

Kinetic study of the oxidative dissolution of metamorphosed sandstone-type uranium in aqueous H₂SO₄ solution

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ABSTRACT

Bench scale experiments were conducted to determine the oxidative dissolution kinetics of metamorphosed sandstone-type uranium in dilute H₂SO₄ solution with H₂O₂ as oxidizing agent. The kinetics results showed that, the rate is controlled by diffusion through the “product” layer composed of the associated concomitants. The leaching process follows the kinetic model $1-2/3X-(1-X)^{2/3}=kt$ with an apparent activation energy of 22.803 kJ/mole. It was found that both sulfuric acid and hydrogen peroxide have significant effects on the leaching rate of uranium species. The reaction orders of H₂SO₄ and H₂O₂ were determined as 1.073 and 2.084, respectively. It is also found that particle size presents a clear effect on uranium leaching rate, and the rate constant (*k*) is proportional to *d*⁻².

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KEYWORDS

Uranium;
H₂SO₄;
Kinetics;
H₂O₂;
Oxidative dissolution.

INTRODUCTION

Sandstone uranium deposits are characterized by medium to coarse-grained sandstones deposited in a continental fluvial or marginal marine sedimentary environment. It constitutes about 18% of world uranium resources. Ore bodies of this type are commonly low to medium grade (0.05-0.4%). Wadi Sikait area belongs to these resources. It is located about 95 km SW of Marsa Alam town in the south Eastern Desert of Egypt. It is highly tectonized and covered by ophiolitic mélange, metamorphosed sandstones, gabbros and porphyritic granites.

The metamorphosed sandstone (20 million Mt. above W. Sikait level) represents the target for uranium and associated minerals. It extends NW-SE for about 2.0 km in length and ranges from 100 - 400 m in width^[1].

Knowledge of the chemistry and kinetics of U(IV) dissolution is necessary for leaching processes are to be understood and optimized.

Oxidative U(IV) dissolution rates under various conditions have been reported in numerous publications. The studies considered here were all performed at room temperature/ 25°C in the presence of O₂ or H₂O₂ and include batch experiments^[2-5], flow experiments and electrochemical experiments^[6-10]. Shoesmith et al.^[11] have performed H₂O₂ experiments on UO₂ electrodes. They have found that the oxidation rate is higher with H₂O₂ than with O₂ saturated solutions. De Pablo et al.^[12] have shown that, the oxidation mechanism of UO₂ by H₂O₂ is thought to occur via OH· and HO₂·. In the presence of carbonate they have found that the dissolution rate is decreased, which is interpreted as a reduction of the efficiency of the oxidant, due to radical

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scavenging. The reactivity of this radical towards the UO_2 surface is expected to be identical to the reactivity of the hydroxyl radical, i.e. the reaction is diffusion controlled^[13].

The dissolution kinetics of U(IV) using various oxidants in alkali metal carbonate solutions at room temperature has previously been reported by Peper et al^[14]. Of the oxidants tested in that study, hydrogen peroxide (H_2O_2) exhibited the most rapid initial dissolution rate. This result was attributed to H_2O_2 acting as both an oxidant and a ligand under alkaline conditions. Moreover, the apparent initial rate of U(IV) oxidation increased with increasing peroxide concentration. Pierce et al^[15] reported the rate of UO_2 dissolution increased by an order of magnitude with a 30 °C increase in temperature. The alkaline dissolution of UO_2 (pH 11–13) in the presence of H_2O_2 , without taking into account added carbonate or H_2O_2 consumption, was modeled via a pseudo first-order reaction^[16]. Gogoleva et al^[17] reported the leaching kinetics of brannerite ore in sulphate solution with iron (III) the results showed that, The leaching rate increased with an increase of H_2SO_4 concentration, and it was proportional to 0.69 power of H_2SO_4 concentration, also the leaching rate of brannerite increased with increase in Fe(III) concentration, and followed a half-order with respect to the ferric iron concentration up to 0.01 M. This paper reports the results of initial rate experiments designed to determine the dissolution rate of U(IV) in dilute H_2SO_4 solution containing H_2O_2 as oxidizing agent.

