RESEARCH ARTICLE

Solvent Leaching Of Total Rare Earth Elements From Phosphate Rocks From Abu-Tartur Plateau

Laila A.Guirguis[1], Ragaa El Sheikh[2], Nagdy M.Farag[1], Mohamed A.Elsayed[1], Mohammed S.Hagag[1]
1- Nuclear Materials Authority, P.O.Box 530 El Maadi, Cairo, Egypt
2- Department of Chemistry, Faculty of Science, Zagazig University, Zagazig, Egypt

Manuscript Info	*Abstract*
	The present work Studied the acid curing of Phosphates rock from Abu-Tartur plateau. The optimizing curing parameters were 500 sulfuric acid kg/t ores with 10% nitric acid relative to quantity of sulfuric acid, 110 ℃ and thus for 2 h. The cured ore was subjected to extraction with solvent leaching for rare earth elements. About 95.6% extraction efficiency was reached under solvent leaching conditions, primene JMT 15% in kerosene, flow rate 1 ml/min, solid/aqueous phase ratio 1:3 and number of contact 5. The loaded organic solvent subjected to the stripping process. Stripping efficiency of rare earth elements from acid cured phosphate ores yielded about 99.8% under the optimum studied conditions which were 3M nitric acid, phase ratio A/O was 3:1 and shaking time was 15 min.

INTRODUCTION

Separation of rare earth elements from phosphate rocks prior to production of phosphoric acid has a great importance, due to saving time, also lowering cost and environmental aspects that is greatly recommended for production of phosphoric acid with lowering impurities. Abu-Tartur plateau which located in Egyptian Western Desert act as a pioneer source of phosphate rocks in Egypt for its huge content from phosphate and percentage of P_2O_5 (25%) . with Many chemical technological procedures were used for separating of rare earth elements from phosphate rocks or phosphoric acid. Such as liquid –liquid extraction[1, 2], ion exchange resin[3], liquid emulsion membrane[4, 5], extraction chromatography[6, 7], chelating resin[8, 9], imprinted polymers[10, 11], flotation[12, 13] and bio accumulation[14, 15].   Solvent leaching is considered as one of the industrial application for separation of some elements. In simplest definition is a conventional leaching of uranium or rare earth elements or any other metals involves mixing the ore (bearing the metals) with an aqueous phase containing solublized chemicals followed by solid-liquid separation and metal recovery by ion exchange / solvent extraction[18]. Solvent leaching in an other word is an analytical technique for extraction of elements this technique is not such famous like other extraction systems e.g. liquid –liquid or solid liquid extraction, Little works is performed to separate of elements with solvent leaching, for example   tri-n-butyl phosphate can be used for uranium extraction from ore that has been previously dampened with acid. With small amount of concentrated acid the ore is pugged and then cured at 100 ℃ for several hour. Nitrate is added next[18]. This step is followed by mixing in static bed or in an agitated vessel, with the TBP in kerosene[18]. The pregnant extract is treated for uranium recovery while the solid residue is washed with diluents to recover TBP. Also DEHPA is used for solvent leaching of uranium from phosphate ores[19] and rare earth elements from some Egyptian ores[20].In the present work Abu-Tartur phosphate rocks were subjected to solvent leaching technique for separation of rare earth elements several parameter were studied.

EXPERIMENTAL
1-Materials and equipments
        All chemical used are in analytical grade, H_2SO_4 98% BDH, NaOH from Sigma-Aldrich, Arzenazo III purchased from Merc, Ascorbic acid 98% from Adwic, formic acid purchased from Sigma-Aldrich, permine JMT purchase from Sigma-Aldrich and nitric acid 69% was purchased from BDH.

2- Instruments
        UV-Vis Shimadzu 1601 used for all spectrophotometric determination and Orion 920 for pH measurements with pH ross combination electrode.
3-Chemical analysis
  A number of chemical and instrumental methods of analyses were used for the quantitative determination of the major, minor and trace element compounds of the present phosphate and black shale rocks.

    An ion exchange method is used for the present study for the analysis of phosphates samples and also applied to black shale samples. This method was applied, and has the advantage over the direct method, in that it separates the phosphate radical completely from the metal cations using the strongly cationic resin Dowex 50 X in the hydrogen form (240 mesh) in a glass column of 100 cm length and 5 cm cross section, the metal cations are retained in the column while the anions passed quantitatively into the effluent. The cations are afterwards eluted from the resin using 4N HCl and determined using suitable methods Thus 1 gm of phosphate and black shale rocks are attacked with mixed acid (15 ml HCl + 5 ml HNO_3 + 15 ml HF + 5 ml $HClO_4$ + 2ml H_2SO_4) till complete dryness and soluble in HCl acid   and passed through the ion exchange column at a rate of 2 ml / minutes. The column is washed by 0.0175 N HCl and the separated anions is collected in 250 ml measuring flask. The retained cations are then eluted with 4N HCl until the column is free from them (iron test) and diluted to 100 ml[19].

- **Determination of Total Rare Earth Elements**
    To 5 ml of cations sample solution pH 1, add 2 ml of 1% ascorbic acid after few minutes add 1 ml of formate buffer and add 4 ml of arsenazo III solution and complete to 40 ml with double distilled water. Adjust the solution pH to 2.6 using 0.1 M NaOH solution, complete to 50 ml with double distilled water and measure the solution absorbance at the maximum absorbance 650 nm.

