

Complete Dissolution of Uranium and Rare Earths in One Step from the Alkaline Uranium Concentrate Residues

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Summary-Abu Zenima wastes with significant contents of uranium and rare earths were leached with sulphuric acid which achieve maximum dissolution for Uranium and Rare earths. A complete dissolution for uranium and about 97.4% for rare earths were performed using 3 mol/L sulfuric acid; 15 min contact time; 1/10 solid/liquid ratio and 500 rpm agitation speed at 90°C leaching temperature. The experimental data were interpreted with a shrinking core model with diffusion control through a porous product layer. The dissolution reaction for uranium and rare earths was found to be pseudo first order, with apparent activation energy of 19.93 and 16.03 kJ /mole.

Introduction

Recovery of uranium and rare earths are still today a matter of greatest concern.^(1, 2) Egypt has a long experience in uranium and rare earth technology, from the ores mining until the separation and production of uranium and rare earth concentrates.⁽³⁻⁵⁾

An enormous amount of work on uranium recovery techniques using sodium carbonate is done on uranium mineralizations from Abu Zenima area, Sinai Desert, Egypt.⁽⁶⁾ A huge amounts of solid wastes are produced after carbonate dissolution processes for Abu Zenima ores, these wastes contain a considerable amount of uranium as sodium di urinate $\text{Na}_2\text{U}_2\text{O}_7$ and some rare earth elements as $\text{REE}(\text{OH})_3$.

Uranium alkaline leaching is highly selective as it reduces the impurities content and more economically preferred than acid leaching if the ore contains more than 12% of carbonates.^(7, 8) Other factors such as efficiency of uranium extraction, reagents cost, water and energy consumption, product quality and environmental impact must also be considered. Some rare earths are completely soluble in carbonate solutions, while others are only partially soluble and finally some are completely insoluble.⁽⁹⁾

Uranium leaching using sulfuric acid solutions is the most widely used process for the extraction of uranium from its ores because of the relatively low cost and wide availability of the

acid. The chemistry of uranium leaching using sulfuric acid is discussed in details by many authors. ⁽¹⁰⁻¹²⁾

Leaching kinetics and reaction mechanism of uranium from a natural sample have been investigated using sulfuric acid with varied temperature under oxidative acidic conditions, ⁽¹³⁾ Suresh et al. had improved the processing of lower grade uraninite bearing ores, ⁽¹⁴⁾ Lasheen et al have developed the leaching processes for uranium and molbednium from sulfuric acid solution ⁽¹⁵⁾ and Kandil et al have improved the rare earths leaching process from Abu Tartur phosphate ore using sulfuric acid .⁽¹⁶⁾

Due to the predicted increase in uranium and rare earths demands and with a decrease in the availability of numerous high quality grade ores, a greater understanding and awareness is needed to improve the mining technology of refractory ore wastes to meet future uranium and rare earths demands. The other point of view is to avoid the environment pollution and provide a pointer to potential environmental management requirements for new projects.

In this concern, the main objective of this work is to investigate the uranium and rare earths dissolution processes, taking into consideration the full dissolution in one step to increase the separation economics of both elements and to avoid any of uranium or rare earths in the wastes again. The kinetic of leaching process using sulfuric acid is performed in order to improve the understanding of the dissolution reaction mechanism for these wastes.

Experimental

Materials and Methods

The solid wastes were produced from hydrometallurgical treatments of uranium concentrates collected from Abu Zenima project, Sinai, Egypt. These treatments were carried out by sodium carbonate in order to get selective leaching for uranium.

A representative sample from the solid wastes was analyzed using X-ray fluorescence analytical instrument at Analytical Lab in Egyptian Atomic Power Energy Agency to determine the components present in the wastes.

