



Kinetic Studies for Thorium and Uranium Leaching process from Nubian Sandstone, Southern Sinai, Egypt

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Abstract

The present study focuses mainly with leaching potentialities and kinetics studies of mineralized basal sandstone in North Ras Mohamed, South Sinai area. The strong acid leaching process has a significant effect in dissolving about 97% of both U and Th. The kinetics experimental data indicate that the rate of the reaction is chemically controlled through the particle surface reaction. Hence, the activation energies of both uranium and thorium were calculated according to Arrhenius equations as 46.08 and 53.998 kJ/mol respectively.

Key words: Kinetic Studies, Nubian sandstone, uranium, thorium, leaching process, Sinai, Ras Mohamed

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I. INTRODUCTION

The most recent geological classification for sandstone uranium deposits in worldwide has been defined by the International Atomic Energy Agency (IAEA) in 2013 and has been adopted in the Red Book since 2014. The deposit types have fundamental characteristics and recognition criteria, and in that respect, while mainly named by host rock, the types are essentially empirical models, based on observable characteristics [1]. Uranium is precipitated in sedimentary environments under reducing conditions caused by a variety of reducing agents within the sandstone including: carbonaceous material (detrital plant debris, amorphous humate, marine algae), sulfides (pyrite, H₂S), hydrocarbons, and interbedded basic volcanic ash with abundant ferro-magnesian minerals (e.g. chlorite) [2]. Sandstone deposits constitute about 28% of world uranium reasonably assured resources and 40% of inferred resources, and are of major economic importance in Kazakhstan, Uzbekistan, USA and Niger [3].

Some of the Paleozoic sedimentary rocks in the southern part of Sinai, including the basal sandstone of Ras Millan, are of great importance especially from the mineralogical and radioactive points of view. It hosts several types of mineral deposits such as copper deposits [4], uranium deposits [5-8] and some transitional metals like Zn, Sn, Ni, Mo and Pt [9]. Shata (2004) [10] studied in detail the basal sandstones of Ras Millan area, Southern Sinai, and concluded that the contact of the lower member of the Araba Formation with granitic rocks has a highest level of radioactivity. The presence of some variations in the radioactivity levels may reflect the fact that, the area under study is covered by rocks of various compositions. Moreover, the variations may be also due to the surface wash-out processes, which reduce the radioactivity levels in place and increase them in another. The sandstone itself is syndepositionally enriched in the elements of detrital origin such as Y, Zr, Nb, V, Cr and Th. These trace elements in the basal sandstone are pathfinders to each other's, as well as to U. He also mentioned that, there are two types of uranium mineralization which exist in the studied basal sandstone; the first is the paleo-placers, including mainly refractory minerals which are detrital from nearby source rocks. The second is the basal-type sandstone and conglomerates, which are unconformably overlying the Precambrian rocks.

Uranium and thorium are the most important elements because of their strategic significance in the energy field. The leaching of uranium and thorium are a term to describe the process of extracting them from its ore which considered as an essential step in the hydrometallurgical test work. Uranium leaching process is carried out via conventional or non-conventional techniques depending on the type of uranium mineral, uranium ore grade, reagents availability, economics of the process and environmental impacts [11]. Several authors studied the extraction of U and Th from different Egyptian ores using acid and alkaline leaching agent. However, acidic leaching using H₂SO₄ acid was used for breakdown the refractory ores involve primary U and Th

minerals, typically thorite, xenotime and to some extent thorogummite [12-17]. Moreover, sulfatization process is used essentially for oxidize tetravalent uranium to hexavalent, and to produce water-soluble Th and U compounds [18-20].

Due to the previously mentioned importance of Southern part of Sinai Peninsula, the present work demonstrates the integration of kinetic leaching studies of radioactive elements (U and Th). In this context, a technological sample was collected from North Ras Mohamed area, Southern Sinai, Egypt assays about 0.1% Th and 0.5% U.

