

# Extraction of gadolinium from El-Garra El-Hamra rare-earth cake, South Western Desert, Egypt

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**Abstract** The study area of El-Garra El-Hamra is one of the igneous masses located in the southern part of the Western Desert of Egypt. This work has been carried out to investigate the process of gadolinium separation from REEs cake obtained from El-Garra El-Hamra ore concentrate. It is considered as a new approach in the Nuclear Materials Authority of Egypt. Firstly; the optimum leaching conditions achieved are 200 gm/L  $H_2SO_4$ , 1/2 solid/liquid ratio, 4 h agitation time, –125 mesh size and at 90 °C temperature. Then by solvent extraction method using 1 mol/L D2EHPA middle REEs were extracted. The organic extractant was stripped by using 2 mol/L HCl and Gd pregnant solution was obtained. Then, the relevant optimum factors were 0.3 mol/L D2EHPA diluted by kerosene, 10 min contact time, and 4/1 organic/aqueous ratio giving 87 % Gd extraction. Then, the scrubbing of the loaded extractant was by 1 mol/L HCL followed by Gd stripping using 5 M HCl, contact time of 30 min and 1/3 organic/aqueous ratio. The strip solution was subjected to evaporation and little amount was dried to obtain  $GdCl_3$  powder having a purity of about 81 % associated with  $YCl_3$  4 %.

**Keywords** El Garra El Hamra area · Rare-earth cake · Gadolinium · Solvent extraction technique

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## Introduction

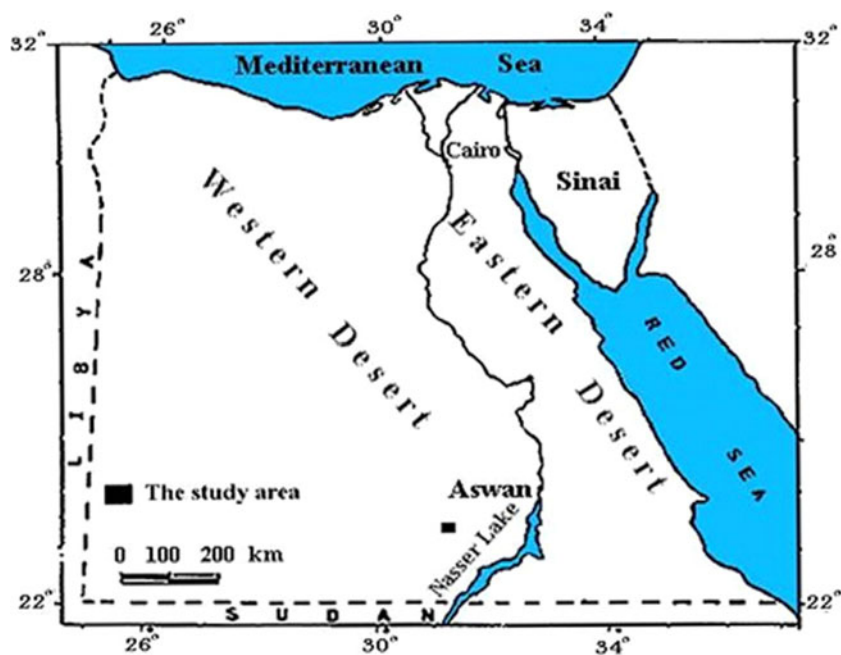
The study area of El-Garra El-Hamra is one of the igneous masses located in the southern part of the western desert of Egypt. It is situated about 270 km southwest of Aswan in the vicinity of Kurkur and Dungul Oases. It is delineated by the lat. 23°24'20"N and long. 3 0°23'25"E. It is an oval shaped isolated hill represented by an igneous body with two peaks surrounded by low country of Phanerozoic sedimentary sequences ranging from Cretaceous to Eocene age [1]. A location map for the studied area is shown in (Fig. 1).

Geologically the whole mass is generally formed of syenitic rocks showing wide variations in colours, mineralogical composition, grain size, texture and radioactivity [1]. These syenites exhibit fine-grained chilled margins along the contact with Nubia sandstone covering the wadi. This implies that the syenitic mass was intruded within the Nubia sandstone rocks. The geological map for the studied area is shown in (Fig. 2).

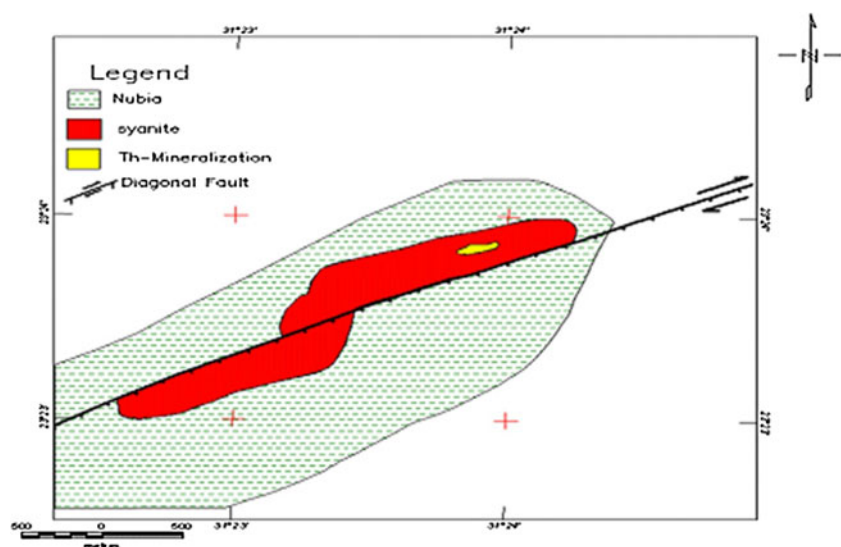
Increasing interest for high-purity rare-earth oxides, such as gadolinium, can be explained by its diversified and expanding applications. Gadolinium (Gd) is one of the most important rare-earths in the nuclear field industry has the highest neutron cross-section among any stable nuclides. This element is effective for the use as shielding agent in nuclear reactors. It is now well known that gadolinium slows the initial reaction rate. Gadolinium is also used as a secondary, emergency shut-down measure in some nuclear reactors, particularly of the CANDU type (1) [2].

