aliphatic chain carbon atom and modifies the polarity of the solvent, promoting the breakage of the stable emulsion and solubilization of its content.

Adding a modifier to the organic phase is the most common method of preventing third phase formation. Methanol has been tested under different concentrations (0.05 M-0.5 M) to show the variation in extraction efficiency values under the same previous conditions of 1:1 phase ratio (organic/aqueous) using cyanex concentration of 0.1 M in kerosene and shaking for 15 min. The results are illustrated in FIG. 6.

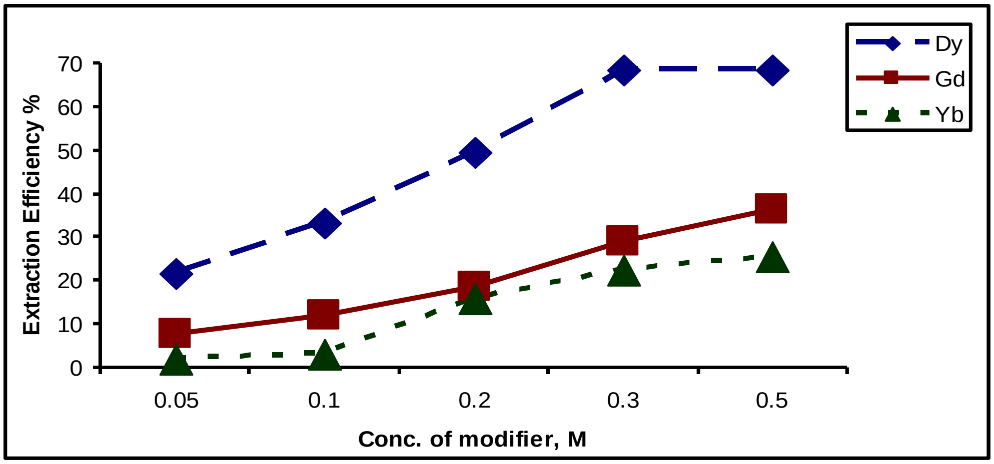


FIG. 6. **Effect of addition of modifier on the extraction process.**

From FIG. 6, the concentration of 0.3 M methanol gives the highest values of extraction efficiency for Dy which corresponds to 68.3% and then an appreciable increase was occurred after this value for Gd and Yb equals 28.9% and 22.3% respectively. The addition of methanol induced the increase of the extraction efficiency because if its ability to soluble in the two phases and the most important influence being recorded for the solvent with lower polarity. Moreover, the volumetric fraction of alcohol controls the number of extractant molecules participating in the interfacial product formation [23,24].

Effect of solvent concentration: The effect of the solvent concentration on rare earth extraction was studied by varying the cyanex 272 concentrations in kerosene from 0.1 M to 1.0 M modified by 0.4 M 1-octanol and dissolved in kerosene. The extraction experiments were carried out using equal (organic/aqueous), a contact time of 15 min and a shaking speed of 150 rpm. The effect of the cyanex concentration on the extraction efficiency is shown in FIG. 7.

