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Successive Leaching of Uranium and Rare Earth Elements from El Sela Mineralization

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Abstract The leaching process of uranium (VI) from El Selarock sample using sulfuric acid solution, and the consecutive leaching of rare earth elements were investigated. The leaching conditions acid concentration, additive concentration, solid-liquid ratio, contact time, particle size, agitation rate, and temperature, were applied. The leaching efficiency of uranium(VI) and rare earths are about 93.62 and 96.25%, respectively at the optimum leaching conditions. Furthermore, the thermodynamic studies for both uranium and REEs ions demonstrate that the negative values of ΔG° and the positive values of ΔH° give the spontaneous reaction and endothermic nature as well as, the positive values of entropy change; ΔS° suggested an increase in randomness.

Keywords Leaching; Uranium; Rare earths; Thermodynamics

1. Introduction

El Sela area is located in the southern eastern Desert of Egypt, between Latitudes of 22° 17′50" North and 22° 18′ 6" N, and longitudes of 36° 13′36" East and 36° 14′ 22" E, at a distance of about 30 km south west of Abu–Ramad city. The field observations proved that the granites of El Sela Mountain are highly weathered, cavernous and exposed with moderate separate hills, which form the outcropping remnants of the granitic pluton. The influences of the ENE–WSW tectonic trend (the main shear zone in El Sela ore) in the successive tectonic events make its evolutionary history a good guide to describe the geologic and tectonic history of El Sela area [1−7]. It formed the outcropping remnants of the granitic pluton. The area is described by its low to moderate relief with some high peaks represented by Gabal El Sela with about 557 m high. It is mainly affected by several valleys sloping towards the Red Sea. The climatic condition is arid proper with rare rainfall less than 50 mm/a. The temperature varies widely; it sometimes exceeds 50 °C in the summer period [8].

Uranium is a relatively abundant element with the highest atomic number of all naturally occurring elements. Uranium is a silvery white metal in actinide series. It occurs as three radioactive isotopes: U–238 (99.28%), U–235 (0.720%), and U–234 (0.0055%). The isotope U–235 is fissile; its nucleus can be split by thermal neutrons, releasing much energy and producing more neutrons, which under the right circumstances can lead to a self–sustaining chain reaction. This reaction is the basis of all nuclear applications. Thus, in uranium processing, it is the uranium–235 component that is the focus of attention. Uranium is one of the most important elements. It represents the corner stone in nuclear energy field through uranium fuel. It is used as a fuel in nuclear power plants [9]. Furthermore, rare earth elements encompass elements which are part of the family of lanthanides in the periodic table with atomic numbers from 57 to 71. Yttrium "Y" of the atomic number 39 is related to the rare earth elements in nature and exhibit very similar chemical properties. Scandium “Sc” with atomic number 21 is also grouped with the lanthanide family because of its similar chemical properties [10]. REEs have massive applications in our life; they are vital to the proper functioning of our computer’s memory, hydrogen storage, nuclear reactors, fluorescent lighting, TV screens, cell phones, DVDs, rechargeable batteries, fiber optic laser cables, car catalytic converters, and nickel–metal hydride batteries and magnets.

Leaching is the process of extracting certain minerals from a solid by dissolving them in a liquid; several leaching techniques have been applied to achieve better efficiencies of uranium dissolution and REEs in industrial or at least in pilot scales. Uranium and rare earth ores materials have to go through several hydrometallurgical procedures which include crushing, grinding, leaching, concentration and purification by solvent extraction and ion exchange, to take the pure form of uranium or rare earth oxides. The leaching stages can be applied by either acidic or alkaline reagents [11–13]. The choice between acid and alkaline leaching is mainly dictated by the mineralization type of the ore materials under consideration. Alkali and ammonium carbonate solutions are the preferred leachants for ores associated with large quantities of acid consuming components such as carbonates (dolomite and calcite) and oxide (magnetite) [14].

Acid leaching is the predominant process for uranium, usually with sulfuric acid because of its relatively low cost and wide availability [15−18]. New tendencies which began to appear include alkaline leaching, pressure leaching, heap leaching, bio−leaching and in−situ leaching [19−21]. The selection of a particular leaching technique depends on the grade, size and permeability characteristics of the ore body as well as on its mineralogical, lithological and chemical properties. In Egypt, some experiments have been conducted to leach uranium and lanthanides from El Selaores [22]. In this regard, the objective of this work is to improve the leaching efficiency of uranium and REEs with minimum dissolution of iron from El Sela mineralization. The current work is investigated a simple leaching process of uranium and rare earth from El Selarock, using the studied optimum conditions.

2. Experimental

2.1. Materials

The studied sample was collected from El Sela area, south eastern, Egypt. It was prepared for analysis by crushing about 5 Kg using a laboratory jaw crusher into pea–size, followed by grinding using a blending mill to different sizes, the pulverized sample was then analyzed using the suitable techniques.

The trace elements in the geologic sample are estimated by XRF technique using Philips unique−II spectrometer with an automatic sample changer PW 1510, (30 positions) connected with computer system using X–40 program for spectrometry (Holland).

Spectrophotometric technique (Arsenazo III method) was used to determine the concentration of uranium and the total REEs in aqueous solutions by a double beam T80 UV/Vis spectrophotometer with 1cm quartz cells; cover the UV–visible range 200–1100 nmat λ_{max} of 655 and 650 nm for uranium and REEs, respectively [23].

The oxidimetric titration method is also employed to analyze uranium ions in leach liquor [24] while, ICP–OES is correspondingly used to analyze the individual REEs.

2.2. Leaching Experiments

The experiments are applied upon El Sela mineralization rock sample to optimize the factors affecting the leaching efficiency. These factors involving acid type and its concentration, the concentration of salt additive, solid: liquid ratio S: L and contact time, as well as the slurry temperature. The studied sample is firstly crushed and ground to the definite size. Several leaching experiments are performed on the powder sample using H_2SO_4, and HCl at a different concentration ranging from 0.25 to 3 M. The different concentration of salts additives $(NH_4)_2SO_4$ or NH_4Cl variable from 0.1 to 0.6 g are added on the leaching process. The effect of solid:liquid ratios is also conducted using the 1:1 to 1:7 ratio. However, the effect of contact time, ranging from 1 to 7 h is actually tested and the effect of leaching temperature, experiments are carried out under different temperature.

After the end of the leaching experiment, the obtained slurry is filtered and the residue left behind is thoroughly washed with distilled water. The obtained filtrate is adjusted to certain volume representing the leach liquor which is then analyzed to determine the concentration of U(VI) and REEs using the suitable techniques. These concentrations are used to obtain the leaching efficiency as this relation:

$$L\% = \left(\frac{C_{a,e}}{C_{s,i}}\right)x100 \qquad (1)$$

Where, $C_{a,e}$ (mg/L) and $C_{s,i}$ (mg/g) are the concentrations of aqueous leaching at equilibrium and initial solid powder sample, respectively for U(VI) and REEs. Also, the thermodynamic isotherms of U(VI) and REEs leaching from El Sela rock sample are investigated.

3. Results and Discussion

3.1. Characterization of El Sela Ore Material

The obtained analytical results indicate actually the nature of the host rock composition and relative to the content of the average element of the parent rock recorded. The SiO_2 assays in El Sela composite sample are about 67.62%, therefore it would be suitable for mild leaching conditions by either acidic or alkaline reagents. Also, it contains the noteworthy amount of phosphate (0.29%). In the meantime, both Na_2O and K_2O are assaying 1.83 and 2.35 % respectively. Investigation of the analyzed trace elements revealed that Cr, Co, Ni, and Cu are 58, 71, 37 and 38 mg/kg, respectively.

Interestingly, it has also been observed that the concentrations of Ga, Pb, and Ba and are 489, 753, and 2862 mg/kg, respectively.Uranium was analysed and estimated as 930 mg/kg, while the total REEs content is 5042.82 mg/kg (Table 2). Additionally, the spectrometric measurement showed that the value of Th in the studied sample is 320 mg/kg. It was found that El Sela area is rich with both U and REEs.