EXPERIMENTAL

Characterization of the working material

The studied sample used in this investigation was obtained from Wadi Sikait area which is located in South Eastern Desert, Egypt. It was crushed to +250 μm and then ground to the required particle size of (-74 μm). It composed mainly of 80.03 % SiO_2 , 2.11 % Al_2O_3 , 0.49% Fe_2O_3 , 2.81% CaO , and 0.65% MgO . Beside the presence of 5081.31 ppm molybdenum and 506.59 ppm uranium. X-ray diffraction (XRD) analysis of the working ore showed the presence of coffinite ($\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$), molybdenite (MoS_2) beside quartz (SiO_2).

Analytical procedures

The sample was analysed for its major and minor elements using the proper analytical methods^[19]. Analysis of uranium was determined spectrophotometrically^[20].

Leaching procedure

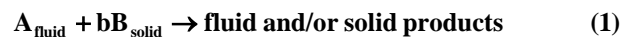
For each run, 70 mL of H_2SO_4 solution of predetermined molarity was charged into 0.25 L conical flask and heated to the required temperature. Thereafter, studied sample (5 g) was added to the conical flask and the contents were well stirred. After leaching, the leaching residue was filtered; the filtrate and leaching residue were analyzed for uranium spectrophotometrically.

RESULTS AND DISCUSSION

Kinetic analysis

Increasing attention is being paid to the study of the chemical kinetics of nonhomogeneous systems. In the classic homogeneous systems, the usual rate laws of first- and second-order kinetics are often sufficient to explain and analyze the experimental data. Leaching is a central unit operation in the hydrometallurgical treatment of ores, and the reactions occurring during the leaching process are typically heterogeneous. Thus, leaching reactions do not often obey simple first- and second-order kinetics. A kinetic analysis of these kinds of reactions is generally performed by noncatalytic heterogeneous reaction models. A kinetic analysis of leaching reactions is required for the effective design of leaching reactors for use in a hydrometallurgical plant.

The leaching reaction of mineral particles by a reagent (a solid–fluid reaction) can be represented by the following reaction:



where A, B, and b represent the fluid reactant, the solid undergoing leaching, and stoichiometric coefficient, respectively. The kinetic of leaching reactions is often described by the shrinking core model. According to the shrinking core model, it is thought that the reaction between solid and fluid reactants takes place on the outer surface of solid. The solid reactant is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk fluid. As the reaction proceeds, the unreacted core of the solid shrinks

toward the center of the solid, and a porous product layer forms around the unreacted core. However, it is assumed that the initial outside radius of the solid does not change while the leaching reaction continues^[18].

The leaching rate of solid is governed by physical and chemical factors. The governing factors are the rate of transport of fluid reactant to and products from the particle surface (i.e., diffusion through the fluid film), the rate of diffusion of fluid reactant and products through the porous product layer that forms on the unreacted core of solid (i.e., diffusion through the product layer), and the rate of the reaction at the surface of unreacted core (i.e., surface chemical reaction). Each of these phenomena affects the rate of the overall leaching reaction. One or more of these factors might control the rate of reaction^[19].

For each step mentioned, the integrated rate equations derived from the shrinking core model are given in the literature. These rate equations can be written as follows:

If the leaching rate is controlled by the diffusion through the liquid film, then the integrated rate equation is:

$$X = k_1 t \quad (2)$$

If the reaction rate is controlled by the diffusion through the ash or product layer, then the integrated rate expression is:

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

If the leaching rate is controlled by the surface chemical reaction, then the integrated rate equation is:

$$1 - (1 - X)^{1/3} = K_c t \quad (4)$$

where X is the conversion fraction of solid particle, k_1 is the apparent rate constant for diffusion through the fluid film, k_d is the apparent rate constant for diffusion through the product layer, k_c is the apparent rate constant for the surface chemical reaction, and t is the reaction time.