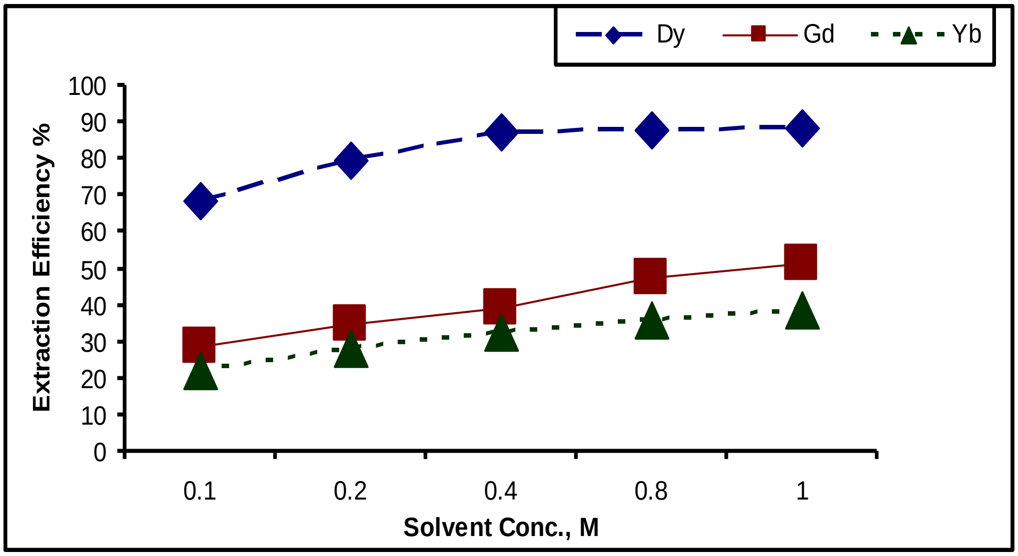


FIG. 7. **Effect of Cyanex 272 concentration on the extraction process.**

From the results, it is noted that the extraction efficiency for Dy increased with the cyanex 272 concentration from 0.1 M to 0.4 M which reach to 87.3% at 0.3 M cyanex 272. However, a slight increase in the extraction efficiency of Dy was observed when the concentration of cyanex 272 was increased at 0.4 M. The extraction of Gd and Yb increased gradually after value of 0.4 M cyanex 272 to reach 51.2% and 38.4% respectively. So, the cyanex 272 concentration of 0.4 M was selected the optimum concentration for Dy extraction.

The plotted data showed that, the extractant concentration plays a significant factor in the extraction process. Cyanex 272 was chosen as the extractant of heavy rare earths due to both its excellent chemical stability and its physical properties. However, it is limited by its high viscosity and density. A diluent such as kerosene reduces the viscosity and density of the organic phase to improve the phase separation characteristics. All of the rare earths typically exhibit in a trivalent oxidation state, while some of them can also occur in the divalent (Sm, Eu and Yb) states. These states are always less stable than the trivalent state. In the divalent state, the elements exhibit markedly different chemical behavior compared with that in the trivalent state (Gupta and Krishnamurthy) [23].

Effect of organic/aqueous ratio: At room temperature, the volumes of cyanex 272 solution (0.4 M) modified in kerosene ranged from 50 ml-400 ml (which corresponding to 0.5:1 up to 4:1 organic/aqueous phase ratio) were contact with 100 ml from each rare earth sample during 15 min. The values of extraction efficiency % of rare earths elements were shown in FIG. 8.

