

Potentiality of Caro's Acid in Leaching of Uranium from Abu-Rusheid Mylonite Rocks, South Eastern Desert, Egypt

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ABSTRACT

Abu Rusheid area is located at the southern Eastern Desert of Egypt and composed of Mylonitic gneiss rocks (mineralized rock), Serpentine rocks, Ophiolitic metagabbro, Ophiolitic mélange, Monzogranites, post-granitic dykes (lamprophyre and dolerite), veins and recent alluvial deposits. The mineralized gneissic rocks and lamprophyre dykes are rich in base metals (Pb, Zn, Cu, and As) and HFSE (Nb, U, Th, Zr, HREE and Y). This paper is concerned with the study of potentiality of sulphuric and Caro's acid in uranium dissolution from Abu Rusheid mineralized rocks. For this purpose, many batch dissolution experiments were conducted. The obtained results showed that 91.5% and 52% uranium leachability for Caro's acid and dilute sulfuric acid respectively, at 1M H₂SO₄, 4hr contact time, room temperature, 1:4 solid: liquid ratio, 300µm grain size and 300rpm stirrer speed. The reaction mechanism was described using shrinking core models, which shows that the reaction is controlled by the diffusion of Caro's acid into the product particle layer. The calculated activation energy E_a is -11.03 and -8.48 kJ/mole for chemical reaction control and diffusion reaction control respectively.

Keywords: Uranium Dissolution; Caro's Acid; Oxidation; Kinetics; Shrinking Core Models; Abu Rusheid Area.

Introduction

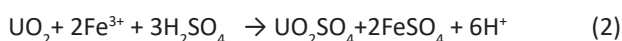
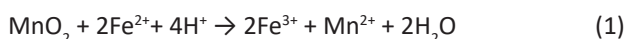
Resulted of many Exploration activities for uranium resources at south Eastern Desert of Egypt, the discovery of hot gneiss rocks (U, Th, Nb, Ta, Zr, Pb, Y, Zn, W, Sn and Ga), in Wadi (W.) Abu Rusheid area, cut by lamprophyre dykes bearing mineralization (U, REEs, Pb, Ag and Zn) along two shear zones [1-4] as well as, low grade metamorphosed sandstone type-uranium deposit (U and Mo) in W. Sikait, 4km from W. Abu Rusheid [5].

Abu Rusheid area is located at the southern part of the Eastern Desert of Egypt, about 95 km to the Southwest of Marsa-Alam City. It is bounded by Latitudes 24° 36' 29" and 24° 39' 22" N and Longitudes 34° 44' 40" and 34° 47' 23" E. It can be reached from the Red Sea coast through W. El Gemal, W. Nugrus and then W. Abu Rusheid. The granite body is located at the eastern margin of the junction between W. Nugrus and Abu Rusheid. The gneiss rocks are subjected to polycyclic deformation and metamorphism and characterized by regional WNW–ESE thrusting. Such thrusting is assigned to an age between 682 Ma (the time of emplacement of the older granitoids) and 565 to 600 Ma, the time of intrusion of the younger granites [6].

The rocks are generally intensively deformed and show clear gradual variation from low grade green schist facies, through the medium grade amphibolite facies (Staurolite – Kyanite – Silliminite facies) [7,8]. Uranium exists naturally in two oxidation states U^{4+} and U^{6+} which termed as primary and secondary respectively. Primary uranium ores include uraninite and pitchblende are predominantly found in veins or pegmatites but are also found in sedimentary and placer deposits [9]. Where the secondary uranium ores are found in weathered zones of primary deposits and precipitated in sediments. These include autinite, torbernite, uranophane, carnotite, and schoepite [10]. Primary uranium is lowering soluble in both dilute acid and carbonate (alkali) solutions than secondary one. So that it economically performs the uranium leaching on proper oxidizing conditions to achieve high uranium extraction.

Uranium leachability is directly proportional to the free acidity of leach solution which range from 20 to 100g/L. However, the using acid leaching medium should not be too strong; very high proton concentrations inhibited the oxidation of U^{4+} to U^{6+} [11]. At concentrations higher than 200g/L the leaching response was inhibited [12]. This consequently leads to an increase in the leachability of other gangues metals associated uranium.

Several trails around the world use, an oxidant such as sodium chlorate, hydrogen peroxide (H_2O_2) and pyrolusite. But that use resulted in accumulating the heavy metal manganese and sodium chloride as the major contaminant in the acidic waste, which restricts its recycling to the mill [13]. Iron oxides minerals such as Hematite and magnetite could be played as oxidizing agent in uranium dissolution process since oxidizing the U^{4+} to U^{6+} as in the following eqns:



Caro's acid is the best alternative oxidant to pyrolusite and sodium chlorate. Since, it was easier to handle, provided better control and a completely automated system, ensured continual oxidant supply and almost eliminating manganese from waste effluents [14, 15].

Batch leaching tests on Ranger, Nabarlek, Koongarra, and Jabiluka ores showed that uranium extraction was unaffected by choice of oxidant, but that Caro's acid reduced acid and lime requirements by 15 - 25% and 20 - 30% respectively [16]. To gain a better understanding of the leaching process and its operation, kinetic studies should be concerned. Since the leaching kinetics interpret the complex behavior of leaching process occur on grain particles [17]. Thus, this study includes investigation and discussion of the leaching kinetics and dissolution of uranium on Caro's acid solution. The shrinking core models considered the best kinetics model chosen to describe the kinetics in heterogeneous reactions like mineral leaching from ores.

For leaching uranium from Abu-Rusheid uranium mineralization, phosphoric acid was examined. Results obtained encourage recommending phosphoric acid as an alternative to sulphuric acid leaching agent for uranium [18]. It is demonstrated by the

laboratory experiment that heap leaching is suited to process Abu-Rusheid uranium mineralization; D263B strong base anion resin can effectively concentrate and purify the obtained pregnant solutions to produce a quality product, namely yellow cake [19].

The present paper concerned with study the leachability of Abu Rusheid uranium minerals ores situated at the Southern Eastern Desert of Egypt. The potentiality of Caro's acid was established in batch experiments followed by kinetics investigation.

