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Leaching of Rare Earth Elements from Gibbsite-bearing Shale of Southwestern Sinai, Egypt using Ammonium Sulfate via Ion Exchange Mechanism

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Abstract

Gibbsite-bearing shale ore, South Western Sinai, Egypt has been identified as containing physically adsorbed rare earth elements (REEs). The investigated material mainly contains an average rare earth elements (REEs) concentration of 6350 ppm. In spite of low grade compared to other rare earth elements (REEs) sources, the low mining cost and the ease of exploitation make it a promising source of rare earth elements (REEs). In this study, experiments were conducted to investigate desorption of rare earth elements (REEs) via ion-exchange mechanism using monovalent electrolyte solution of ammonium sulfate. All laboratory experiments were conducted at ambient temperature by using a batch leaching technique. The impact process factors that affect the leaching of rare earth elements (REEs) such as the ionic strength of $(NH_4)_2SO_4$, the solution's pH, liquid/solid (L/S) ratio and the reaction contact time have been optimized. Rare earth elements (REEs) maximum leaching efficiency of 93.8% was achieved with combination of 0.5 M $(NH_4)_2SO_4$, 30 minutes contact time, L/S ratio of 3:1 at pH 5. The selectivity of REEs has been enhanced and improved as a result of the fast-leaching rate and the ease of the ion exchange process. The simplicity with which REEs can be desorbed from gibbsite surface by ion exchange is due to that the rare earth cations are more hydrated than NH_4^+ monovalent cation which results in attachment of NH_4^+ to gibbsite surface and desorption of rare earth cations to the liquid phase.

Keywords: Rare earth elements; ion-exchange; ammonium sulfate; rare earth desorption; gibbsite.

1. Introduction

Modern industries are in dire need of the availability of rare earth elements due to their unique chemical and physical properties. They are widely utilized in the creation of novel materials, energy efficiency, powerful permanent magnets, lasers, fiber optics, electronic devices as well as in military weapon systems [1-2]. The increasing development in advanced, clean and efficient technologies have led to an accelerated increase in the demand for rare earth elements (REE)s in the international markets, with focusing on finding new resources to ensure a sufficient supply for use in the present and future [3, 4].

A collection of 17 chemical elements known as "rare earth elements" includes 15 lanthanides with atomic numbers ranging from 57 lanthanum (La) to 71 lutetium (Lu) of the periodic table, yttrium (Y) and scandium (Sc) due to their shared chemical and physical characteristics with lanthanides [5-7].

Between lanthanum and neodymium, samarium and dysprosium, and holmium and lutetium, rare earth elements are categorized into three groups [8-10]. Since oxygen is their primary bonding partner, all rare earth elements are lithophiles, and they are naturally occur as oxides, carbonates, silicates, or phosphates [11]. There are about 200 identified REE-containing minerals, however due to their geological characteristics; the majority is not concentrated in commercially viable ore deposits. The main commercially significant sources fall into the following categories [12-14]:

1) Carbonaceous source: Bastnasite, (REE, Ce)(CO$_3$)F, is a fluorocarbonate mineral, which basically contains light rare earth elements.

2) Phosphate source: Monazite, (REE)PO$_4$ is a light rare earth phosphate minerals, the major components of which are rare earth oxides (REO), usually found in placer deposits, while Xenotimes (Y,REE)PO$_4$ are phosphate minerals, the main constituent of which is

yttrium orthophosphate and other heavy REE.

   3) Clay minerals source: where the REEs are adsorbed on the clay minerals surfaces such as kaolinite, illite, and smectites or montmorillonites. This can be attributed to in situ weathering of the rare earth-bearing rocks resulting in its adsorption to the clay's surfaces.