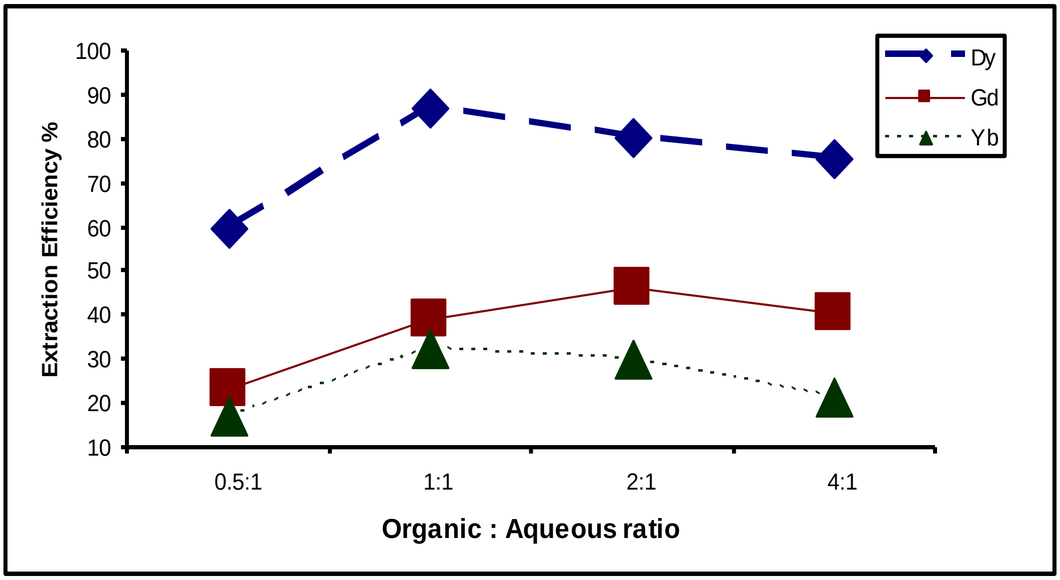


FIG. 8. **Effect of organic/aqueous ratio on the extraction process.**

The data show that there is a general increase in the extraction efficiency of rare earths till equal 1, which corresponding to 87.3%, 39.1% and 32.5% for Dy, Gd and Yb respectively. After this ratio (for Dy) the effect of organic/aqueous ratio on the extraction process was reversible, i.e. by increasing organic/aqueous ratio, the extraction efficiency decreases gradually. This behavior indicates that the extraction efficiency was affected by the viscosity of the solvent as the low viscosity leads to low pressure drop and good mass transfer [21,22].

Successive extraction steps

The extraction operation of heavy rare earths by 0.4 M cyanex 272, modified by 0.3 M methanol, in kerosene was carried out three times using equal (organic/aqueous) phase ratio, at room temperature for 15 min. The results are graphically represented in FIG. 9.

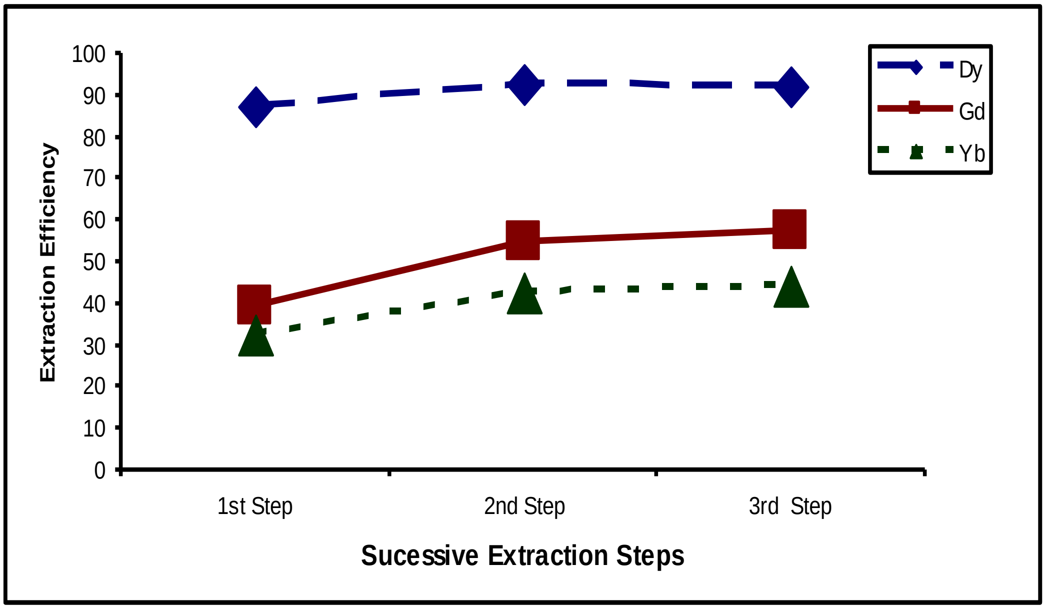


FIG. 9. **Effect of successive extraction steps on the extraction process.**

The results indicate that, the extraction efficiency % of Dy, Gd and Yb increases after the second successive step which becomes 92.7%, 54.7% and 42.5%, while in the third leaching process, the extraction efficiency was increased very slightly due to the effect of distribution coefficient [25]. It is more efficient to perform two extractions with 1/2 volume of extracting solvent than 1 large volume.

Stripping investigations: The stripping investigations were carried out using diluted HCl to determine the optimum conditions for successfully recovering of dysprosium from the organic solution. The effect of experimental time, HCl concentration and aqueous/organic phase ratio was studied.

Effect of stripping time: The effect of stripping time on the recovery of Dy, Gd and Yb from cyanex solution was investigated using 0.05 M HCl FIG. 10. The process was performed using equal phase ratio (1st step) at room temperature, while the contact time was ranged from 5 min to 20 min.