Geologic setting

Regional geology

Abu Rusheid outcrops over an area of ca. 73.5 km² in the south Eastern Desert of Egypt as a small part of the southern region of the Arabian-Nubian Shield (ANS). The shield covers more than 6 x 10⁶ km² [20,21] and represents one of the largest Neoproterozoic crustal growth events on earth and was exposed after uplift and erosion during Oligocene and younger times [22,23]. The Arabian-Nubian Shield (ANS) consists of Precambrian rocks on the both flanks of the Red Sea in western Arabia and northeastern Africa (Fig. 1a; [24]. The ANS is dominantly juvenile continental crust, i.e. crust formed from mantle-derived melts [25-27]. It is formed between 900 and 550 Ma when the Mozambique ocean closed by accretion of arc terranes [22]. The Arabian Nubian Shield covers several countries, mainly Egypt, Eritrea, Ethiopia, Saudi Arabia, Somalia, Sudan, Oman and Yemen. The Abu Rusheid area is a part of the Arabian-Nubian Shield and can be considered a key domain in that shield, beside its very complex structures. This area lies in the Wadi Al Gemal basin and hosts a wealth of sources of uranium and other nuclear elements. In addition, this area is considered as the southeastern extension of the Migif-Hafafit metamorphic complex [28-30], which is highly tectonized and characterized by presence of several types of mineralization and alteration processes along time spans. Abu Rusheid-Sikait area is bordering to the major shear zone recognized by many authors as the Nugrus thrust fault [31] or the Nugrus strike-slip fault [32] and or Shait-Nugrus shear zone [33].

Geology of the study area

The main rock units encountered in this area are grouped from older to younger as follows; - (a) Mylonitic gneiss rocks, (b) Serpentinite rocks, (c) Ophiolitic metagabbro, (d) Ophiolitic mélangé, (e) Monzogranite rocks, (f) Post-granitic dykes and veins (Fig.1b). The mylonitic gneiss rocks (2.0 km²) represent the oldest rocks exposed in W. Abu-Rusheid area. These mylonitic gneisses were originally identified as psammitic gneisses [34-37], occur in the field down thrust the ophiolitic mélangé and foliated in ENE-WSW direction (Fig. 2a). The mylonitic gneiss rocks of Abu Rusheid area is characterized by development of mylonitic fabric close to the shear and contact zones, low to moderate topography and highly sheared as well as show a well-developed planer banding, gneissosity and folding. These rocks are light gray to gray in color, fine to coarse grained and exhibit both gneissosity and augen structures and characterized by absence of enclaves. The altered rock acquires reddish to yellowish color due to staining with iron solutions. Some pyrite crystals were oxidized leaving vugs filled with quartz, iron oxides, carbonates and secondary U minerals. They are highly metasomatized and reflect high radioactive anomalies that contain abundant crystals of thorite, uranothorite, zircon, fluorite and Nb-bearing minerals (samarskite, pyrochlore, betafite) [38]. They are cross cut by three main shear zones; the first two shear zones are parallel to each other (NNW- SSE) and perpendicular to the third one (ENE-WSW), the NNW-SSE shear zones were emplaced by lamprophyre dykes which act as a good barrier (physical and chemical trap) capturing, adsorbing and protecting the uranium minerals that introduced to the gneiss with moving the uranium-rich hydrothermal solution (Fig. 2b-d). The two main shear zones are discontinuous and irregular in shape extending about 1.5 km.

They are variable in thickness from 1m to 2m, highly tectonized and rich with Zn, REEs, U, Y, Cu, Ag in decreasing order. They have general NNW trend and dips steeply (80°-85°) toward SW. The serpentinite is only found in a small part in the NW corner of the mapped area. The ophiolitic metagabbros are observed in sheeted mass overlying the ophiolitic mélangé. These rocks are highly tectonized

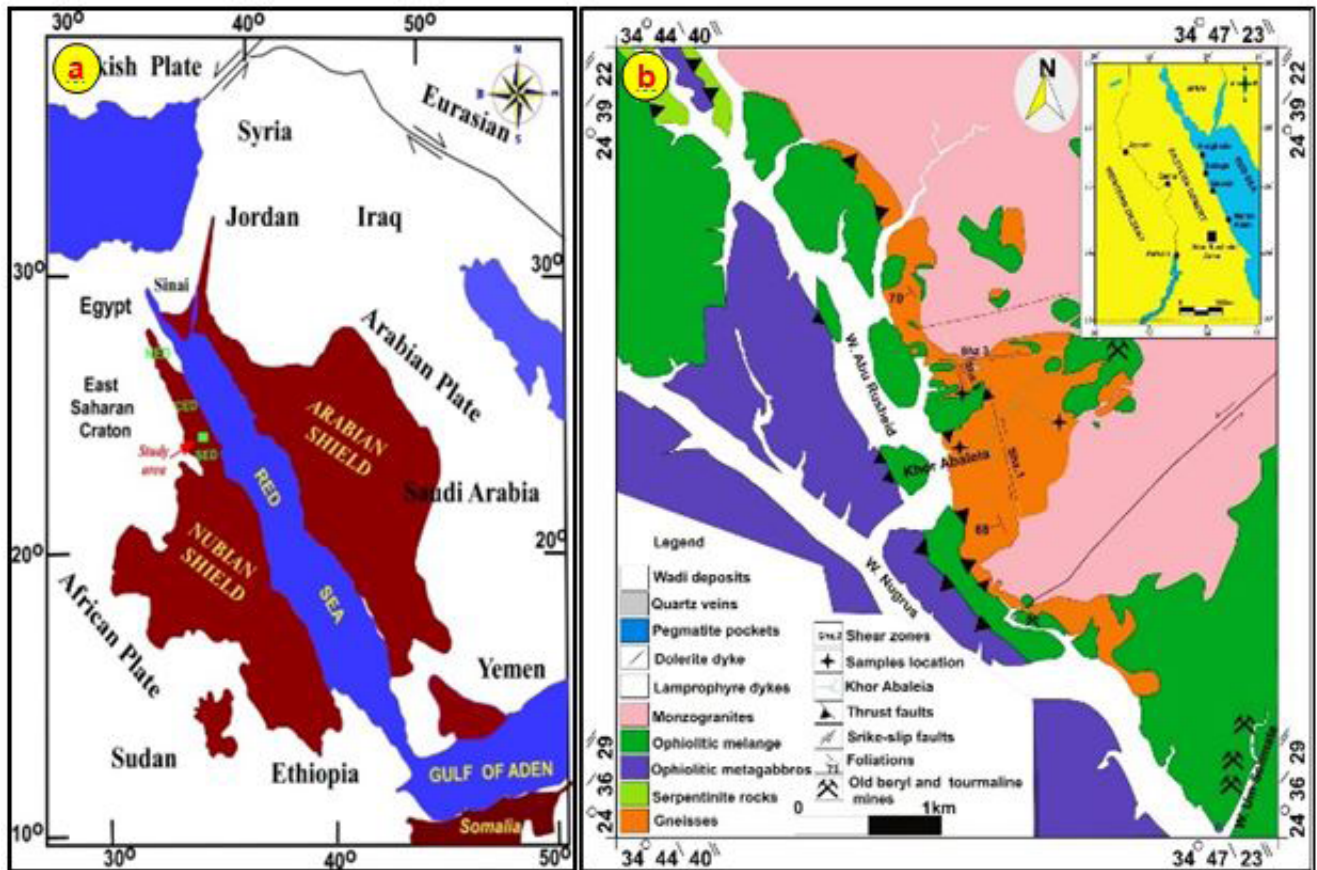


Figure 1: (a) Map of the Arabian-Nubian Shield (ANS) modified after Stern et al. (2006) [23]. (b) Geologic map of Abu Rusheid area, SED, Egypt, (after Ibrahim et al., 2004) [39].