Effect of temperature

The effect of temperature on reaction rate was examined in the range of 298–368°K under the conditions of -74 μ m particle size, 2.5 M H₂SO₄, 0.6 M H₂O₂ and 1:14 solid : liquid ratio over a period of 120 min. The results, shown in Figure 1, indicate that temperature has significant effect on the rate of leaching and overall extraction efficiency of uranium. To determine

the kinetic parameters and rate-controlling step of the leaching of uranium in sulfate solutions, the data obtained in Figure 1 were analyzed based on the shrinking core model using the rate expression given in Eqs. [2] through [4]. By applying the rate expression in Eqs. [2] through [4] it was found that, Only the following diffusion-controlled kinetic equation was found to fit the data best from 0 to 120 min:

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

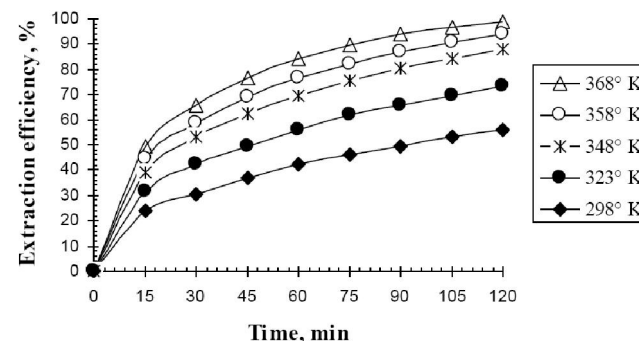


Figure 1 : Effect of temperature on leaching rate of uranium at (2.5M H₂SO₄, 0.5M H₂O₂, -74 μ m).

The relationship between $[1 - 2/3(X) - (1 - X)^{2/3}]$ values and leaching time for uranium at various temperatures are plotted in Figure 2), regression analysis shows all R squares for the equations at the five temperatures are greater than 0.99. Such results indicate that the linear relationship between $[1 - 2/3(X) - (1 - X)^{2/3}]$ and leaching time(t) is significant and suggest that the leaching rate of uranium in presence of H₂O₂ is controlled by diffusion through the “product” layer. Since, from the above discussion, no insoluble product forms, it is inferred that the insoluble oxide minerals (quartz, etc.) associated with uranium play the role of the “product” layer.

The apparent activation energy was determined based on the Arrhenius equation:

$$k = A \exp(-Ea/R - T) \quad (6)$$

$$\text{or } \ln k = \ln A - Ea/RT \quad (7)$$

Where k is a reaction rate constant, A is the frequency factor, Ea is the apparent activation energy and R is the gas constant. the $\ln k$ versus $1/T$ data for the five temperatures are graphed in Figure 3. The regression analysis showed that the linear relationship is also significant. The apparent activation energy (Ea) was, hence, determined to be 22.803 kJ/mol.

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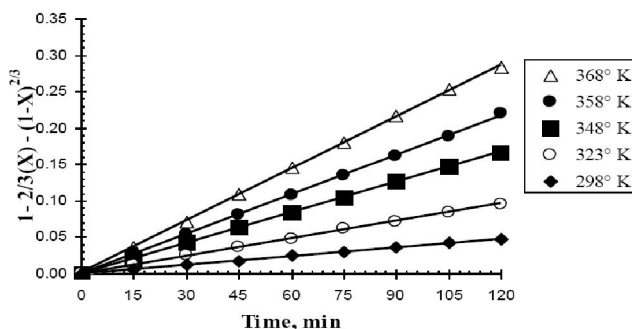


Figure 2 : Relationship between $[1 - 2/3(X) - (1-X)^{2/3}]$ and leaching time for uranium leaching at various temperature at (2.5 M H_2SO_4 , 0.5 M H_2O_2 , -74 μm).