II. EXPERIMENTAL WORK

2.1. Samples preparation and analytical techniques

Representative quotient of sample was obtained through systematic quartering. Sample was crushed using a small hummer then further pulverization continued for representative portion to 75 μ . The collected representative sample was chemically analyzed for major oxides and trace elements using the Inductive Coupled Plasma Mass Spectrometer (ICP-MS) of ACME Lab in Vancouver, Canada.

2.1.1. Determination of radioactive elements

Uranium determination was carried out via titration method using ammonium meta-vanadate as titrant and di-amino 4-sulfonic acid as indicator. The advantages of this method are the low detection limits, low interfering elements and high accuracy. The concentration of ammonium meta-vanadate differs according to the concentration of uranium in samples [21]. On the other hand, determination of thorium (IV) using Arsenazo III and spectrophotometer model Prolabo, Jean and constant U.V. Hence, this method can be used for analysis of thorium in many materials and ores without preliminary separation [22].

2.2- Leaching procedures:

In the present work, several pug leaching tests were performed using 10 g ore sample fractions ground to 75 μ (to be more efficient) to which different amounts of concentrated H₂SO₄ acid are added and well mixed. The acid treated ore was then left to cure under different conditions. After curing, agitation leaching with distilled water was performed using a solid-liquid ratio of 1/10 for 1 h at room temperature. At the end of each leaching experiment, filtration was carried out and the obtained filtrate was analyzed for metal values under consideration.

2.3. Kinetics Leaching procedures

The kinetic analysis was tested according to the shrinking core model (SCM), it was first developed by Yagi and Kunii (1955) [23]. In the establishment of the SCM, the solid reactant is considered to be non-porous and is initially surrounded by a fluid film through which mass transfer occurs between the solid particle and the bulk of the fluid.

III. RESULTS AND DISCUSSIONS

3.1. Chemical composition of the basal sandstone

From the obtained chemical analysis data of the study basal sandstone given in table (1), it is clearly evident that it is mainly composed of SiO₂ (83.27%) besides Al₂O₃ (6.86) and significant high contents of Fe₂O₃ and P₂O₅ which may reflect, to some extent, its sedimentary nature. With respect to the economic metal values, it was found that U and Th were amounted to 0.05, 0.13% respectively. In addition to presence of considerable amount of rare earth elements (REE=0.13 ppm). From mineralogical point of view, basal sandstone of Ras Millan area refers to presence of thorite and uranothorite as the main radioactive minerals besides some other minerals such as plumbogummite, anatase, chlorite and iron oxy-hydroxides minerals [20].

Table (1): The ICP-MS chemical analysis of Basal Sandstone

Oxides	(%)
SiO ₂	82.54
Al ₂ O ₃	6.86
TiO ₂	0.43
Fe ₂ O ₃	4.96
CaO	0.62
MgO	0.05
Na ₂ O ₃	0.34
K ₂ O	0.17
Cl	0.19
P ₂ O ₅	1.2
L.O.I.(Loss Of Ignition)	1.8
U	0.05
Th	0.13
REE	0.13
Total	99.87

3.2. Results of leaching studies upon the basal sandstone sample

3.2.1. Effect of solid/ liquid ratio (w/v)

The effect of solid/liquid (S/L) ratio (amount of sample/Conc. H_2SO_4) upon the U and Th leaching efficiencies of the studied sample was considered in the range of 1/0.25 to 1/1.5 using Conc. H_2SO_4 on 74 μ , for different leaching time ranging from 50 to 350 min at 150-200°C. The obtained results plotted in figure (1) indicate that, leaching efficiencies of the both U and Th increase by decreasing S/L ratio from 1/0.25 to 1/1.5 with different magnitudes. The more efficient leaching condition was observed at S/L ratio of 1/1.5 for both U (82.7%) and Th (92.2%) at 200 and 180 min respectively. This may be due to the refractory nature of the corresponding minerals (thorite and uranothorite) which need high amount concentrated H_2SO_4 acid and high S/L ratio [20].