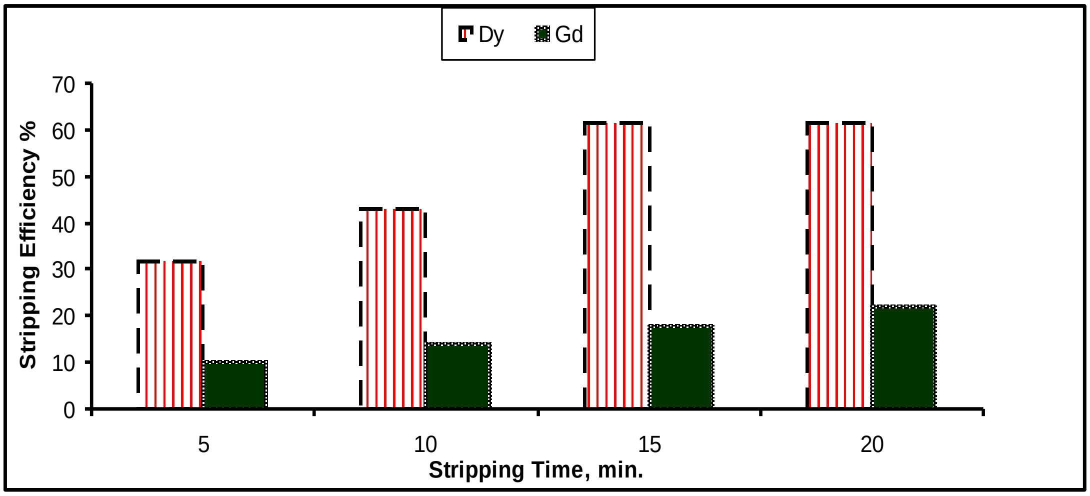


FIG. 10. **Effect of time on the stripping process.**

The results in FIG. 10 indicate that, the stripping efficiency % slightly increases from 5 min to 15 min. and then remains constant till 20 min. This indicates that the process is rapid, i.e. is not a diffusion controlled process. At 10 min the stripping percent of Dy and Gd equals 61.4 and 19.3 respectively, while the value % of Yb was not detected.

Effect of HCl concentration: For the best stripping of dysprosium uploaded on cyanex 272, the concentration of HCl was varied from 0.05 M to 0.3 M and the process were carried out under room temperature in time equal 15 min. The results were diagrammatically shown in FIG. 11.

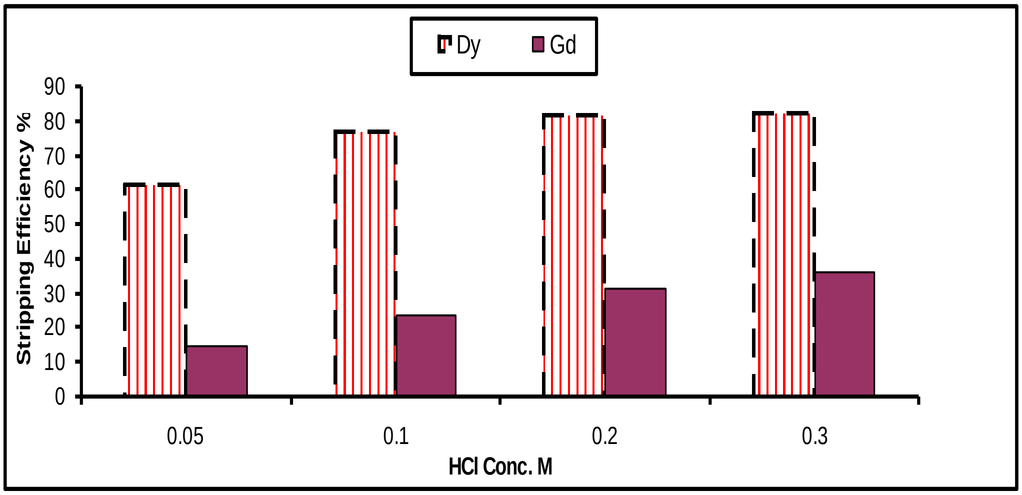


FIG. 11. **Effect of HCl conc. on the stripping process.**

The results indicate that, by increasing the conc. of HCl from 0.05 → 0.2 M, the stripping efficiency become 81.4% and 31.8% for Dy and Gd respectively. After this concentration, the value of stripping efficiency increases very slightly due to decrease the capacity of carbonate solution as well as the viscosity of organic phase which lead to increase the reversible effect of solvent as well as decrease the mass transfer [22].

