ISSN NO. 2320-5407

Journal Homepage: - www.journalijar.com

INTERNATIONAL JOURNAL OF
ADVANCED RESEARCH (IJAR)

Article DOI: 10.21474/IJAR01/1548
DOI URL: http://dx.doi.org/10.21474/IJAR01/1548

RESEARCH ARTICLE

LEACHING AND RECOVERY OF RARE EARTH ELEMENTS FROM ALTERED ALKALINE GRANITE ROCK FROM NUSAB EL-BALGUM AREA, SOUTH WESTERN DESERT, EGYPT.

Taysser A. Lashen[1], Saeyda A. Mohamed[2], Mohamed F. Cheira*[1], Doaa I. Zaki[1] and Eman M. Allam[1].
1. Nuclear Materials Authority, P.O. Box 530 El Maadi, Cairo, Egypt.
2. Chemistry Department, Faculty of Science, Menoufiya University, Egypt.

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Manuscript Info

Manuscript History

Received: 12 July 2016
Final Accepted: 13 August 2016
Published: September 2016

Key words:-
Rare earth, Leaching, Hydrochloric acid, Thermodynamics, Separation, Three-liquid-phase system.

Abstract

Leaching and recovery parameters controlling the releasing of rare earth elements from Nusab El-Balgum altered alkaline granite rock are studied and determined. The optimum conditions of batch leaching are attained at 3 M of HCl concentration, 200 rpm stirring speed and 1/6 solid to liquid ratio for 180 min contact time at room temperature. Under the optimized conditions, the ∑REEs leaching efficiency was 92.4%. The thermodynamic data showed positive values of both ΔH and ΔS which indicates that the leaching process is indeed endothermic and random while the obtained negative values of ΔG indicate that REEs dissolution process is spontaneous in nature. Three-liquid-phase system (Cyanex 272/PEG 2000/$(NH_4)_2SO_4$–H_2O) is employed for rare earths separation from associated impurities in the obtained leach liquor. The relevant factors controlling and selective enrichment of those ions in aqueous salt phase are investigated. The optimized conditions are occurred at pH 2, 3g of PEG, and 1.6 M of $(NH_4)_2SO_4$. Separation of REEs ions from bottom aqueous phase after removal of impurities is achieved and precipitated by adding oxalic acid.

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Introduction:-

Rare earth elements (REEs) have unique physicochemical properties that have led to their application in wide range of high-value market sectors including phosphors, optical glass, lasers, advanced ceramics, capacitors, metal alloys, critical military applications, nuclear and the manufacturing of high intensity magnets[1,2]. Since REEs have become an indispensable part of modern life, their extraction procedures now hold huge importance[3]. Actually, the rare-earth deposits are associated with of several rock types and in some mineral concentrate[4-5]. They occur in low concentrations of few mg/kg in many rock formations and their major minerals, such as bastnaesite, monazite, allanite, gadolinite and xenotime[6]. These minerals occur in concentrations of 5-10% in carbonatites formations, iron ores and phosphate rocks[7].

Numerous studies have been reported on the leaching of REEs using mineral acids and their salts solutions. The choice of leaching agent depends on the selectivity in the separation of rare-earth elements, type of gangue minerals in the ore and the type of the reagents to be used in the further extraction procedures[8-14]. In this context ion-adsorption clays are leached with concentrated inorganic salt solutions of monovalent cations. The physisorbed REEs are relatively easily and selectively desorbed and substituted on the substrate by these ions and transferred into

Corresponding Author:- Mohamed F. Cheira.
Address:- Nuclear Materials Authority, P.O. Box 530 El Maadi, Cairo, Egypt.

solution as soluble sulfates or chlorides[15]. Ammonium chloride and ammonium nitrate were used as a mixed leachate to treat weathered deposited rare earth ores[16]. Other researchers suggested magnesium sulfate as leaching agent for ion-adsorption type rare earth ore to reduce or even eliminate ammonia-nitrogen emissions[17,18]. On the other hand releasing of rare earth ions from a mineral concentrate containing minerals require severe conditions to destroy their structure. Xue et al., reported that the hydrochloric acid leaching process of the activated bastnaesite occurred at 90 ℃ leaching temperature and 20:1 liquid to solid ratio[19]. In fact, leaching ores by HCl are environmentally beneficial for those containing bastnaesite.

Solvent extraction and ion-exchange techniques have been reported to produce high purity single rare earth element solutions or compounds. In this context, several extractants have been suggested with various ligands[20-29]. Also, commercial ion exchangers in the hydrogen, sodium and chloride forms that are available under the trade names of Amberlite, Duolite, Dowex, Ionac, and Purolite are used for extraction of REEs. These techniques have the advantage of allowing the recovery of the metallic ions, but they are expensive and sophisticated[30-36].

Three-liquid-phase system (TLPS) is a process for simultaneous extraction and separation of multiple target components even with slight differences in physicochemical properties. In a well-designed TLPS, multiphase extraction and selective separation of different components respectively into three different liquid phases can be achieved by only one-step of extraction[37]. TLPE is composed of an organic solvent-rich top phase, a polymer-rich middle phase and a salt-rich bottom phase. According to the strategy developed by Sui et al., it is possible to separate REEs in groups and also from undesirable ions by this approach[38]. They concluded that most of the rare earths in their solutions remained in salt-rich bottom phase due to the formation of hydrophilic complexes between them and complexing agents. On the basis of this data, it could be separate and recover ∑REEs in relatively pure form by controlling variant parameters whereas the obtained leach liquor containing about 90% light rare earth ions.

The current work aimed to study the leaching and recovery parameters of total REEs from Nusab EI Balgum altered alkaline granite rock sample. The leaching parameters included the type of leaching agents, the concentration of hydrochloric acid, agitation time, solid/liquid ratio, stirring rate, grain particle size and leaching temperature are studied. The leaching performance of total iron which is the primary impurity ion in the leachate is also investigated. In addition, thermodynamic parameters of the leaching process are also determined. Recovery of total REEs from the obtained leach liquor is carried out using the three-liquid-phase system. The effect of acidity, concentration of ammonium sulfate and the suitable amount of polyethylene glycol are determined.

Materials and methods:-

Characteristic of working sample:-

The studied sample is obtained from Nusab EI Balgum area, in the central southwestern desert of Egypt. The area is bounded by latitudes 23° 15/ to 23° 20/ N and longitudes 29° 15/ to 29° 20/ E. It covers about 40 km^2 and forms the northern part of Bir Safsaf area. It consists mainly of sandstone, volcanic rocks, altered granitic. The working sample is firstly subjected to preparation through crushing, grinding and sieving followed by proper quartering, then analyzed quantitatively after complete dissolution using the suitable techniques.

Reagents:-

The chemicals and reagents used in this work are of the analytical grade in all experiments, double-distilled water was used for aqueous solutions preparation and dilution. The main chemicals used in this work are hydrochloric acid 37% obtained from Adwic, ascorbic acid from Sigma-Aldrich, formic acid from Prolabo and Arsenazo III from BDH, England. Bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272, purity of 85 wt%) is supplied by Sigma, polyethylene glycol (PEG) with average molecular weight of 2000 is purchased from Loba Chemie. The stock solution of $(NH_4)_2SO_4$ salt is prepared by dissolving an appropriate amount of $(NH_4)_2SO_4$ in double distilled water, ethylene diamine tetraacetic acid (EDTA) is supplied from Loba Chemie and 1,10- phenanthroline (phen) is obtained from Sigma-Aldrich.