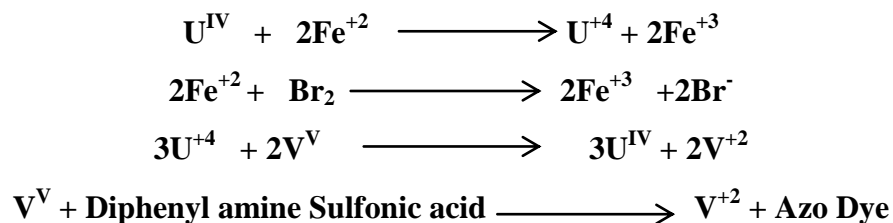
The experiments were carried out under the following fixed conditions:

- The chemicals and reagents used (sulfuric acid, nitric acid and sodium carbonate) were of analytical grade from Sigma-Aldrich and all dissolution experiments were carried out using double distilled water.
- The dissolution experiments were carried out in 100 mL glass beaker using hot plat magnetic stirrer.
- Temperature measurements were done using pH-mv-temp Meter from HAANA instruments.

- After each experiment, the retained leach pulp was allowed to cool to ambient temperature and then filtered out using filter paper (Whatman 41), the filtrate was analyzed for uranium and rare earths content and the leaching efficiency was calculated by the following equation.

$$\text{U or REEs Leach. Eff., \%} = \frac{\text{Leached U (VI) or REEs (III) conc.}}{\text{U (VI) or REEs (III) conc. in solid waste}} \times 100$$

- Uranium and total rare earths in original solid waste were determined by complete dissolution for 0.5 gram of a representative sample which heated with 12 mL of mixture concentrated nitric/perchloric acids in the ratio 1/3 in 100 mL Teflon beaker till complete evaporation, then 25 mL hydrofluoric acid was added and left to dry. Finally 30 mL of hydrochloric acid of 18% treated the attacked residue and a clear solution was obtained containing U (IV) and REE (III) ⁽¹⁷⁾.
- Uranium concentrations in the solid waste or in the leach liquor were calculated by oxidometric titration method against ammonium metavanadate after a prior uranium reduction in the presence of a diphenylamine sulfonic acid indicator until violet end point according to the following equations ⁽¹⁸⁾.



- Total REEs or individual elements in the solid waste or in the leach liquor were determined by Arsenazo III. In weakly acidic media (pH 2.3-2.7), the lanthanides and yttrium react with Arsenazo III to form coloured complex. The absorbance of its complex was measured at the wavelength 650 nm using UV-spectrophotometer “single beam multi-cells-positions model SP-8001”, Metretech Inc. ⁽¹⁹⁾

Batch tests for solid wastes dissolution

Many dissolution trials for uranium and rare earths were firstly performed by sodium carbonate, sulfuric acid and nitric acid with a fixed conditions of 1 mol/L acid or alkali, 1/10 solid/leaching solution ratio, 15 minutes contact time and 500 rpm agitation speed at 25 °C. These trials were conducted to select the more convenient leaching agent which achieve the

purpose of this study and succeeded in complete dissolution of both uranium and rare earths in one step.

Sulfuric acid was the preferred leachate in our study. So, several dissolution experiments was performed for a representative sample of Abu Zenima wastes using sulfuric acid, the studied factors affecting the dissolution of uranium and rare earths from the solid wastes were; sulfuric acid molarity, solid/leaching acid ratio, contact time, leaching temperature and agitation speed. These factors were summarized in Table 1.

Table 1: The Studied dissolution conditions for U and REEs from Abu Zenima wastes

| Factor | Variation range | Fixed conditions |
|--------------------------------------|--|-------------------------------------|
| Sulfuric acid molarity, mol/L | 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 | 1/10- 15 min.-100 °C-500 rpm |
| Solid/Leach Acid ratio, wt/v | 2/5, 1/5, 1/10, 1/15 and 1/20 | 3M- 15 min.-100 °C-500 rpm |
| Contact time, min. | 5, 10, 15, 20, 25 and 30 min | 3M-1/10- 100 °C- 500rpm |
| Temperature, °C | 20, 40, 60, 80 and 100 °C | 3M-15 min.-1/10-500 rpm |
| Agitation speed, rpm | 200, 300, 400, 500 and 600 | 3M-15 Min.-1/10-100 °C |

Results and Discussion

The waste characterization

A representative sample from Abu Zenima waste is undergoes to complete analysis for major and trace elements, the analytical results is indicated in Table 2 and Fig. 1 which proves the presence of a considerable uranium and rare earths content.