Figure 2: Field photographs showing, (a) Ophiolitic melange thrust over mylonitic gneiss. (b) NNW shear zone (2). (c) Lamprophyre dyke. (d) Altered lamprophyre dyke associated with secondary uranium mineralization.

and form fold thrust sheets around W. Nugrus, W. Abu Rusheid, where the ophiolitic metagabbros are thrust over both ophiolitic mélangé and mylonitic gneiss rocks (NW-SE and dips 330/NE). Abu-Rusheid –Sikait granitic pluton is an elongated body extending NW-SE for about 12 km with width about 3 km. The granitic rocks occupy the major part of the mapped area surrounding the mylonitic gneisses (Fig.1b). They are represented from the NW direction by porphyritic biotite monzogranite followed by deformed biotite monzogranite and two mica monzogranite, whereas the muscovite granites occupy the SE part of the pluton [39].

Characteristics of the Radioactive Mineralization

The mylonitic gneiss rocks are characterized by well-developed Li, U, Th, Nb, Y, Au, As, Pb, Zn, Sn and Cu enrichments respectively. The common minerals that have been recognized in both mylonitic gneiss and lamprophyres are represented by zinnwaldite, U- minerals (soddyite, uranophane, autunite, kasolite, torbernite and meta- zeunerite) (Fig. 3a,b), Th-minerals (thorite and uranothorite), and gold, cassiterite, scheelite, xenotime (Y), allanite, zircon, fluorite, monazite (Ce) and Nb-Ta minerals. Thorium minerals (thorite and uranothorite) are clear in gneissic rocks only. Others minerals were recorded and studied such as (sulphides, tin, zinc–Manganese Minerals, fluorite, xenotime, zircon, allanite, monazite, iron oxide minerals, clay minerals (illite + kaolinite) and calcite and micas at Abu Rusheid area, Rashed, (2005). The average U/Th ratio in mylonite and lamprophyre dykes (1.32 and 40.0) is exceeding than average of crust (0.33), illustrate uranium gain, whereas in mylonitic gneiss samples, their U/Th ratio (0.24) is less than the average of crust, denote uranium loss. Also, testing of uranium equilibrium by recorded major chemical U addition ($U_{chem} / eU = 3$) in the mylonite gneiss and lamprophyre samples as indication for young surficial uranyl mineralization.

The descending (infiltrational) mineralization-bearing hydrothermal solutions are mainly derived from meteoric water, migrating under gravity from high relief peripheral hot uraniferous muscovite-biotite granite to low central part of the basin (mylonitic gneiss rocks) and redeposited along banding planes and fractures in mylonitic gneiss.

After the emplacement of lamprophyre dykes (mantled-derived with high temperature and volatiles, as well as, CO_2), the ascending (exfiltrational) hydrothermal solutions are dominantly derived from groundwater, and are mainly derived by high gas pressures penetrating into the basin, along banding planes and fractures in the host rocks with low

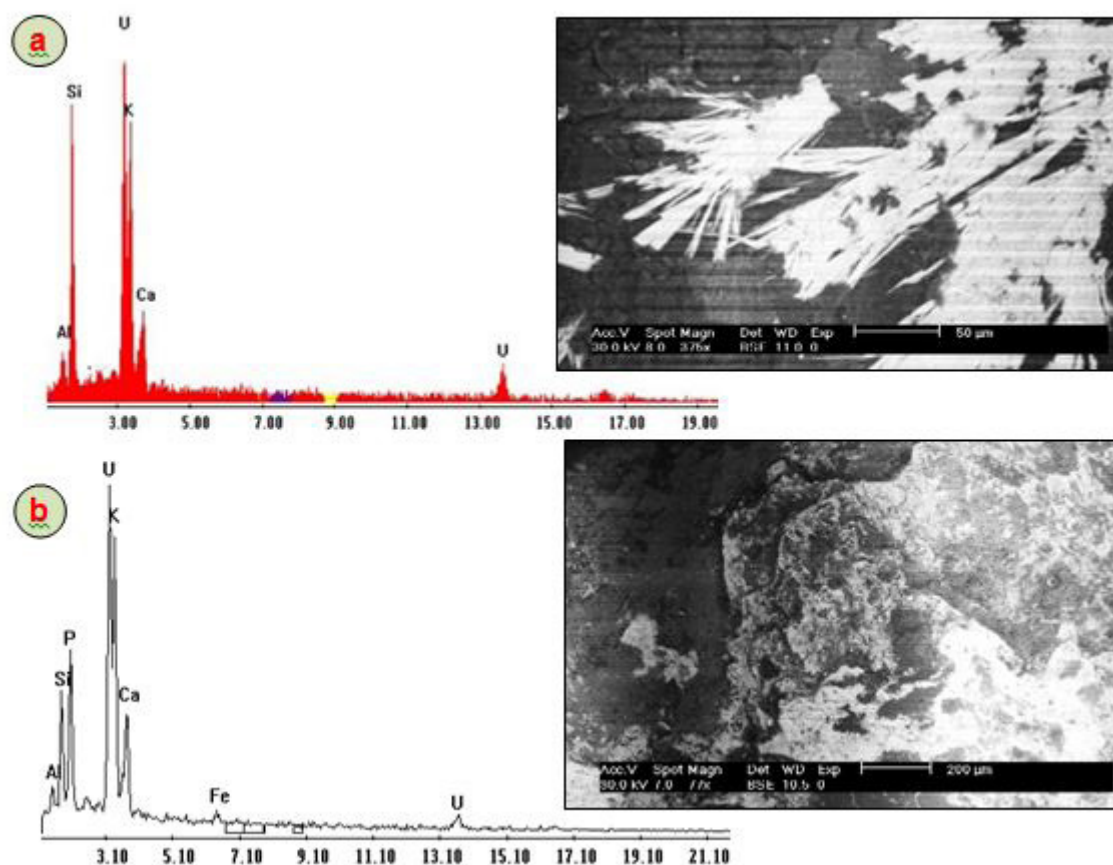


Figure 3: ESEM Micrograph and EDX chart of, a) - Uranophane and b) -Autunite of investigated rocks at Abu Rusheid area.

temperatures and containing $F1^-$ and CO_3^{2-} , PO_4^{3-} and H_2O caused redistribution; transportation and redeposition of the base metals (Pb, Zn, Cu and As), precious metals (Au and Ag) and in HFSE (e.g. Nb, HREE and Y), along the channel ways (banding of the gneissic rocks and fractures) to the shear zones (NNW-SSE) and precipitated in boxworks and adsorbed on clay minerals.