Analytical methods:-

The mineralogical analyses of working sample are assayed by X-ray Diffraction analysis (XRD), which is used to determine bulk mineral assemblages based on the diffraction of X-rays interacting with a rock sample. The quantitative analysis of the studied sample after its digestion is then carried out for the determination of the major oxides and trace elements. The major oxides SiO_2, Al_2O_3 and TiO_2 have been spectrophotometrically analyzed using Unicam UV2-100 UV/Vis spectrometer according to standard methods of analysis while Na and K oxides have determined by the flame photometric technique. The Fe_2O_3, MgO and CaO have however been titrimetrically determined[39]. In the meantime, the concentration of the trace elements in the working sample has been determined through the inductively coupled plasma optical emission spectrometry (ICP-OES). The ∑REEs concentration in the leachate solution is spectrophotometrically determined by Arsenazo III at 650 nm[40]. All analysis is repeated 3 times for each sample.

Leaching procedure:-

Studies of acid leaching experiments are conducted to achieve the goal of dissolving maximum REEs constituents under optimum conditions with the minimum dissolution of the other undesirable gangues. The leaching experiments are carried out in a 500 mL beaker at different acid types, concentrations of HCl acid ranging from 0.5 to 5 M, solid to liquid ratio (1/1 - 1/8), leaching time (up to 300 min), stirring rate (100 - 350 rpm), grain size (40 - 200 mesh) and temperature (25 - 80 °C) of the solution on the extent of dissolution of metal species. In order to monitor the progress of leaching samples are taken out at different parameters and analyzed. At the end of leaching, the residue is filtered and washed with distilled water. The concentrations of leachable metal ions in the obtained liquor are quantitatively analyzed.

Three-liquid-phase extraction:-

Prescribed volumes of the prepared leach liquor are placed in graduated centrifuge tubes. The phase-forming reagents are the organic extractant (Cyanex 272 in the top), polymer (PEG 2000 in the middle) and inorganic salt $(NH_4)_2SO_4$ in the bottom). The complexing agents such as EDTA and 1,10 phenanthroline are added at room temperature. The pH value of the aqueous solution is adjusted by adding either dilute NaOH solution or HCl acid. The loaded tubes are then shaken for 10 min on a mechanical shaker to ensure complete mixing. The separation of each phase is enhanced by centrifugation for 30 min at a speed of 4000 rpm. After separation, phase volumes are measured and the concentrations of ∑REEs in the bottom phase are analyzed.

Results and Discussion:-

Characterization of working sample:-

The representative sample is subjected to complete chemical analysis using the mentioned procedures and the obtained results are shown in Table (1). From these results, it is clearly evident that the concentration of silica, alumina, Fe_2O_3, K_2O and CaO are assaying 72.2, 3.4, 16.8, 1.4 and 0.59% respectively. Individual analysis of REEs concentrations by ICP-OES technique are given in Table (2) that refer to an enrichment of light REEs than heavy REEs. These results agree with X-ray powder diffraction (XRD) identification (Figure 1) whereas bastnaesite mineral incorporated REEs. Bastnaesite found as solid solutions adsorbed on quartz and iron oxides and not found as separated mineral[41]. Besides, the silicon minerals seem as quartz. The total REE concentration is around 0.34 wt%.

Table 1:- Chemical analysis of the working sample.

Oxide	Wt.,%	Trace element	mg/L
SiO_2	72.2	**U^{6+}**	74
Al_2O_3	3.4	**∑REEs**	3451
TiO_2	0.45	**Ba^{2+}**	135
Fe_2O_3	16.8	**Pb^{2+}**	23
MnO	0.27	**Cr^{3+}**	10
MgO	0.28	**Cu^{2+}**	7
CaO	0.59	**Ni^{2+}**	16
K_2O	1.4	**Cd^{2+}**	7
Na_2O	0.1	**Sr^{2+}**	20
P_2O_5	0.53	**Co^{3+}**	12
L.O.I*	3.11	**Zn^{2+}**	592

*Total Loss of Ignition at 1000 ^{0}C

Table 2:- Chemical analysis of individual REEs of the working sample.

Metal ion	mg/L	Metal ion	mg/L
La^{3+}	517	**Dy^{3+}**	77
Ce^{3+}	1200	**Ho^{3+}**	16
Pr^{3+}	166	**Er^{3+}**	34
Nd^{3+}	942	**Tm^{3+}**	5
Sm^{3+}	288	**Yb^{3+}**	47
Eu^{3+}	10	**Lu^{3+}**	4
Gd^{3+}	59	**Sc^{3+}**	23
Tb^{3+}	13	**Y^{3+}**	50

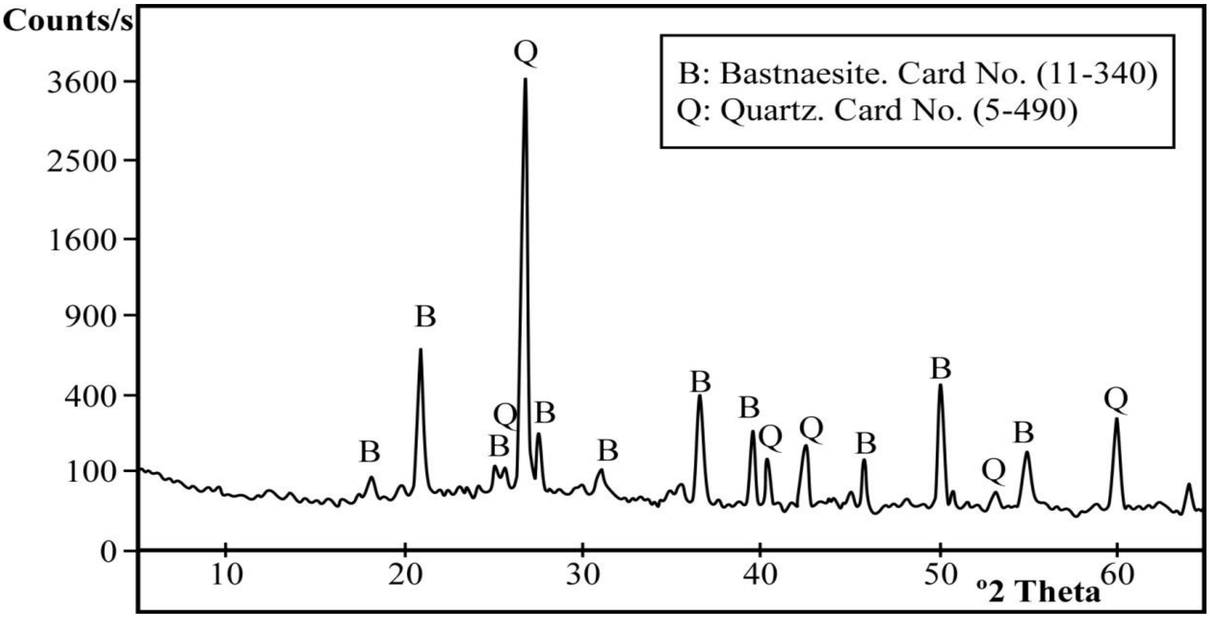

Figure 1:- XRD pattern of the working sample.