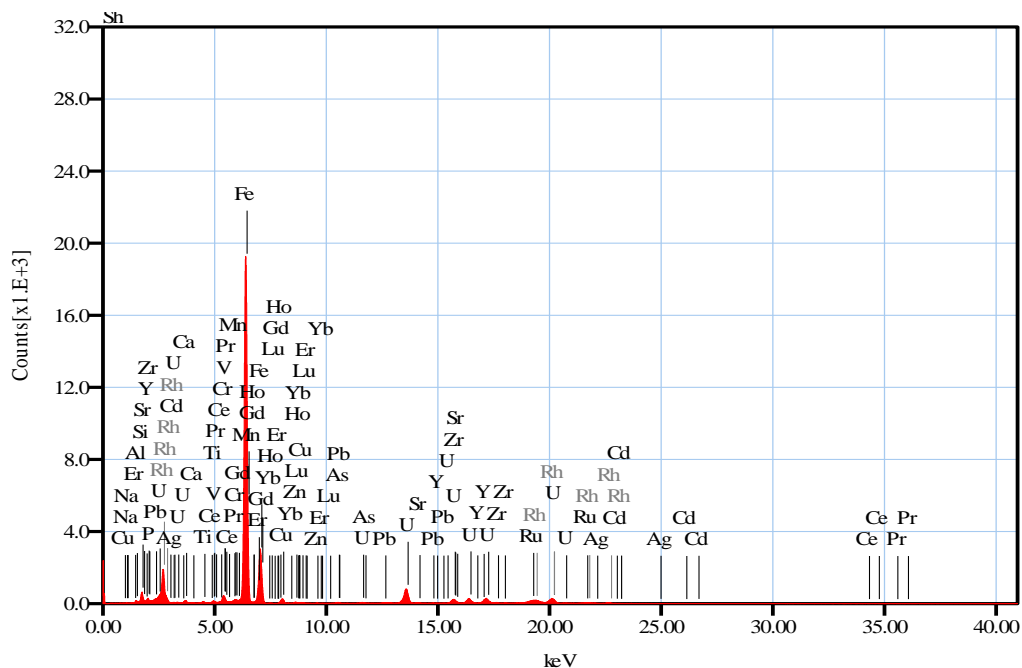


Fig. 1: XRF-chart for Abu Zenima wastes

Table 2: XRF-Elemental analysis of Abu Zenima waste

| Element | Ms%* | Element | ms% | Element | ms% | Element | ms% |
|--------------------------------|-------|--------------------------------|-------|-------------------------------|------|---------------------------------|------|
| Na ₂ O | 6.45 | Cr ₂ O ₃ | 1.04 | Y ₂ O ₃ | 0.01 | Gd ₂ O ₃ | 0.16 |
| Al ₂ O ₃ | 6.82 | MnO | 0.05 | ZrO ₂ | 0.36 | Ho ₂ O ₃ | 0.27 |
| SiO ₂ | 13.32 | Fe ₂ O ₃ | 62.63 | RuO ₂ | 0.06 | Er ₂ O ₃ | 0.22 |
| P ₂ O ₅ | 0.81 | CuO | 1.09 | Ag ₂ O | 0.01 | Yb ₂ O ₃ | 0.22 |
| CaO | 1.01 | ZnO | 0.25 | CdO | 0.03 | Lu ₂ O ₃ | 0.01 |
| TiO ₂ | 0.26 | As ₂ O ₃ | 0.15 | PbO | 0.01 | Pr ₆ O ₁₁ | 0.33 |
| V ₂ O ₅ | 0.44 | SrO | 0.03 | CeO ₂ | 0.37 | U ₃ O ₈ | 3.59 |

* Mass percentage

Results of dissolution trials

According to the nature of these wastes and its preparation after carbonate dissolution processes for Abu Zenima uranium minerals, the leaching efficiencies of uranium and rare earths are tested using sulfuric and nitric acids each separately using fixed conditions of 3 mol/L of leaching solution, 1/10 solid/leaching solution ratio, 15 minutes contact time and 500 rpm

agitation speed at 80 °C. From the experimental results as shown in Fig. 2, the three leaching agents don't succeed in differentiate between uranium and rare earths and a partial or complete dissolution for uranium and rare earths are carried out. However, maximum dissolution for uranium and rare earths is achieved using sulfuric acid as a leaching agent. So, sulfuric acid is the convenient leachate to achieve the dissolution of uranium and rare earths in one step.