4-Acid curing of the phosphate ores
        Collected technological sample of phosphate rocks from Abu-Tartur plateau, ores was milled to -150 mesh and subjected to chemical analysis for major elements determination table (1). Ore was cured at 110 ºC with sulfuric acid 98% about 550kg/t and 55kg/t nitric acid required thus for 2 h curing time. The cured ores was packed into column of 1 cm diameter and 50 cm length and subjected for solvent diffusion through tube for studying proper solvent leaching parameter for controlled rare earth elements extraction.
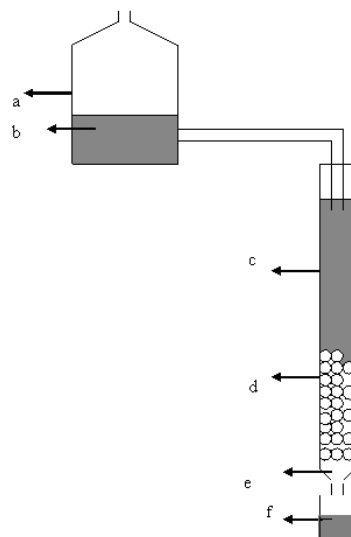
Solvent leaching process
        The pre-cured ore was packed in the solvent leaching column tube. The parameter controlling the extraction process such as type of diluents, concentration of solvent, flow rate, number of contact and phase ratio was studied. The output solvent was periodically collected every 20 ml through put volume for rare earth elements analysis (fig 1 shows the solvent leaching system), also residual of cured ores after solvent leaching process was washed with dilluent (to remove adsorbed solvent

        on cured ores) and then drying at oven at 100 ºC for 2 h and then 1 g of the residual was breaking down with mixed acid (2 ml sulfuric acid + 10 ml nitric acid + 20 ml hydrochloric acid) and subjected to spectrophotometric determination of uranium or rare earth elements to compared with that obtained from loaded organic. But in case of solid phase ratio and number of contact, after determination of latter parameter (type of diluents, concentration of solvent, and flow rate) certain amount of pre-cured ore was packed into column and certain volume of solvent (primene JMT) passed through ores and repassed many times for determination of (solid phase ratio and number of contact).

Table :(1)Analysis of technological sample from Abu-Tartur Phosphate rock.

Elements	concentration
U	27 ppm
REE	2103 ppm
Zr	595 ppm
CaO	35.6 %
MgO	2.4 %
P_2O_5	21.8 %
Fe_2O_3	11 %
Al_2O_3	4 %
SiO_2	8.3 %
Na_2O	2.44 %
K_2O	0.405 %
Ti_2O	1.4 %
Weight loss at 110 C	2.6 %
Weight loss at 550 C	4 %
Weight loss at 1000 C	3.5 %

a: solvent container
b: primene jmt solvent in kerosene
c: solvent leaching column
d: acid cured phosphate ores
e: glass wool
f: loaded solvent
Figure (1) Solvent leaching system for rare earth elements extraction from acid cured phosphate ores.

Stripping process

In order to strip rare earth elements from a the loaded organic phase, it was brought into contact with a suitable aqueous solution (strip solution). Controlling the stripping process were studied such as stripping agent type, concentration of stripping agent, phase ratio and shaking time.

RESULTS

Effect of sulfuric acid amount

This effect was studied by applying different acid quantities ranging from 100 up to 750 kg/t ore, however 10 % of this amount is replaced with nitric acid while keeping the other factor constant, figure (2) shows that sulfuric acid quantity 500 kg/t ore is the optimum acid. acid quantity which is required for amenable of rare earth elements from phosphate ores (to be extracted through primene JMT) which was increased to 91% where, below 500 kg/t gave lesser extraction of rare earth elements. Also when quantity of sulfuric acid > 500 kg/t lead to that ores sample converted into paste with very hard difficulty to be packed in solvent leaching column and completely prevent the solvent to be diffused through the ores.
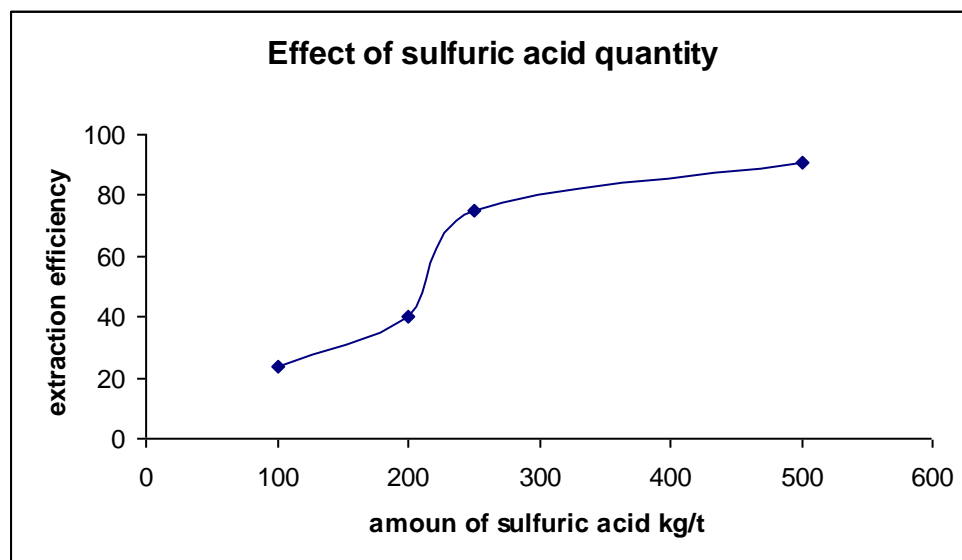

Figure (2) Effect of sulfuric acid quantity for acid curing of phosphates rock on extraction efficiency.