On the other hand, the major minerals are identified by XRD shown in Figure (1). The data of X−ray diffraction pattern reveal that El Sela study sample is composed essentially of quartz SiO_2, and hydroxylapatite $Ca_5(PO_3)_4.OH$ with basal spacing 3.33, and 2.79 at 2Θ = 26.695°, and 31.975°, respectively.

Table 1: Chemical analysis of El Sela working sample

Constituents	**Wt,%**	**Constituents**	**Conc., mg/kg**
SiO_2	67.62	Ga	489
Al_2O_3	13.30	Pb	753
Fe_2O_3	8.54	Sr	31
CaO	1.248	Zn	186
MgO	2.184	Cu	38
TiO_2	1.44	Cr	58
Na_2O	1.83	V	116
K_2O	2.35	Ni	37
P_2O_5	0.108	Co	71.6
L.O.I.	0.75	Ba	2862
U	0.093	Zr	71
∑REEs	0.5043	Rb	U.D
Th	0.032	Nb	3

L.O.I: Total Loss of Ignition at 1000 °C.*

Table 2: Chemical analysis of individual REEs of the studied sample

Element	**Conc.(mg/kg)**	**Element**	**Conc.(mg/kg)**
Sc	ND*	Gd	78.96
Y	2003.75	Tb	9.78
La	2000	Dy	13.9
Ce	410	Ho	2.76
Pr	228.8	Er	4.44
Nd	125.6	Tm	ND
Sm	55.94	Yb	ND
Eu	6.34	Lu	31.6

ND = non detected*

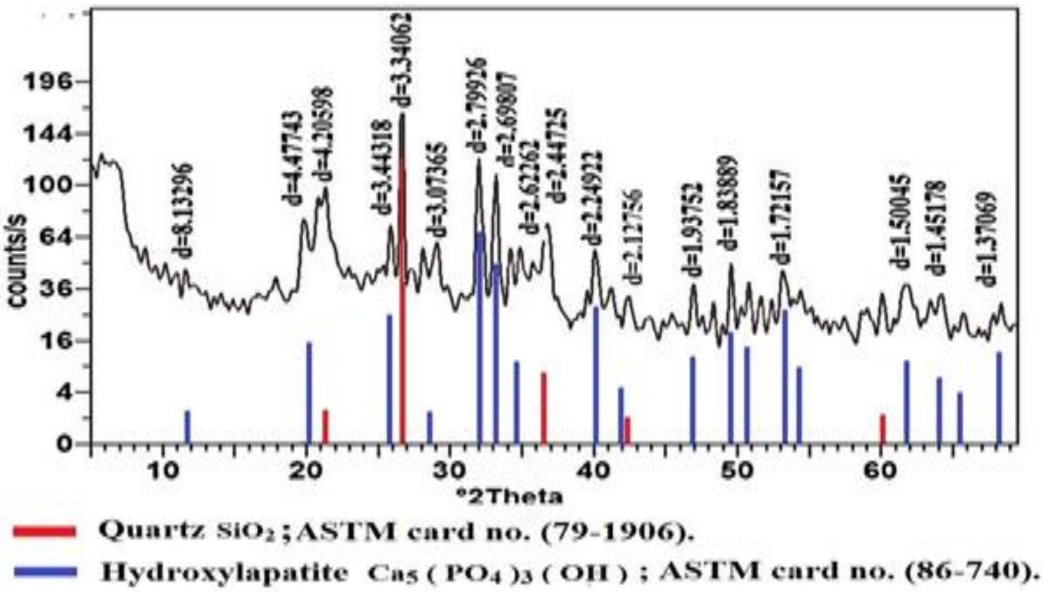

Figure 1: XRD pattern of El Sela composite

3.2. Leaching Studies of Uranium and REEs

Leaching is one of the most important techniques for extractionand it is used to leach uranium and REEs from their resources. The previous results of mineralogical and chemical analysis of El Sela rock sample indicated the presence of radioactive elements such as uranium and REEs beside some associated elements such as iron. To study the leaching of uranium and REEs elements, the rock sample crush and grind initially to definite particle sizes. Then, the leaching processes are applied. Different acid leaching such as H_2SO_4, HNO_3, and HCl is used to investigate the influence of acid type on leaching efficiency. The leaching experiments are performed using 20 g of powdered sample (149-100 µm particle size) and 60 ml of 150 mg/L individual acid leaching agent (1:3, S:L ratio) and 200 rpm stirring speed for 4 h contact time at room temperature. Afterward, the obtained rock sludge is filtered and the residue is thoroughly washed with distilled water. The obtained filtrate is adjusted to certain volume representing the leach liquor which is then analyzed.

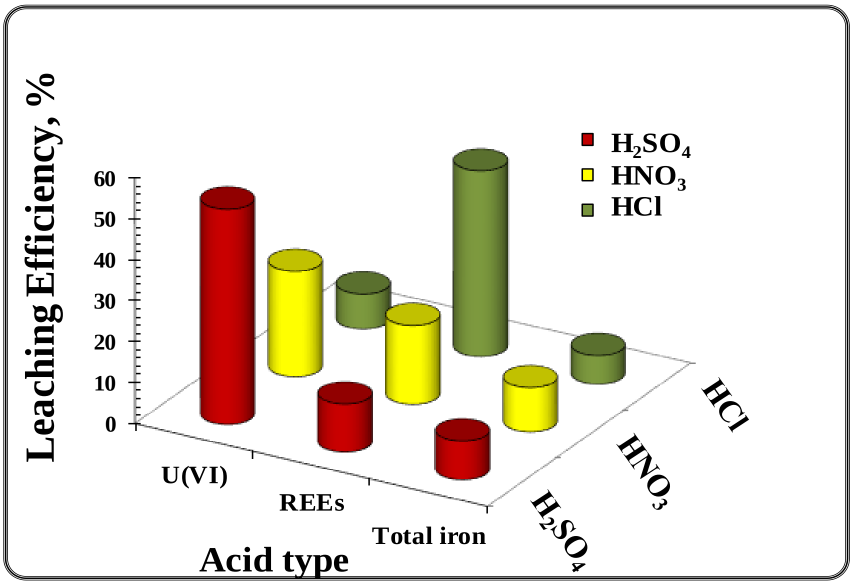

Figure 2: Effect of different acid types on leaching efficiencies of U(VI), REEs, and total iron from El Sela sample (150 g/L leaching agents concentration, 1:3 S:L phase ratio, 200 rpm stirring speed, 149-100 µm particle size, 4h contact time, room temperature).

From the data presented in Figure (2), the maximum leaching efficiency of uranium is 52.55% by 150 mg/L H_2SO_4, while the maximum REEs leaching efficiency (45.32%) is achieved using 150 mg/L HCl. On the other hand, the effect of HNO_3 on leaching efficiency of uranium ions and REEs ions was not much significant comparing with H_2SO_4 and HCl acids. However, the total iron leaching efficiency is 9.43% and 6.98% for sulfuric acid and hydrochloric acid, respectively. In view of that, sulfuric acid is selected to carry out the acid leaching process for uranium ions, and hydrochloric acid is advised as an alternate leaching agent during the leaching process of REEs.

3.2.1. Uranium leaching

The optimum uranium leaching conditions are achieved through investigating the influence of the concentration of sulfuric acid leaching, solid to liquid phase ratio (S:L), additive type and its concentration, leaching time, stirring speed, practical size, and temperature.

3.2.1.1. Effect of leaching concentration

Different concentrations of H_2SO_4 acid are employed to study uranium leaching efficiency from the ore material. The concentration of H_2SO_4 is ranging from 25 to 300 g/L and the other experimental factors are fixed at 1:3 (S:L) ratio, 200 rpm stirring speed, and 149-100 µm particle size, for 4h contact time at room temperature. The results are given in Figure (3) reveal that the leaching efficiency of uranium from the studied sample is increased by increasing the concentration of H_2SO_4 increased until the maximum leaching efficiency at 52.55% using 150 g/L H_2SO_4. The leachability of U(VI) does not improve moreover 150 g/L H_2SO_4.On the other side, the REEs and total iron in leach liquor are undesirable impurities during the extraction of uranium. The concentrations of REEs and iron are measured and found trivial regarding uranium leaching efficiency. Finally, it is obvious that the 150 g/L H_2SO_4 can dissolve the maximum amount of uranium ions from the studied sample with proper efficiency.