Results of sulfuric acid dissolution experiments

The dissolution efficiencies for uranium and rare earths from Abu Zenima solid wastes are investigated using sulfuric acid which is one of the most convenient leaching agents.

Sulfuric acid molarity

By varying the Sulfuric acid molarity from 0.5 to 4 mol/L (under fixed conditions of a solid/liquid S/L ratio of 1/10, 15 min leaching time and a stirring rate of 500 rpm at 100 °C). As shown in Fig. 2, the sulfuric acid of 3 mol/L is the preferred acid concentration which applies in the subsequent leaching experiments.

Solid /liquid ratio

Effect of solid /liquid (S/L) ratio from 2/5 to 1/20 is studied under fixed conditions of 3 mol/L H₂SO₄, and agitation for 15 minutes with 500 rpm at 100 °C. From Fig. 2, it is noticed that the leaching efficiency of both uranium and rare earths are improved by altering the S/L ratio from 2/5 to 1/10. However, there isn't any increase in the leaching efficiencies above 1/10 ratio. So, solid /liquid ratio of 1/10 is considered the preferred ratio.

Agitation time

The effect of agitation times ranged from 5 to 30 minutes on the leaching efficiencies of uranium and rare earths is studied using fixed conditions of 3 mol/L H₂SO₄, solid/liquid ratio 1/10 and 500 rpm agitating rate at 100 °C. From Fig. 2, the leaching efficiencies of uranium and rare earths are increased by prolonging