Optimization of leaching parameters:-

Effect of acid type:-

The effect of the acid type upon the REEs leaching efficiency from the powdered sample is tested using 3M of H_2SO_4, HNO_3 and HCl under the 1/3 solid/liquid ratio, 80 mesh particle size, 200 rpm stirring rate for 60 min agitation time at room temperature. Under these mentioned conditions, the ∑REEs leaching efficiencies are 24.70, 28.22 and 66.00% while the iron dissolution efficiencies are 9.30, 10.78 and 13.63% for H_2SO_4, HNO_3 and HCl respectively. The latter results are graphically represented in Figure (2), as can be seen the use of HCl attains the higher dissolution efficiency (66.00%) than the other two acids. Moreover, processing of ore bearing bastnaesite is more favorites with HCl than H_2SO_4 to avoid fluoride emission, it causes series air pollution. Also, it is interesting to mention here that the choice of HCl as leachant is very useful for further procedure suggested for recovery of total REEs. Therefore, it is the preferred choice for the next experiments of leaching process.

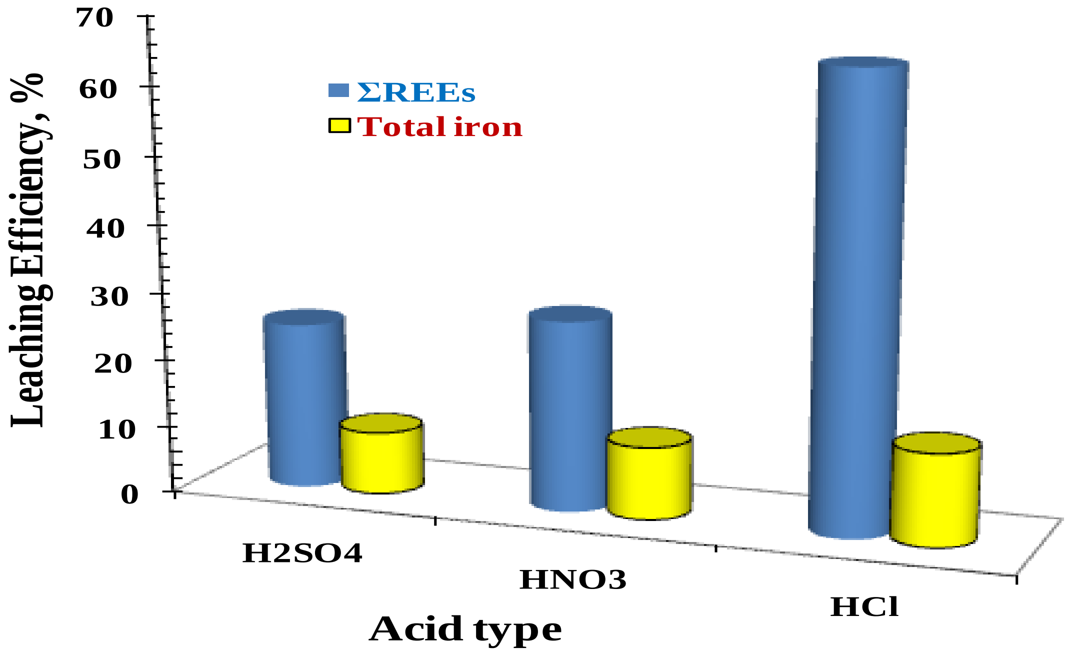

Figure 2:- Effect of acid type on the leaching efficiencies of ∑REEs and total iron.

Effect of hydrochloric acid concentration:-

A series of experiments are performed to determine the optimum concentration of HCl for the total REEs leaching from the studied sample. The concentration is varied from 0.5 to 5 M under the conditions of 80 mesh particle size, 1:3 S/L ratio and 200 rpm stirring rate for 60 min leaching time at ambient temperature. The results of the obtained leaching data are graphically represented in Figure (3). It shows an increase in the leaching efficiency of ∑REEs from 15.33 to 66.08% with increasing the acid concentration from 0.5 to 3 M HCl. The increase of acid consumption from 3 to 5 M, more the undesirable impurities are dissolved, especially iron species that lead to serious defects in the purity of the final product.

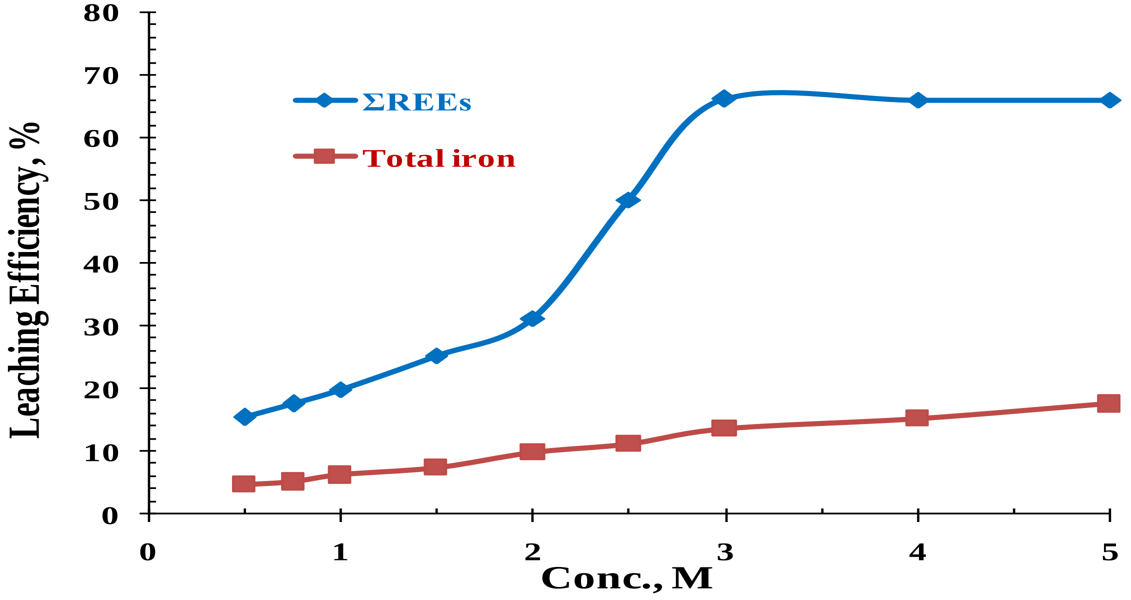

Figure 3:- Effect of HCl concentration on the leaching efficiencies of ∑REEs and total iron.

Effect of agitation time:-

The effect of agitation time on REEs releasing from sample material is studied from 30 to 300 min under the constant conditions at 80 mesh, 3M HCl, 1:3 S/L ratio and 200 rpm agitating rate at ambient temperature. The obtained results in Figure (4), indicates that maximum dissolution of REEs (75.20%) occurred after 180 min, above this period there is no increase in the solubility of REEs.