Effect of phase ratio: Different phase ratios of HCl and cyanex 272 (bearing Dy, Gd and Yb) were studied ranging from 0.5 → 3 at room temperature during 15 min to show the maximum efficiency of for stripping of HREEs from the organic phase. The data was illustrated in FIG. 12.

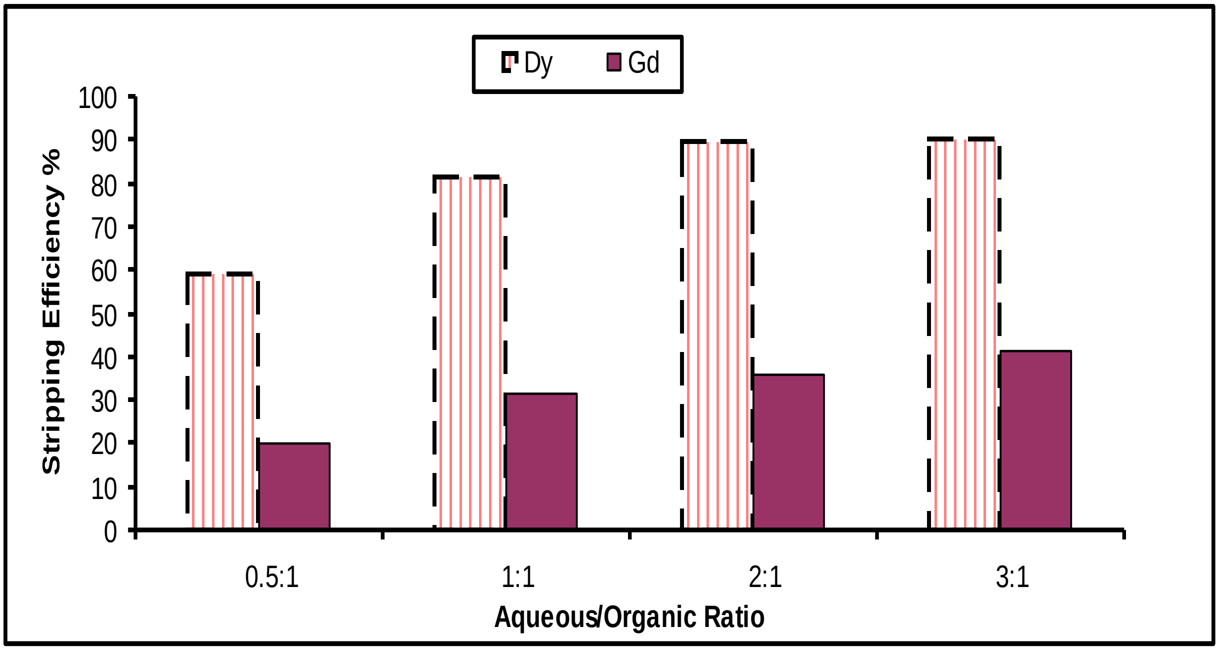


FIG. 12. **Effect of aqueous/organic ratio on the stripping process.**

By increasing aqueous/organic ratio, the stripping efficiency was increased and reached the maximum value at 2:1 which corresponding to stripping 89.6% and 36.3% of Dy and Gd FIG. 12 respectively. Further increase in organic/aqueous ratio was associated with a very slight increase in stripping percent. Accordingly, 2:1 aqueous/organic phase ratio is recommended for stripping when using HCl solution. For the stripping of dysprosium from cyanex 272 modified in kerosene, the process should be performed using 2:1 phase ratio of 0.2 M HCl at room temperature for 15 min contact time.