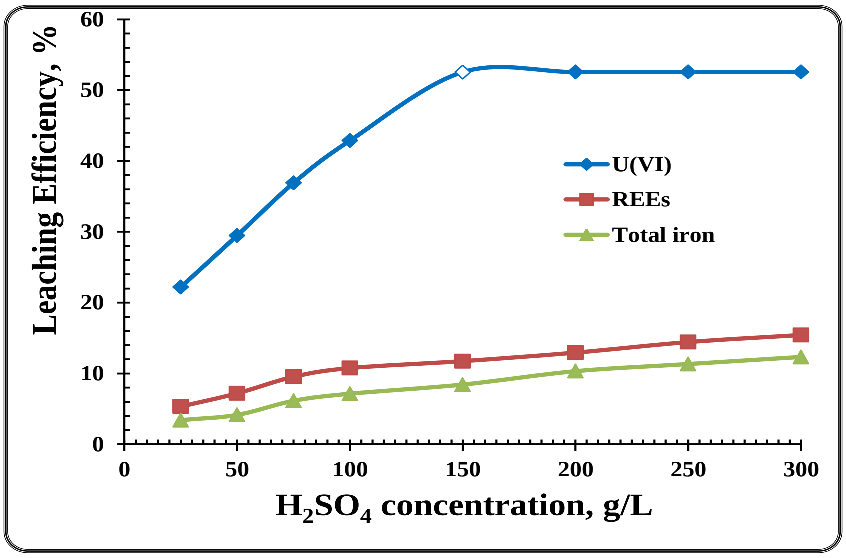

Figure 3: Effect of sulfuric acid concentration on leaching efficiency of U(VI) from El Sela sample (1:3 S:L phase ratio, 200 rpm stirring speed, 149-100 µm particle size, 4h contact time, room temperature)

3.2.1.2. Effect of solid: liquid phase ratio

A lot of experiments are performed in order to study the effect of solid to liquid phase ratio (S:L) upon the leaching efficiency of uranium from the studied sample, these experiments by varying (S:L) ratio from 1:1 to 1:7 at 150 g/L of H_2SO_4 concentration,149-100 µm particle size, and 200 rpm stirring speed, for 4 h contact time at room temperature.

As illustrated in Figure (4), the leaching efficiency of uranium is progressively increased from 32.23% to 60.33% as the (S:L) ratio increased from 1:1 to 1:4. However, the uranium leaching efficiency is constant by increasing the solid to liquid ratio (S:L) from 1:4 to 1:7. In consequence, the best solid: liquid phase ratio nominated is 1:4, whereas, the leaching efficiencies of REEs and total iron are 13.64% and 10.43%which are ignored during extraction process of U(VI).

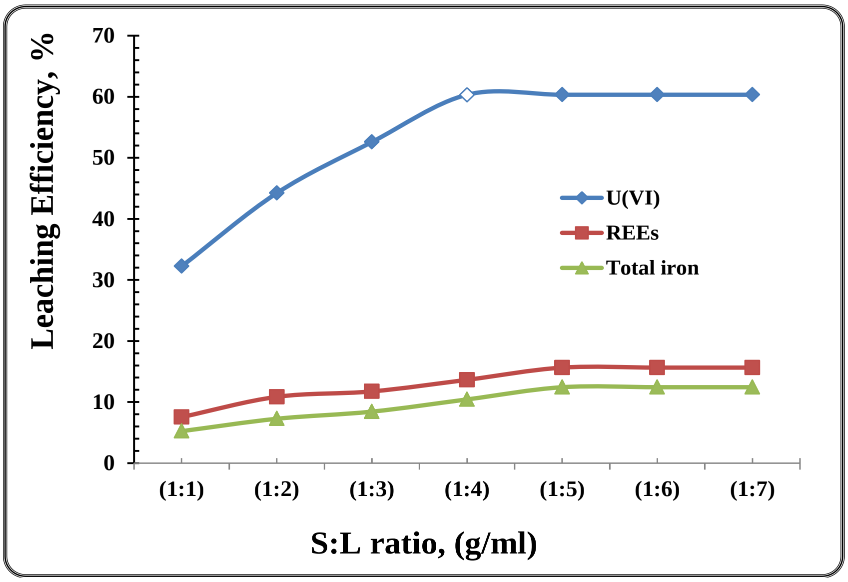

Figure 4: Effect of solid to liquid ratio on leaching efficiency of U(VI) from El Sela sample (150 g/L sulfuric acid, 200 rpm stirring speed, 149-100 µm particle size, 4h contact time, room temperature)

3.2.1.3. Effect of additive type

The additive materials have been suggested to improve leaching efficiency of uranium from its ores materials [25]. To study the effect of additive type on uranium leaching efficiency, three different additives ammonium sulfate, sodium sulfate, and potassium sulfate assaying 150 mg/L are used at 150 g/L of sulfuric acid, 1:4 S/L phase ratio, 200 rpm speed of stirring, and 149-100 µm particle size, for 4 h contact time at room temperature. From the data in Figure (5) reveals that $(NH_4)_2SO_4$ attained the maximum leaching efficiency of uranium comparing with other types of additives used. Thus, ammonium sulfate $(NH_4)_2SO_4$ is used to be an additive during uranium leaching, as it is commercially available [26].

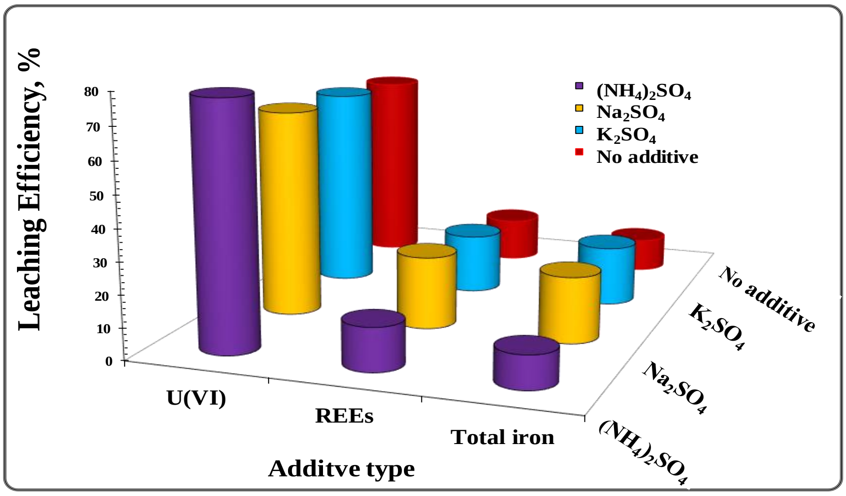

Figure 5: Effect of additive types on leaching efficiency of uranium from El Sela sample (150 g/L additive type, 150 g/L sulfuric acid,1:4 S:L phase ratio, 200 rpm stirring speed, 149-100 µm particle size, 4h contact time, room temperature).

3.2.1.4. Effect of ammonium sulfate concentration

The influence of ammonium sulfate concentration on uranium leaching efficiency is studied using different concentrations of $(NH_4)_2SO_4$ ranging from 25 to 300 g/L, while the other experimental conditions are fixed at 150 g/L sulfuric acid, 1:4 solid:liquid ratio, 200 rpm stirring speed, and 149-100 µm particle size for 4 h leaching time at room temperature.

As displayed in Figure (6), the uranium leaching efficiency is increased from 61.19 to 77.33% with increasing the concentration of $(NH_4)_2SO_4$ from 25 to 150 g/L, in turn, followed by constancy in leaching efficiency with different concentration of ammonium sulfate from 150 to 300 g/L. Correspondingly, the maximum of leachability for REEs and total iron are 13.73% and 10.55%, respectively. As a result, 150 g/L of $(NH_4)_2SO_4$ is recommended as an optimum concentration in the following uranium leaching investigation.