Effect of nitric acid

This factor was studied by variation the percentage of nitric acid from (5- 30%) relative to sulfuric acid amount. addition of nitric acid gave a good enhancements in rare earth elements extraction , the effect of replacing of 10 % of the sulfuric acid by nitric acid justified by several investigators[20]. Besides its value as a fertilizer constituent, it also improves the solublize of rare earth elements from cured phosphate ores, also it can minimize the rare earth elements in the gypsum residue as shown in fig (3).
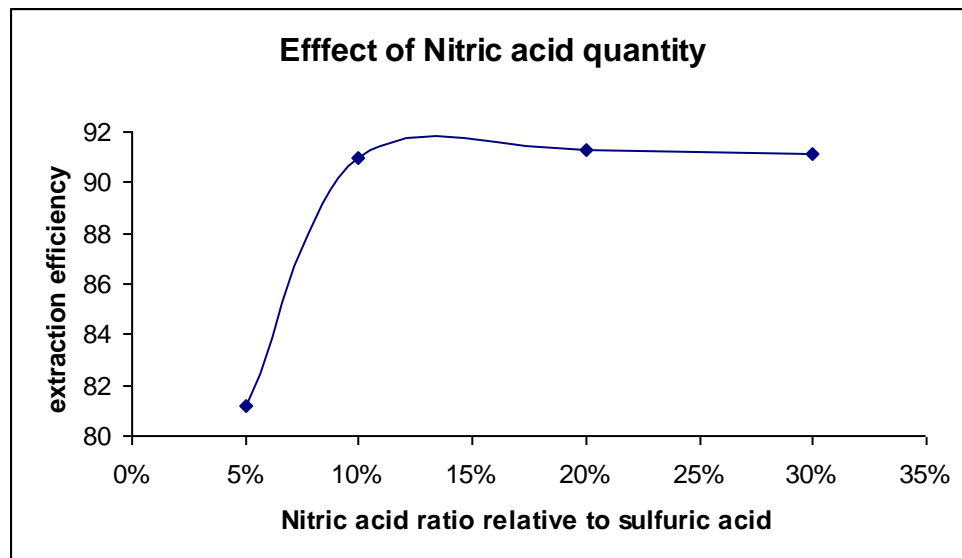
Figure (3) Effect of nitric acid quantity relative to sulfuric acid on acid curing for rare earth extraction from phosphates rock

Effect of curing time

        The curing time was varied from 1-5 hours while keeping the other operating acid curing conditions constant such as sulfuric acid 550 kg/t of ore, 10 % nitric acid relative to sulfuric acid amount. The results were illustrated below on fig (4). The curing time of 2 h can be considered as optimum one which yielded 91 % of rare earth elements content. Over which on any remarkable increase in the extraction efficiency.
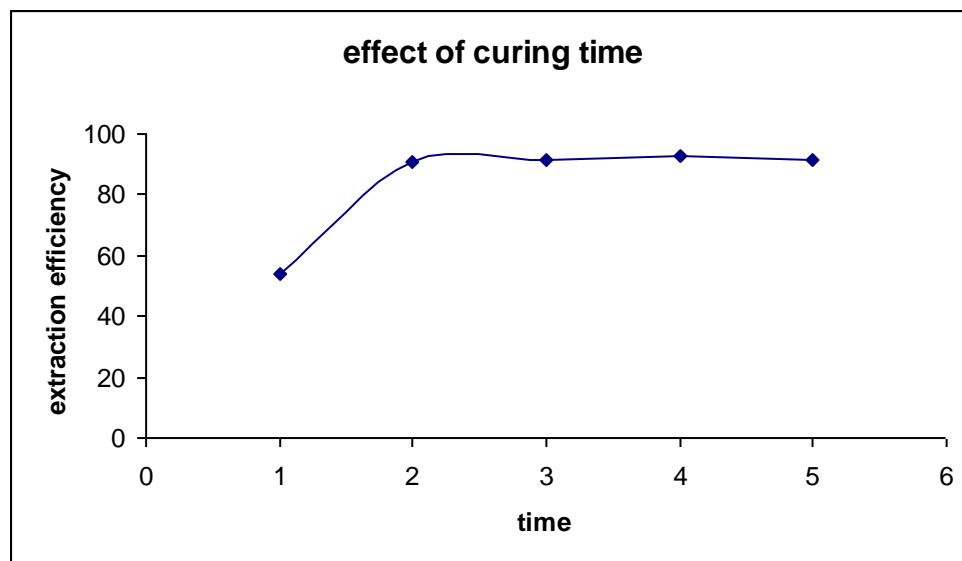

Figure (4) Effect of time curing for phosphate rocks on extraction efficiency of rare earth elements.

Effect of temperature

To study this effect the temperature was varied from 30-120 ºC. Curing at temperature 110 ºC yielded higher extraction efficiency of rare earth elements with primene JMT compared with lower one as shown figure (5) when temperature elevated>110ºC no remarkable increase in extraction efficiency also below 110 ºC gave lesser extraction of rare earth elements.
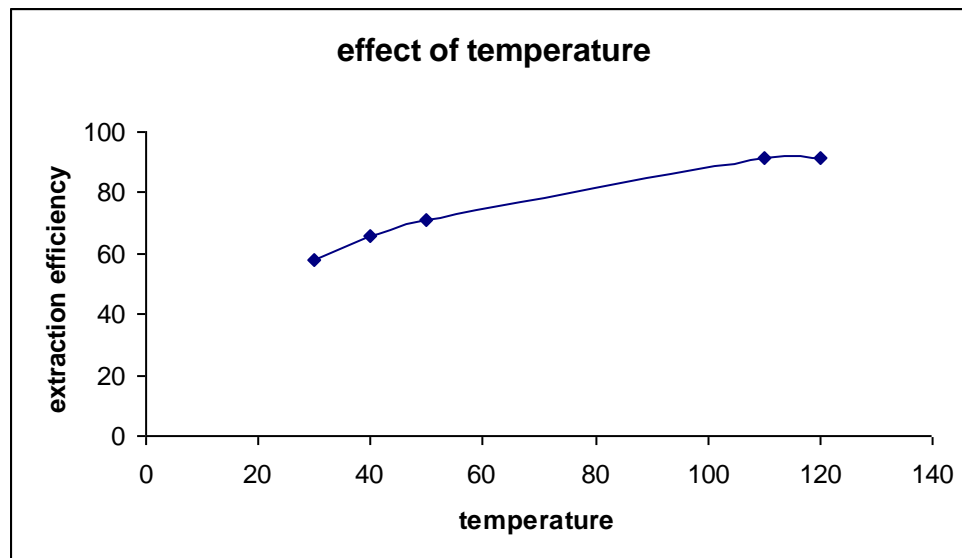
Figure (5) Effect of curing temperature of phosphate rocks on extraction efficiency of rare earth elements.

Solvent leaching process
The factors affect the solvent leaching process were studied such as: Effect of diluents type, concentration of diluents type, phase ratio and number of contact.