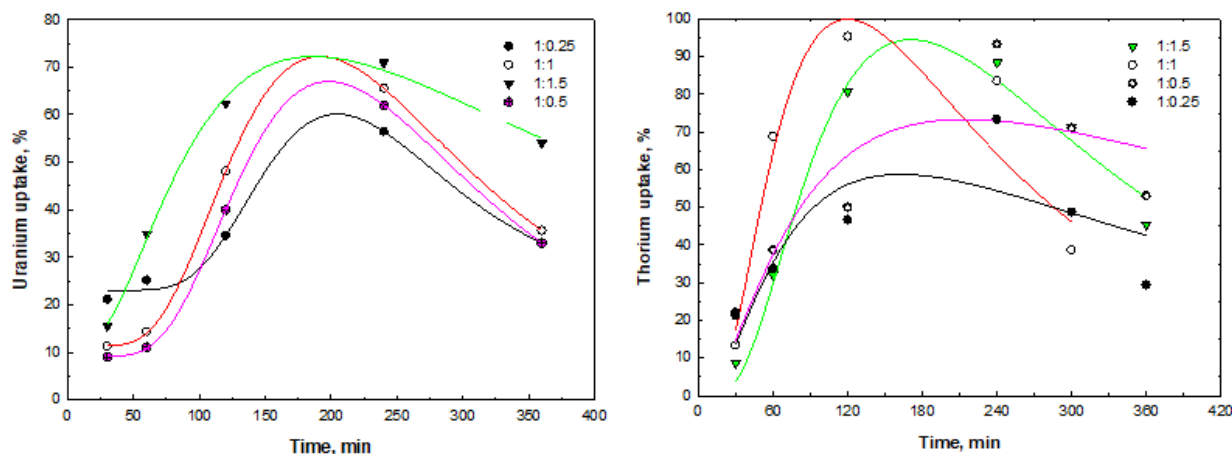


Figure (1): Effect of solid/liquid ratio upon the leaching efficiencies of U and Th

3.2.2. Effect of temperature

The effect of the curing temperature upon the leaching efficiencies of the U and Th from the basal sandstone was studied between temperatures ranging from 100 to 200°C while fixing Conc. H_2SO_4 with 1/1.5 (S/L), at different leaching time, the obtained results are plotted in Fig. (2). From these data, it is clear that as the curing temperature increases, the leaching efficiencies of U and Th of basal sandstone increase till curing temperature of 200°C at about 190-200 min and assaying about (95.4 and 97.1 %) respectively. Beyond the latter temperature, the leaching efficiencies of these metal values decrease to varying degrees. This may be due to the dissolving of undesirable constituents at high temperature.