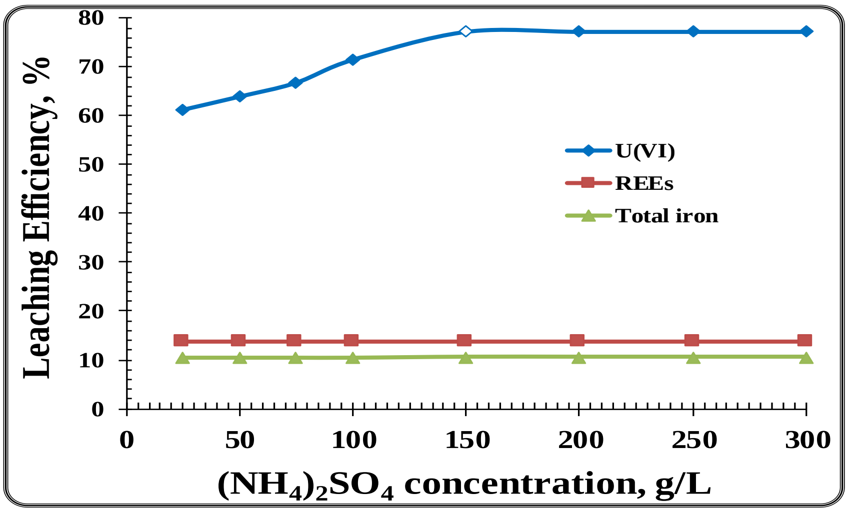

Figure 6: Effect of $(NH_4)_2SO_4$ concentration on leaching efficiency of uranium from El Sela sample (150 g/L sulfuric acid,1:4 S:L phase ratio, 200 rpm stirring speed, 149-100 µm particle size, 4h contact time, room temperature)

3.2.1.5. Effect of contact time

The leaching time plays a remarkable role in the uranium leaching efficiency. The effect of leaching time on uranium leaching efficiency is studied by varying the contact time from 1 to 8 h, and the other experimental circumstances are set fixed at 150 g/L sulfuric acid, 150 g/L $(NH_4)_2SO_4$, 1:4 solid:liquid ratio, 200 rpm speed of stirring, and 149-100 µm particle size at room temperature. The results are presented in Figure (7), the leaching efficiency of uranium is clearly rose from 41.76 to 87.35% by increasing the contact time from 1 to 6 h. Then, there is no change recorded in leaching efficiency after increasing the leaching time higher than 6 hours. Alternatively, the leaching efficiencies of REEs and total iron are 15.98 and 12.66%, respectively. Based on these results, the leaching time is set to 6 h for further leaching process of El Sela sample.

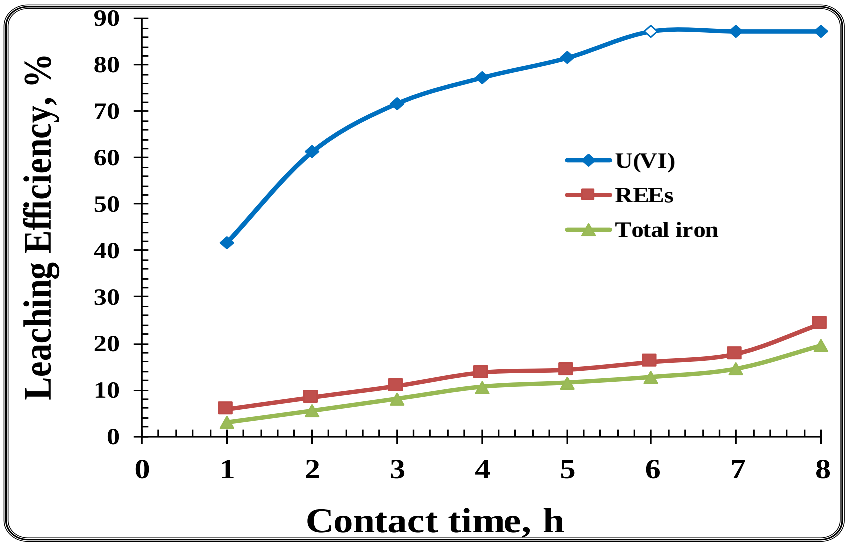

Figure 7: Effect of contact time on leaching efficiency of uranium from El Sela sample (150 g/L sulfuric acid, 150 g/L $(NH_4)_2SO_4$, 200 rpm, 1:4 S:L phase ratio, 149-100 µm particle size, room temperature)

3.2.1.6. Effect of stirring speed

The stirring speed is studied to investigate the impact of speed rating on the leaching efficiency of uranium. The experimental conditions are fixed at 150 g/L sulfuric acid, 150 g/L $(NH_4)_2SO_4$, 1:4 S:L phase ratio, and 149-100 µm particle size at room temperature for 6 h contact time, while the stirring rate is changed from 50 to 300 rpm. From the results in Figure (8), it indicates that the most extent of uranium leaching efficiency is 87.35%, is recorded after using speed rate 200 rpm. The leaching efficiency of REEs and total iron was 15.98% and 12.66%, successively. Furthermore, higher stirring speed than 200 rpm leads to the same leaching efficiency. Hence, the 200 rpm stirring speed is considered the most favorable stirring rate in the following experiments.

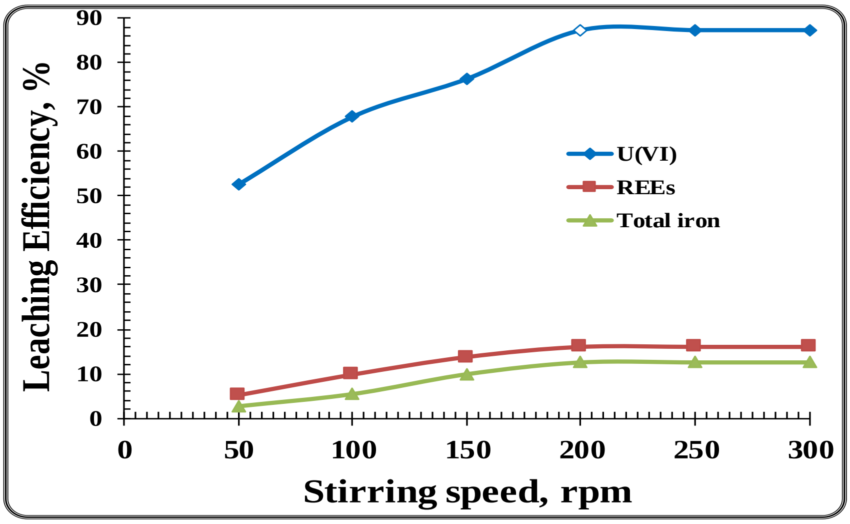

Figure 8: Effect of stirring speed on leaching efficiency of uranium from El Sela sample (150 g/L sulfuric acid, 150 g/L $(NH_4)_2SO_4$, 1:4 S/L phase ratio, 6 h contact time,149-100 µm particle size, room temperature)

3.2.1.7. Effect of particle size

Different particle size fractions of the studied ore material are used in the range 400 to 32 µm to study the effect of particle size on uranium leaching efficiency and The other experimental variables are constant at the 150 g/L H_2SO_4, 150 g/L $(NH_4)2SO_4$, 1:4 S/L phase ratio, and 200 rpm stirring rate for 6 h leaching time at room temperature. As given in Figure (9), the utmost uranium leaching efficiency was about 93.62% at 100-63 µm particle size fraction used and persistent when various tiny fractions of El Sela samples used. Consecutively, the leaching efficiency of both REEs and total iron are 16.35 and 13.11% respectively. Accordingly, the particle size 100-63 µm is the most recommended to be used in uranium leaching experiments.