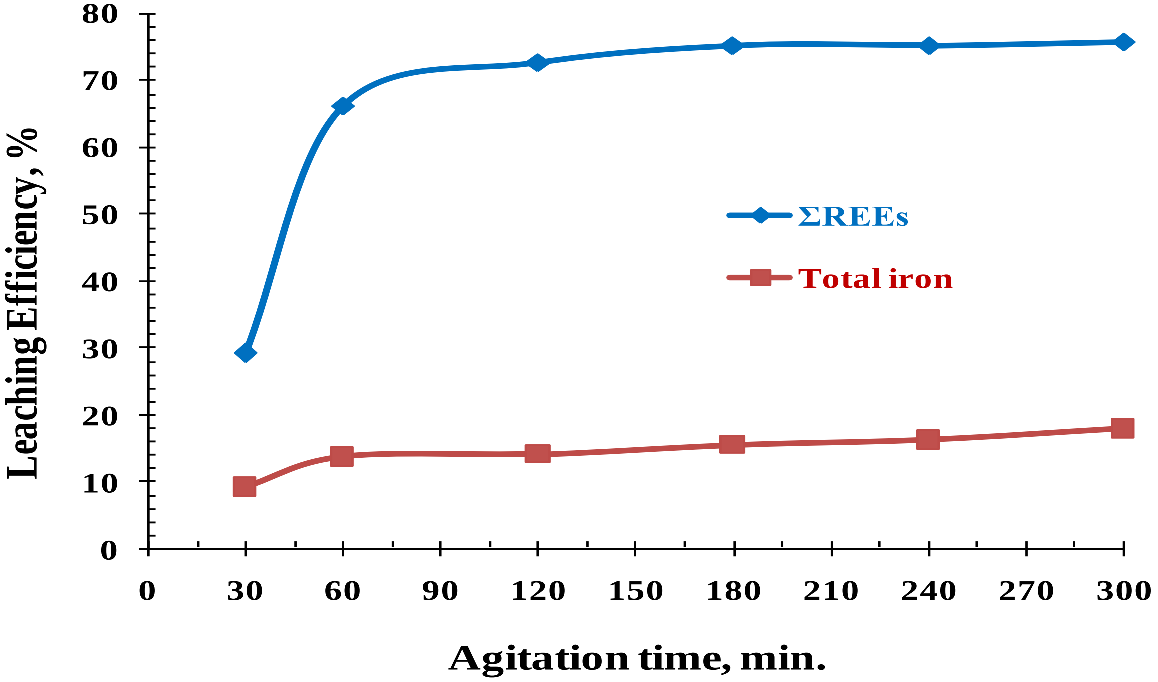

Figure 4:- Effect of agitation time on the leaching efficiencies of ∑REEs and total iron.

Effect of solid/liquid ratio:-

The effect of solid/liquid (S/L) ratio from 1/1 to 1/8 is studied under the other optimized conditions. The obtained results are featured in Figure (5) indicate that the leaching efficiency of total REEs is increased from 39.91% to 92.24%. In the main time, the iron solubility increased from10.02 to 15.50%. Thus, the optimum ratio used for the subsequent experiment is 1/6.

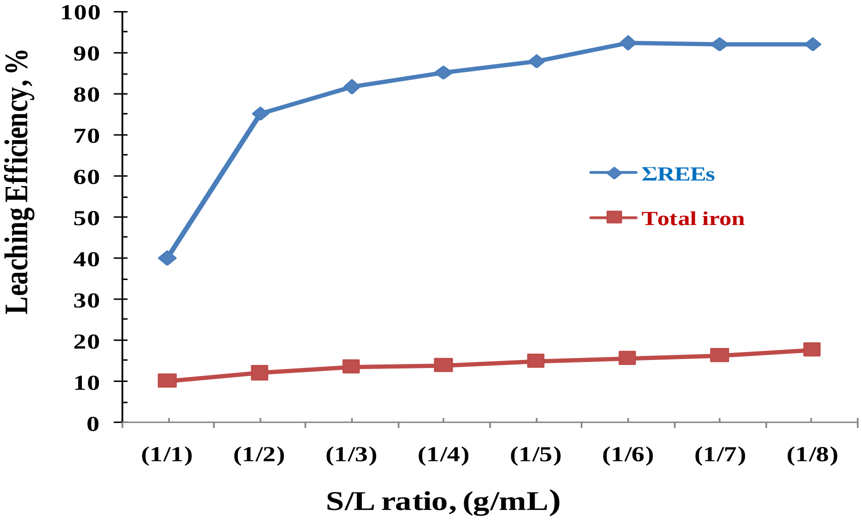

Figure 5:- Effect of solid/liquid ratio on leaching efficiencies of ∑REEs and total iron.

Effect of stirring rate:-

The effect of stirring rate on the ∑REEs leaching efficiency is investigated from 100 rpm to 350 rpm under the previous recommended conditions. The obtained data indicates that the leachability of REEs is increased from 73.31 to 92.24% as the stirring speed increased from 100 to 200 rpm but it remains almost constant above 200 rpm (Figure 6). Increasing the stirring rate more than the latter value leads to more iron releasing in the leach liquor. Therefore, the chosen stirring rate is 200 rpm for the subsequent tests.

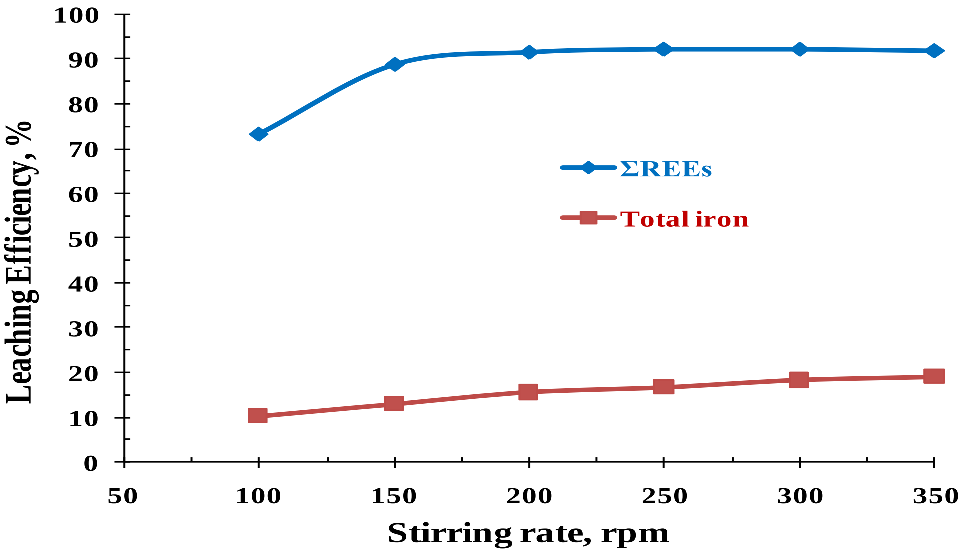

Figure 6:- Effect of stirring rate on leaching efficiencies of ∑REEs and total iron.