Effect of diluents type
        Four diluents were used in solvent leaching of rare earth elements from cured phosphate ores (n- hexane, xylene, kerosene and carbon –tetra-chloride) with 10 % **Primene JMT**as solvent . Results showing that kerosene gave highest extraction efficiency (72.2 %) as shown below in fig (6) i.e. (kerosene> n- hexane > xylene > CCl_4) 72.2 %, 36.3 % , 25.6 % , 18.2 % respectively.
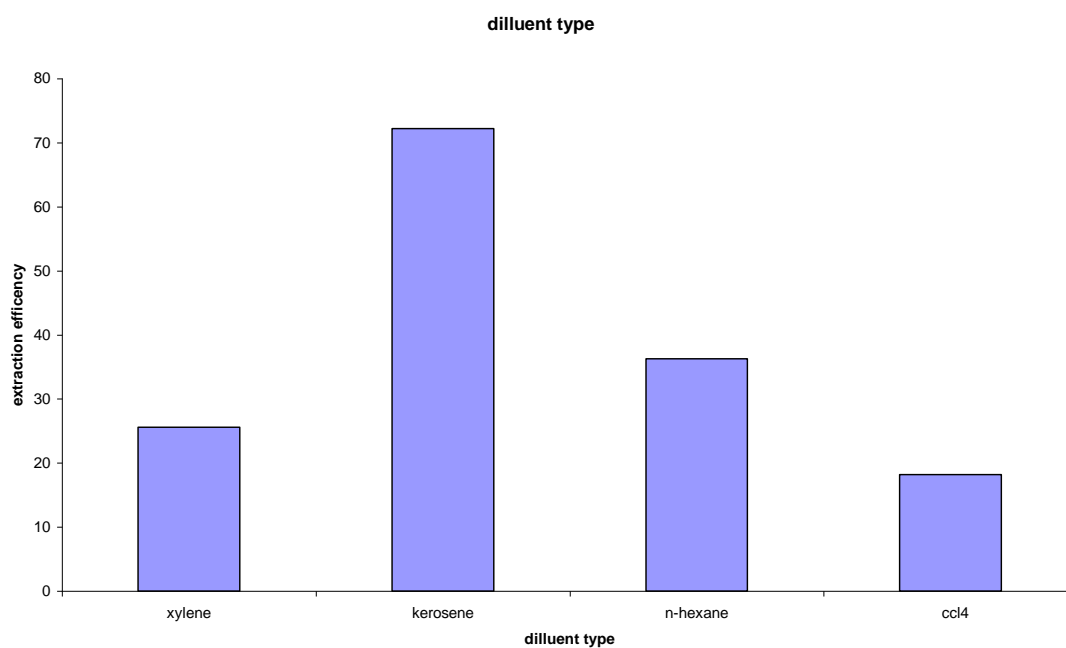

Figure (6) Effect of diluents type for solvent leaching of acid curing phosphate ore with Primene JMT as solvent.

Effect of Primene JMT concentration

The results were shown below in figure (7). It was clear that extraction efficiency increased from 5 % primene jmt in kerosene till reach 15 % primene jmt in kerosene after that it remained almost constant. And so on 15 % primene jmt in kerosene considered as optimum concentration.
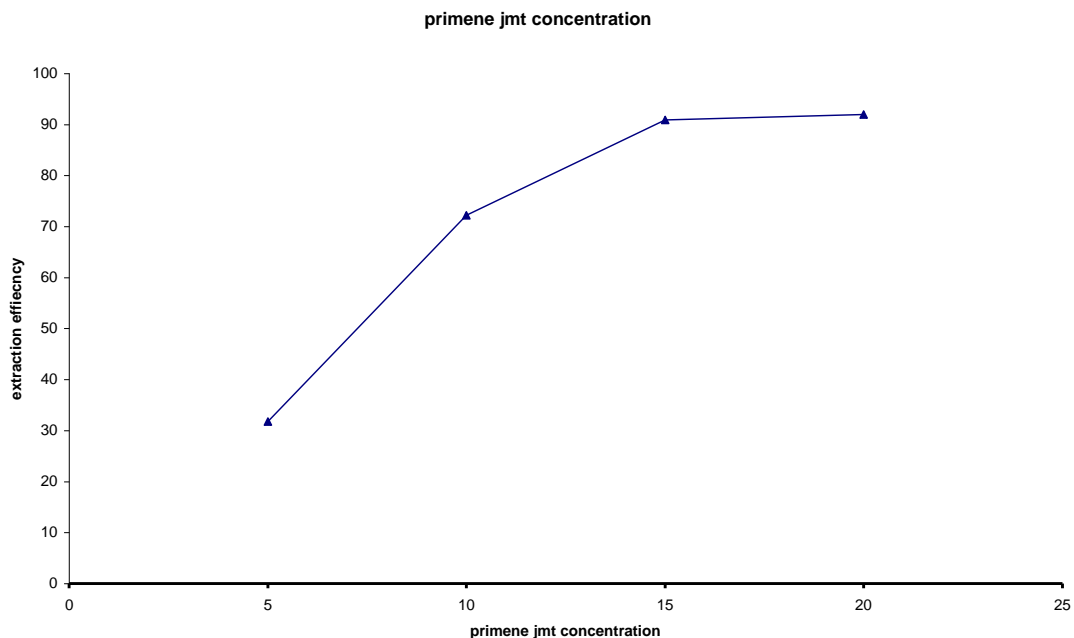
primene jmt concentration

Figure (7) Effect of solvent concentration on the solvent leaching of the rare earth elements from acid cured phosphate ore from Abu- Tartur.