Precipitation of Dy_2O_3

In the bench-scale work, the mixed lanthanides Dy and Gd were precipitated from the strip liquors by the addition of excess of oxalic acid with stirring for 1 h. The precipitated oxalate was filtered, washed with distilled water and calcined in a muffle furnace at 850°C for 2 h to obtain a dysprosium oxide (Dy_2O_3) [17]. The rare earth oxide (ΣREO) product, analyzed by ICP-MS apparatus, contains 88.2% and 9.7% of Dy_2O_3 and Gd_2O_3 respectively. The scan electron microscopy (SEM) for the REO was shown in FIG. 13. The mixed rare earth oxide was in the form of light brownish powder. Analysis of the rare earth oxides in about 0.25 g of the product gave ΣREO content of 97.9%.

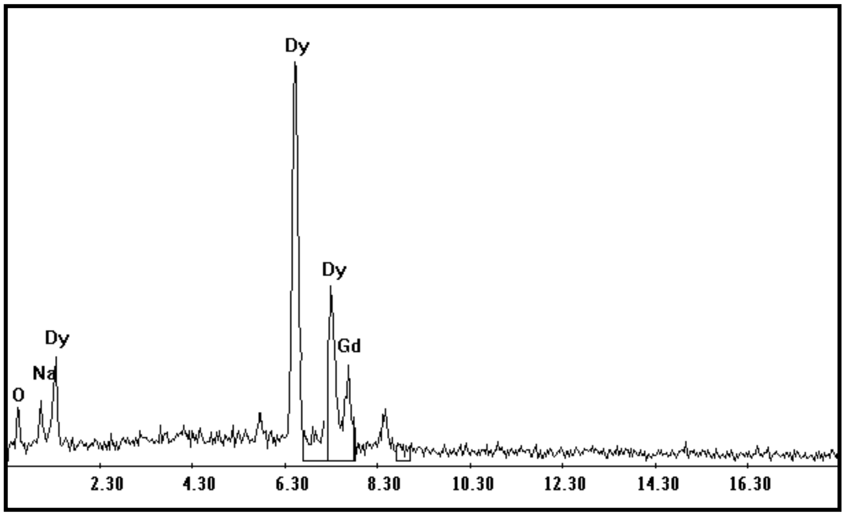


FIG. 13. **Scan electron microscopy (SEM) for rare earth oxide product.**

Conclusions

A successful extraction procedure of some heavy rare earths (yttrium and dysprosium) from rare earths concentrate is obtained. The latter is prepared from digestion of xenotime bearing ferruginous sandstone by sulfuric acid followed by its precipitation using oxalic acid. This was possible through treatment of the concentrate by Na_2CO_3 and extraction of Dy using cyanex 272 in kerosene using methanol as modifier. The corresponding relevant factors were studied and the conclusions can be summarized as follows:

- For the dissolution of rare earths concentrate, HCl was used and the treatment was carried out by Na_2CO_3. The optimum conditions, at which the process was performed, are contact time of 20 min. using 5% of carbonate solution. The solubility efficiency reached the highest values of 88.3, 84.2, 64.6, 57.3 and 46.2 for Y, Dy, Er, Gd and Yb respectively, while Ho not soluble as well as detected in the analysis. By the addition of (80 ml) H_2O_2, the heavy rare earths (Dy, Gd and Yb) was precipitated while Y and Er left behind in the filtrate which undergone precipitation by oxalic acid after being acidified and fired to oxide.

- Extraction of Dy from the obtained peroxy precipitate (after dissolution with HCl) was performed using cyanex 272 (modified by methanol) in kerosene. The efficiency for extraction process was 87.3%, 39.1% and 32.5% for Dy, Gd and Yb respectively under 15 min. in equal phase ratio of 0.4 M cyanex 272 in 0.3 M methanol as modifier. The efficiency of Cyanex 272 for extraction of Dy was increased after the separation of Y.

- The extraction efficiency for Dy, Gd and Yb was reached 92.7%, 54.7% and 42.5% respectively after 2nd extraction step. The stripping of 89.6% and 36.3% of Dy and Gd respectively was obtained using 0.2 M HCl (2:1 aqueous/organic phase ratio) at 15 min. Dy is precipitated from the latter solution using oxalic acid.

- Pure oxides of Y and Dy are obtained after calcination at 850°C for 2 h. The latter oxides are subjected to ICP-MS and SEM analysis. The amount contains 0.25 g of the product gave a ΣREO content of 97.9%.