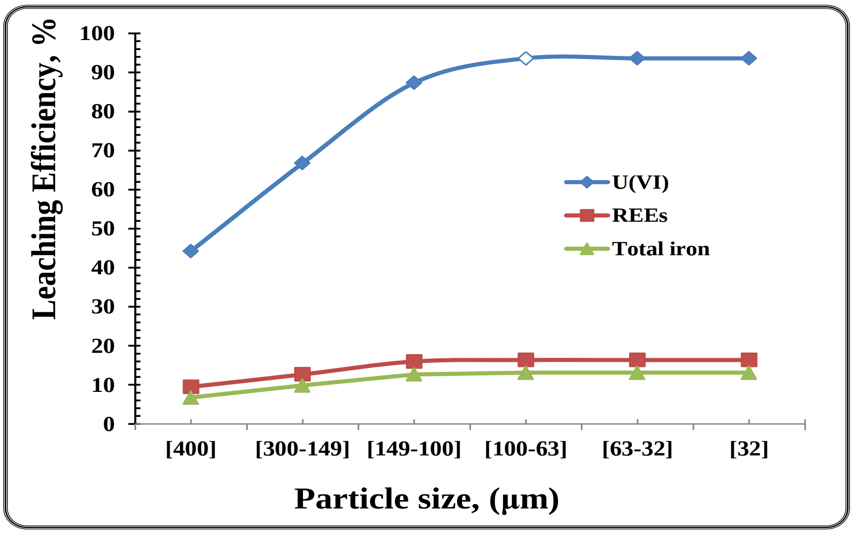

Figure 9: Effect of particle size on leaching efficiency of uranium from El Sela sample (150 g/L sulfuric acid, 150 g/L $(NH_4)_2SO_4$, 1:4 S:L phase ratio, 200 rpm stirring speed, 6 h contact time, room temperature)

3.2.1.8. Effect of temperature

The uranium leaching efficiency is affected by temperature extensively. A wide range of temperature varying from 25 to 80ºC has been applied to investigate the optimum temperature required throughout the leaching process while the other factors of leaching are remained constant at 150 g/L H_2SO_4 concentration, 150 g/L ammonium sulfate, 1:4 S:L phase ratio, 200 rpm stirring speed, and 100-63 µm particle size for 6 h leaching time. As can be seen from the data in Figure (10), the results pointed out that the leachability of uranium is slowly increased from 93.62% to 97.75% as the temperature of the leaching process increased at 80 ºC. It supports the idea that the uranium leaching process is endothermic and almost of the uranium content into the ore can be leached. However, running the leaching process at high temperature (40-80º C) is unreasonable, as the feasibility is not much comparing with the expenses. Moreover, the REEs and iron leaching efficiency are increasing with increasing the temperature. Besides, the suggested leaching facility is in the Egyptian Eastern desert and the average temperature is 40-50º C particularly in summer. Therefore, the leaching temperature of room temperature is usually chosen in uranium leaching.

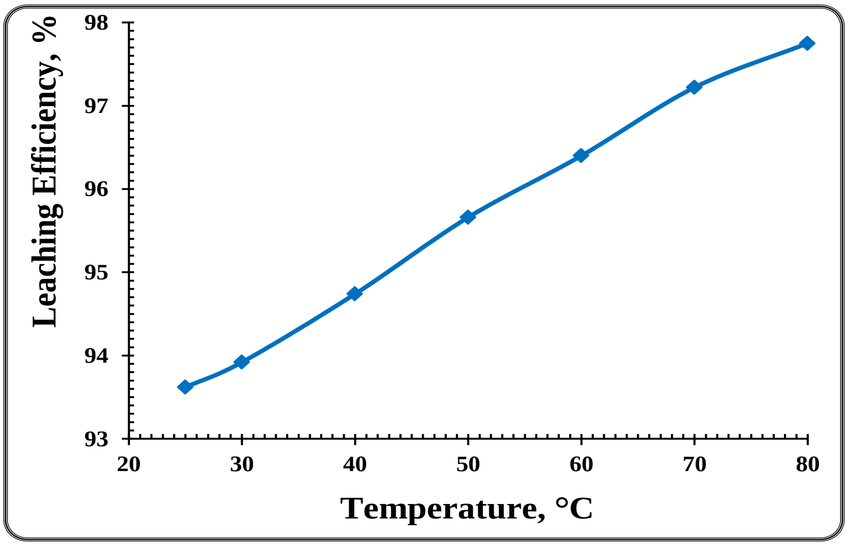

Figure 10: Effect of temperature on leaching efficiency of uranium from El Sela sample150 g/L sulfuric acid, 150 g/L $(NH_4)_2SO_4$, 1:4 S:L phase ratio, 200 rpm stirring speed, 149-100 µm particle size, 6 h contact time)

3.2.1.9. Leaching thermodynamic of uranium

In order to gain insight into the acidic leaching of uranium from the El Sela sample using sulfuric acid, the thermodynamic parameters for leaching process including Gibbes free energy of adsorption ΔG° (kJ/mol), enthalpy change ΔH° (kJ/mol), and entropy change ΔS° (J/mol.K), were calculated using Van't Hoff equations:

$$Log\ K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (2)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

$$\Delta G^\circ = -2.303RT\ Log\ K_d \quad (4)$$

Where, R is the universal gas constant (8.314 J/mol.K), and T is the absolute temperature (K), and K_d is the distribution coefficient calculated as stated by the following equation:

$$K_d = \frac{C_L}{C_S} \quad (5)$$

Where, C_L and C_S are the amounts of metal ions in leaching solution (mg) and in the solid sample (mg) at equilibrium (mg metal/kg solid sample), respectively. The plots of log k_d against 1/T for the uranium leachingare displayed in Figure (11). Both values of ΔH° and ΔS° values can be calculated from the slope and intercept, respectively. The values of thermodynamic parameters based on the above functions are tabulated in Table (3). The negative value of ΔG° points out that the leaching of uranium ions is the spontaneous reaction.

The increase in ΔG° value with increasing the temperature implies that the reaction is more favorable at room temperature. But the positive values of Gibbs free energy of REEs and iron ions are expected the non-spontaneous reaction at any temperature and the decrease in ΔG° value with increasing the temperature implies that the reaction is not favorable at room temperature. he positive values of enthalpy change, ΔH, for uranium and REE and total iron confirmed the endothermic nature of the acid leaching of these metals from the working sample. Likewise, the positive values of entropy change, ΔS, for the studied metal ions, suggested an increase in randomness due to the leaching of the metal ions from the studied sample.

Table 3: Thermodynamic parameters for U(VI), REEs and iron ions leaching from El Sela sample.

Metal ions	ΔH kJ/mol	ΔS kJ/mol.K	ΔG (KJ/mol)						
			298 K	303 K	313 K	323 K	333 K	343 K	353 K
U(VI)	17.39	0.08	-6.469	-6.869	-7.669	-8.471	-9.271	-10.07	-10.87
REEs	7.87	0.012	4.032	3.967	3.838	3.709	3.581	3.452	3.323
Iron	8.61	0.013	4.627	4.561	4.427	4.293	4.159	4.025	3.892

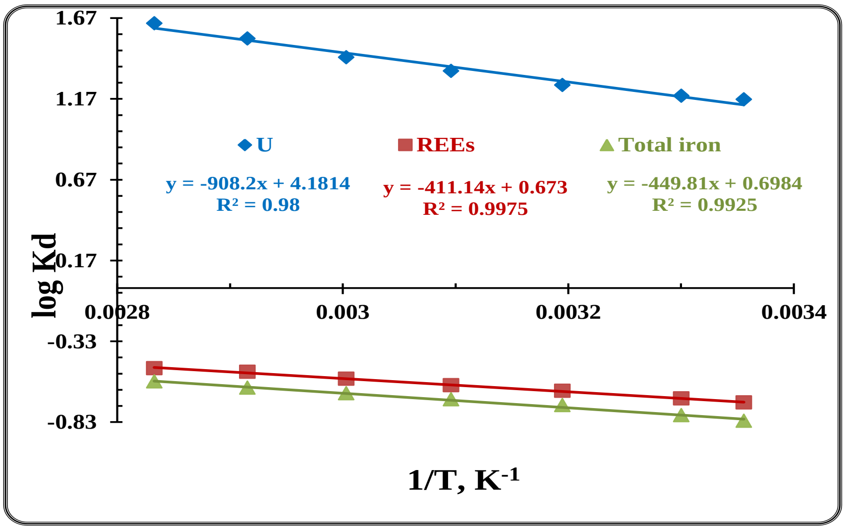

Figure 11: Plot of Log K_d versus 1/T for uranium, REEs and total iron leaching from El Sela sample

3.2.2. REEs leaching

As mentioned before the hydrochloric acid is proposed as a leaching agent in the leaching process of REEs. The optimum leaching conditions are achieved through investigating the influence of the concentration of leaching agent, additives, and its appropriate concentration, solid to liquid (S:L) phase ratio, leaching time, stirring speed, practical size, and temperature.