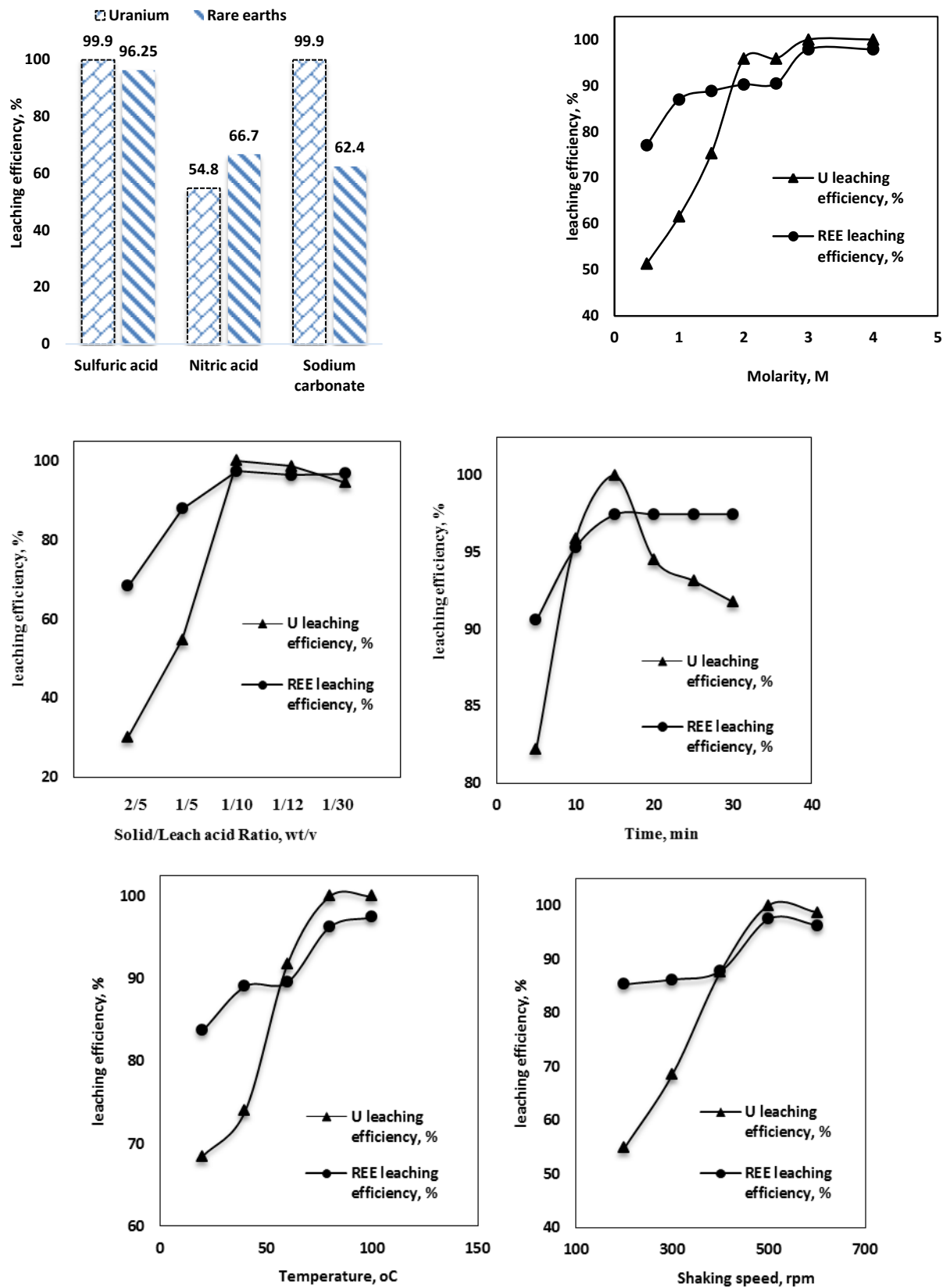


Fig. 2 The studied factors affected on the leaching efficiency of U (VI) and REEs (III)

The time from 5 to 15 minutes. There are not any enhancements in leaching efficiencies by prolonging the stirring time over 15 minutes.

Leaching temperature

The effect of leaching temperature on the leaching efficiencies of uranium and rare earths is studied from 20 to 100 °C under conditions of 3 mol/L H₂SO₄, solid /liquid ratio of 1/10 and agitated with 500 rpm for 15 minutes. From Fig. 2, as the dissolution temperature enhances from 20 to 100 °C as the leaching efficiencies of uranium and rare earths increase from 68.5 to 100% and from 83.7 to 97.4%, respectively.

Agitation speed

Maximum dissolution for uranium and rare earths are performed using the agitation speed of 500 rpm under the optimum conditions of 3 mol/L H₂SO₄, solids/liquid ratio 1/10, contact time 15 min at 100 °C. This is observed from the agitation speed plotted curve with several agitation speeds as shown in Fig. 2.

Uranium dissolution kinetics

In order to determine the kinetic terms and rate-controlling step for the dissolution processes for uranium and rare earths by sulfuric acid, the experimental data are analyzed using fluid–solid heterogeneous reaction models. The validity of the experimental data into the integral rate is tested by statistical and graphical methods. The rate of reaction between the solid particle and the acid may be controlled by one of the following steps: diffusion through the ash/product layer, diffusion through the fluid film, or the chemical reaction at the surface.

The integrated equations for fluid–solid heterogeneous reactions are: ^(20, 21)

For ash layer diffusion control:

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = k_1 t, \quad (1)$$

For chemical reaction control:

$$1 - (1 - X)^{1/3} = k_2 t \quad (2)$$

For surface diffusion control:

$$1 - (1 - X)^{2/3} = k_3 t \quad (3)$$

And for film diffusion control:

$$X = k_4 t \quad (4)$$

Where k_1 , k_2 , k_3 and k_4 are the apparent reaction rate constants (min^{-1}) for each case respectively and t is the leaching time and X is the fractional conversion for U (VI) and REE (III) expressed as

$$X = \frac{\text{U or REEs conc. in the leached solution}}{\text{U or REEs conc. in the feed solution}}$$

U or REEs conc. in the original solid waste

By plotting $[1-3(1-X)^{2/3} + 2(1-X)]$, $[1-(1-X)^{2/3}]$ and $[1-(1-X)^{1/3}]$, $[X]$ each separately versus the time at various temperature (20, 40, 60, 80 and 100 °C) for uranium and rare earths dissolution processes and from the R-squares values which illustrated in Table 3, it is indicated that Eq. (3) which represented the ash layer diffusion control equation has the greatest R-squared values for all the lines and has the most compliant with the experimental data.