The lamprophyre dykes and mylonitic gneiss are characterized by ferrugination (high total iron). The latter indicates the presence of alkali hydrothermal solution, may precipitate Fe^{+3} and U^{+6} within micro-fractures in the form of iron-oxy-hydroxides rich in uranium. The occurrences of U-minerals in the pores (fractures and veins) indicate that, these minerals were deposited from solutions descending or ascending that permeated the micro-porous. Desulfidization process took place in the mylonitic gneiss rocks and lamprophyre dykes, where sulfide minerals such as pyrite, chalcopyrite and sphalerite are easily oxidized by ground water in the presence of oxygen to produce either ferric oxide or its hydrate analog, leaving box works. The release of Ca and F during illitization of plagioclases and biotite may combine together to form calcium fluoride ($Ca F_2$). This kind of alteration by acid solution is responsible for leaching mineralization from the banded mylonitic gneiss rocks, transported and adsorbed on the margins of NNW-SSE lamprophyre dykes (chemical trap for mineralization). However, it is important to test the nature of the uranium bearing minerals (whether an easily leachable uranium phase exists).

Experimental

Characterization of Abu Rusheid mylonite uranium mineralization

Abu Rusheid mylonite representative samples were collected from Abu Rusheid area which is located in the South Eastern Desert, Egypt. The ore sample was firstly crushed to 297 μm and 149 μm then ground to 74 μm particle sizes. Sample characterization by XRF showed the presence of Ba, Pb, Fe, Mo, Nb, Zr, Y, Sr, U, Zn, Mn, Ca, K, S, Si and Al. The representative sample is characterized chemically as major and trace elements by ignition at 1000 °C before preparing solutions A and B of Shapiro and Brannock method for analysis of silicate rock [40]. Uranium analysis was performed spectrophotometrically using Arsenazo (I) method [41]. Analysis performed using UV-spectrophotometer "single beam multi-cells-positions model SP-8001", Metretech Inc., version 1.02.

Leaching Experiments

Leaching experiments were conducted with a conical flask placed in a constant temperature water bath, with mechanical stirring and a thermometer for temperature control. 250 g of representative sample was introduced into the reactor to yield a solid/liquid ratio of 1/3. After leaching, the sample was washed with acidified water. The effects of changing various parameters such as sulfuric acid and H_2O_2 concentration, temperature, leaching time, grain size, S/L ratio and Eh were investigated. Used reagents (H_2SO_4 and H_2O_2) are of the analytical grade. Eh and pH were measured accurately using the pH- meter model (HAANA pH-mV-temp). Uranium was analyzed by titration against ammonium meta vanadate [42].

Results and discussion

Chemical characterization of uranium mineralization sample

Analysis of the working technological uraniferous mylonite sample has revealed a uranium assay of 400 ppm. Major elements analyzed involved 73.8% SiO_2 , 11.9% Al_2O_3 and 2.9% total iron as Fe_2O_3 as shown in Table (1) as well as some trace elements. The leaching of uranium minerals by sulfuric acid requires the presence of Fe^{+3} in order to oxidize U^{+4} to U^{+6} to form $U(SO_4)_4$ dissolved in leach liquor but Fe^{+2} is abundant than Fe^{+3} in the studied sample. Thus, it's necessary to presence of oxidant to oxidize Fe^{+2} to Fe^{+3} , which their presence serves an electron transfer catalyst between an oxidant and UO_2 [43].



Oxides	Wt%	Trace elements	Ppm
SiO ₂	73.8	Nb	680
TiO ₂	0.1	Zr	2650
Al ₂ O ₃	13.9	Y	750
Fe ₂ O ₃	0.7	Pb	800
FeO	2.2	Ga	85
MnO	0.1	Cu	190
MgO	0.85	Zn	1450
CaO	0.67	U	400
Na ₂ O	3.0	Th	573
K ₂ O	4.3	Nd	84
P ₂ O ₅	1.06	As	12
L.O.I	0.16	Sn	21

Table 1: The rock composition of Abu-Rusheid technological sample

Nerenest derived equation (1); could follow the ferric iron concentration on leach liquor, since it's correlated the redox potential with Fe³⁺ / Fe²⁺ ratio:

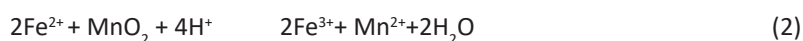
$$E_c = 397 + 0.1984T \log ([Fe^{3+}]/[Fe^{2+}]),$$

Where E_c is the solution potential relative to the saturated calomel electrode (mV) at 35°C, T is in K. The another model equation is predicted from plant data of hartebeestfontein operation:

$$E_c = 399.8 + 0.14 \log A + 0.2 \log ([Fe^{3+}]/[Fe^{2+}])$$

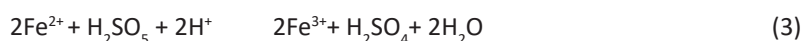
Where A is the sulfuric acid concentration (g/L) [44].

The presence of MnO (0.1%) in mineralized ore could be useful as oxidant of iron as in the following equation (2)



The above equation shows that the reaction requires large amounts of hydrogen ions to take place, which consequently consume the acid leach.

The acid required to achieve the pervious equivalent oxidation of ferrous ion could be reduced by 50% if using another oxidant such as sodium chlorate or Caro's acid as evident in the following equation:



The Nabarlek mill in Northern Australia use Caro's acid (H₂SO₅) as oxidant agent which manufactured on site by the reaction of concentrated sulfuric acid with 50-70% hydrogen peroxide in ratio of 3:1. Because of its greater stability, Caro's acid is a more efficient oxidant than hydrogen peroxide itself [45].