Effect of the grain particle size:-

The effect of changing grain particle size is studied from 40 to 200 mesh sizes under the previous optimum conditions. The obtained results for total REEs and total iron leaching efficiencies are illustrated in Figure (7). It is found that the ∑REEs leaching efficiency increases by decreasing the particle size from 40 to 80 mesh. On this regard, the leaching efficiency is increased from 44.25 to 92.4%, while the leaching efficiency of iron is increased from 3.75 to 15.5%. It is worthy to mention that more grinding would increase the dissolution of the most amounts of gangue constituents as well as increase the complication of the filtration and the washing steps, in addition to the costs of the grinding step itself. Thus, the particle size of 80 mesh is considered the preferred particle size to perform the leaching process.

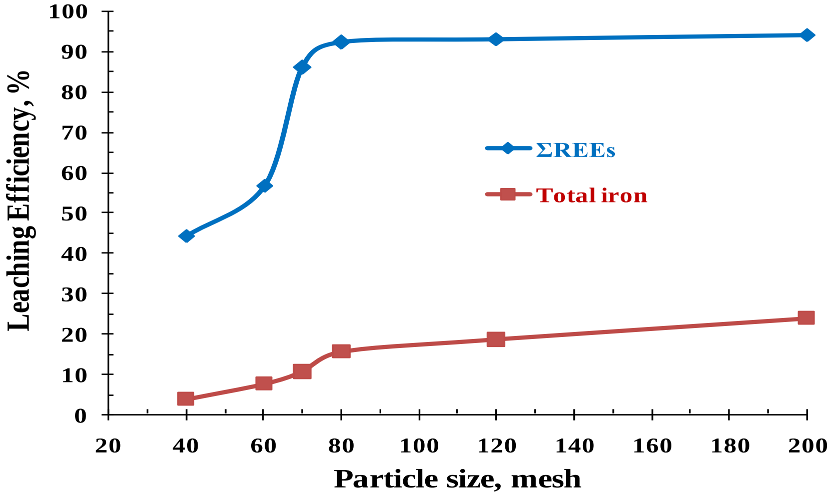

Figure 7:- Effect of grain particle size on leaching efficiencies of ∑REEs and total iron.

Effect of leaching temperature:-

The effect of leaching temperature is examined in the range from 25 to 80 °C under the constant conditions of 3 M HCl concentration, 200 rpm stirring speed and 1/6 solid to liquid ratio for 180 min contact time. From the obtained results (Table 3), it is found that the leaching efficiency of ∑REEs is slightly increased from 92.4 to 95.5% with increasing the leaching temperature from 25 to 80 °C respectively. Besides, the iron leaching efficiency is increased with increasing the temperature. Therefore, the leaching temperature of 25 °C is chosen in actual production to avoid the rare earth ions hydrolysis and economize the operating cost.

Table 3:- Effect of temperature on the leaching efficiencies of ∑REEs and total iron.

	Leaching efficiency, %	
Temperature, °C	**∑REEs**	**Total iron**
25	92.4	15.3
30	92.7	16.7
40	93.5	18.4
50	94.2	19.3
60	94.8	21.4
70	95.0	23.3
80	95.5	25.2

Thermodynamic leaching studies:-

The acidic leaching of REEs and total iron from the working sample are thermodynamically studied to explore the feasibility and spontaneity of the leaching process through the determination of thermodynamic parameters. The thermodynamic parameters are calculated from the variation of the thermodynamic distribution coefficient K_d with a change in temperature according to the following equation:

$$K_d = \frac{C_L}{C_S}$$

where C_L and C_S are the amounts of metal ions in leaching solution (mg) and the solid sample (mg) at equilibrium (mg metal/kg solid sample), respectively. The thermodynamic parameters including the Gibbs free energy ΔG (kJ/mol), the enthalpy ΔH (kJ/mol) and the entropy ΔS (J/mol.K) are calculated for this system using the following Van't Hoff equations[42].

$$\log K_d = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}$$

$$\Delta G = \Delta H - T\,\Delta S$$

where R is the universal gas constant (8.314 J/mol.K) and T is temperature (K). Accordingly, the values of both the enthalpy ΔH and the entropy ΔS are calculated from the slope (-ΔH/R) and intercept (ΔS/R) of the Log K_d versus 1/T plot (Figure 8). From the obtained data, the values of R^2 of thermodynamic model are near to unity, indicating a good linearity. The values of ΔH, ΔS and ΔG for leaching process are obtained and reported in Table (4). It has to be mentioned in this regard that the enthalpy change values (ΔH) are found to be positive +8.93 and +9.45 kJ/mole for ∑REE and total iron respectively, confirmed the endothermic nature of the acid leaching of these species from the working sample while the positive values of entropy change (ΔS), +50.74 and +17.65 J/(mole.K) for ∑REEs and total iron respectively, suggested an increase in randomness due to the leaching of the metal ions from the studied sample. The positive values of Gibbs free energy of iron ions impurities would be expected the non-spontaneous reaction. On the other hand, the negative values of ΔG of the ∑REEs leaching would be expected for a product-favored and spontaneous reaction, indicating the high affinity of the metal ions towards the acidic leaching solution and the spontaneity of the leaching process.

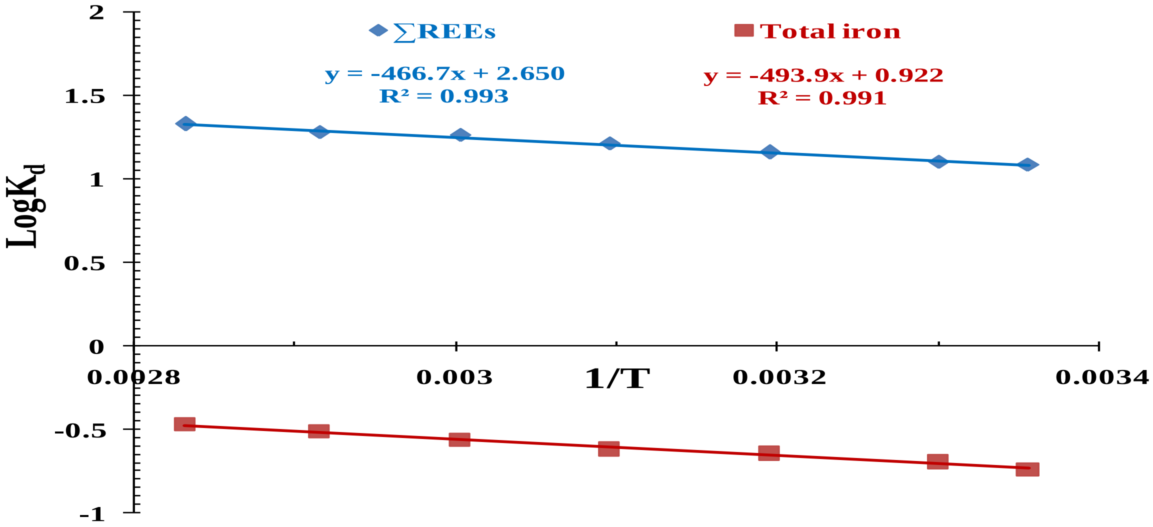

Figure 8:- Plot of Log K_d versus 1/T (K^{-1}) for REEs and total iron leaching.

Table 4:- Thermodynamic parameters for ∑REEs and total iron leaching from the studied sample using acidic leaching agent.