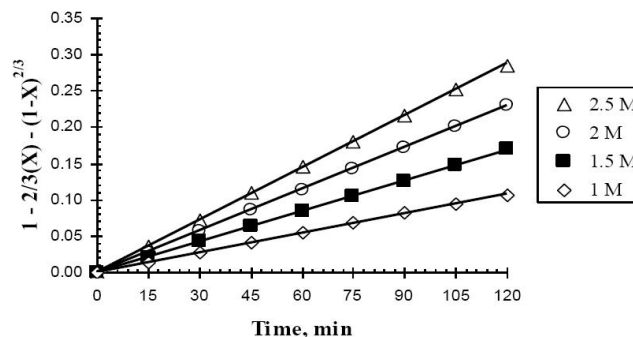


Figure 5 : Relationship between $[1 - 2/3(X) - (1-X)^{2/3}]$ and leaching time for uranium leaching at various H_2SO_4 concentration at (0.5 M H_2O_2 , 95° C, -74 μm).

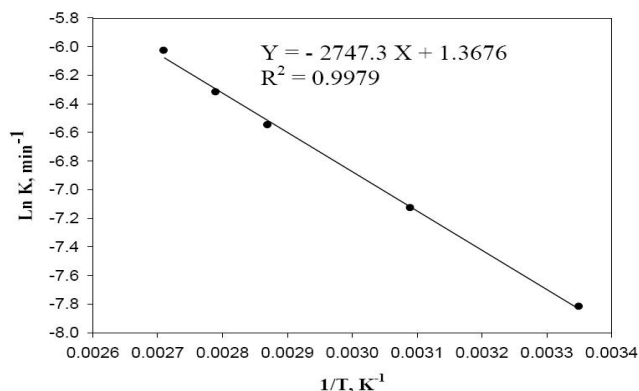


Figure 3 : Arrhenius plot for uranium leaching at (2.5 M H_2SO_4 , 0.5 M H_2O_2 , -74 μm).

Effect of H_2SO_4 concentration

The effect of H_2SO_4 concentration was carried out by varying the concentration from 1 to 2.5 M under the conditions of -74 μm particle size, 0.5 M H_2O_2 , and 1:14 solid/liquid ratio. The leaching results are in Figure 4. The corresponding results of $[1 - 2/3(X) - (1-X)^{2/3}]$ values against time at various concentration are shown in Figure 5. It can be seen that, increase in H_2SO_4 concentration causes a distinct increase in the leaching rate of uranium. An initial H_2SO_4 concentration of 2.5 M is necessary to obtain a high dissolution rate of uranium.

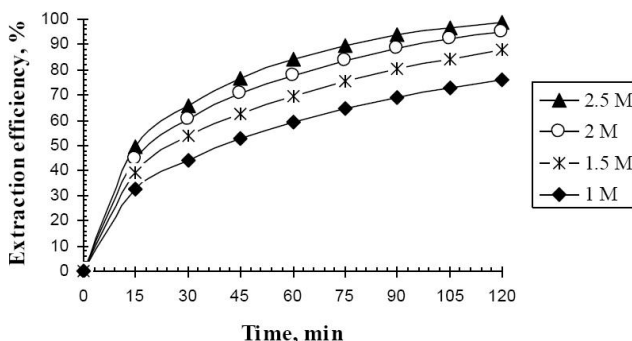


Figure 4 : Effect of H_2SO_4 concentration on leaching rate of uranium at (0.5 M H_2O_2 , 95° C, -74 μm).

In order to obtain the reaction order of H_2SO_4 acid the log-log results of the rate constants versus the concentration of H_2SO_4 acid are plotted in Figure 6. The slope of the line, or the reaction order of H_2SO_4 acid, is found to be 1.0733 Hence the leaching rate of uranium strongly depends on the acid concentration.

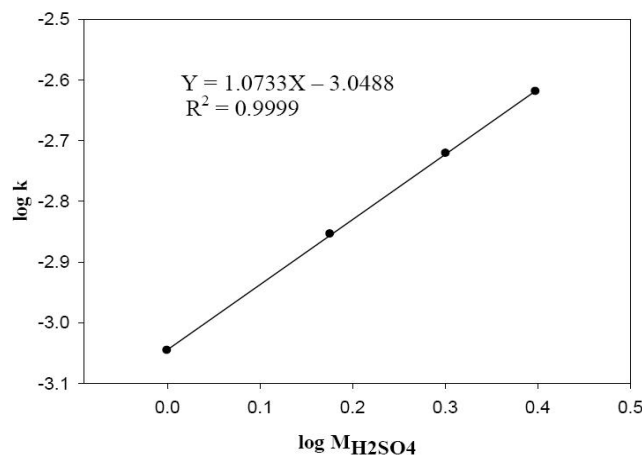


Figure 6 : Log - log plot between rate constant versus total H_2SO_4 concentration at (0.500 M H_2O_2 , 95.000° C, -74.000 μm).