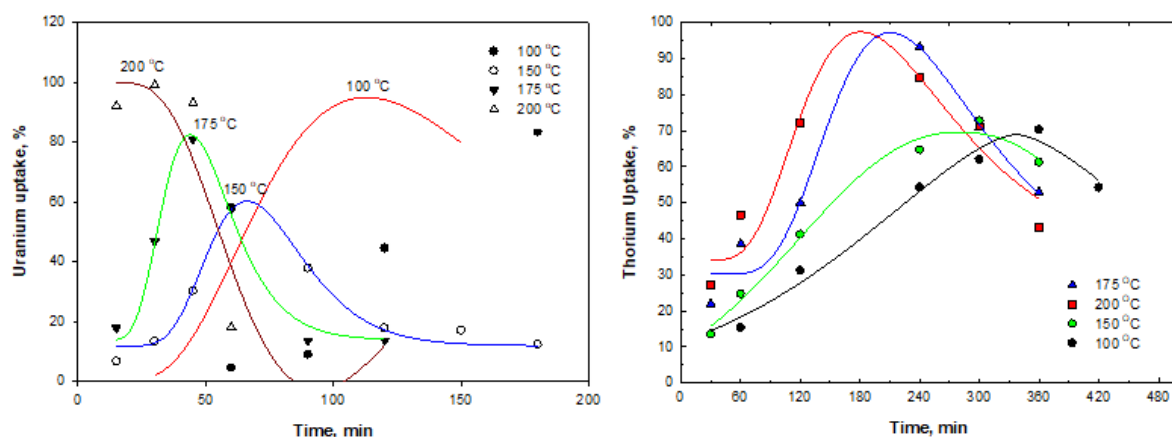


Figure (2): Effect of temperature upon the leaching efficiencies of U and Th

3.2.3. Effect of contact time

Fixing the Conc. H_2SO_4 with 1/1.5 (S/L), a number of pug leaching experiments were performed for a curing time varying from 50-420 min and the curing temperature about 200°C. From the obtained leaching efficiencies of the studied metal values plotted in Fig. (3), it was found that the latter have increased by increasing the curing time from 50 till 200 min and at 200°C. It can thus be concluding that, increasing curing time above 200 min, hydrolysis may occur and hence the dissolution extent of metal values decreases.

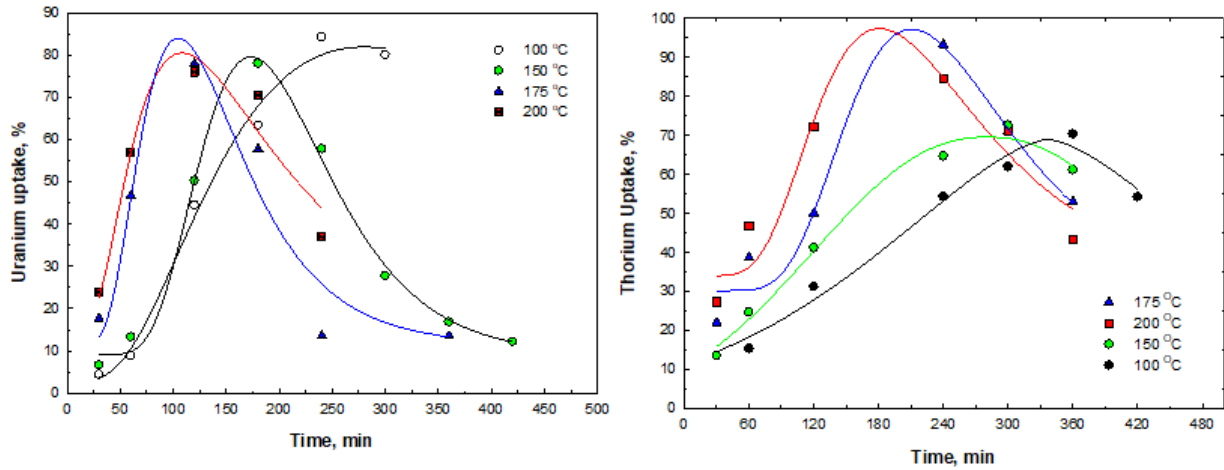


Figure (3): Effect of contact time upon the leaching efficiencies of U and Th

3.3. Dissolution kinetic models

3.3.1. Rate control by diffusion through the product layer

If the rate of the reaction is controlled by diffusion through the product layer, the integrated rate equation is described as follows:

$$1 - \frac{2}{3}X - (1-X)^{2/3} = \frac{2M_s D C_A}{\rho_s \beta r_0^2} t = k_d t \quad (1)$$

where X is the fraction reacted, k_c is the kinetic constant, M_s is the molecular weight of the solid, C_A is the concentration of the dissolved lixiviant A in the bulk of the solution, ρ_s density of the mineral, β is the stoichiometric coefficient of the reagent in the leaching reaction, r_0 is the initial radius of the solid particle, t is the reaction time, D is the diffusion coefficient in the porous product layer, k_d and k_r are the rate constants which are calculated from Eqs. (1) and (2), respectively. An attempt was made to fit the obtained experimental data to the model equation described in Eq. (1), and this is presented in Fig. (4) for both uranium and thorium dissolution from thorite and uranothorite minerals.