3.2.2.1. Effect of HCl concentration

The influence of HCl concentration is tested using different concentrations varying from 25 to 300 g/L, while other experimental factors are kept at 1:3 solid:liquid phase ratio, 149-100 µm particle size of ore material, and 200 rpm stirring speed for 4 h leaching time at room temperature. From data given in Figure (12);it is obvious that the leachability of REEs is increased from 15.14% to 57.43% when the concentration of HCl is to 200 g/L. Additionally, the leaching efficiency of uranium and total iron is 11.94% and 9.32%, respectively. Nevertheless, the leaching efficiency of REEs is fixed at 57.43%, by increasing the HCl concentration from 200 to 300 g/L. In consequence, 200 g/L is recommended as an effective concentration for HCl acid on leaching process of REEs [27].

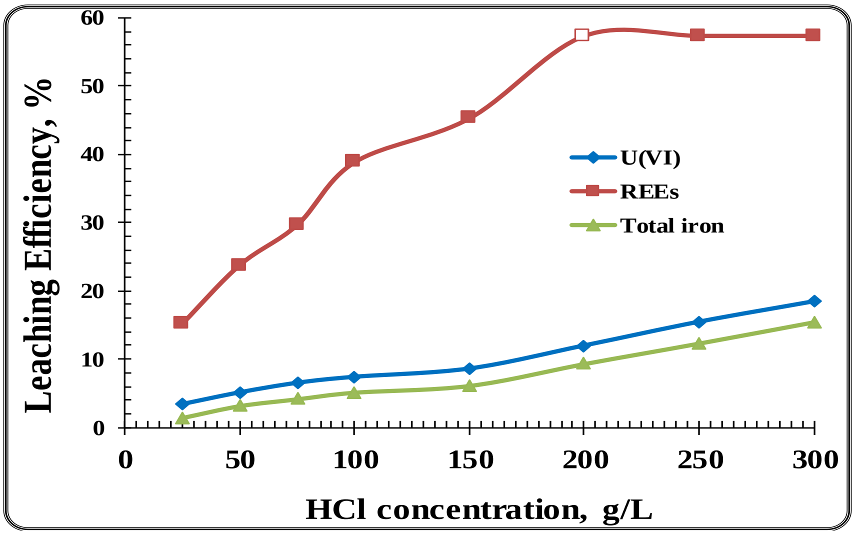

Figure 12: Effect of HCl concentration on leaching efficiency of REEs from El Sela sample (1:3 S:L phase ratio, 200 rpm stirring speed, 149-100 µm particle size, 4h contact time, room temperature)

3.2.2.2. Effect of solid: liquid phase ratio

The effect of solid to liquid phase ratio is undertaken in these experiments. Different S:L phase ratios ranging from 1:1 to 1:7 are employed while the other circumstances of leaching are fixed at 200 g/L hydrochloric acid, 200 rpm stirring speed, and 149-100 µm particle size for 4 h contact time, at room temperature. The obtained results established that the leaching efficiency of REEs tends to rise from 27.43% to 63.55% with increasing the solid: liquid phase ratio from 1:1 to 1:4. Also, the REEs leaching efficiency is persistent at 63.55% with increasing the (S:L) phase radio from 1:4 to 1:7 (Figure 13). Meanwhile, the uranium and total iron leaching efficiencies are 13.27% and 11.43% respectively. Thus, the solid: liquid ratio 1:4 is the appropriate S/L phase ratio on leaching efficiency of REEs.

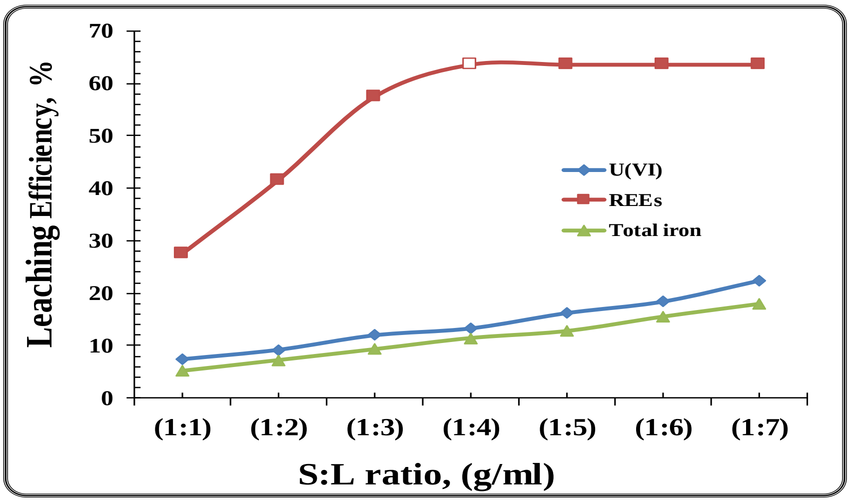

Figure 13: Effect of S:L phase ratio on leaching efficiency of REEs from El Sela sample (200 g/L hydrochloric acid, 200 rpm stirring speed, 149-100 µm particle size, 4 h contact time, room temperature)

3.5.2.2.3. Effect of additive type

In order to increase the leaching efficiency of REEs from El Sela sample, different types of chloride salts additives (ammonium chloride, sodium chloride, and potassium chloride) are used and the experimental parameters are kept consistent at 200 g/L HCl acid, 150 g/L additive types, 1:4 S:L phase ratio, 200 rpm stirring rate, and 149-100 µm particle size for 4 h leaching time at room temperature. From the data in Figure (14) reveals that the ultimate leaching efficiency of REEs is 77.54% achieved with NH_4Cl. Hence, ammonium chloride proposed as an additive material through leaching process of REEs later.

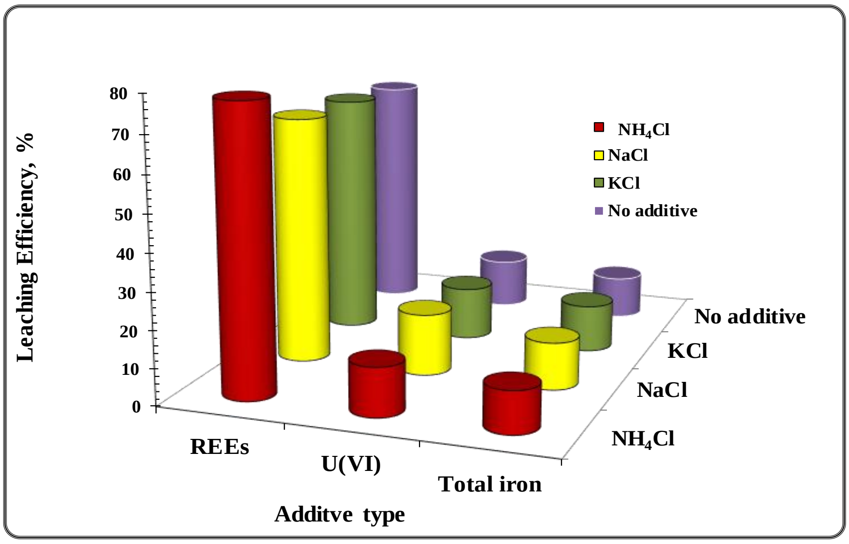

Figure (14): Effect of different additive types on leaching efficiency of REEs from El Sela sample (200 g/L HCl, 150 g/L additive type, 1:4 S:L phase ratio, 200 rpm stirring speed,149-100 μm particle size, 4h contact time, room temperature)

3.2.2.4. Effect of ammonium chloride concentration

Different concentrations of NH_4Cl from 25 to 300 g/L are used to study the leaching efficiency of REEs at 200 g/L HCl, 1:4 solid/liquid phase ratio, 200 rpm stirring speed, and 149-100 μm particle size, for4 h contact time at room temperature. From the result in Figure (15), it is seen that the REEs leaching efficiency is augmented from 63.55 % to 86.65% with increasing the concentration of NH_4Cl from 25 to 200 g/L. Meanwhile, the leaching efficiency of uranium and total iron ions are 13.27% and 11.55%, respectively. After that, the experiments are conducted using 250 and 300 g/L of ammonium chloride, the leaching efficiency of REEs is constant at 86.65%. It is obvious that the proper concentration of NH_4Cl is 200 g/L to achieve a valuable leaching content of REEs.