Effect of solvent flow rate

In order to study the flow rate effect upon rare earth elements solvent leaching efficiency from acid cured ore, a series of experiments were performed using various solvent flow rates ranging from 0.5 up to 3 ml per min. The experiments were performed under the following fixed conditions: 20 g ore sample solvent concentration primene jmt 15% in kerosene. figure (8) shown that 1 ml per second is the optimum flow rate where there was no any significant effect on solvent leaching at flow rate 0.5 ml per min also sharp decrease on solvent leaching at flow rate 2 and 3 ml per min this may be due to the reduction contact time between solvent and the cured phosphate sample.
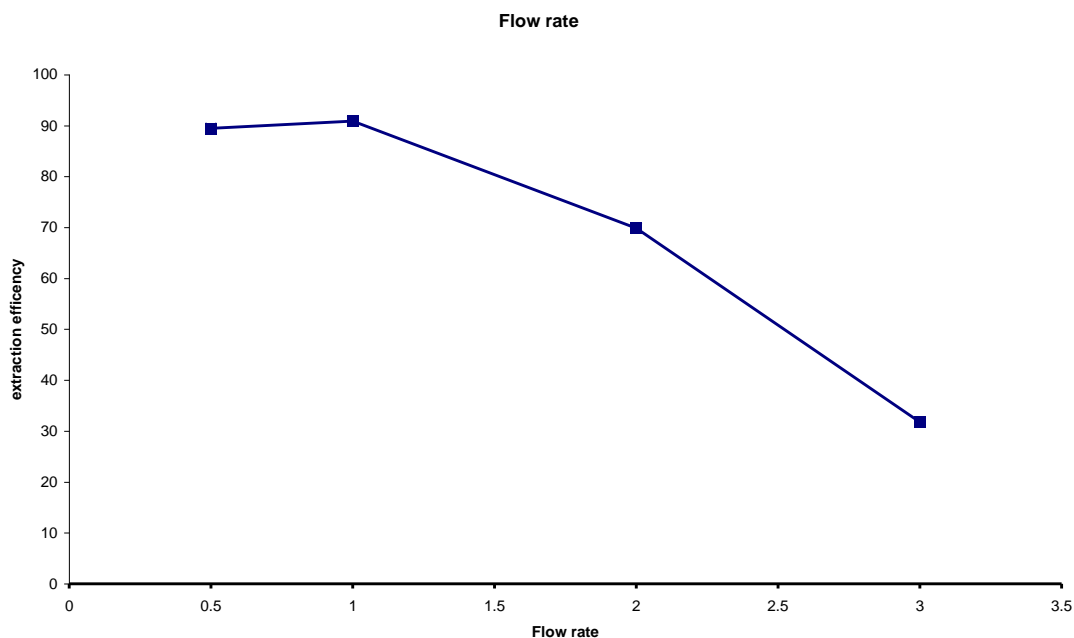
Flow rate

Figure (8) Effect of solvent flow rate on solvent leaching of acid cured phosphate ore from Abu-Tartour with 15% primene jmt in kerosene.

Effect of Solid / Solvent Ratio

The effect of the solid/solvent ratio on the solvent leaching of rare earth elements from the cured sample was studied. Different volumes of 15% primene jmt in kerosene and 1ml/ min flow rate were used for the detecting phase ratio varied from 1:1 , 1:2 , 1:3 and 1:4, O/S (ore / solvent) was used and recycled about 4 times through the solvent leaching glass column which was packed with 20 gm of acid cured phosphate sample, the results shown below in fig (9). its clear from experiments gave that 1:3 O/S (ore / solvent) was the optimum one for the extraction of rare earth elements through solvent leaching.
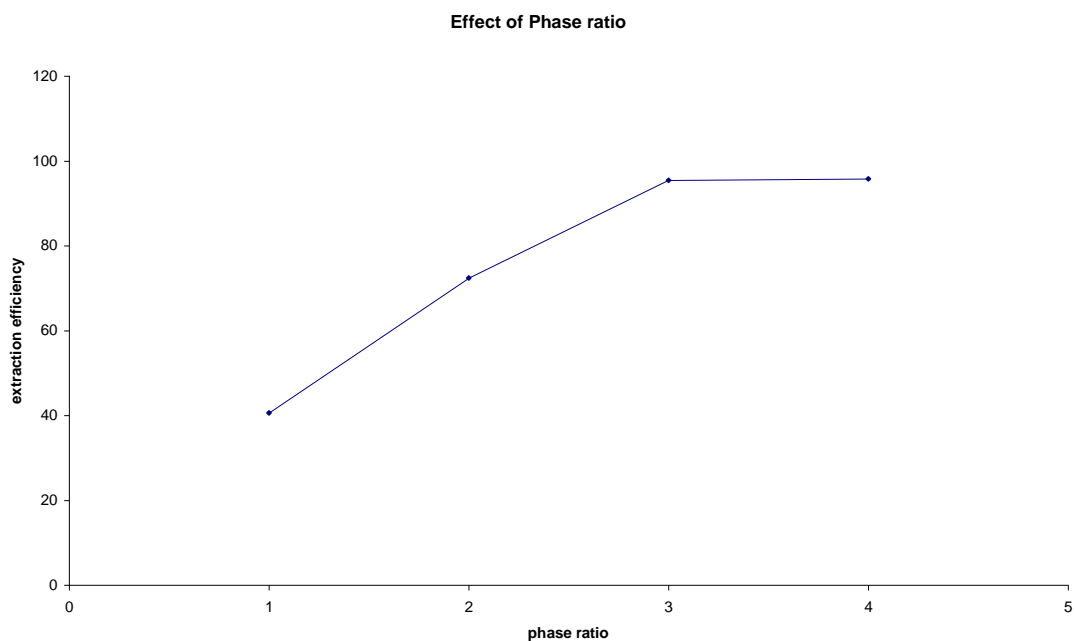
Effect of Phase ratio

Figure (9) Effect of solid/solvent ratio for solvent leaching of acid cured phosphate ore from Abu-Tartur with 15% primene jmt in kerosene.