Metal ions	ΔH (KJ/mol)	ΔS J/(mol K)	ΔG (KJ/mol)						
			298 K	**303K**	**313 K**	**323K**	**333K**	**343K**	**353K**
∑REEs	8.93	50.74	-6.19	-6.44	-6.95	-7.46	-7.96	-8.47	-8.98
Total iron	9.45	17.65	4.19	4.10	3.92	3.78	3.57	3.39	3.22

Preparation of leach liquor:-

A leach liquor is prepared by treating 1 kg of 80 mesh size properly ground sample with 6 liters of 3 M hydrochloric acid solution for 180 min and agitated at room temperature. The insoluble gangue residue is then filtered and the obtained leach liquor is found to assay 532 mg/L of total REEs indicating a leaching efficiency of 92.4%. The complete chemical analysis of leach liquor using the mentioned procedures is shown in Table (5).

Table 5:- Chemical analysis of the working leach liquor.

Metal ions	g/L	Metal ions	mg/L
Si^{4+}	8.3	U^{6+}	7
Al^{3+}	1.3	∑REEs	532
Ti^{4+}	0.1	Ba^{2+}	19
Fe^{3+}	4.3	Pb^{2+}	5
Mn^{2+}	1.6	Cr^{3+}	6
Mg^{2+}	0.06	Cu^{2+}	3
Ca^{2+}	0.12	Ni^{2+}	16
K^{+}	0.23	Sr^{2+}	4
Na^{+}	0.08	Co^{3+}	3
P^{5+}	0.38	Zn^{2+}	66

Three-liquid-phase extraction studies:-

In this study, the three-liquid-phase extraction approach composed of Cyanex 272/PEG 2000/ $(NH_4)_2SO_4$–H_2O which is used to remove impurities from the working leach solution which contains total REEs by controlling partitioning and selective enrichment of those impurities and rare earths in the three-liquid-phase system.

Factors affect on the partition of REEs in TLPS:-

Effect of pH:-

The effect of partition of ∑REEs in salt-rich bottom phase of TLPS versus aqueous pH value is carried out within the pH range from 1 to 3 to avoid Fe (III) and Al (III) hydrolysis. The obtained result plotted in Figure (9), indicates that the partition of ∑REEs in bottom phase increased with the increase of pH value up to 2 then decreased. It might be due to partition of some rare earth ions in other phases. Actually, the distribution of rare earth ions in three phases depends mainly on pH value and complexing behavior of the used extractants.

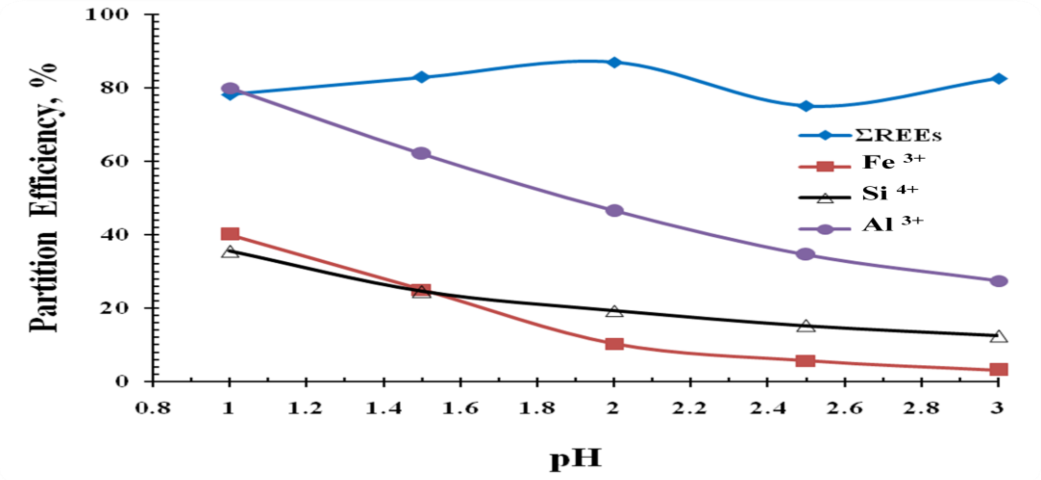

Figure 9:- Effect of pH value on the partition of Fe, Al, Si ions and ∑REEs in the bottom phase of TLPS.

Influence of 1, 10- phenanthroline and EDTA addition to TLPS:-

Addition of 1, 10- phenanthroline (phen) and EDTA (1/1) into the TLPS are shown to be effective in enhancing the separation of impurities onto polymer-rich middle phase. On addition of phen and EDTA into the leach liquor in presence of reducing agent (hydroxyl amine hydrochloride), an enrichment of iron (II) and Al (III) into the PEG-rich phase are observed. In fact, the complexing stability of Fe(II)-phen is higher than Fe(II)-Cl chelate, thus, phen is reported as an effective complexing agent for iron species. The extraction of Fe(II) is due to the interaction of Fe(II)–phen complexes with active C-O-C groups in PEG molecular chains. However, the addition of phen has no impact on the partition behavior of Al(III), it is due to weaker complexing ability of phen with Al(III) compared to that with Fe(II). Complexation of Al(III) with EDTA is strongly dependent on aqueous pH value. The interaction of Al(III)–EDTA chelates with PEG molecular chains enables the transfer of Al ions from salt-rich. The influence of addition of phen and EDTA on the partition of REEs, Fe, Al and Si ions ions in bottom TLPS are illustrated in Figure (10). As shown the partition efficiencies of Fe, Al and Si impurities are decreased with increasing the concentration of both phen and EDTA until 200 mmole while the partition efficiency of ∑ REEs is not affected.

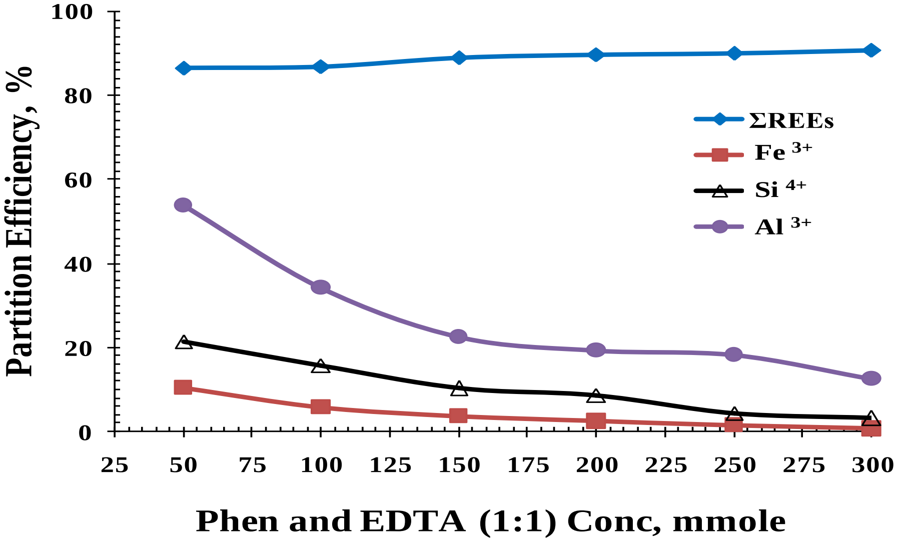

Figure 10:- Influence of the addition of phen and EDTA on the partition of ∑REEs, Fe, Al and Si ions in bottom phase of TLPS.