Potentiality of Caro's acid of uranium dissolution from Abu Rusheid mineralized sample was investigated by performs batch experiments as the following;

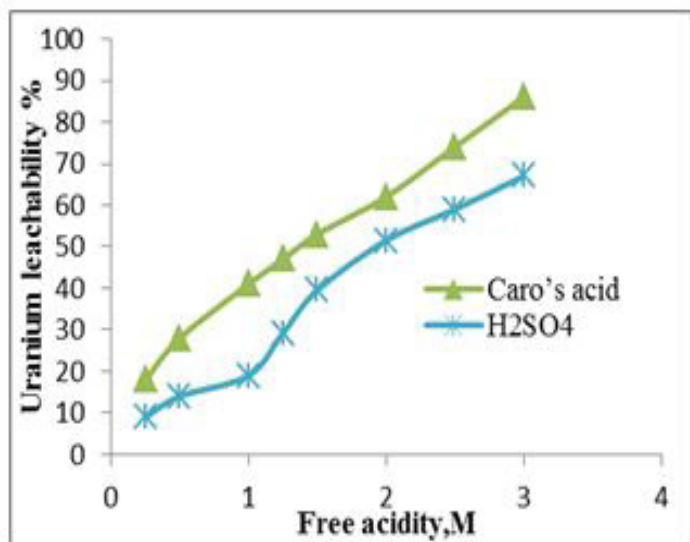


Figure 4: Effect of free acidity of leach solution (H₂SO₄ and Caro's acid) on uranium leachability

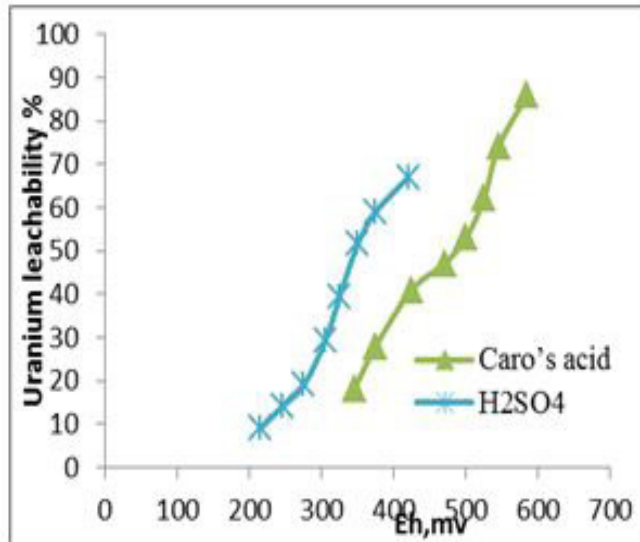


Figure 5: Effect of Eh on uranium leachability (H₂SO₄ and Caro's acid)

Relevant dissolution factors

Effect of Free acidity

Investigation of free acidity effect was achieved by varying acid strength from 0.25 M to 3 M, at 3:1 ratio of hydrogen peroxide (Caro's acid) at constant, temperature (40 °C), particle size (300µm) ,1:2 solid –liquid ratio and stirring speed (300 rpm) for 6hr. Uranium concentration and Eh were analyzed after solid liquid separation at each experiment. The obtained data was graphed as the following Figures 4 and 5.

As shown in Figure 4, the mineralized ore need large amounts of sulfuric acid to achieve almost uranium leaching. Since the leachability record low percent 9 to19% at free acidity 0.25M to 1M with redox potential 215 to 275 mv then increase periodically as in Figure 5. Which; owing to the studying mineralized ore containing a lot of acid consumer minerals such as fluorite mica.

Introducing the oxidant as H₂O₂ mixed with sulfuric acid as the leach liquor improve the leaching performance and increase the leachability from 19 to 41% and redox potential from 275 to 425mv. Since increase the oxidation rate of iron consequently increase the uranium dissolution. In other hand, reduce consuming of sulfuric acid by gangues metals associated uranium and oxidation. 1M sulfuric acid was used as the maximum concentration of ore leaching to decrease the dissolution of gangues metals such as silica and alumina which exist as the major oxides in ore. High free acidity, access to the uranium inside individual particles.

Effect of contact time

By varying the parameter in the range of 3–7 hr with keeping other variables as follows: 1M free acidity, temperature 40°C, particle size 300µm and solid/liquid ratio 1:2.

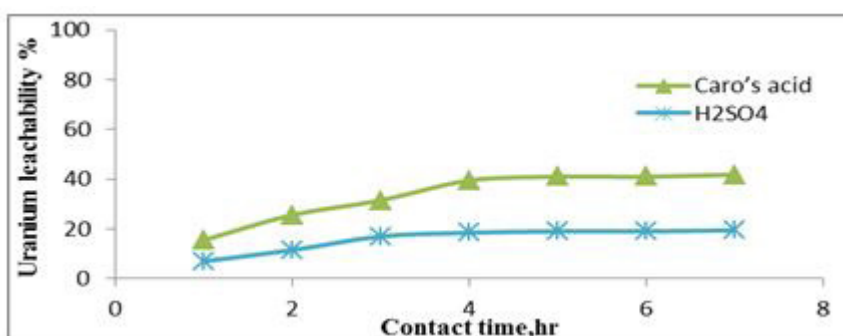


Figure 6: Effect of contact time on uranium leachability %using H₂SO₄ and Caro's acid

The results are shown in Figure 6, about 31.5, 17 % of uranium values were leached in 3 hr using 1M H₂SO₄ and Caro's acid respectively. Then, gradually increased to about 41.8, and 19.5% in 4-7 hr reaction time, respectively. The less increase in leachability of uranium is result of simultaneous increase of acid consumption, during leaching in case of using only sulfuric acid since.

Effect of grain size

The leachability as function of grain size was established by varying the grain size from 425 to 75 μm and constant the other parameters and illustrated in Figure7. As shown in Figure 7, the leachability increase gradually with grain size decrease could be attributed to increase in the area of reaction consequently increase dissolution of the contained uranium and oxidant (MnO) on solution.

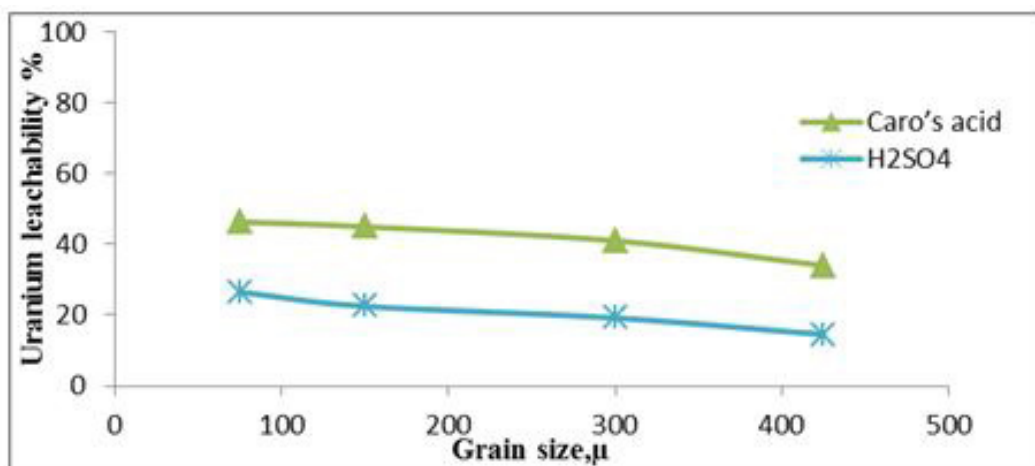


Figure 7: Effect of grain size on uranium leachability %using H₂SO₄ and Caro's acid

Effect of temperature

Temperature studied range were from room temperature to lower 85 °C to avoid dissolution of associated minerals like monazite and rare earth silicate [40]. Consequently, temperature effect was investigated by varying reaction temperature from 30 to 70°C and fixing the other parameters to avoid dissolution of associated minerals like monazite and rare earth elements silicate. Consequently, temperature effect was investigated by varying reaction temperature. Figure 8, shows that, gradual increase in uranium leachability with temperature increase, as increase from 19.2 to 36% at temperature from 30 to 70 °C in case of diluted H₂SO₄. On using Caro's acid, there is slightly increase in leachability from 41 to 44 at temperature 30-50 °C, then tend to decrease with temperature increase from 50 to 70 °C.