Effect of number of contact on solvent leaching

The number of times of passing solvent through the cured ore s to get saturation of the solvent with rare earth elements; in other words ores is nearly depleted or solvent was loaded with maximum amount of rare earth elements from the ore sample that it can be loaded were studied. Solvent is passing several times (1 – 6) through ores till solvent saturation while other solvent leaching parameter as 1:3 phase ratio, 15% primene jmt in kerosene and 1 ml/min as flow rare. figure (10) illustrated that 5 times of contact is the optimum condition till solvent completely saturated with rare earth elements from cured phosphate ores with extraction efficiency 95 %.
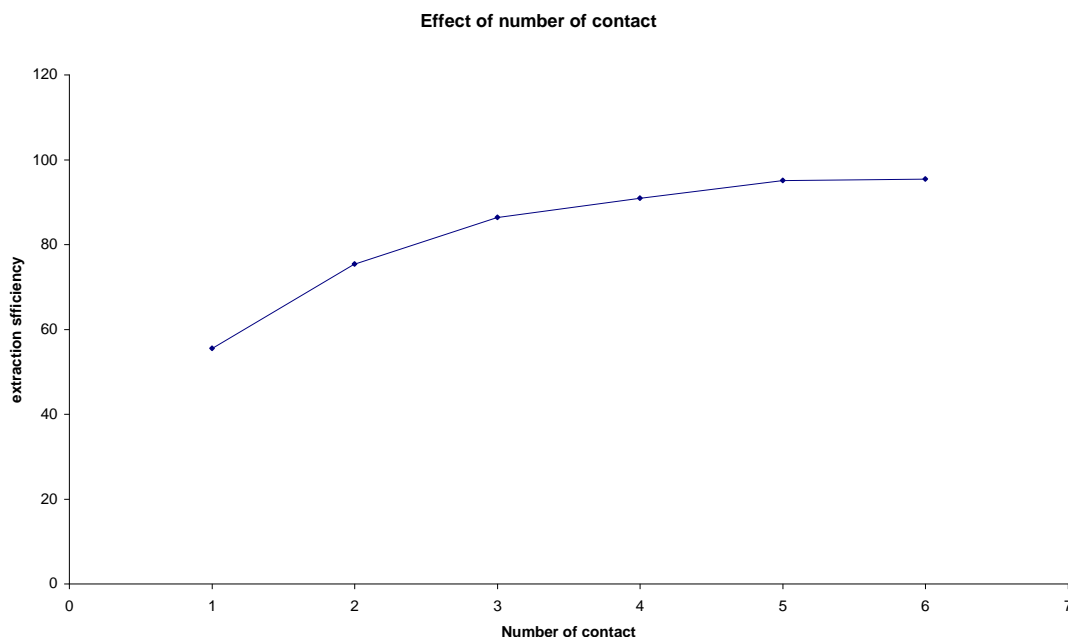
Effect of number of contact

Figure (10) Effect of number of contact solvent leaching of acid cured phosphate ore from Abu-Tartur with 15% primene jmt in kerosene.

Stripping process

The stripping conditions such as stripping agent type, concentration of stripping agent, phase ratio and shaking time were studied.

Effect of the stripping agent

Four stripping agent were used such sodium carbonate, hydrochloric acid, nitric acid and sulfuric acid at the following concentrations 3M. The stripping efficiency was calculated by measuring the concentration of the rare earth elements in the aqueous phase, the results were shown below in fig (11) showed that 3M of HNO_3 has the highest solvent leaching efficiency 69.3 % whereas H_2SO_4, HCl and Na_2CO_3 results was 30%, 36.6%, 18.2% respectively.
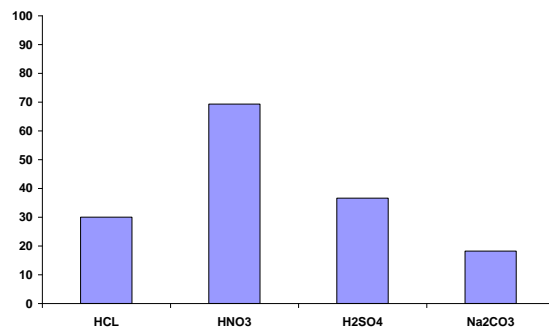
Figure(11) Effect of type of stripping agent for rare earth elements that loaded on primene jmt from solvent leaching of acid cured phosphate ore Abu-Tartour plateau.

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Effect of nitric acid concentration

To study this effect different concentrations of nitric acid ranged from (1- 10) used at the following operating conditions phase ratio 1/2 (O/A) and shaking time 10 min. stripping efficiency of rare earth elements from the loaded organic solvent reached about 53.2% the results were shown below in fig (12). The stripping efficiency increases as the concentration of nitric acid increased from (1-3) Mafter that it remained constant. And so no 3 M nitric acid was the optimum conditions. whereas stripping at 10 M nitric solvent (primene jmt 15 % in kerosene) is damaged and could not be regenerated again.
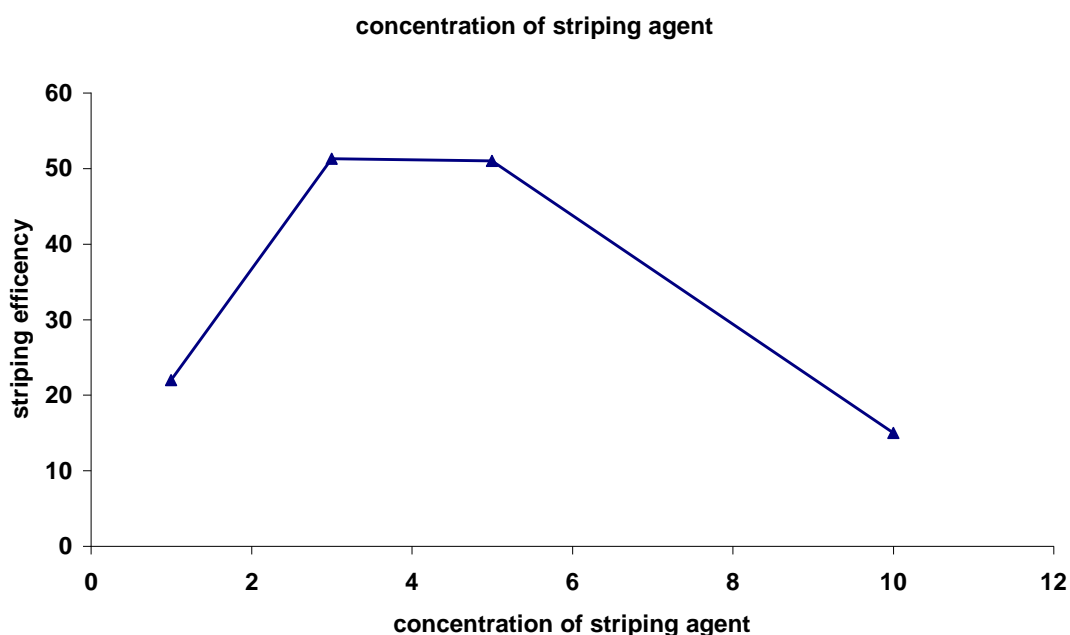
concentration of striping agent