These consequences indicated that the linear relationship between $[1-3(1-X)^{2/3} + 2(1-X)]$ and the leaching time is significant and proved that the leaching rate of uranium and rare earths were diffusion controlled.

Table 3 R-squares of plotting $(1-3(1-X)^{2/3} + 2(1-X))$, $(1-(1-X)^{1/3})$, $(1-(1-X)^{2/3})$ and (X) versus time at various temperatures for uranium and rare earths dissolution reactions

| | | R ² for the line obtained from plotting of | | | |
|-----------------------------|--------------------|---|---------------------------------|---------------------------------|---------------|
| | At temperature, °C | $1-3(1-X)^{2/3}+2(1-X)$ versus time | $1 - (1 - X)^{1/3}$ versus time | $1 - (1 - X)^{2/3}$ versus time | X versus time |
| For Uranium dissolution | 20 | 0.931 | 0.796 | 0.705 | 0.56 |
| | 40 | 0.919 | 0.756 | 0.659 | 0.485 |
| | 60 | 0.91 | 0.752 | 0.659 | 0.381 |
| | 80 | 0.921 | 0.884 | 0.624 | 0.252 |
| | 100 | 0.938 | 0.864 | 0.636 | 0.2 |
| For Rare Earths dissolution | 20 | 0.921 | 0.737 | 0.483 | 0.532 |
| | 40 | 0.901 | 0.735 | 0.378 | 0.489 |
| | 60 | 0.904 | 0.752 | 0.449 | 0.461 |
| | 80 | 0.911 | 0.842 | 0.262 | 0.396 |
| | 100 | 0.904 | 0.897 | 0.209 | 0.372 |

3.5 Determining the order of the reaction

In order to determine the rate law for uranium and rare earths dissolution processes by sulfuric acid, the plotting of $\ln [C]$, $1/[C]$ or $[C]$ versus time are carried out which are in fact expressing to first order, second order or zero order, respectively, an indication on whether the

plotting is a straight line has to be found where, C represents the total concentration of uranium or rare earths dissolved.

By plotting the curves of uranium and rare earths dissolutions, the R-squared values for all lines are illustrated in Table 4. Plotting of $\ln [C]$ against time curve for uranium dissolution (Fig. 3) is the more fitting and has straight lines of high R-square values at the five studied temperatures (20, 40, 60, 80 and 100 °C). So, the uranium dissolution process is pseudo first order. On the other hand, plotting of $\ln[C]$ against time curve for rare earths dissolution (Fig. 4) is the more fitting curve and has straight lines of high R-square values at the five studied temperatures. So, the rare earths dissolution process is pseudo first order.

Table 3 R-squares values for U (VI) and REEs (III) dissolution lines at different temperatures

| | R ² for the line obtained from plotting of | | | |
|-------------------------------------|---|----------------------|-------------------|-----------------|
| | At Temperature, °C | $\ln[C]$ versus time | 1/[C] versus time | [C] versus time |
| For Uranium dissolution process | 20 | 0.945 | 0.958 | 0.748 |
| | 40 | 0.953 | 0.792 | 0.726 |
| | 60 | 0.96 | 0.836 | 0.633 |
| | 80 | 0.967 | 0.599 | 0.548 |
| | 100 | 0.977 | 0.726 | 0.516 |
| For Rare earths dissolution process | 20 | 0.931 | 0.907 | 0.664 |
| | 40 | 0.917 | 0.949 | 0.608 |
| | 60 | 0.974 | 0.71 | 0.607 |
| | 80 | 0.942 | 0.467 | 0.515 |
| | 100 | 0.982 | 0.692 | 0.493 |