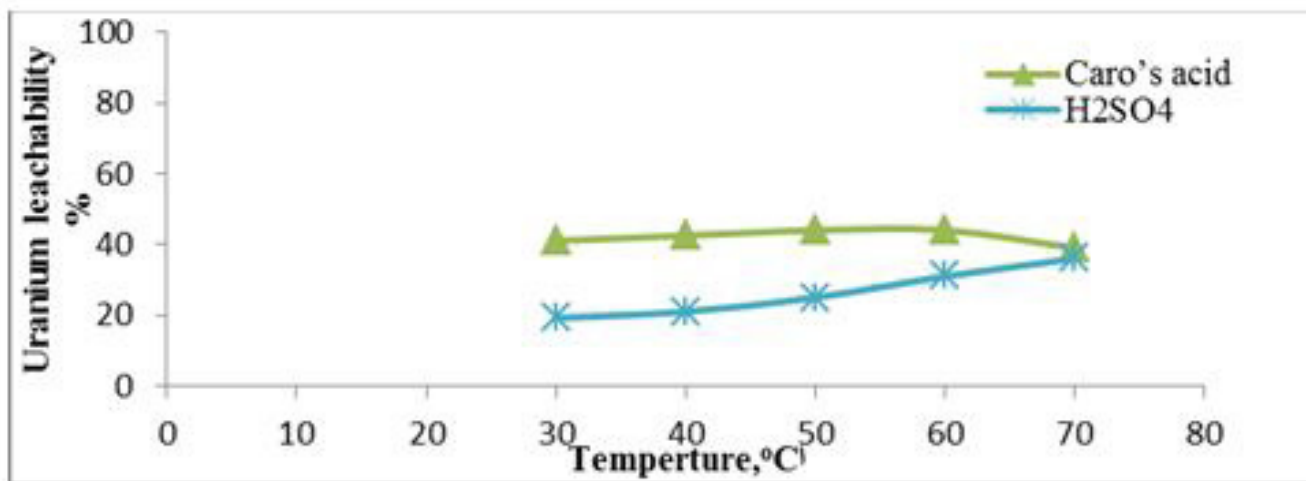


Figure 8: Effect of Temperature on uranium leachability %using H₂SO₄ and Caro's acid

From above, we can concluded that the high temperature accelerate the uranium dissolution when using diluted H_2SO_4 . On other hand, accelerate firstly then decrease after that on using Caro's acid which can be attributed to the dissociation of H_2SO_5 into H_2SO_4 and water at temperature above $50^\circ C$.

Effect of S/L ratio

The effect of S/L ratio was investigated by varying through the S/L ratio range between 1:2 to 1:5, while fixing the other parameters. The obtained results (Figure 9) show that the uranium leachability increased gradually as the ratio decrease from 1:2 to 1:5 in case of H_2SO_4 . On other hand, multiplied as ratio decrease from 1/2 to 1/3 then increase gradually to reach 96.5% from 1/3 to 1/5 ratio. Which proved that the Caro's acid save in sulfuric acid consuming during leaching and give concentrated uranium leach liquor.

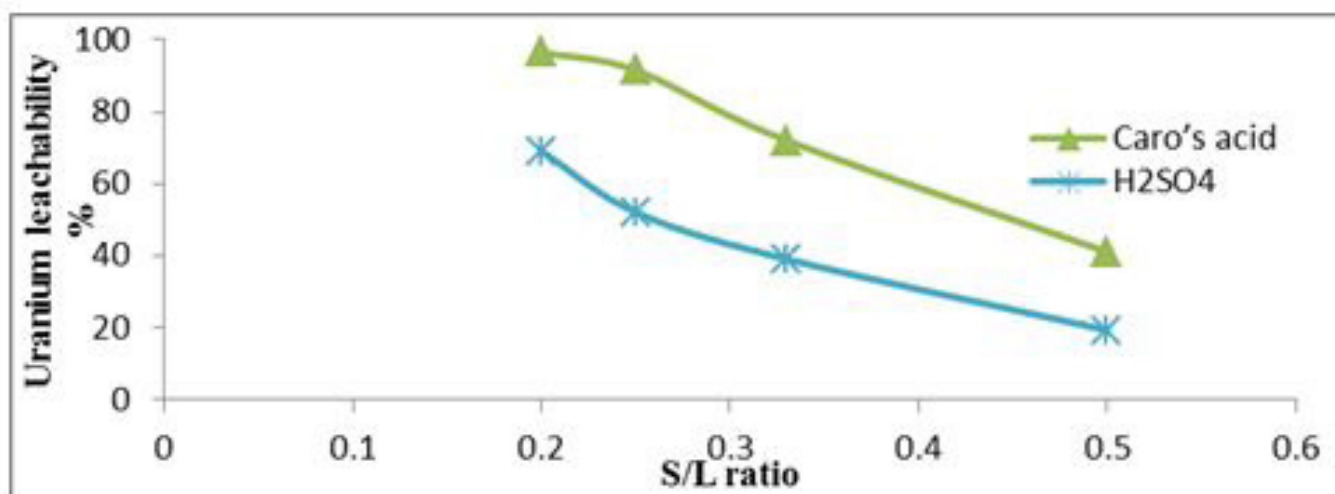


Figure 9: Effect of S/L ratio on uranium leachability % using H_2SO_4 and Caro's acid

Leaching kinetics

In order to gain more understood of leaching behavior ,the uranium leachability % values were determined along each experiment performed with time .The obtained results would be formulated in core shrinking models which the best model can describe the kinetics and reaction mechanism.

Shrinking core model derived equations as the following [46].

$$1-3(1-X)^{2/3} + 2(1-X) = K_d t, \tag{5}$$

when the leaching rate controlled by diffusion through product layer

$$1 - (1 - X)^{1/3} = K_c t, \tag{6}$$

when the leaching rate controlled by chemical reaction on surface layer

$$X = K_f t, \tag{7}$$

when leaching rate controlled by film diffusion

While K_d , K_c and K_f are the apparent rate constants (min^{-1}), t is the leaching time, and X is the metal fraction.