On the other hand, gadolinium is an efficient catalyst used for decarboxylation of oxalo acetic acid, conversion of ortho-hydrogen to parahydrogen and polymerization of ethylene [2]. Gadolinium also possesses unusual metallurgic properties, with as little as 1 % of gadolinium improving the workability and resistance of iron, chromium, and related alloys to high temperatures and oxidation. Gadolinium is paramagnetic at

**Fig. 1** Map of Egypt showing the study area



**Fig. 2** The geological map of El-Garra El-Hamra area, South Western Desert, Egypt [1]



room temperature and this trait makes gadolinium useful for magnetic resonance imaging MRI scan devices. Besides MRI, gadolinium is also used in other imaging systems such as in X-ray by enhancing the imaging quality of the X-ray that is exposed to the photographic film. Due to extremely high neutron cross-section of gadolinium, this element is very effective for use with neutron radiography.

## Experimental

### Reagents

The main chemicals and reagents used in this work are listed in Table (1).

Stock solutions of rare-earth elements were prepared by dissolving 10 g. of rare-earth cake previously prepared was subjected to dissolution in 6 M HCl acid until it completely dissolved, then complete with water upto 1 L.

An organic phase was prepared by adding 0.3 mol/L of all types of the tested solvents to the required diluent kerosene. The applied extractants are di-2-ethylhexyl phosphoric acid (D2EHPA), di-2,4,4-trimethylpentyle phosphinic acid (Cyanex272) and tri-*n*-octylphosphine oxide (TOPO).

A 0.01, 0.03, 0.07, 0.1, 0.2 and 0.3 mol/L D2EHPA/ Kerosene was prepared by dissolving the appropriate amount of D2EHPA in kerosene.

**Table 1** Chemicals specifications of reagents

Chemical	Formula	Product	Purity
Gadolinium standard solution (1,000 µg/ml)	Gd(NO <sub>3</sub> ) <sub>3</sub>	Science lab.	
Thorium standard solution (1,000 µg/ml)	Th(NO <sub>3</sub> ) <sub>3</sub>	Aldrich	A.R.
Arsenazo III	C <sub>22</sub> N <sub>16</sub> As <sub>2</sub> N <sub>4</sub> Na <sub>2</sub> O <sub>14</sub> S <sub>2</sub>	Merck	A.R.
Arsenazo I	C <sub>16</sub> H <sub>10</sub> O <sub>11</sub> N <sub>2</sub> S <sub>2</sub> AsNa <sub>3</sub>	SIGMA	A.R.
Hydrofluoric acid	HF	Pharma	A.R.
Oxalic acid	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	Adwic	A.R.
Hydrochloric acid	HCl	Analar	A.R.
Nitric acid	HNO <sub>3</sub>	Adwic	A.R.
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	Adwic	
Sodium hydroxide	NaOH	Star chemic	A.R.
Urea	NH <sub>2</sub> ·CO·NH <sub>2</sub>	ADWIC	A.R.
Ammonium carbonate	NH <sub>4</sub> HCO <sub>3</sub> and NH <sub>2</sub> CO <sub>2</sub>	Fine chem. limited	
Ammonium bicarbonate	NH <sub>4</sub> HCO <sub>3</sub>	Nice chemicals	
Carbon tetrachloride	CCl <sub>4</sub>	Adwic	99 %
Chloroform	CHCl <sub>3</sub>	Adwic	99 %
D2EHPA di-2-ethylhexyl phosphoric acid	C <sub>16</sub> H <sub>35</sub> O <sub>4</sub> P	MERCK	A.R.
Kerosene		Misr Petroleum Co.	Pure
Benzene	C <sub>6</sub> H <sub>6</sub>	Adwic	99 %
Iso-octylphenoxy polyethoxy ethanol (Triton × 100)		Loba chemic	
Ammonia solution	NH <sub>4</sub> OH	ADWIC	A.R.
Boric acid	H <sub>3</sub> BO <sub>3</sub>	Fluka	
Ascorbic acid	C <sub>6</sub> H <sub>7</sub> O <sub>6</sub> Na	MERCK	A.R.
Sodium tetraborate	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	Fluka	
Formic acid	HCOOH	ADWIK	85 %
Sodium acetate		Star chemic	Pure
-5-Sulphosalysilic acid	C <sub>7</sub> H <sub>6</sub> O <sub>6</sub> S·2H <sub>2</sub> O	Ubichem limited uk	
1,10-phenanthroline monohydrate	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> ·H <sub>2</sub> O	Loba chemie	A.R.
Tributyl phosphate (TBP)	(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> PO	Merck	A.R.
Ammonia solution	NH <sub>4</sub> OH	ADWIC	A.R.
Cyanex 272	C <sub>16</sub> H <sub>31</sub> O <sub>2</sub> P		85 %
TOPO	C <sub>24</sub> H <sub>51</sub> PO		A.R.
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	Analar	A.R.