The analysis of the plots of diffusion controlled process at the interface represented by Eq. (1) did not give a perfect straight line, since neither a correlation coefficient straight nor a zero point intercept was obtained in both figures of uranium and thorium. Even at high temperature a straight line with zero-point intercept indicated in case of thorium, however a weak correlation coefficient was obtained.

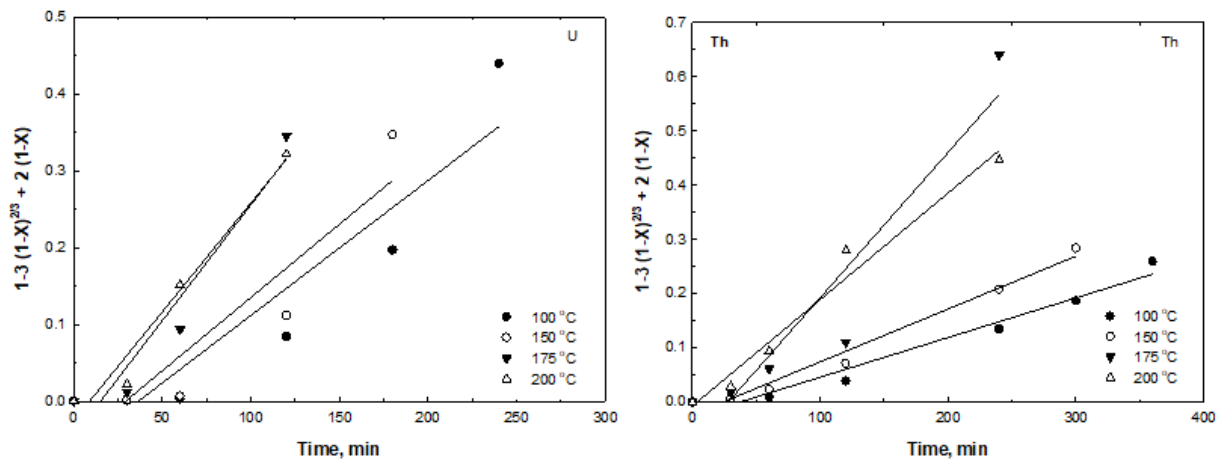


Figure (4): A plot of $1 - 3(1-X)^{2/3} + 2(1-X)$ vs. time at various reaction temperatures for mineralized basal sandstone dissolution in sulfuric acid solution

3.3.2. Rate control by chemical reaction

When surface chemical reaction is rate controlling, the kinetics may be correlated graphically using Eq. (2).

$$1 - (1-X)^{1/3} = \frac{k_r M_s C_A}{\rho_s \beta r_0} t = k_r t. \quad (2)$$

Application of Eq. (2) to the experimental data obtained, at different temperatures, resulted in linear plots presented in Fig. 2. It is observed, from both plots, during the whole reaction time that the data in these figures are linear and gave an average correlation coefficient of 0.9943 and 0.9970 for uranium and Thorium respectively, this is shown in Fig. (5), which indicate that the rate of the reaction is chemically controlled through the particle surface reaction. The slopes of the straight lines from each figure were estimated which is equivalent to the rate constants, k_r .