Effect of free acidity

To elucidate the mechanism of the Caro's acid concentration on uranium dissolution, the shrinking core models as described by Eqns. (5) and (6) are operated and graphed as in Figure (10a, b).

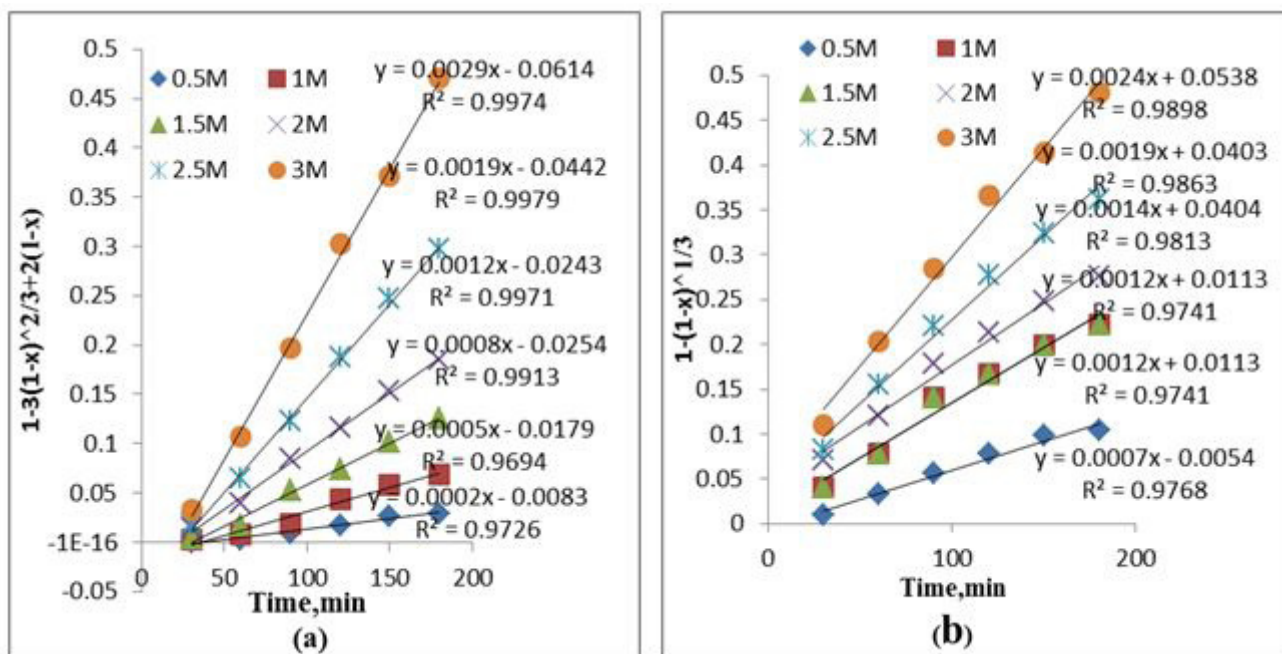


Figure 10: The kinetic curve of uranium leaching at different concentration of Caro's acid based on different models. (a) diffusion reaction control; (b) Chemical reaction control

As shown in Figure 10 a,b ,there are a linearity relation of slopes > 0.9 between the uranium fraction mole dissolved at varied times and Caro's acid concentration. There are very little changes between two reaction models, so that another relationship will be plotted between logarithm apparent rate constant against logarithm M H₂SO₄ as in Figure 11 to differentiate between them.

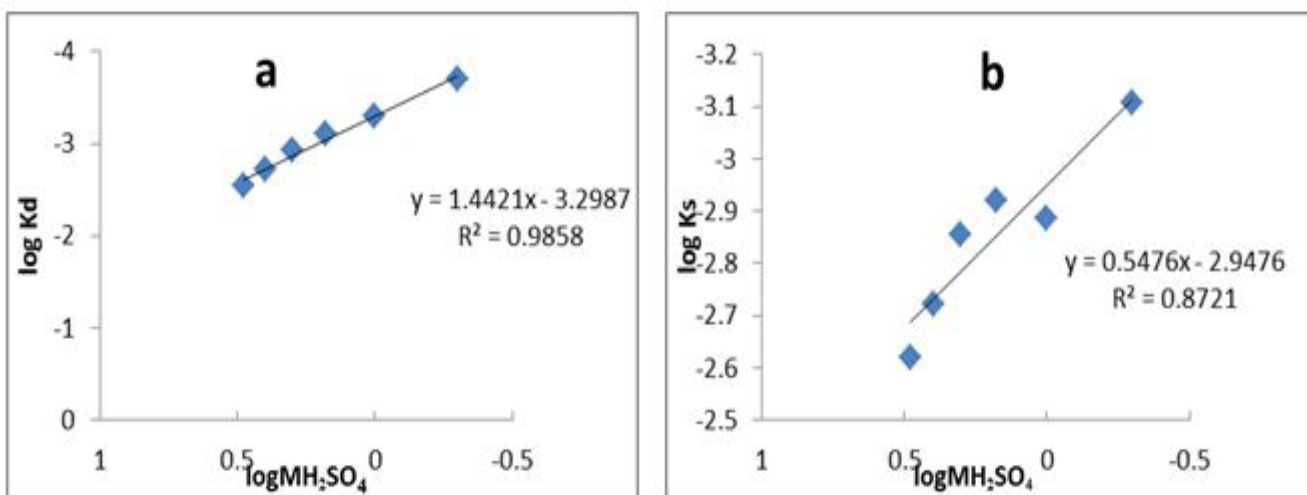


Figure 11: log-log plot of the rate constant versus H₂SO₄ concentration based on different models.(a) diffusion reaction control; (b) Chemical reaction control

Figure 11, shows that the linearity in diffusion model than other chemical one, which proved that the leaching rate is controlled by diffusion process. The slope of 0.986 indicates strong dependence of the rate on sulfuric acid concentration.

Effect of Temperature

Measuring uranium adsorbed each time interval during dissolution experiments with varying reaction temperature and fixes other conditions. The obtained resulted used in construction of two shrinking core models to be examined at different temperatures as shown Figures 12 a,b.