## Apparatus

Methods used for gadolinium determination are: 1-the flame atomic absorption spectrometry.

The Environmental Scanning Electron Microscope model XL30 (ESEM) was used and the product purity was calculated from the result. Operating conditions are listed as; vacuum 30 kV and BSE equals 10.0 BSE (Back Scattered Electron) procedure.

The apparatus used for the colorimetric determination is [Metertech Inc model SP-8001, UV-visible (UV-Vis) spectrophotometer]. This apparatus is a single beam recording spectrophotometer and covers the UV-Vis range 200–1,100 nm with wave length accuracy of ±1 nm. Deuterium lamp (UV range) and halogen lamp (Visible

range) as light sources were utilized. One match of 5 cm<sup>3</sup> quartz cell with a path length of 1 cm was used for both working and blank reagent samples. All measurements were performed at the Nuclear Materials Authority (NMA).

## Ore material

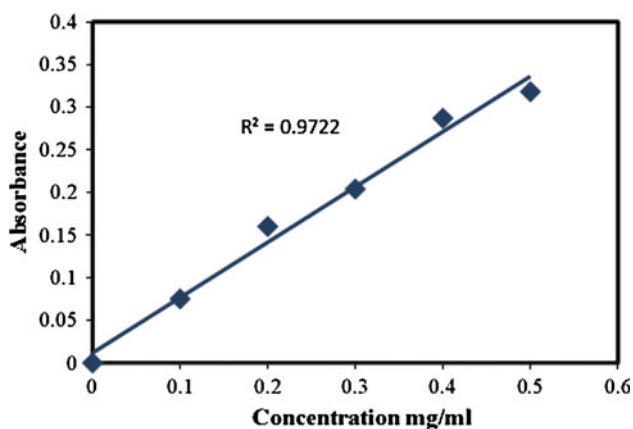
The ore sample was a concentrate prepared by Mahdy et al. [3], using the various methods of physical mineral separations proposed namely (heavy liquid, isodynamic, gravitation by shaking tables and lift magnet). The physical separation of El-Garra El-Hamra mineralized synthetic ore material was conducted by obtaining a heavy fraction of the shaking tables separation step followed by subsection to lift magnet at 2.5 A its mineralogical composition is shown in Table (2).

**Table 2** Mineralogical composition of the study sample

Mineral	Content (%)
Thorogumite	53
Bastanaesite	7
Hematite	9
Goethite	6
Others (quartz and green silicate)	25

**Table 3** Chemical analysis of El-Garra El-Hamra concentrate

Element	Wt%
Al <sub>2</sub> O <sub>3</sub>	1.49
SiO <sub>2</sub>	19.92
ZrO <sub>2</sub>	7.59
UO <sub>2</sub>	5.67
CaO	1.61
TiO <sub>2</sub>	0.75
Ce <sub>2</sub> O <sub>3</sub>	0.8
FeO	16.01
NiO	1.51
ZnO	1.25
ThO <sub>2</sub>	30.1
Y <sub>2</sub> O <sub>3</sub>	13.3
Total	100

**Fig. 3** Calibration curve of gadolinium (III)—(5-Br-PADAP) Complex

Chemical analysis of El-Garra El-Hamra concentrate carried out using ESEM is shown in Table (3).

#### Procedure

Gd III—2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) PADAP calibration curve was demonstrated. Calibration curve Fig. 3 of Gadolinium-(5-Br-

PADAP) complex was carried out, by taking different concentration of standard Gadolinium solutions. The operative conditions such as pH and homogeneity of solution were adjusted to fulfill the spectrophotometric determination of Gd measuring the sample absorbance at 580  $\mu\text{m}$  against a reagent blank solution [4].

Equal volumes (10 ml) of aqueous and solvent solutions were mixed by a magnetic stirrer. After equilibration, complete separation of the two phases was obtained by the settling time nearly 5 min. Concentration of the gadolinium ion in organic phase was measured by subtracting its concentration in aqueous phase after extraction from the concentration of the metal ion before extraction.

The rare-earth elements extracted from rare-earth solution using 1 mol/L D2EHPA/Kerosene. Stripping of the middle rare-earths that contains gadolinium was conducted using 2 mol/L HCl. This solution might contain gadolinium, samarium and europium.

Strip solution was subjected to gadolinium extraction by applying different extraction factors such as solvent type, solvent concentration, diluents, contact time, pH of the aqueous solution and organic/aqueous ratio.

Scrubbing was carried out by washing the loaded solvent for several times with a small quantity of 1 M HCl to remove the undesired elements.

The loaded organic was subjected gadolinium stripping by applying different stripping factors such as acid type, acid concentration, contact time and aqueous/organic ratio.

## Results and discussions

### El-Garra El-Hamra REE cake preparation

The relevant leaching factors affecting ore concentrate leaching efficiency such as acid type and its concentration, stirring time, grain size, and solid/liquid ratio were studied. The optimum conditions have been achieved thus 40 % leaching efficiency was obtained at first stage using 200 gm/L H<sub>2</sub>SO<sub>4</sub>, 1/2 solid/liquid ratio, 4 h agitation time, –125 mesh size and at 90 °C temperature. However, the low leaching efficiency can be promoted. Almost complete leaching of El-Garra El-Hamra rare-earth elements concentrate can be predicted by applying 2 or 3 stages of the leaching. After solid/liquid separation thorium/rare-earth elements cake was precipitated as oxalate using 10 % oxalic acid with stirring and heating at 60 °C until saturation. When applying 150 g/L ammonium carbonate/ammonium bicarbonate solution mixture the insoluble rare-earth elements carbonate was formed and separated by filtration. Then the rare-earth elements cake was then dissolved in hydrochloric acid to be available for gadolinium separation from chloride solution by organic