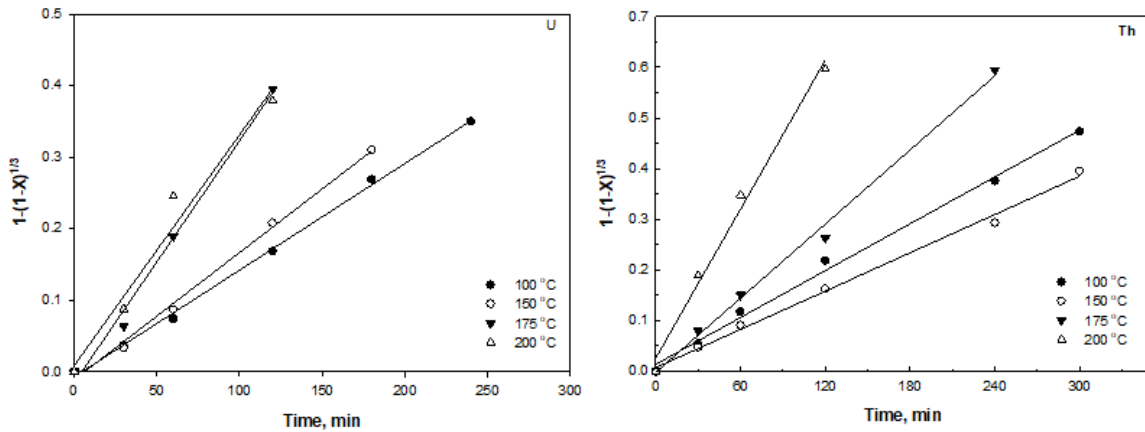


Figure (5): A plot of $1 - (1-X)^{1/3}$ vs. time at various reaction temperatures for mineralized basal sandstone dissolution in sulfuric acid solution

3.3.3. Calculation of the activation energy

A process may be regarded either as diffusion rate controlled through the porous layer when the activation energy of the process is from 4 to 12 kJ/mol or chemical rate controlled through the particle surface reaction when its activation energy is greater than 42 kJ/mol [24]. The temperature dependence of the chemical reactions can be given by the Arrhenius equation [25] as follows:

$$k_r = A \exp(-E_a / RT) \quad (3)$$

where A is the frequency factor and E_a is the apparent activation energy. The Arrhenius plot shown in Fig. (6) was made by plotting the natural logarithm of the rate constant ($\ln k_r$) against the reciprocal of the temperature ($1/T$). Hence, the activation energies of uranium and thorium were calculated from the slopes of the Arrhenius plots presented in Fig 5 as 46.08 kJ/mol and 53.998 kJ/mol respectively, which is in agreement with the reported activation energy for a chemically controlled process [24]. Since the calculated activation energies are high, it can be concluded that the dissolution rate of uranium and thorium from mineralized basal sandstone by sulfuric acid solution is very sensitive to temperature.

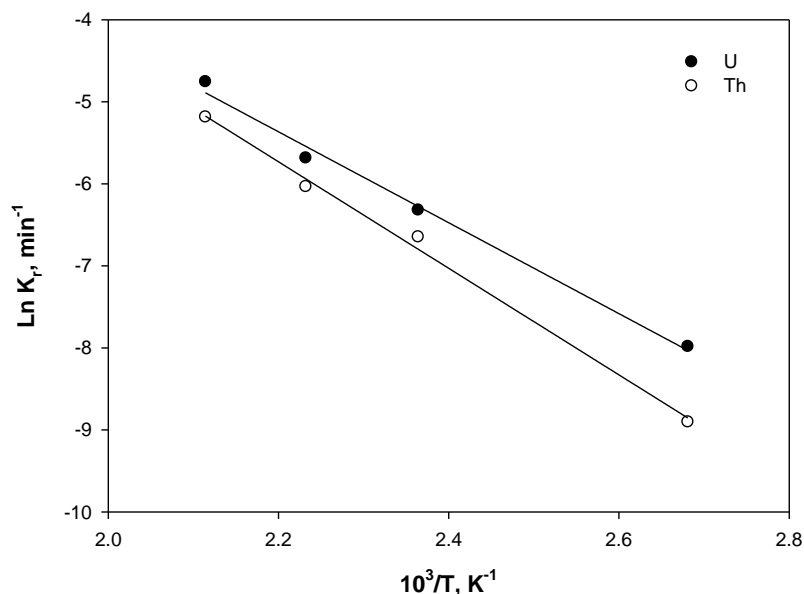


Figure (6): $\ln k_r$ vs. $1000/T$ (K^{-1}): Arrhenius plot for determining activation energy, E_a , for mineralized basal sandstone dissolution in 18 M H_2SO_4