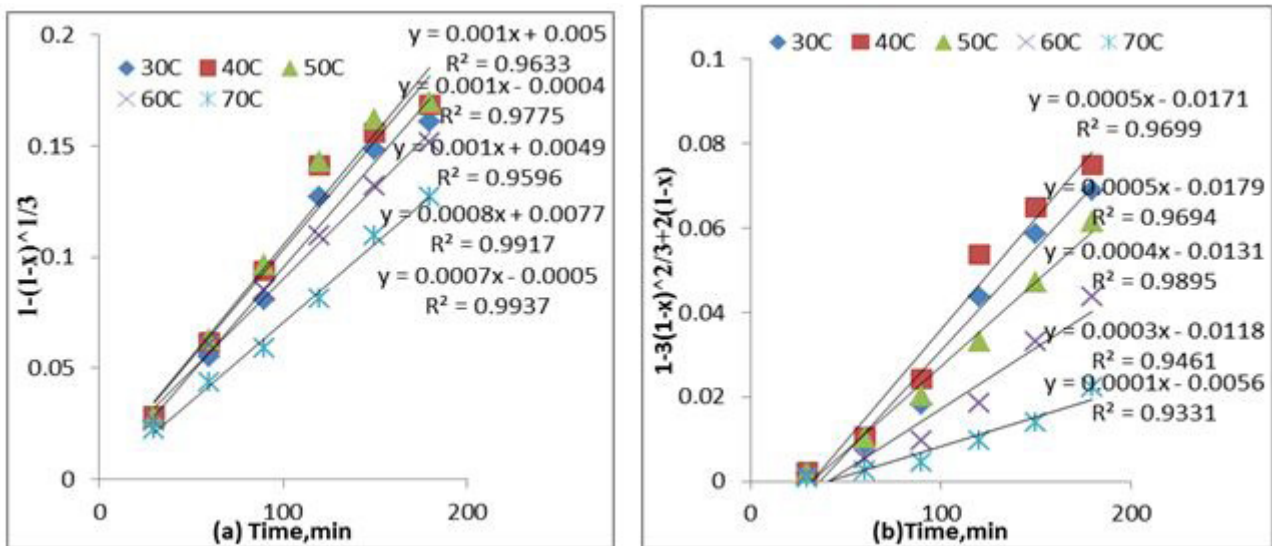


Figure 12: The kinetic curve of uranium leaching at different temperatures based on different models (a) Diffusion reaction control; (b) Chemical reaction control

As observed, the two models have good linear fits and their R² values are close to each other. Therefore, it is difficult to distinguish between these reaction models.

Activation energy is the important parameter that can be used to justify the rate-determining step in hydrometallurgical process. It was calculated based on the Arrhenius equation [47]:

$$K = A e^{-E_a/RT}; \quad \ln K = \ln A - E_a/RT \quad (8)$$

Where *K* is the rate constant, *E_a* is the activation energy, *R* is the ideal-gas constant (8.314 J/Kmol), *T* is the temperature in K and *A* the frequency or pre-exponential factor.

As shown in Figure 13, Arrhenius equation was plotted as Ln(*K*) versus (1/*T*) for each temperature, and the activation energies were calculated from the slopes of straight lines where the slope is -*E_a*/*R*.

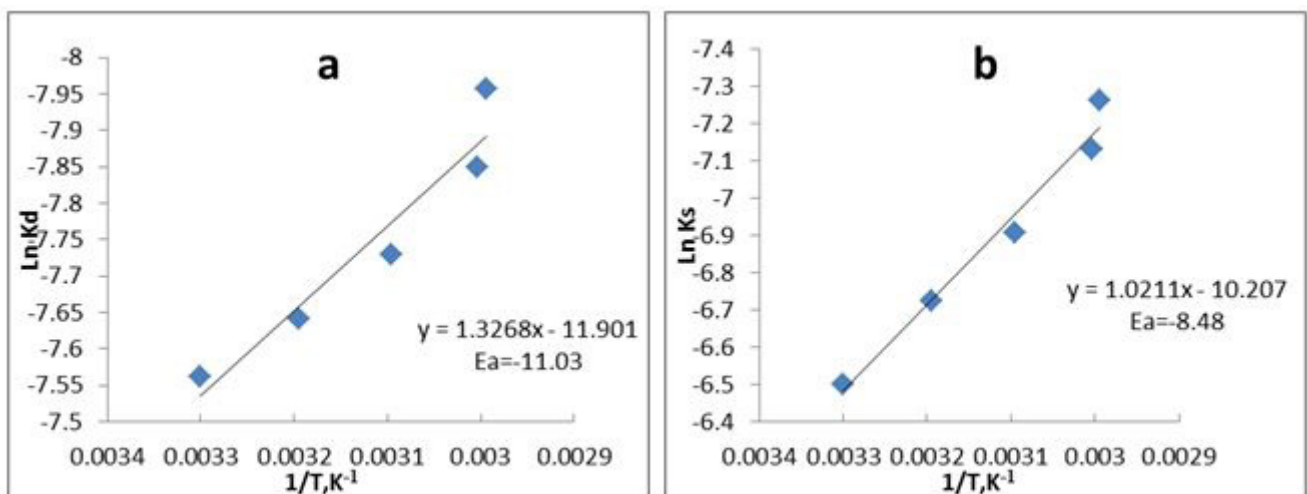


Figure 13: Arrhenius plot for the uranium leaching at different Temperatures based on different models (a) Diffusion reaction control; (b) Chemical reaction control

From above Figure the calculated activation energy E_a are -11.03 and -8.48 kJ/mole for chemical reaction control and diffusion reaction control respectively. These indicate that the reaction rate is controlled by chemical reaction on the particle surface. Consequently, temperature have pronounced effect on reaction rate since, its increase lead to dissociate the Caro's acid into H_2O and H_2SO_4 on the particle surface, then increase the diffusion of ions dissociated through the liquid film and particle layer.

Conclusion and Future Applications

Caro's acid effectiveness on uranium dissolution from Abu Rushied mineralized ore in comparison with dilute sulfuric acid leaching was studied by batch experiments and kinetic modulations. Batch experiments show the superiority of Caro's acid in uranium dissolution with low concentration than dilute sulfuric acid. Leachability of 91.5% and 52% uranium for Caro's acid and dilute sulfuric acid respectively was obtained. Shrinking core models used to determines the reaction mechanism, which shows that the uranium dissolution in Caro's acid controlled by diffusion reaction model. However, controlled by chemical surface reaction model with elevated the temperature. Arrhenius plot were constructed to calculate the activation energy, which is found ranging from -11.03 to -8.48kJ/mole. In future, we can applied a two-stage leaching for achieving maximum uranium solubilisation with minimum dissolution of gangue elements like chlorite and biotite in sulfuric acid leaching of uranium ore. Firstly, leaching with Caro's with optimized concentration of less than 100g/l H_2SO_4 until Eh and pH of leach liquor reached 450 and 1.6 respectively followed by leaching with diluted H_2SO_4 that keep the Eh and pH of leach liquor at the same values.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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