Effect of PEG 2000 amount:-

The effect of partition of total REEs with the added amount of PEG 2000 is illustrated in Figure (11). From the obtained results, it is clearly evident that the partition of total ∑REEs in the bottom salt-rich phase of TLPS varied with increase of PEG 2000 up to 3 g, more increase than this value has no effect on the partition of ∑REEs in the latter phase. The increase of PEG 2000 could lead to the transfer of H_2O molecules from salt-rich phase to PEG–rich phase, which in favor of the transferring of hydrophilic complexes making discordancy in the partition of ions in three phases.

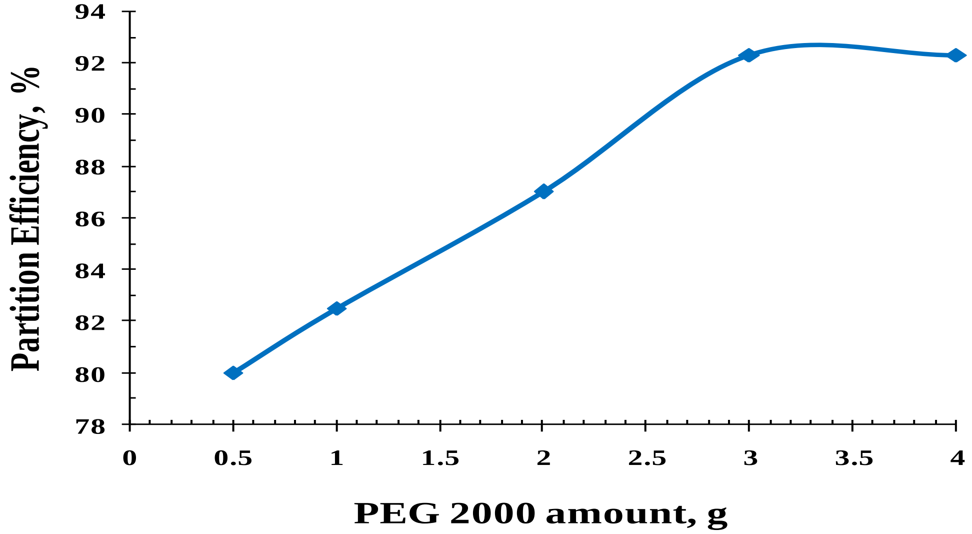

Figure 11:- Effect of PEG 2000 amount on the partition of ∑REEs in bottom phase of TLPS.

Effect of $(NH_4)_2SO_4$ Concentration:-

The effect of $(NH_4)_2SO_4$ concentration on the partition of ∑REEs in the bottom salt rich layer is presented in Figure (12).The obtained data showed an enrichment of ∑REEs in this layer. It increases with increasing the $(NH_4)_2SO_4$ concentration up to 1.6 M. Over the later value of $(NH_4)_2SO_4$ concentration has, it is no effect on ∑REEs extraction in bottom phase. However, the increase of salt concentration in aqueous phase could result in stripping of the hydration shell of the polymer molecular chain, and thereby has a significant influence on the partitioning of rare-earth ions.

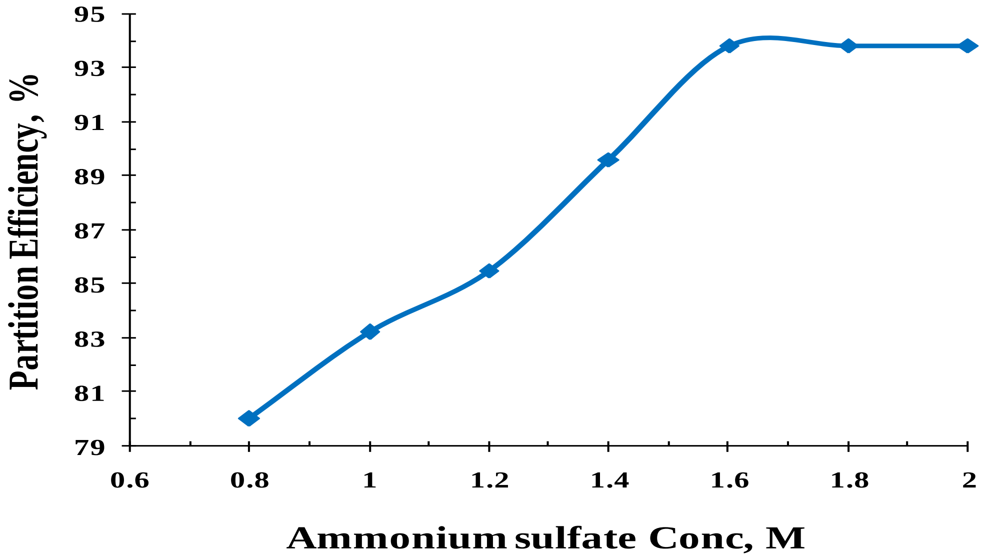

Figure 12:- Effect of $(NH_4)_2SO_4$ concentration on the partition of ∑REEs in salt-rich phase of TLPS.

Precipitation of ∑REEs by oxalic acid:-

Precipitation of the collected rare earth elements separated from the salt bottom layer is carried out using oxalic acid and then roasted to produce rare earth oxides. A common observation in REEs precipitation of REEs by oxalic acid is conducted where the 20% oxalic acid is gradually added with continuous stirring at pH1[43]. The obtained precipitate has been identified using the environmental scanning electron microscope (ESEM) (Figure 13) and then analysed quantitatively using ICP-OES technique to identify its chemical constituents and individual REEs distribution in oxalate and oxides forms (Tables 6, 7). The obtained data seemed that the rare earth oxides are assaying 44.37 and 98.60% in oxalate and oxide concentrates respectively. Finally, a schematic flow sheet of leaching and recovery of REEs is constructed and presented in Figure (14).

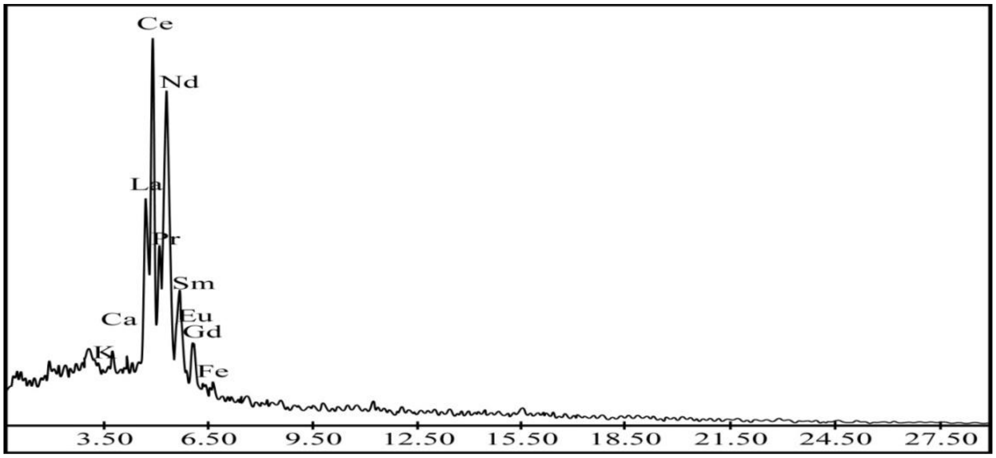

Figure 13:- The environmental scanning electron microscope of the obtained RE oxalate.