**Table 4** Trace elements and rare earth elements distribution in El-Garra El-Hamra REE cake

Element	Wt%
UO <sub>2</sub>	0
SiO <sub>2</sub>	0.41
ThO <sub>2</sub>	8.2
FeO	0
La <sub>2</sub> O <sub>3</sub>	6.9
Ce <sub>2</sub> O <sub>3</sub>	16.11
Nd <sub>2</sub> O <sub>3</sub>	7.98
Sm <sub>2</sub> O <sub>3</sub>	1.6
Gd <sub>2</sub> O <sub>3</sub>	3.7
Dy <sub>2</sub> O <sub>3</sub>	7.13
Er <sub>2</sub> O <sub>3</sub>	2.7
Yb <sub>2</sub> O <sub>3</sub>	2.89
Y <sub>2</sub> O <sub>3</sub>	39.83
Total	100

**Table 5** Semi-quantitative ESEM analysis pattern of the gadolinium concentrate precipitate

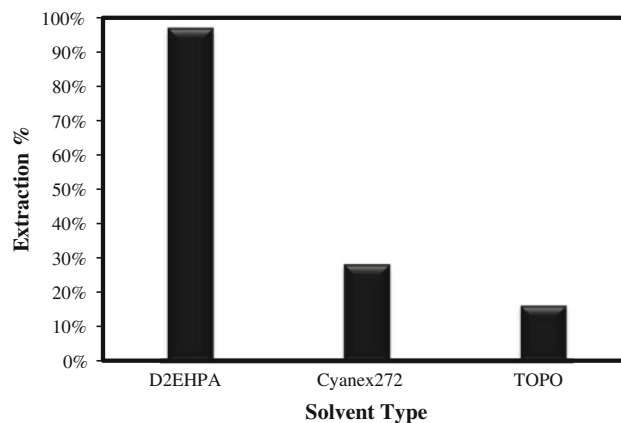
Element	Wt%
Mg	5.86
Cl	27.37
Ca	2.49
Gd	58.06
Fe	2.54
Y	3.68
Total	100

solvents. Tables (4, 5) describes the REE cake composition obtained from El-Garra El-Hamra ore concentrate. From this table it is clear that it contains high content of the heavy rare-earth elements (Y, Gd, Dy, Yb, Ho, and Er) and barren of iron and uranium. This gives a special economic importance to this REE cake.

Extraction of gadolinium from El-Garra El-Hamra REE cake stock solution

According to HSAB theory [5], lanthanides can react with acids to form hard acids compounds while with considered extractants they can also react with bases to form hard bases compounds. With increasing the atomic number of lanthanides, the hardness increases and resulted in increase in extraction abilities.

As a matter of fact, extraction from chloride media produces higher separation factors than nitrate or sulphate. Ritcey and Lucas [6] showed that variation in pH and extractant concentration allowed separation of some

**Fig. 4** Effect of solvent type upon gadolinium extraction efficiency (0.03 mol/L, 10 min pH 1, 1/1 O/A phase ratio)

adjacent rare earths. However; it was feasible to separate heavy rare earths from lights by variation of pH, solvent molarity, and a number of extraction stages.

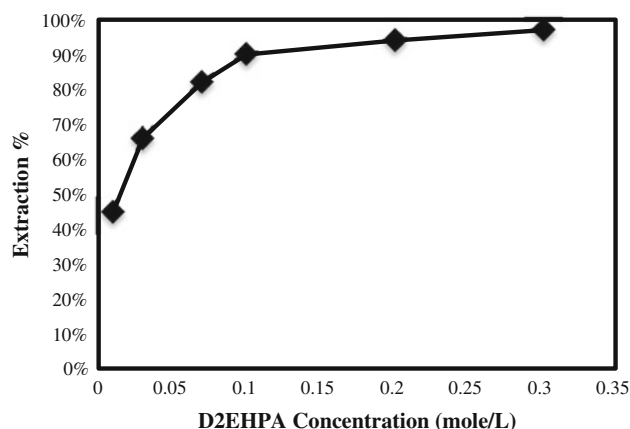
In general, all heavy and intermediate rare earths can be extracted while the light rare earths remain in the raffinate. This is because extraction increases as the atomic number of rare earth increase this was attributed to increased electrostatic interactions between the acid anion and the rare-earth cation as the size of the latter decreased. Variation of the pH of the feed allows control of the degree of extraction, thus a high pH favours extraction of light earths whereas the heavy elements can be extracted even at low pH.

Different extraction factors were investigated such as solvent type, solvent concentration, organic/aqueous ratio, contact time, diluents and pH of the aqueous solution.

#### *Effect of solvent type upon gadolinium extraction efficiency*

Different types of solvents were used in Gd extraction experiments including D2EHPA, Di-2, 4, 4-trimethylpentyle phosphinic acid (Cyanex 272) and TOPO. The obtained extraction efficiency percent results are presented in Fig. 4.