The value of the rate constant k is determined from the slope of the resultant lines. Since the uranium and rare earths dissolution processes are first order, the slope of the line would equal -k, where

$$\text{Slope} = \frac{\Delta (\ln[C])}{\Delta t} = -K$$

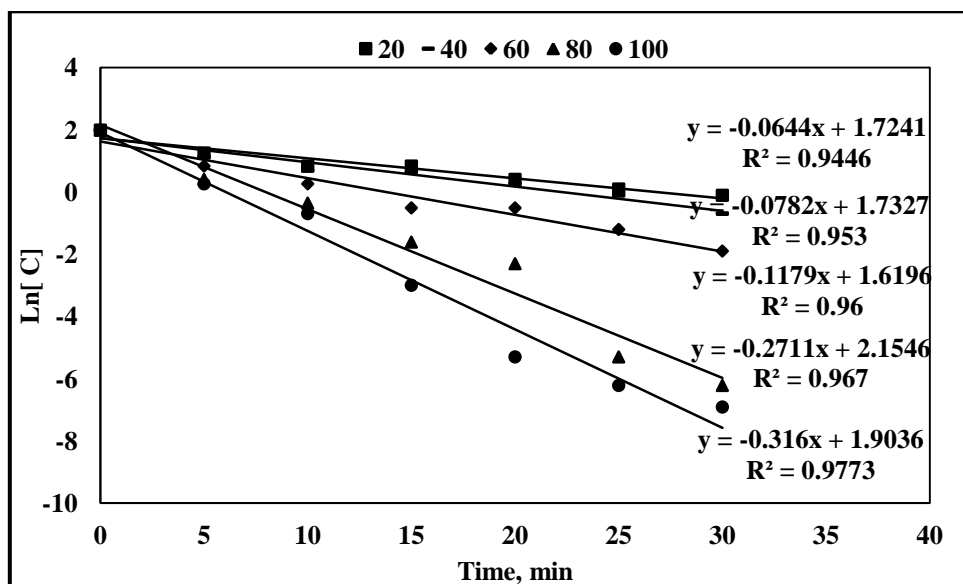


Fig. 3 plotting of $\ln [C]$ versus time for U (VI) dissolution process
(3 mol/L H_2SO_4 , S/L 1/2, 500rpm)

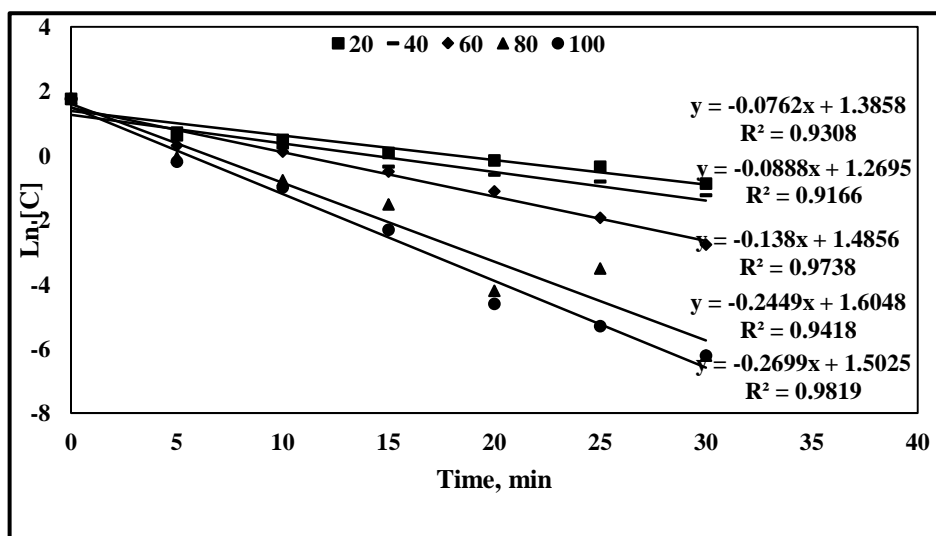


Fig. 4 plotting of $\ln [C]$ versus time for REEs (III) dissolution process
(3 mol/L H_2SO_4 , S/L 1/2, 500rpm)

From Table 5, it is observed that rate constant for uranium and rare earths dissolution processes increased gradually by increasing the temperature which indicates that the rate of dissolution reaction enhances with the increasing of reaction temperature.