Table 6:- Chemical analysis of RE oxalate and RE oxide products.

Constituents	**Conc.,%**		**Constituents**	**Conc.,%**	
	Oxalate	**Oxide**		**Oxalate**	**Oxide**
SiO_2	N.d.	N.d.	**RE_2O_3**	44.32	98.60
Al_2O_3	N.d.	N.d.	**Ba^{2+}**	N.d.	N.d.
TiO_2	0.06	0.07	**Pb^{2+}**	N.d.	N.d.
Fe_2O_3	0.1	0.15	**Cr^{3+}**	0.001	0.02
MnO	0.003	0.03	**Cu^{2+}**	N.d.	N.d.
MgO	0.001	0.02	**Ni^{2+}**	N.d.	N.d.
CaO	0.07	0.09	**Zn^{2+}**	0.004	0.05
K_2O	0.01	0.02	**LOI****	28.32	0
Na_2O	0.05	0.07	**LOI*****	25.78	0

N.d. = Not detected
**Loss of Ignition at 110 ^{0}C
*** Loss of Ignition at 1000 ^{0}C

Table 7:- Chemical analysis of individual REEs in the RE oxalate and RE oxide products.

Metal ion	**mg/L**		**Metal ion**	**mg/L**	
	Oxalate	**Oxide**		**Oxalate**	**Oxide**
La^{3+}	98247	217660	**Dy^{3+}**	3251.5	7204
Ce^{3+}	161086	356904	**Ho^{3+}**	336.5	773
Pr^{3+}	33174	73513	**Er^{3+}**	664.5	1462
Nd^{3+}	56610	125443	**Tm^{3+}**	50	100
Sm^{3+}	12820	28422	**Yb^{3+}**	218	492
Eu^{3+}	410	930	**Lu^{3+}**	92	191
Gd^{3+}	8067	17851	**Sc^{3+}**	481	1063
Tb^{3+}	124	292	**Y^{3+}**	8130	18032

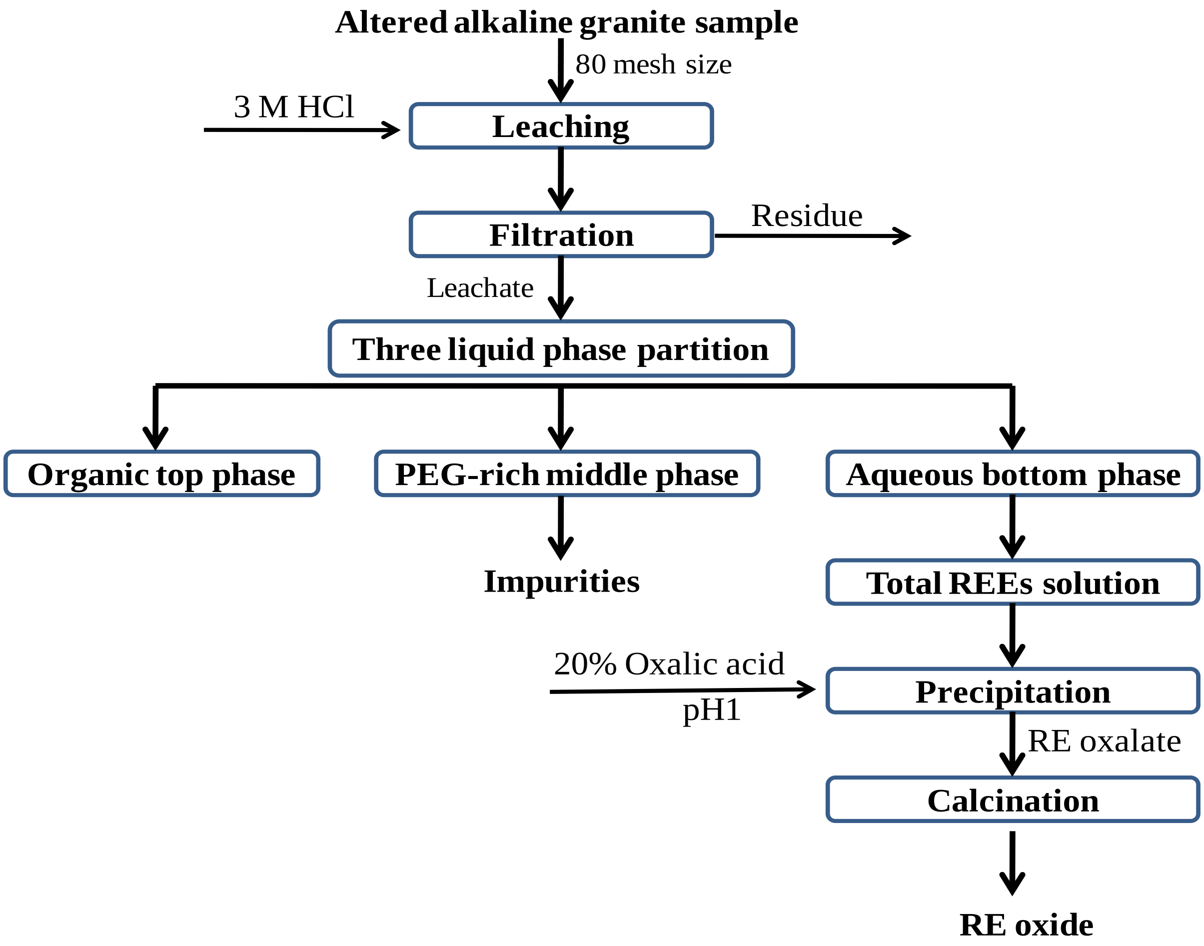

Figure 14:- A schematic flow sheet for leaching and recovery of ∑REEs from Nusab EL-Bulgum rock sample.

Conclusion:-

The leaching procedures of REEs using HCl acid form the Nusab El-Balgum altered alkaline granite rock sample have indicated that REEs dissolution is strongly dependent on the HCl acid concentration. The maximum leaching efficiency (92.4 %) is obtained at 3 M hydrochloric acid concentration, 200 rpm stirring speed and 1/6 S/L ratio for 180 min contact time at room temperature. The thermodynamic results of negative ΔG value confirm the feasibility and the spontaneous nature of the studied leaching process of ∑REEs while the positive ΔH value reflects the endothermic nature of dissolution. On the contrary, the positive ΔS value suggests an increase in randomness at the S/L interface during dissolution. It is also indicated that the rare earth ions are most probably transported from the solid phase into the bulk of solution to improve the leaching efficiency.

The optimized parameters affect on the recovery of REEs from chloride media using Cyanex 272/PEG2000/$(NH_4)_2SO_4$–H_2O occurred at pH 2, 200 mmole phen and EDTA, 3 g of PEG 2000 and 1.6 M $(NH_4)_2SO_4$. About 93.8% of the leached REEs are separated in the salt-rich bottom phase. Precipitation of rare earths from their solutions is performed using oxalic acid as rare earth oxalates. The obtained product assayed 98.60 % as oxide.

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