   A net negative charge is formed on the surface of clay minerals as a result of replacing a cation of lower charge in the place of a cation of a greater charge during the entry of these cations that present in solutions to the interlayer of the clay minerals, thus enhances the potential of clay minerals to adsorb rare earth element [15, 16]. Because of their complexity, carbonaceous and phosphate sources require strong processing conditions, which presents challenges in exploiting them as sources for rare earth elements. Although clay minerals contain a low concentration of rare earth elements, they are characterized by the ease of dissolving the REEs through simple process, which making them one of the important sources of rare earth elements [17-19].

   Aside from adhering to clay minerals surfaces, REEs are attached to naturally occurring Al-Fe-hydroxides such gibbsite (AlOOH) and goethite (FeOOH). While adsorption is most likely the most common route of enriching rare earth elements (REEs) in ion adsorption clay, they are also, to a considerably lesser extent, absorbed into the crystal lattice of secondary oxides as hematite and silicates [20, 21]. By leaching at room temperature with monovalent sulphate or chloride salt solutions these adsorbed rare earth elements (REEs) can be recovered yielding a high-grade rare earth oxides product [22, 23].

   The purpose of this study is to investigate the leaching of rare earth elements (REEs) adsorbed on gibbsite-bearing shale using monovalent ammonium sulfate as lixiviant and establishing the optimum leaching conditions which maximize extraction efficiency of the rare earth elements (REEs). In addition to exploiting of low –concentration gibbsite ore as an important and promising source of rare earth elements.

2. Experimental
2.1 Characterization of ore sample
   A representative gibbsite-bearing shale sample portion was ground to - 60 mesh size for complete chemical analysis. The major oxides as Al_2O_3, Fe_2O_3, TiO_2, CaO, P_2O_5, MgO and SiO_2 were analysed according to Shapiro and Brannock [24]. Trace elements such as Zn, Ni, Co, Cu and V were estimated using a Unicam atomic absorption spectrometer model-969 (AAS) flame type at principal wavelengths. A flame photometric technique was used for the determination of Na and K contents. Total REEs was determined by Arsenazo III, where the absorbance of its complex was measured at λ654 nm

as Y reference using a UV-VIS spectrophotometer (Shimadzu UV-160) [25]. An oxidimetric titration method was used for analyzing uranium against ammonium metavanadate [26]. Gravimetric analysis was used for determination of loss on ignition (L.O.I). Table 1 provides the chemical composition.

Table 1. The gibbsite sample's chemical composition.

Major Contents	Conc. (%)	Trace elements	Conc. (ppm)
SiO_2	22.8	U	390
Al_2O_3	21.1	REEs	6350
Fe_2O_3	13	Zn	8430
TiO_2	0.18	Co	2800
CaO	6.88	Ni	980
MgO	5.55	Cu	4600
MnO	3.35	V	105
Na_2O	1.65		
K_2O	0.32		
P_2O_5	0.1		
Cl	3		
$L.O.I$	21.45		

The X-ray diffraction analysis (using Phillips PW-3710) indicated that quartz (SiO_2), kaolinite [$Al_2Si_2O_5(OH)_4$] and Gibbsite [$Al(OH)_3$] were the main crystalline phases and no other crystalline structures of were observed, suggesting that concentration is below the detection limit (Fig.1).
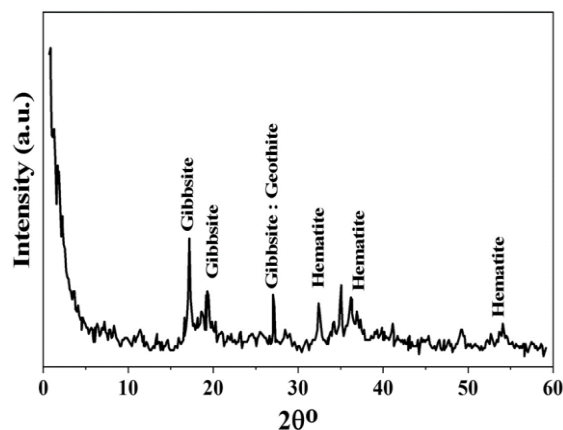

Fig.1 The X-ray diffraction analysis of the gibbsite-bearing shale representative sample.