IV. CONCLUSIONS

The present work demonstrates, accomplished testwork on the leaching potentialities and kinetic studies of basal sandstone in Ras Millan, South Sinai area. Identification of radioactive minerals (thorite and uranothorite) together with the determination of the deleterious gangue amounts of the studied basal sandstone provide information that assist in each stage of the hydrometallurgical testwork. In this context, the H_2SO_4 acid leaching process has a significant effect in dissolving U and Th and achieve to about 97%. Hence, the activation energies of uranium and thorium were calculated from the slopes of the Arrhenius plots as 46.08 kJ/mol and 53.998 kJ/mol respectively, which is in agreement with the reported activation energy for a chemically controlled process.

Compliance with ethical standards

The present paper is an original work and all the authors declare that they have no conflicts of interest.

REFERENCES

- [1]. **Geology of uranium, world uranium association (2020):** <https://www.world-nuclear.org/information-library/nuclear-fuel-cycle/uranium-resources/geology-of-uranium-deposits.aspx>.
- [2]. **IAEA-TECDOC-1842 (2018):** Geological Classification of Uranium Deposits and Description of Selected Examples. IAEA TECDOC SERIES, International Atomic Energy Agency, Vienna.
- [3]. **McKay, A., and Miezitis, Y., (2001):** Australia's Uranium Resources, Geology and Development Of Deposits, Geoscience Australia (2001), ISBN 0642467161.
- [4]. **El Sharkawi, M. A., El Aref, M. M. and Abdel Motelib, A. A. (1990):** Syngenetic and paleo karstic copper mineralization in Paleozoic platform sediments of west central Sinai, Egypt. BL: sediment hosted mineral deposits. Spec. Publ. Int. Assoc. Sedimentol., pp. 159-170.
- [5]. **El Aassy, I., Botros, N. H., Abdel Razik, A., El Shamy, A. S., Ibrahim, S. K., Sherif, H. Y., Attia, K. E. and Moufei, A. A. (1986):** Report on proving of some radioactive occurrences in west central Sinai. Int. Rept. N.M.A., Cairo, Egypt.
- [6]. **Dabbour, G. M. and Mahdy, M. A. (1988):** Mineralogical studies on the lower uraniferous sediments of W. Naseib, Sinai, Egypt. In: C.N.S.A. Conference, Cairo.
- [7]. **Abu Khoziem, H. A. (2017):** Recovery of Cu, REEs, U and V from Abu Zienema Poly-mineralized Carbonaceous Shale Ore Material, Southwestern Sinai, Egypt. Bull. Fac. Sci. Zagazig Univ., 39
- [8]. **Raslan, F. M. Fawzy, M. M, and Abu-Khoziem, H. A. (2017):** Mineralogy of mineralized pegmatite of Ras Mohamed granite, Southern Sinai, Egypt. Inter. J. of Geology, Earth & Environmental Sciences. 7 (1) 65-80.
- [9]. **Ahmed, F. Y. (2003):** Contribution to the crystal chemistry of the mineralized Paleozoic dolostone of Um Bogma, Southwestern Sinai, Egypt. J. Geol. Vol. 47 (1), pp. 527-540.
- [10]. **Shata, A. E. (2004):** Rare earth elements and uranium mobilization in the radioactive Cambro-ordovician sandstones of Ras Millan area, South Sinai; Proceeding of the 7th P Conf. Geology of Sinai for Development Ismailia, pp. 181-197.
- [11]. **Atia B. M., Gado M. A. Cheira M. F., (2018):** Kinetics of uranium and iron dissolution by sulfuric acid from Abu Zeneima ferruginous siltstone, Southwestern Sinai, Egypt? Euro-Mediterranean Journal for Environmental Integration. pp. 3:39
- [12]. **Afifi, S. Y., Morsy, M. A., El-Sheikh, E. M., El Kady, M. A., and Mahdy, M. A., 2006,** "Recovery of some valuable elements from El Garra El Hamra sulfate leach liquors by modified lignocellulosic cotton stalks," Arabian Journal of Nuclear Science and Application, Vol.39, No. 2, pp. 22-41.