Effect of H_2O_2 concentration

The effect of H_2O_2 concentration on the leaching rate of uranium was studied by varying the total initial concentration of H_2O_2 from 0.1 to 0.5 M under the conditions of 95° C, 2.5 M H_2SO_4 , -74 μm particle size. The leaching results are plotted in Figure 7. The corresponding $[1 - 2/3(X) - (1-X)^{2/3}]$ values against time at various H_2O_2 concentration are shown in Figure 8.

As mentioned above, the log-log results between the rate constant versus the total H_2O_2 concentration are illustrated in Figure 9. The reaction order is determined to be 2.084 hence the leaching efficiency strongly depends on the H_2O_2 concentration. The mechanism

of the oxidation of U (IV) by H_2O_2 in sulfuric acid medium may be considered as follows^[20]:

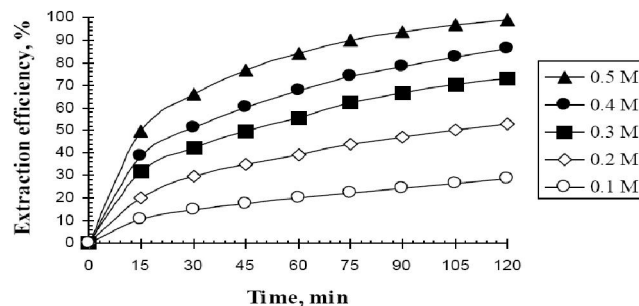
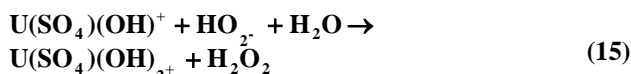
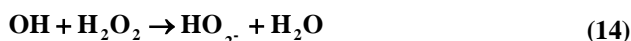
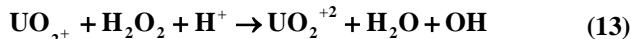
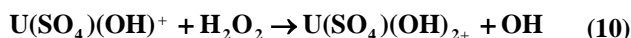
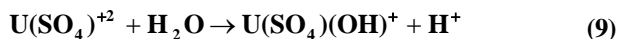


Figure 7 : Effect of H_2O_2 concentration on leaching rate of uranium at ($2.5 \text{ M H}_2\text{SO}_4$, 95°C , $-74 \mu\text{m}$).

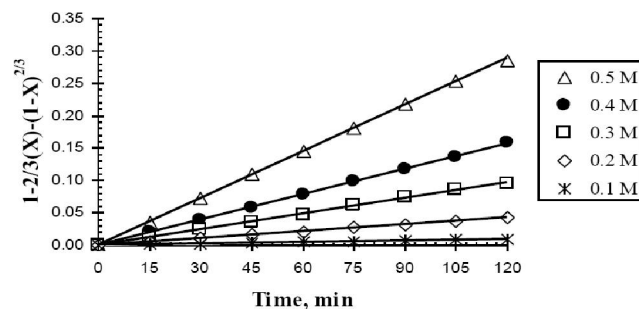


Figure 8 : Relationship between $[1 - 2/3(X) - (1-X)^{2/3}]$ and leaching time for uranium leaching at various H_2O_2 concentration at ($2.5 \text{ M H}_2\text{SO}_4$, 95°C , $-74 \mu\text{m}$).