Comparing the application of Cyanex 272 and D2EHPA organic solvents in the Gd extraction one can notice that extraction by Cyanex 272 takes place at lower aqueous acidity than with D2EHPA. Also, steric hindrance effects and selectivity of the former are superior to D2EHPA. However, it was not possible through preliminary Gd extraction experiments to attain a satisfactory operational condition for the separation of Gd using Cyanex 272 because the pH that must be maintained for efficient separation is high, calling for controls more sensitive than those available. When pH decreased almost no extraction occur and if pH increased an emulsion formed as a result of precipitation of the elements. So for the previously



**Fig. 5** Effect of extractant concentration upon gadolinium extraction efficiency (10 min, pH 1, 1/1 O/A phase ratio)

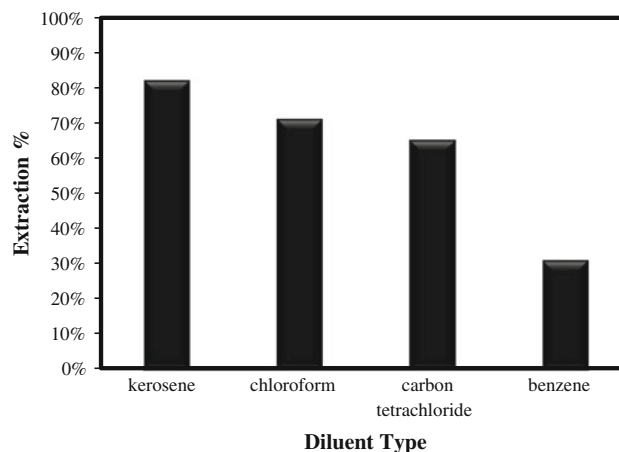
mentioned reasons, the extraction efficiency is diminished when using Cyanex 272. The organic solvent D2EHPA was chosen where it is available, effective, cheap and suitable for gadolinium extraction.

It is clear that D2EHPA shows higher extraction efficiency more than the other two extractants under the same extraction conditions. That may be due to the fact that TOPO (Gd extraction efficiency 16 %) is a solvating extractant which tends to be rather unselective, i.e. extracting a wide range of neutral complexes and under certain conditions free acid. While in the case of Cyanex 272 (Gd extraction efficiency 28 %) this may be due to the fact that Preston and du Preez [7] Cyanex 272 can extract more metal ions from the aqueous solution, when pH of the aqueous solution is higher than 6.20. This is in contrast with the fact that the extraction with Cyanex 272 is more effective for gadolinium separation with high purity compared to D2EHPA. This is mainly due to the higher gadolinium  $pK_a$  value for Cyanex 272 (2.93) than those for D2EHPA (1.26).

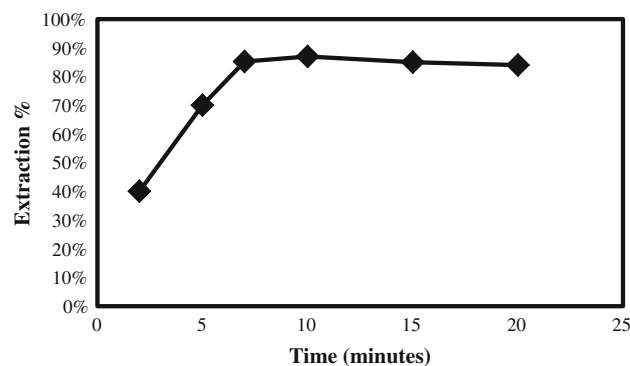
#### *Effect of solvent concentration upon gadolinium extraction efficiency*

Effect of D2EHPA concentration on Gd extraction efficiency was studied, where as the concentration of solvent increase the extraction increases. From the obtained results plotted in Fig. 5, it is clear that Gd extraction efficiency increases sharply with extractant concentration increase upto 0.1 mol/l however further increase in solvent concentration will result in relatively small increase in the Gd extraction results.

Indeed, the distribution coefficient for Gadolinium when using D2EHPA as extractant is directly dependent on the third power of the concentration of D2EHPA in the equilibrated organic phase and inversely dependent on the third power of the  $H^+$  concentration in the aqueous phase.



**Fig. 6** Effect of diluent type upon gadolinium extraction efficiency (0.07 mol/L D2EHPA, 10 min, pH 1, 1/1 O/A phase ratio)



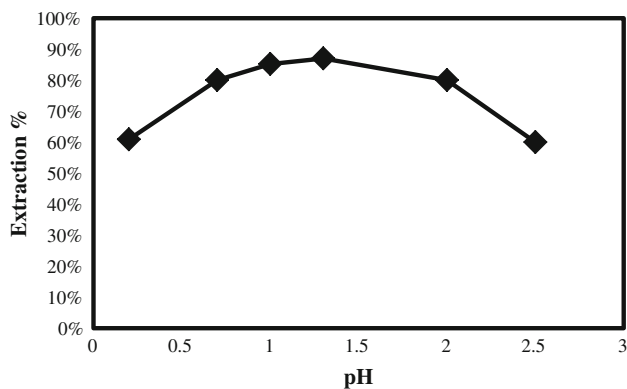
**Fig. 7** Effect of contact time upon Gd extraction efficiency (0.03 mol/L D2EHPA, pH 1, 1/1 O/A phase ratio, kerosene)

On the other hand, Gd distribution coefficient is limited by the formation of a gelatinous third phase when the solute concentration in the organic phase was too high [8].