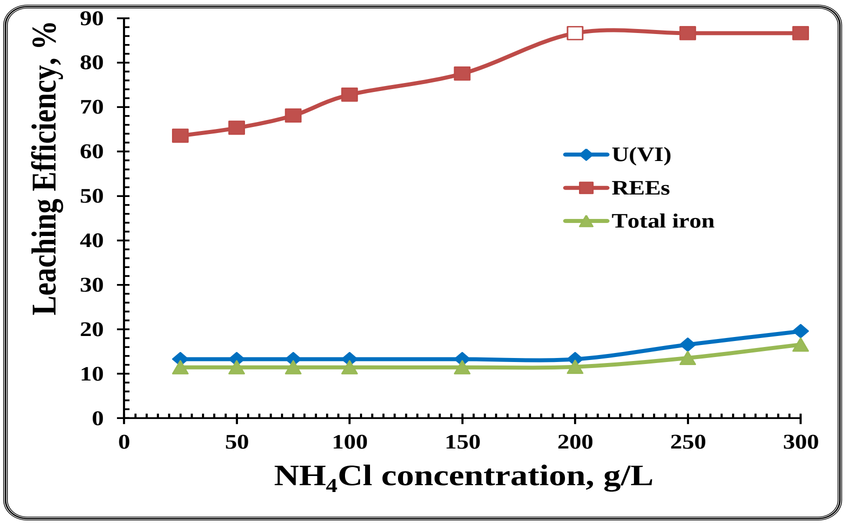

Figure 15: Effect of NH_4Clconcentration on leaching efficiency of REEs from El Sela sample (200 g/L HCl, 1:4 S:L phase ratio, 200 rpm stirring speed, 149-100 μm particle size, 4h contact time, room temperature).

3.2.2.5. Effect of contact time

The leaching time is considered a crucial factor controlling the maximum REEs leaching efficiency. The influence of leaching time is studied at the different time varying from 1 to 8 h whereas the other experimental conditions are remained constant at 200 g/L HCl, 200 g/L NH_4Cl, 1:4 S:L phase ratio, 200 rpm stirring speed, and 149-100 µm particle size at room temperature. The results are shown in Figure (16), it reveals that REEs leaching efficiency is gradually increased from 55.67% to 91.55% regarding raising the leaching time from 1 to 5 h, respectively. Moreover, the leaching efficiency of uranium and total ions after 5 h are 14.15% and 11.77%, respectively. The achieved leaching efficiency of REEs after 5 h is fixed at 91.55% so that it is conceivable that the 5 h is a reasonable leaching time for El Sela ore material for the subsequent leaching stages.

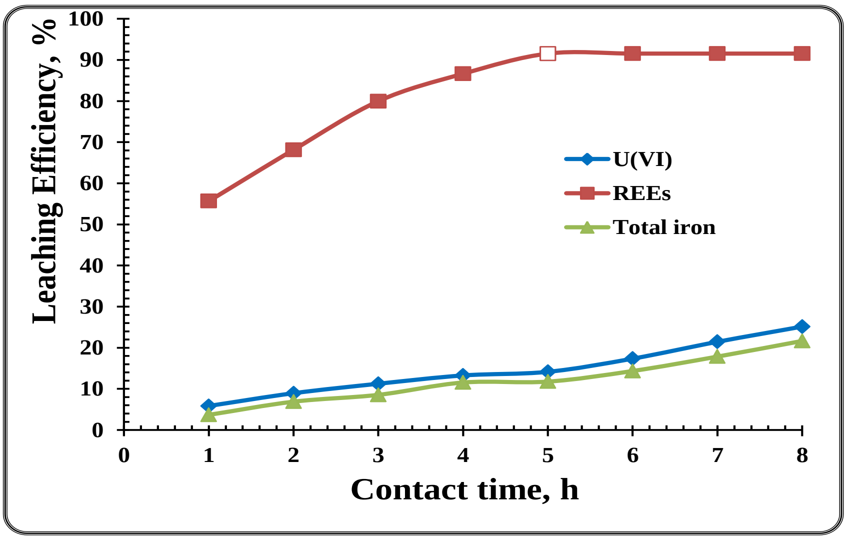

Figure 16: Effect of contact time on leaching efficiency of REEs from El Sela sample (200 g/L HCl, 200 g/L NH_4Cl, 1:4 S:L phase ratio, 200 rpm stirring speed, 149-100 µm particle size, room temperature)

3.2.2.6. Effect of stirring speed

Experiments are undertaken using variable stirring rates to detect the effect of stirring speed on the leaching efficiency of REEs. The other experimental parameters are kept constant at 200 g/L HCl acid, 200 g/L for NH_4Cl, 1:4 S:L phase ratio, and 149-100 µm particle size at room temperature for 5 h contact time, whereas the stirring rate is varied from 50 to 300 rpm. The data shown in Figure (17), it reveals that the maximum leaching efficiency of REEs is 91.55%, it is obtained by stirring speed 200 rpm. Astonishing, the recorded leaching efficiency of REEs is persistent at 91.55% when the stirring speed increased above 200 rpm. Additionally, the leaching efficiencies of uranium and total iron in leach liquor are 14.15% and 11.77%, respectively. As a result, the speed of stirring 200 rpm reflected the adequate speed of stirring in next experiments.

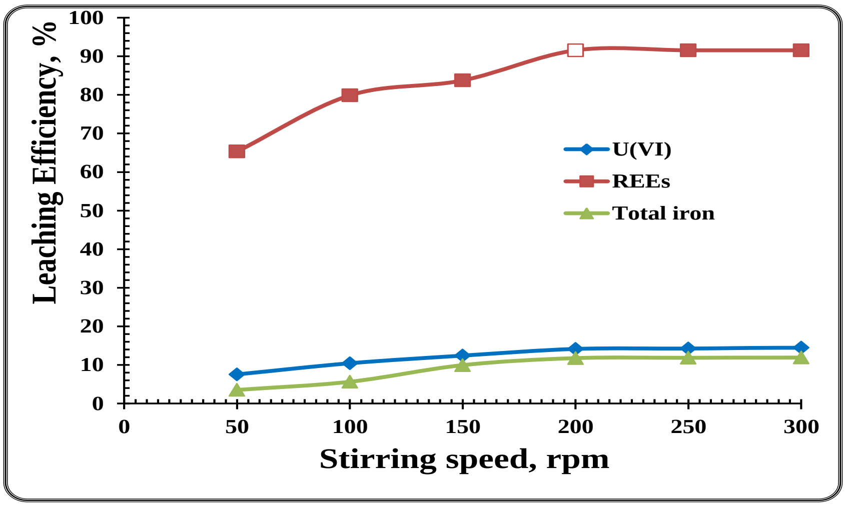

Figure 17: Effect of stirring speed on leaching efficiency of REEs from El Sela sample (200 g/L HCl, 200 g/L NH_4Cl, 1:4 S:L phase ratio, 149-100 µm particle size, 5 h contact time, room temperature)

3.2.2.7. Effect of particle size on leaching efficiency

Figure (18) represents the influence of particle size of ore material on the REEs leaching efficiency. The study is conducted using constant experimental factors at 200 g/L HCl, 200 g/L NH_4Cl, 1:4 S:L phase ratio, and 200 rpm stirring speed for 5 h contact time at room temperature. It is obvious that the leaching efficiency of REEs is increased with decreasing the particle size of the studied sample. The particle size 100-63 µm has achieved the optimum leaching efficiency of REEs (96.25%). The latter value of REEs leaching efficiency is attained using smaller particle size 63-32 µm and 32 µm. As a consequence, 100-63 µm is the proposed particle size of studied samples during REEs leaching process.