2.2 Batch Leaching Tests
   Dissolution experiments have been conducted using batch technique at ambient temperature. The effect of various parameters on the leaching process including the concentration of $(NH_4)_2SO_4$ solution, the solution pH, L/S ratio and the leaching time were optimized. Each variable was studied separately by

changing its range and fixing the other influencing variables. The scope of each controlling variable was as follow: the concentration of ammonium sulphate $(NH_4)_2SO_4$ solutions was from 0.1 to 1 M, pH range was from 1 to 7, L/S ratio was from 1:1 to 5:1 and leaching time was from 5 to 60 minutes. Equilibrium adsorption experiments were conducted using magnetic stirrer at 300 rpm. In all stages of the experiments, 0.1 N normal solutions of NaOH and H_2SO_4 were used to adjust pH. The pH measurements were performed by a digital pH meter model DM-21 and a combination glass electrode purchased from HANA. The solid residue after each experiment was filtered using vacuum filtration, then washed several times with distilled water and dried in the oven at 105°C for 12 h, then weighted and taken in preparation for analysis. The utilized chemicals were of analytical grade, and water that had undergone two deionization processes was used to prepare all tests.

3. Results and discussion

3.1 Effect of $(NH_4)_2 SO_4$ concentration.

To be able to obtain the optimum concentration of $(NH_4)_2SO_4$ solution required for maximum leaching of REEs, several batch experiments were carried out by differentiating concentration of $(NH_4)_2SO_4$ solution from 0.1 to 1 M and the other parameters were kept constant at leaching time of 60 minutes, L/S ratio of 4:1 and pH of 3.0 at ambient temperature using magnetic stirrer at 300 rpm. Absorption of lixiviant by the ore sample and / or sampling during leaching results in changes in lixiviant volume, so the final solid residue is taken as a reference in the calculus of the dissolved mass of REE. The leaching efficiency is calculated from equations 1 and 2.

Leaching efficiency % = [(mass REE) dissolved/ (mass REE) in sample initially] x100   (1)
(Mass REE) dissolved = (mass REE) in ore sample initially – (mass REE) in final residue   (2)

The adsorption of NH_4^+ occurs through the cation exchange mechanism.
Clay-REE^{+3} +3NH_4^+= Clay-$(NH_4^+)_3$ +REE^{+3} (3)

According to the supposed hydration theory, division of the cation exchange between minerals surface, where REEs are physically adsorbed, and the aqueous solution provided two different cations, the more highly hydrated ion is favoured to be in the liquid phase since it would demand a lot of energy to be dehydrated and attached to the mineral surface, whereas the more likely hydrated will tend to link the mineral. The hydration numbers for REEs are between 8 and 9, while ~4 for NH_4^+ monovalent cation. This explains the ore sample's performance for monovalent cations over trivalent rare earth elements and, in turn, the simplicity with which REEs can be desorbed from mineral surface by ion exchange [27, 28].

Figure 2 showed that raising $(NH_4)_2SO_4$ concentration from 0.1 to 1 M. significantly enhanced the overall quantity of REE recovery from 35.6% to 74.6%. Further increase of ammonium sulfate concentration beyond 0.5 M becomes less pronounced and provided no appreciable improvement in the recovery of REEs. 0.5 M was chosen to be the optimum ammonium sulfate concentration.
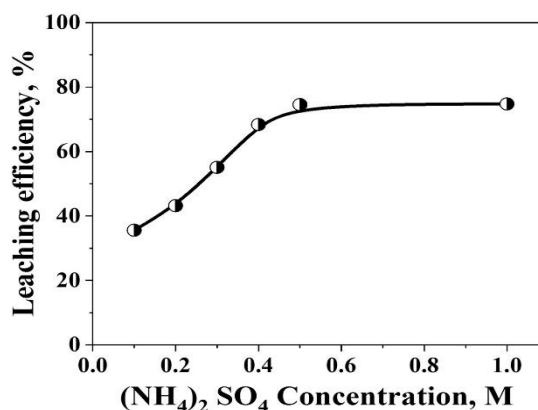