A technological flow sheet FIG. 14 for the recovery of yttrium and dysprosium from the xenotime bearing ferruginous sandstone of southwestern Sinai has been formulated.

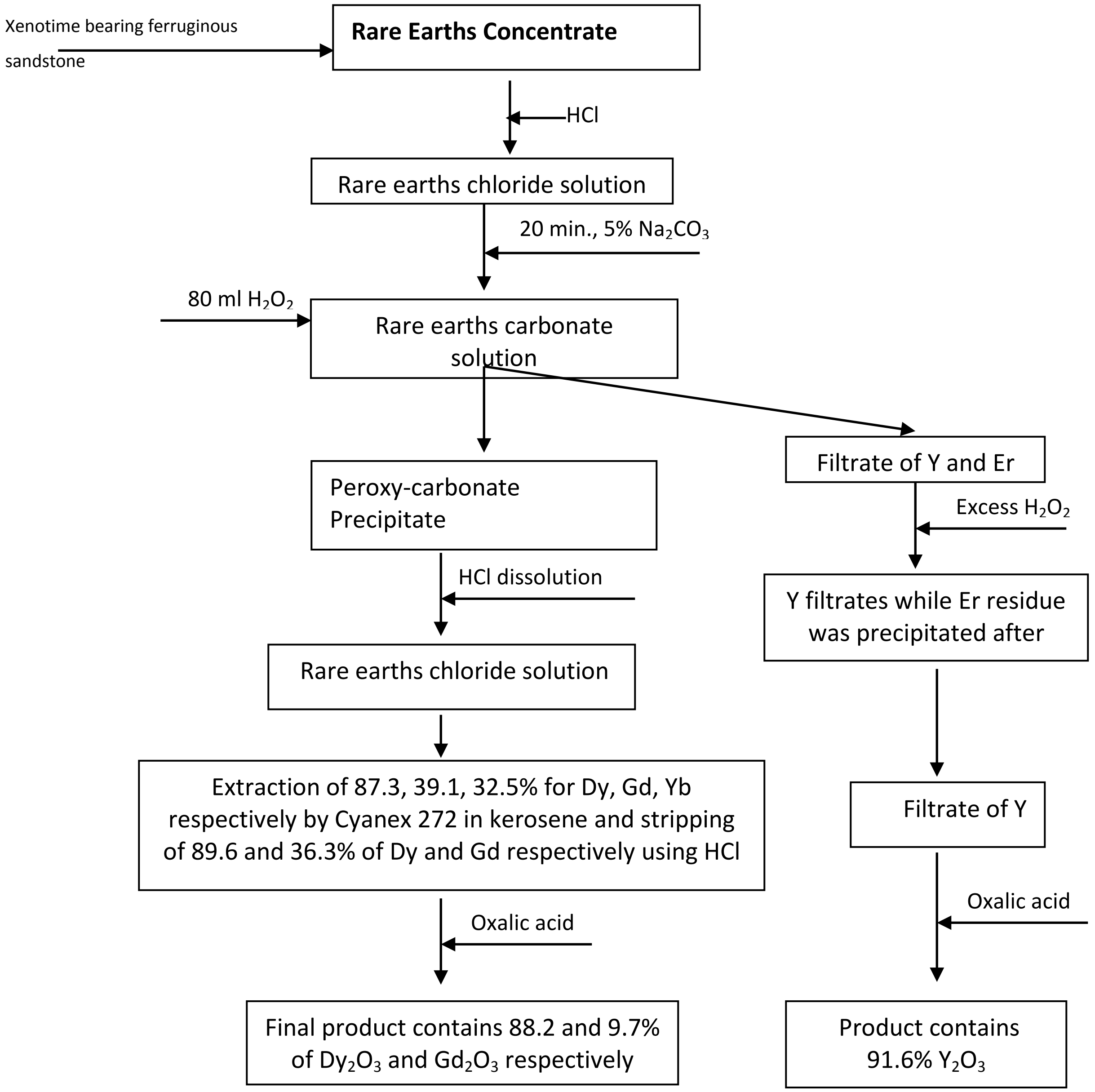


FIG. 14. **Flow sheet for extraction of Y and Dy from the xenotime bearing ferruginous sandstone of southwestern Sinai.**

Acknowledgement

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