Figure (12) Effect of concentration of nitric as stripping agent for rare earth elements that loaded on Primene JMT from solvent leaching of acid cured phosphate ore Abu-Tartur plateau.

Effect of phase ratio

In order to study the effect of aqueous/organic phase ratio upon the stripping efficiency of the rare earth elements from the loaded organic solvent. A series of stripping experiments were performed using different A/O ratios ranging from 1/4 - 4/1. The other stripping conditions were fixed at 3M nitric acid concentrations and shaking time 10 min. the results shown below in fig (13). Results showed that the stripping efficiency increases from 1/1 (A/O) till reach (3/1) (A/O) after that it remained almost constant. And so on (3/) (A/O) colud be considered as the optimum phase ratio.
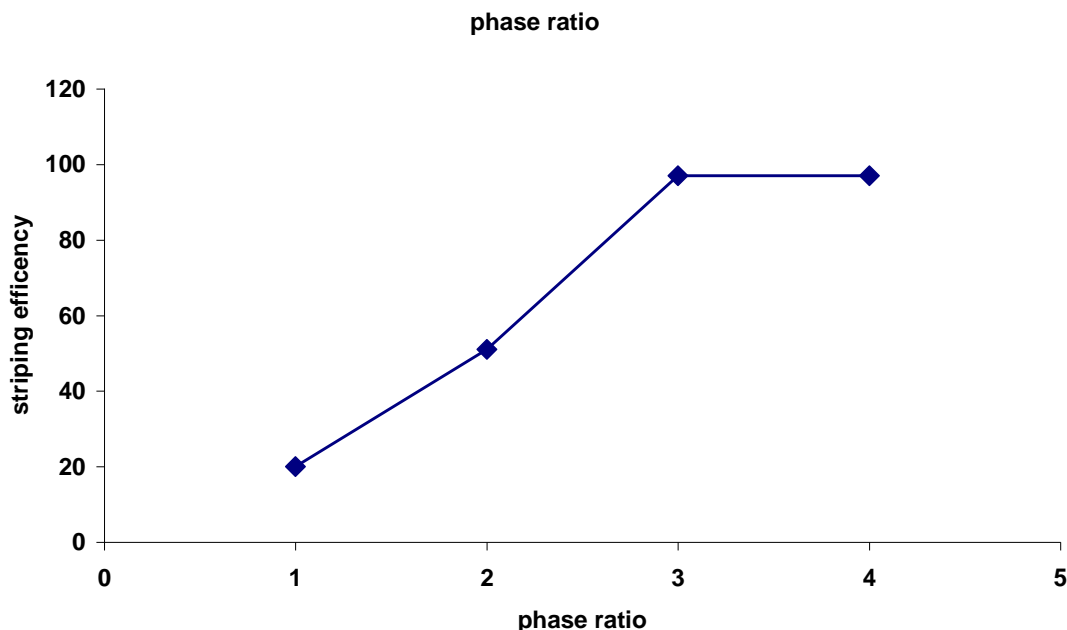
phase ratio

Figure (13) Effec of A/O Phase Ratio upon rare earth elements Stripping from loaded 15% primene jmt in kerosene from phosphate ore Abu-Tartur plateau.

Effect Of Shaking Time

the effect of shaking time upon rare earth elements stripping efficiency from the loaded organic solvent was studied using the following conditions 3 M nitric acid and phase ratio 3;1 A/O. shaking time was varied from (2- 20) minute applied for optimization the best shaking time for stripping process. The results shown below in fig (14) revealed that 2 minute was needed to get 38.2 % stripping efficiency of rare earth elements this is gave rise to 90.1% stripping efficiency of rare earth elements at 5 minute also reached 97.2% at 10 min. shaking time where it reached 99.8 % (stripping efficiency) at 15 min shaking time which was the same at 20 min shaking time. And so on 15 min was the optimum shaking time.
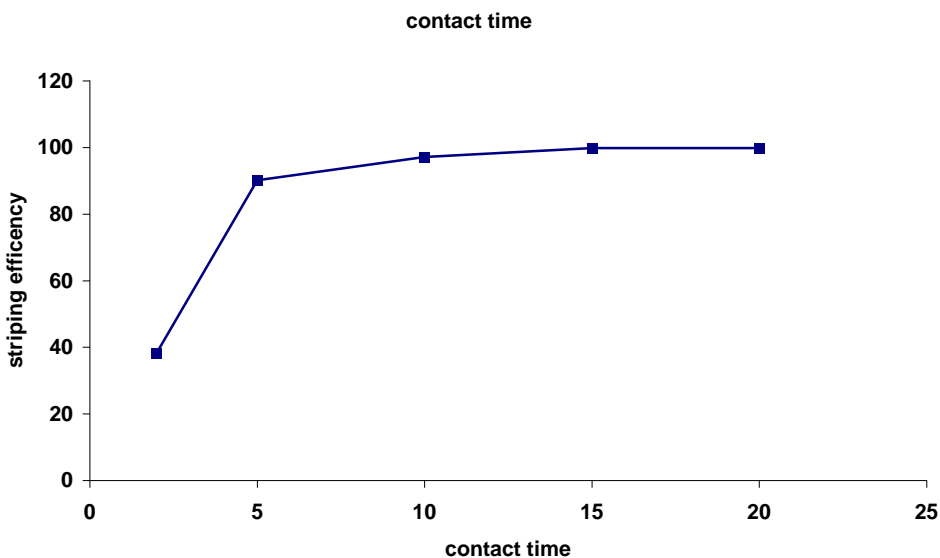
contact time

Figure (14) Effect of shaking time for stripping of rare earth elements that loaded on primene jmt from solvent leaching of acid cured phosphate ore Abu-Tartur plateau.