Fig.2 Shows how the concentration of $(NH_4)_2SO_4$ solution affects how effectively total rare earth elements are leached (25°C, 300 rpm, L/S 4:1 at pH 3)

3.2 pH effect

To assess how well rare earth elements are being leached and how much of an impact pH has, several batch experiments were conducted for pH values ranging from 1 to 7 and the other factors were held constant at 0.5 M ammonium sulfate concentration, leaching time of 60 minutes and 4:1 L/S ratio at ambient temperature via magnetic stirrer at 300 rpm. The obtained results shown in Fig.3 revealed that the leaching efficiency for REEs improved from 53.3 % at pH 1 to 93.8 % at pH 5 then decreased at pH 6.

The REEs cations form sulfate complexes with sulfate at acidic range of pH and near neutral pH. At the previous pH range, the liberation and the releasing of REEs cations from minerals surfaces into the $(NH_4)_2SO_4$ solution increases. Hence, results in higher leaching efficiency levels of REEs via ion-exchange mechanism with $(NH_4)_2SO_4$. Beyond the neutral pH the REEs are lost due to hydrolysis and formation of REEs hydroxide complexes which are predominant at neutral at pH rang> 6, which can negatively impact the REEs ability to be leached via ion-exchange mechanism.
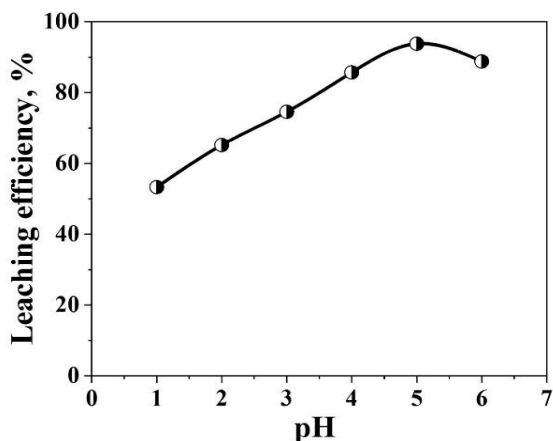
Fig. 3 Leaching efficiency of total rare earth elements as a function of solution pH (25°C, 300 rpm, L/S: 4:1 and 0.5 M $(NH_4)_2 SO_4$).

3.3 Effect of liquid –to- solid ratio

A series of leaching experiments have been conducted to examine the effect of the liquid to solid ratio on the extraction efficiency of REEs under the following circumstances: 0.5 M ammonium sulfate concentration, 60 minutes leaching time and pH of 5 at ambient temperature using magnetic stirrer at 300 rpm. The Liquid to solid ratios used in the studies were in the order of 1:1, 2:1, 3:1, 4:1 and 5:1. From Figure 4 it can be illustrated that, in case of lower liquid to solid ratio (1:1), the solid particles aggregate, coalcence and results in reducing the required surface area for complete interaction with the ammonium sulfate solution. Consequently, decrease REEs' leaching efficiency of to 75.6%.

On the other hand, the increase of the liquid/ solid ratio would yield free motion for the solid particles up to highest level and results in increase of the attacking force of the ammonium sulfate solution. Also achieve diffusion of the lixiviant cations (NH_4^+) from the solution to the surface of the solid particles where the REEs adsorbed causing REEs to diffuse out of the particle surface to the solution. Thereby, the extraction efficiency of the REEs was increased to 93.8% in case of L/S ratio of 3:1.

The effectiveness of the REEs is unaffected by increasing the liquid/solid ratio to 4:1 and 5:1. Hence, the optimum recommended L/S ratio is 3:1.