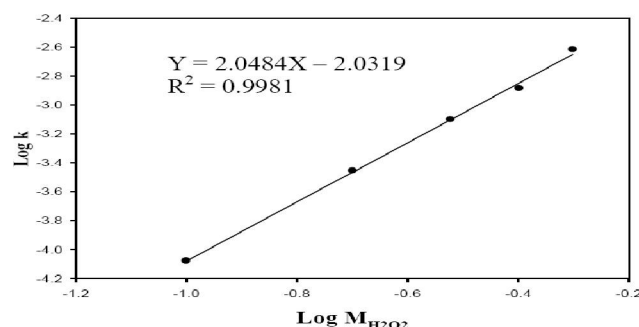


Figure 9 : Log – log plot between rate constant versus total H_2O_2 concentration at ($2.5 \text{ M H}_2\text{SO}_4$, 95°C , $-74 \mu\text{m}$).

Effect of particle size

Effect of particle size on the rate of reaction of uranium in the range of 250 to $74 \mu\text{m}$ in presence of $2.5 \text{ M H}_2\text{SO}_4$, $0.5 \text{ M H}_2\text{O}_2$ and 1:14 solid/liquid ratio are presented in Figure 10, the obtained results showed that, as the particle size decrease the extraction efficiency of uranium increased.

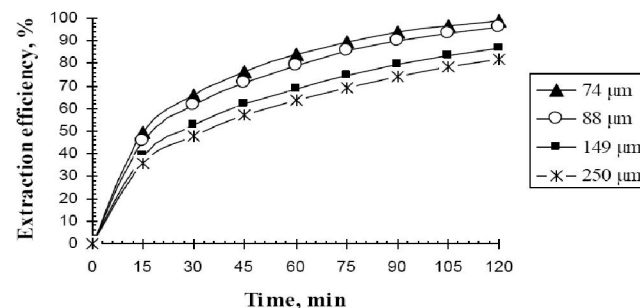


Figure 10 : Effect of particle size on leaching rate of uranium at ($2.5 \text{ M H}_2\text{SO}_4$, $0.5 \text{ M H}_2\text{O}_2$, 95°C).

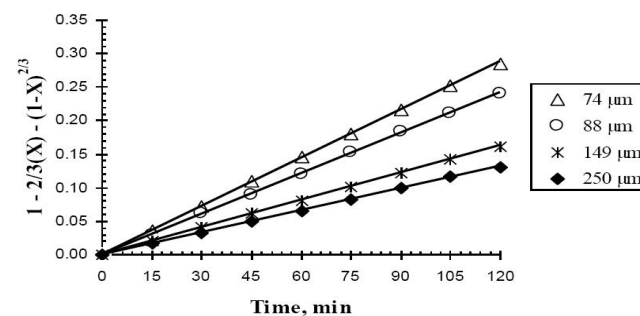


Figure 11 : Relationship between $[1 - 2/3(X) - (1-X)^{2/3}]$ and leaching time for uranium leaching at different particle size at ($2.5 \text{ M H}_2\text{SO}_4$, $0.5 \text{ M H}_2\text{O}_2$, 95°C).

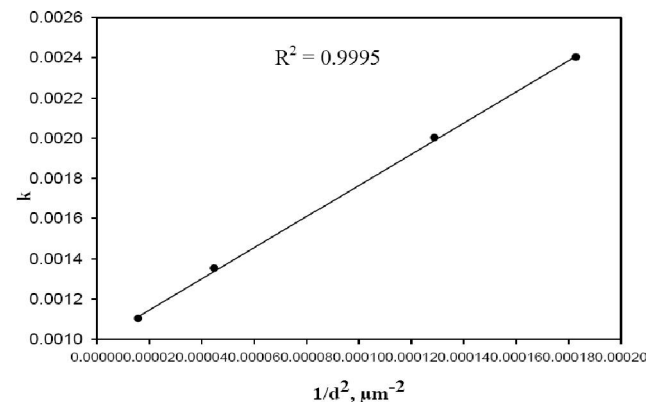


Figure 12 : Plot between rate constant versus the inverse of square particle diameter at ($2.5 \text{ M H}_2\text{SO}_4$, $0.5 \text{ M H}_2\text{O}_2$, 95°C).