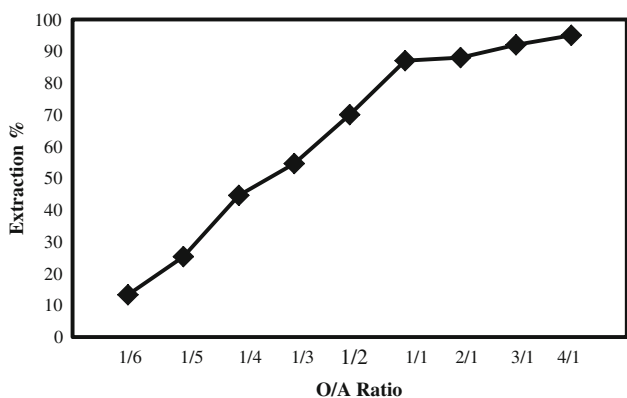
#### *Effect of diluent type upon gadolinium extraction efficiency*

It is worthy to mention that the nature of the diluent, i.e. aliphatic or aromatic, plays an important role in the stoichiometries of the metal complexes formed during the solvent extraction of metals from aqueous solutions [9]. The flash point of the diluent is very important in the selection of suitable diluent for metal solvent extraction. Kerosene and benzene have approximately the same dielectric constant but kerosene is more efficient in extraction of gadolinium (III) because Kerosene has a very low flash point ( $\sim 32^\circ F$ ), be insoluble in the aqueous phase, have a low surface tension, and be cheap and readily available [8] so it was preferred as the diluent for further gadolinium (III) extraction studies.

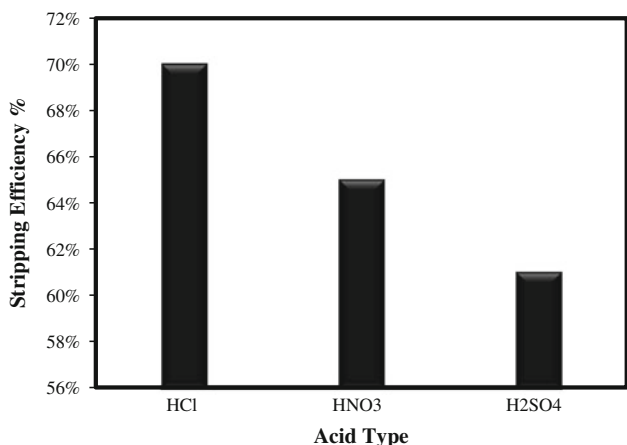
The effect of diluent type upon gadolinium extraction efficiency was performed using either aliphatic diluents



**Fig. 8** Effect of pH upon gadolinium extraction efficiency (0.07 mol/L D2EHPA, 10 min, 1/1 O/A phase ratio, kerosene)

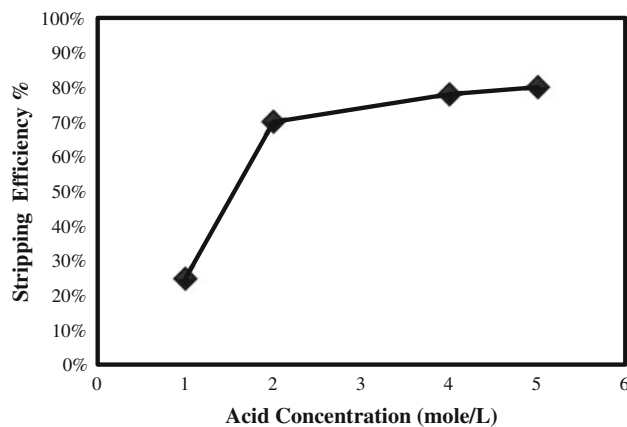


**Fig. 9** Effect of organic/aqueous ratio upon gadolinium extraction efficiency (0.07 mol/L D2EHPA, 10 min, pH 1.3, kerosene)

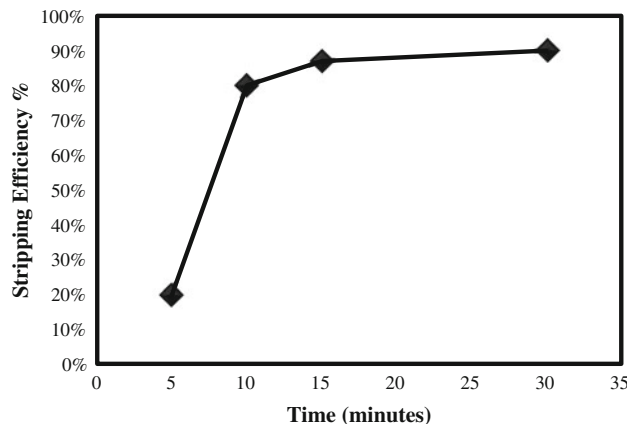


**Fig. 10** Effect of acid type upon gadolinium stripping efficiency (2.5 mol/L, 15 min, 2/1 A/O phase ratio)

(kerosene, carbon tetrachloride and chloroform) which are more effective than the aromatic one (benzene). The obtained results shown in Fig. 6 proved that the aliphatic diluents have higher gadolinium extraction efficiency



**Fig. 11** Effect of acid concentration upon gadolinium stripping efficiency (5 mol/L HCl, 15 min, 2/1 A/O phase ratio)

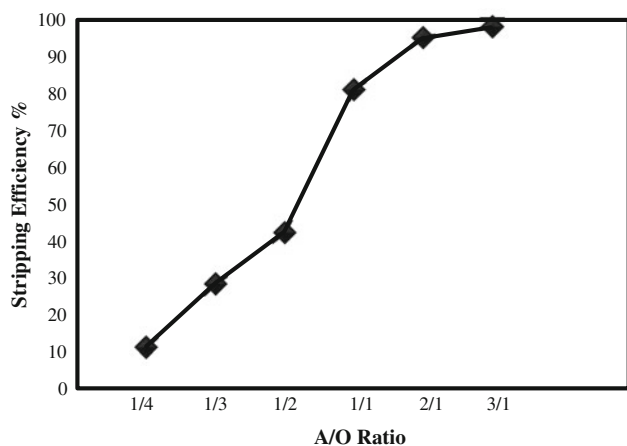


**Fig. 12** Effect of contact time upon gadolinium stripping efficiency (5 mol/L HCl, 2/1 A/O phase ratio)

(more than 87 %) while aromatic diluents have lower gadolinium extraction efficiency (30.9 %). The obtained results clarify that the applied diluents can be classified in the order kerosene, chloroform, carbon tetrachloride, benzene.