- [13]. **Bowell, R. J., Gorgan, J., Hutton-Ashkenny, M., Brough, C., Penman, K., and Sapsford, D. J. (2011)** Geometallurgy of uranium deposits, *Minerals Engineering*, Vol.24, No.12, pp.1305-1313, <https://doi.org/10.1016/j.mineng.2011.05.005>.
- [14]. **Ram, R., Charalambous, F. A., McMaster, S., Pownceby, M.I., Tardio, J., and Bhargava, S.K., 2013**, "An investigation on the dissolution of natural uraninite ores," *Mineral Engineering*, Vol. 50-51, pp. 83-92, <https://doi.org/10.1016/j.mineng.2013.06.013>.
- [15]. **Bhargava, S. K., Ram, R., Pownceby, M., Grocott, S. Ring, B., Tardio, J., and Jones, L. (2015)**: A review of acid leaching of uraninite, *Hydrometallurgy*, Vol. 151, pp. 10-24.
- [16]. **Abu Elatta S. A., Abdellah W. M., Abu Khoziem H. A. (2018)**: Mineralogy, geochemistry and leaching characteristics of the high-grade Th-U-Y zone of altered syenite at El Garra El Hamra, Southwestern Desert, Egypt. *Minerals & Metallurgical Processing*, 53(4), pp.230-243.
- [17]. **Abdellah, W. M.** Preparation of Pure Uranium, Thorium and Yttrium Oxides from El-Garra El-Hamra Sulfate Leach Liquor. *Journal of Radiochemistry*, 2020, vol. 62, no. 3, pp. 347-358.
- [18]. **El-Hazek, M.N. Amer, T.E. Issa, R.M. Abu El-Azm, M.G., Omar, S.A. and El-Hady, S. M. (2009)** Characterization and Breakdown of South Gabal EL A'urf Polymineralized ore Material". *Eurasian Chem. Tech. J.*, Vol. 11, pp. 149-158.
- [19]. **Venter, R., and Boylett, M., 2009**, "The evaluation of various oxidants used in acid leaching of uranium," *Hydrometallurgy Conference*, Feb. 24-26, 2009, Southern African Institute of Mining and Metallurgy, pp. 445-456.
- [20]. **Amer, T. E., El Assay, I. E., Rezk, A. A., El Kammar, A. A., El Manawy, A.W. and Abu Khoziem, H. A. (2014)**: Geometallurgy and Processing of North Ras Mohamed Ore Deposits, South Sinai, Egypt. *Inte. J. of Mineral Processing*, 129, 12-21.
- [21]. **Mathew, K. J., Burger, S., Ogt, S. V., Mason, P. M., and Narayanan, U. I. (2009)**: Uranium assay determination using Davies and Gray titration. *Processing the Eighth International Conference on Methods and Applications of Radioanalytical Chemistry (Marc VIII) Kaailua-Kona, Hawaii, P.5.*
- [22]. **Marczenko, Z. (2000)**: Spectrophotometric determination of elements, John Wiley and Sons, Harwood, New York,
- [23]. **Yagis, and Kuniid (1955)**: *Proc. 5th Inst. Symp. Combustion*, p. 231. *Churn. Engng (Japan) 1955* 19 500.
- [24]. **Habashi, F (1980)**: Recovery of uranium from phosphate rock. *Process and problems. 2nd international congress on phosphorus compound proceedings*
- [25]. **Laidler K. J. (1984)**: The development of the Arrhenius equation. *J. Chem. Educ.* ;61:494-498. doi: 10.1021/ed061p494.