The corresponding results of $[1 - 2/3(X) - (1-X)^{2/3}]$ values against time at various concentrations are graphed in Figure 11. The apparent rate constant are determined and plotted versus the inverse of the square particle diameter, d^{-2} as in Figure 12. The regression

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equation is found to have R square of 0.995. The directly proportional linear relationship of rate constants to d^{-2} supports the conclusion that the leaching of uranium in the presence of H_2O_2 from the working sample is diffusion controlled.

CONCLUSION

The leaching kinetics of uranium from metamorphosed sandstone-type uranium show that, the rate of U(VI) leaching using dilute H_2SO_4 in presence of H_2O_2 is controlled by diffusion through a "product" layer and follows a shrinking core kinetic model $1 - \frac{2}{3X} (1 - X)^{3/2} = kt$ with an apparent activation energy of 22.803 kJ/mole. The kinetics study also shows strong dependence on acid and H_2O_2 concentration with a reaction order of 1.074 for total H_2SO_4 concentration and a reaction order of 2.084 for H_2O_2 . It is also found that particle size presents a clear effect on uranium leaching rate, and the rate constant (k) is proportional to d^2 .

REFERENCES

- [1] M.E.Ibrahim, G.M.Saleh, W.S.Ibrahim; Journal of Geology and Mining Research, **2(6)**, 129 (2010).
- [2] J.Casas, V.Giménez, M.E.Martí, J.D.P.Torrero; Radiochim.Acta., **66/67**, 23 (1994).
- [3] J.Giménez, F.Clarens, I.Casas, M.Rovira, J.de Pablo; J.Nucl.Mater., **345**, 232 (2005).
- [4] G.I.Park, H.K.Lee; J.Korean.Nucl.Soc., **28**, 349 (1996).
- [5] M.E.Torrero, E.Baraj, J.de Pablo, J.Giménez, I.Casas; Int.J.Chem.Kinet., **29**, 261 (1997).
- [6] W.J.Gray, S.A.Steward, J.C.Tait, D.W.Shoesmith; Radioactive waste management, **4**, 2597 (1994).
- [7] J.de Pablo, I.Casas, J.Giménez, M.Molera, M.E.Torrero; Mat.Res.Soc.Symp.Proc., **465**, 535 (1997).
- [8] M.J.Nicol, C.R.S.Needs, N.P.Finkelstein; In: Leaching Reduct. Hydrometall. A.R.Burkin (Ed); (IMM, London), **1** (1973).
- [9] D.W.Shoesmith; J.Nucl.Mater., **282**, 1 (2000).
- [10] D.W.Shoesmith, S.Sunder; J.Nucl.Mater., **190**, 20 (1992).
- [11] D.W.Shoesmith, S.Sunder, M.G.Bailey, G.J.Wallance; Corros.Sci., **29**, 1115 (1989).
- [12] J.de Pablo, I.Casas; Mater.Res.Soc.Symp. Proc., **663**, 409 (2001).
- [13] E.Ekeröth, M.Jonsson; J.Nucl.Mater., **322**, 242 (2003).
- [14] S.M.Peper, L.F.Brodnax, S.E.Field, R.A.Zehnder, S.N.Valdez, W.H.Runde; Ind.Eng.Chem. Res., **43**, 8188 (2004).
- [15] E.M.Pierce, J.P.Icenhower, R.J.Serne, J.G.Catalano; J.Nucl.Mater., **345**, 206 (2005).
- [16] S.Meca, V.Marti, J.de Pablo, J.Gimenez, I.Casas; Radiochim.Acta., **96**, 535 (2008).
- [17] E.M.Gogoleva; J.Radioanal.Nucl.Chem., **293**, 185 (2012).
- [18] O.Levenspiel; Chemical Reaction Engineering. John Wiley & Sons, Inc, New York, (1999).
- [19] F.Habashi; Principles of Extractive Metallurgy: General Principles, Gordon and Breach, New York. **1**, (1980).
- [20] P.K.Bhattacharyya, R.D.Saini, P.B.Ruikar; International Journal of Chemical Kinetics, **13**, 385 (1981).