*Effect of contact time upon gadolinium extraction efficiency*

The data obtained from studying the effect of the contact time upon gadolinium (III) extraction efficiency is plotted in Fig. 7. Data shows that the extraction efficiency was directly related to the contact time and more than 10 min is required to reach the equilibrium for the Gd(III) under the experimental conditions indicating that there will be no more transfer of Gd(III) from the aqueous phase to organic phase on further contacting. Thus 10 min is sufficient to extract 87 % of gadolinium from D2EHPA.



**Fig. 13** Effect of aqueous/organic ratio upon gadolinium stripping efficiency (5 mol/L HCl, 30 min)

#### *Effect of pH upon gadolinium extraction efficiency*

Acidity of the metal feed solution is usually a variable of great importance in the solvent extraction process. Data obtained when studying the effect of pH value upon Gd(III) extraction efficiency is plotted in Fig. 8. Extraction increases upto pH 1.3 then it decrease again, as higher pH values could not be used as the equilibration led to the formation of a turbid aqueous solution probably owing to micro emulsion formation as a result of precipitation of the rare-earth elements. However, lower pH values enhance

the reverse reaction and thus extraction decreases again. Accordingly the obtained results indicate that at pH 1.3 of Gd aqueous solution is performed for effective gadolinium extraction in a chloride medium.

#### *Effect of organic/aqueous ratio upon gadolinium extraction efficiency*

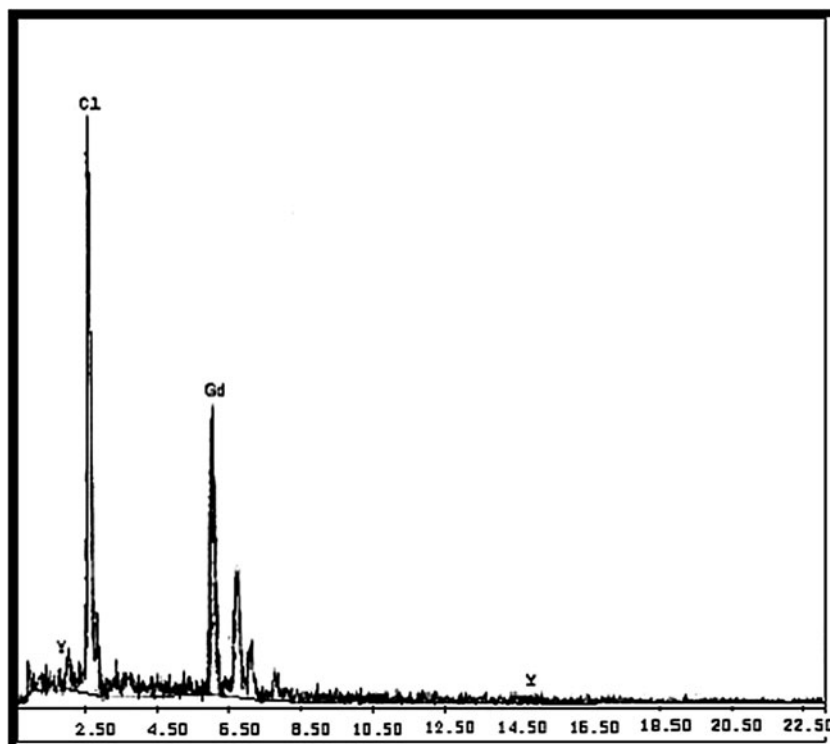
It is well known that the volume ratio of the two phases is called the phase ratio; it plays an important role in the extraction process. In fact, a low organic/aqueous ratio although advantageous from the theoretical point of view however, it is sometimes undesirable because it may lead to high solvent losses. On the other hand, a high organic/aqueous ratio requires a large inventory of solvent can occur which may be considered as a financial burden [10].

The effect of organic/aqueous ratio upon gadolinium extraction efficiency was performed in this study. From the obtained results plotted in Fig. 9 it is clear that; as the concentration of organic increase the extraction efficiency increases.

#### Results of gadolinium stripping from loaded solvent

Stripping of the loaded organic phase can be achieved by a wide variety of stripping solutions such as chlorides, sulphate or nitrate. The choice is depending on the subsequent recovery process used for the interested metal. In this work,

**Fig. 14** Qualitative ESEM analysis of Gd concentrate precipitate





different Stripping factors were investigated such as acid type, acid concentration, contact time and organic/aqueous ratio.

*Effect of acid type upon gadolinium stripping efficiency*

Different acidic stripping agents were used namely HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>. In all cases, the concentration of all acids used was 2 mol/L and the phase ratio of organic solvent to stripping solution was 1:1, the considered equilibration time was 10 min at room temperature. From the obtained results shown in Fig. 10, it is clear from the obtained results that HCl is the best stripping agent for Gadolinium (III) and then it was chosen in the present work as the stripping agent.

*Effect of acid concentration upon gadolinium stripping efficiency*

Influence of HCl concentration on gadolinium stripping from the loaded D2EHPA was investigated. In this study, HCl concentration varied from 1 to 5 mol/L. The obtained experimental results (Fig. 11) show that gadolinium stripping efficiency was directly related to acid concentration.

Stripping of gadolinium reached 80 % from the loaded D2EHPA using 5 mol/L HCl.