Table 5 Rate constant values for uranium dissolution processes at different temperatures

| At Temperature, °C | Rate constant “K” for U(VI) dissolution process | Rate constant “K” for REEs(III) dissolution process |
|--------------------|---|---|
| 20 | 0.0717 | 0.0762 |
| 40 | 0.0788 | 0.0888 |
| 60 | 0.1268 | 0.138 |
| 80 | 0.2199 | 0.2449 |
| 100 | 0.3566 | 0.2699 |

The apparent activation energy for uranium and rare earths dissolution reactions are determined from the Arrhenius equation: ^(22, 23)

$$\ln k = \ln A - E_a/RT \quad (5)$$

Where k is the reaction rate constant, A is the frequency factor, E_a is the apparent activation energy and R is the ideal gas constant. By plotting of $\ln k$ versus $1/T$ for uranium and rare earths dissolution results as shown in Fig. 7, the regression analysis for this plot shows a respectable linear relationship and the apparent activation energy (E_a) for uranium and rare earths dissolution are 19.93 and 16.03 KJ/mol respectively. It is worthy to mention that activation energies values suggested that the dissolution reactions are carried out through a diffusion controlled process.

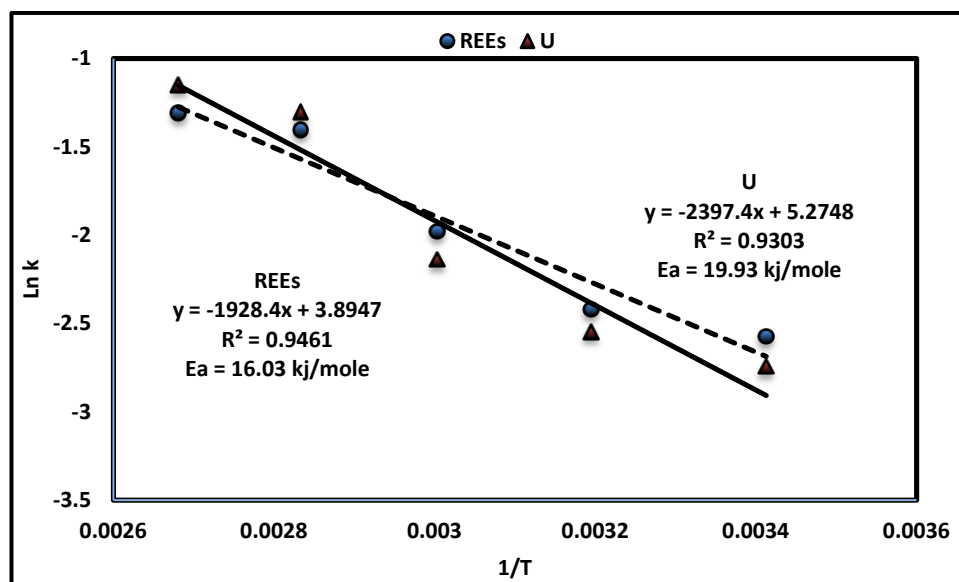


Fig. 7 Arrhenius plot for uranium and rare earths dissolution (3 mol/L H_2SO_4 , 1/10 solid/ liquid ratio, contact time 15 min)

Conclusion

Optimum dissolution results for uranium and rare earths from Abu Zenima wastes are achieved in one step using sulfuric acid. So, the separation of uranium from rare earths solutions is carried out through the extraction process using a selective organic solvent.

Dissolution processes for uranium and rare earths using H₂SO₄ acid are optimized by conditions of 3 mol/L H₂SO₄, 500 rpm agitation speed, 1/10 solid/liquid ratio and 15 minutes agitation time at 100 °C. Leaching efficiencies of 100% for uranium and 97.9% for rare earths are obtained by the optimum leaching conditions.

The leaching kinetics of uranium and rare earths using sulfuric acid are ash layer diffusion controlled and follows the shrinking core model $1-3(1-X)^{2/3} + 2(1-X) = kt$.

The kinetics studies prove that the reaction rates of uranium and rare earths dissolution processes are enhanced by increasing the leaching temperature and the order of reactions are first order for uranium and rare earths with apparent activation energy of 19.93 kJ/mol for U (VI) and 16.03 kJ/mol for REEs (III).

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