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Conclusion

Rare earth elements extracted from Abu-Tartur phosphate rock. Different stages were applied till reached extraction efficiency 95.4%. ore was subjected to acid curing with sulfuric acid (500 kg/t) ore, nitric acid 10 % relative to amount of sulfuric acid for 2h at 110°C. solvent leaching conditions was applied such as 15 % primene jmt in kerosene, flow rate 1 ml/min, solid/organic phase ratio 1:3 and with 5 number of contact. Stripping conditions applied 3 M nitric acid, 1:3 O/A phase ratio and 10 min shaking time which yielded 99.8 % stripping efficiency fig (15) is showing flow sheet for curing, solvent leaching and stripping process .
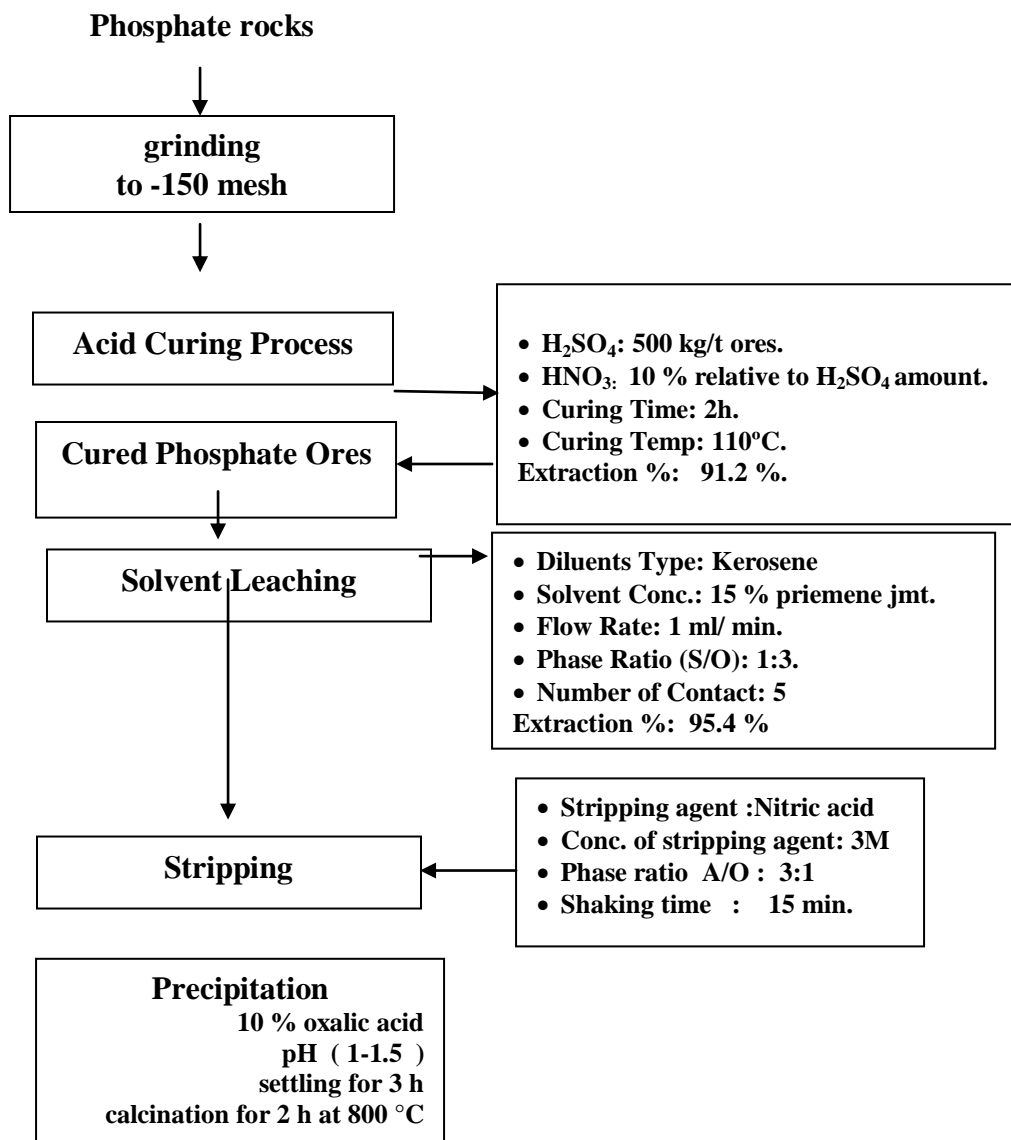
Phosphate rocks

**grinding
to -150 mesh**

Acid Curing Process

- H_2SO_4: 500 kg/t ores.
- HNO_3: 10 % relative to H_2SO_4 amount.
- Curing Time: 2h.
- Curing Temp: 110°C.

Extraction %:   91.2 %.

Cured Phosphate Ores

Solvent Leaching

- Diluents Type: Kerosene
- Solvent Conc.: 15 % priemene jmt.
- Flow Rate: 1 ml/ min.
- Phase Ratio (S/O): 1:3.
- Number of Contact: 5

Extraction %: 95.4 %

Stripping

- Stripping agent :Nitric acid
- Conc. of stripping agent: 3M
- Phase ratio A/O : 3:1
- Shaking time   :   15 min.

**Precipitation
10 % oxalic acid
pH（1-1.5）
settling for 3 h
calcination for 2 h at 800 °C**

Figure (15): Proposed Flow sheet for Rare earth elements recovery from Abu-Trtur phosphate rocks.

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