3.4 Impact of stirring duration

The Leaching time's impact on the effectiveness the REEs' extraction was studied under the following fixed conditions: 0.5 M ammonium sulfate concentration, L/S ratio of 3:1 and pH 5 using magnetic stirrer at a speed of 300 rpm at room temperature (25 °C±1) using a range of leaching time up to 60 minutes. From Fig. 5 it can be noted that the leaching efficiency of the REEs increases dramatically to 87.6 % after 5 min and 93.8 % after 10 min. Extending of the stirring time beyond 10 min has no

discernible impact on the effectiveness of REEs and may be results in loss of REE due to hydrolysis. The selectivity is improved as a result of the fast leaching kinetics.
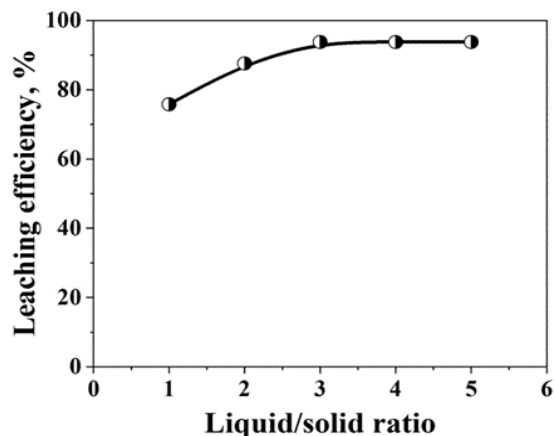

Fig. 4 Leaching efficiency of total rare earth elements as a function of L/S ratio (25°C, 300 rpm, 60 min a stirring time, pH 5 and 0.5 M $(NH_4)_2SO_4$).
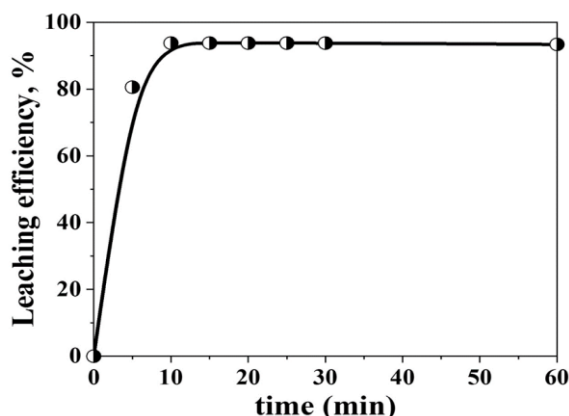

Fig. 5: Leaching efficiency of total rare earth elements as a function of stirring time (25°C, 300 rpm, pH 5 and 0.5 M $(NH_4)_2SO_4$).

4. Conclusion

The current study investigated the effects of experimental variables, including the lixiviant concentration, pH, liquid/solid ratio and stirring duration, on the process of desorption of rare earth ions that have been adsorbed on gibbsite-bearing shale ore by leaching with monovalent electrolyte solution of ammonium sulfate $(NH_4)_2SO_4$ at ambient temperature. This ore consists substantially from gibbsite, iron oxide, iron hydroxide, quartz and contains an average REEs concentration of 6350 PPm. In this study, the exploitation of this ore as a promising source for REEs rather than conventional sources is considered. REEs were extracted with ease via ion-exchange mechanism. The leaching efficiency of REEs (93.8%) was maxed out when the operating factors were as follow:

0.5M $(NH_4)_2SO_4$ achieved the maximum extraction level of REEs and ensures the stoichiometric ratio 3:1 between the trivalent REEs and the exchange cation NH_4^+. It was found that, the leaching of REEs is dependent on pH of $(NH_4)_2SO_4$ solution and the maximum leaching efficiency was given at pH of 5. The optimum liquid/solid ratio for obtaining maximum leaching efficiency of REEs was found to be 3:1, where this ratio offers free motion for the solid particles to complete the ion exchange process with the lixiviant solution. The leaching kinetics were fast, in less than 10 min. the maximum leaching efficiency can be reached, resulting in selectivity improvement. The recommended leaching time is 30 min.

Conflicts of interest: There are no conflicts to declare.

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