It is worthy to mention that this high acidity of the stripping solution is due to high stability of the Gd-D2EHPA complex.

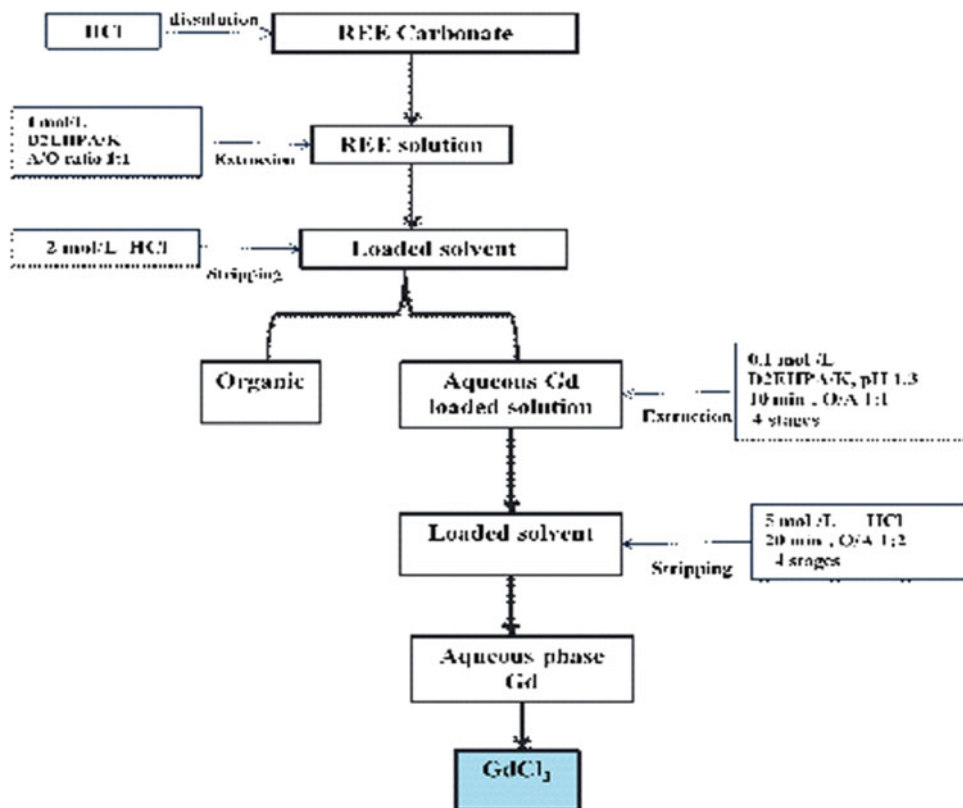
*Effect of contact time upon gadolinium stripping efficiency*

Effect of contact time upon gadolinium stripping efficiency was conducted in the range from 5 to 30 min. The obtained experimental results (Fig. 12) show that the stripping efficiency was directly related to the contact time. Thus 30 min is sufficient to extract 90 % of gadolinium from D2EHPA.

*Effect of aqueous/organic ratio upon gadolinium stripping efficiency*

Effect of aqueous/organic ratio upon gadolinium stripping efficiency from loaded organic solvent was studied from aqueous/organic ratio 1/4 to 3/1. The obtained data (Fig. 13) show that the extraction efficiency increased from 11.4 % to almost complete stripping (98 %) by increasing the aqueous/organic ratio upto 3/1.

**Fig. 15** Proposed flow sheet for separation of gadolinium from El-Garra El-Hamra rare earth elements cake



## Gadolinium precipitation results

The strip solution was firstly evaporated; the obtained gadolinium precipitate was subjected to characterization using the Environmental Scanning Electron Microscope model XL30 ESEM. The obtained data showed that the precipitate has gadolinium chloride content 81 %. Rest of impurities composes 14 % which is namely;  $MgCl_2$ ,  $CaCl_2$ ,  $FeCl_2$ . The  $YCl_3$  may reach 4 % of the precipitate. Results are listed in Table 2 and shown in (Fig. 14). It is worthy to mention herein that, as far as the author knows, it is the first time to obtain  $GdCl_3$  concentrate from the processing of thorumite-bastnaesite ore material.

## Proposed flow sheet

From the obtained results concerning the performed extraction and precipitation experiments, a proposed flow sheet for gadolinium recovery presented from El-Garra El-Hamra rare-earth cake.

According to the proposed flow sheet (Fig. 15), the REE cake is dissolved in hydrochloric acid. REE pregnant solution can be then treated with 1 mol/L D2EHPA as organic solvent dissolved in kerosene as a diluent. After separation of organic and aqueous solutions, middle rare earth stripping can be carried out upon the loaded organic solvent with 2 mol/L HCl. The gadolinium pregnant solution is then subjected to gadolinium extraction using 0.1 mol/L D2EHPA diluted by kerosene, 10 min contact time, and 1/1 organic/aqueous ratio. Thus, more than 87 % of the gadolinium present in the solution was extracted. After that, about 95 % of the extracted gadolinium has been stripped from the loaded organic solvent. The obtained data shows that the gadolinium optimum stripping conditions are 5 M HCl solution, 15 min contact time, and 1/2 organic/aqueous ratio.

The strip solution dried to obtain  $GdCl_3$  having a purity of about 81 % associated with  $YCl_3$  (4 %).

## Conclusion

Gadolinium as an important rare-earth element in the nuclear field, it is successfully extracted from the enriched El-Garra El-Hamra concentrate with purity 81 % using the organic solvent extraction technique. This paper is considered as a new approach in the Nuclear Materials Authority of Egypt.

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