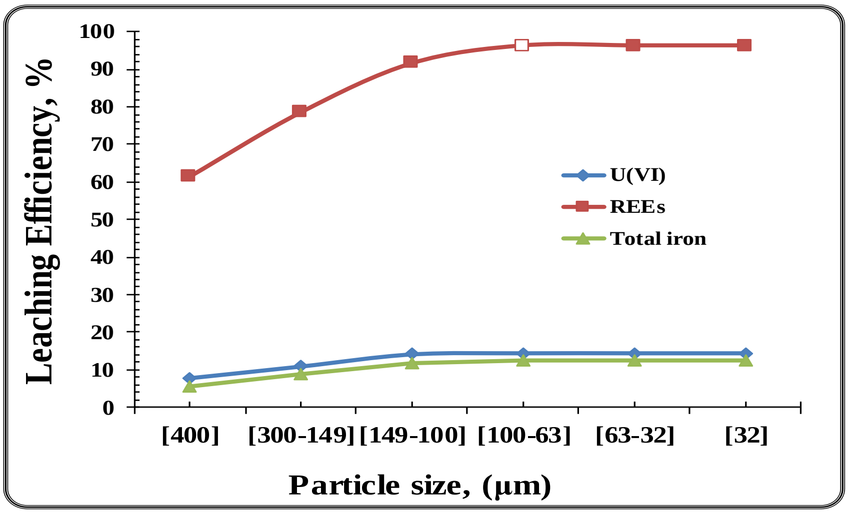

Figure 18: Effect of particle size on leaching efficiency of REEs from El Sela sample (200 g/L HCl, 200 g/L NH_4Cl, 1:4 S:L phase ratio, 200 rpm stirring speed, 5 h contact time, room temperature).

3.2.2.8. Effect of temperature on leaching efficiency

To study the effect of temperature of the leaching efficiency of REEs, several experiments of uranium leaching processes are applied at different temperature changing from 25 to 80 °C. The other experimental parameters are fixed on 200 g/L HCl, 200 g/L NH_4Cl, 1:4 S:L phase ratio, 100-63µm particle size, 200 rpm stirring speed for 5 h contact time. From the results obtained in Figure (19). It seems that the leaching process of REEs is an endothermic process since the leachability of REEs improved from 96.25% at room temperature 25 °C to 99.15% at 80 °C. The change in REEs leaching efficiency is not much. According to feasibility, the leaching of REEs should be at 25 °C to economize the expenditure. Positively, the weather of Egypt is warm enough to help to carry out the leaching process at 40~50 °C.

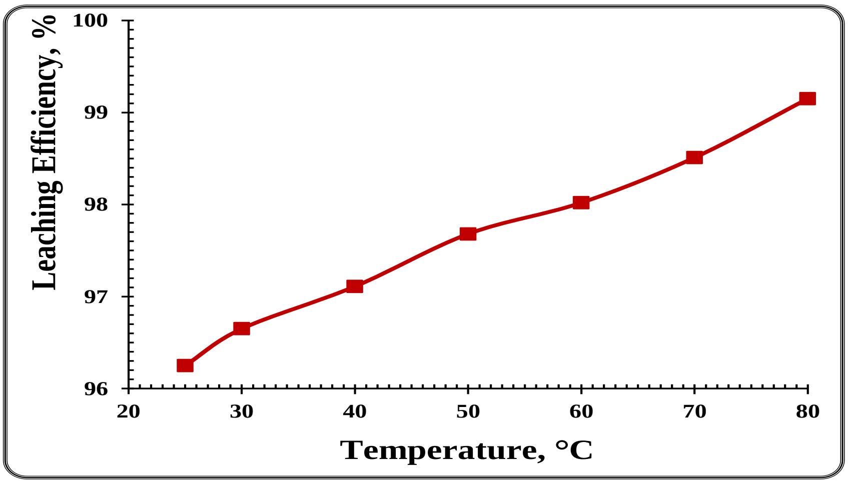

Figure 19: Effect of temperature on leaching efficiency of REEs from El Sela sample (200 g/L HCl, 200 g/L NH_4Cl, 1:4 S:L phase ratio, 200 rpm stirring speed, 5 h contact time, room temperature)

3.2.2.9. Leaching thermodynamic of REEs

The acidic leaching of REEs from the El Sela sample using hydrochloric acid is thermodynamically studied to explore the feasibility and spontaneity of the leaching process through the determination of thermodynamic parameters. The thermodynamic parameters are calculated according to the previous equations (2-5).

The values of both ΔH° and ΔS° are calculated from the slope (-ΔH°/R) and intercept (ΔS°/2.303R) of the Log K_d versus 1/T plot, presented in Figure (20). From the obtained data, the values of R^2 of the thermodynamic model are near to unity, indicating a good linearity. The values of ΔH°, ΔS° and ΔG° for leaching process is obtained and presented in Table (4). It has to be mentioned in this regard that the value of change in enthalpy (ΔH°) is found to be positive for REEs, confirmed the endothermic nature of the acid leaching of total REEs from the studied sample; while the positive value of change in entropy (ΔS°) suggested an increase in randomness due to the leaching of the metal ions from the working sample. The negative value 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. Meanwhile, the positive values of Gibbs free energy of uranium and iron ions are expected the non-spontaneous reaction at any temperature and the decrease in ΔG° value with increasing the temperature implies that the reaction is not favorable at room temperature.

Table 4: Thermodynamic parameters for REEs, U(VI), and iron ions leaching from El Sela sample.

Metal ions	ΔH	ΔS	ΔG (KJ/mol)						
	kJ/mol	kJ/mol.K	298 K	303 K	313 K	323 K	333 K	343 K	353 K
REEs	17.58	0.085	-7.897	-8.32	-9.179	-10.03	-10.89	-11.74	-12.59
U(VI)	9.67	0.017	4.434	4.346	4.171	3.995	3.819	3.643	3.467
Iron	10.56	0.019	4.843	4.747	4.556	4.364	4.172	3.981	3.789

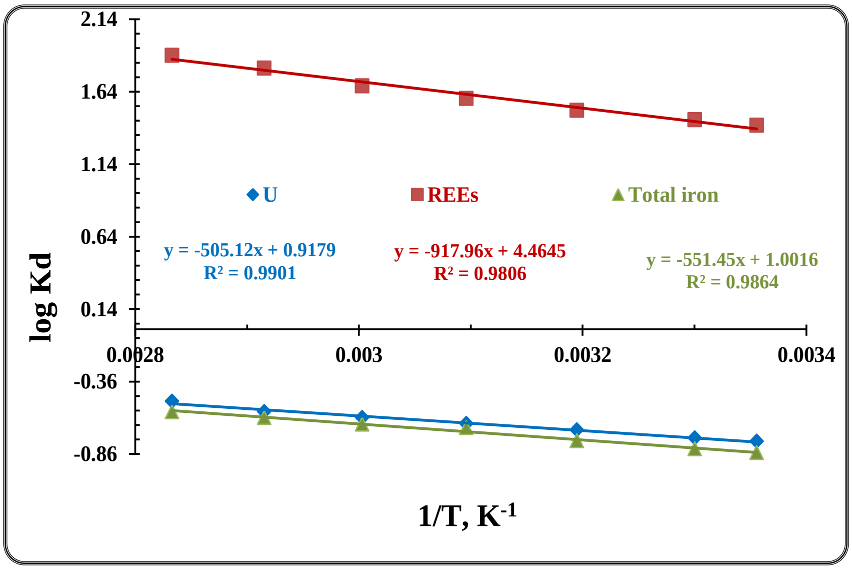

Figure 20: Plot of Log K_d versus 1/T for REEs, uranium, and total iron leaching from El Sela sample

4. Conclusions

The chemical analysis of El Sela sample manifests that uranium and REEs concentrations are 0.093% and 0.504%, respectively, indicating abundance of these elements. The maximum uranium leaching efficiency was conducted using 150 mg/L sulfuric acid in presence of 150 mg/L $(NH_4)_2SO_4$, 1:4 S:L phase ratio, for 6 h of contact time, 200 rpm stirring speed, and 149-100 µm particle size at room temperature. Whilst, the optimum leaching efficiency of REEs was attained using 200 mg/L hydrochloric acid 200 mg/L NH_4Cl, 1:4 S:L phase ratio, for 5 h of contact time, 200 rpm stirring speed, and 149-100 µm particle size at room temperature. Additionally, the thermodynamic studies demonstrate that the leaching process for both uranium and REEs ions are endothermic nature. The negative value of ΔG° points out that the leaching is spontaneous reaction.

Whereas, the positive values of entropy change, ΔSº, for the studied metal ions, suggested an increase in randomness due to the leaching of the metal ions from the studied sample.

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