1. Introduction

The Carboniferous rock sequence at Southwestern Sinai represents indeed a promising facies for uranium and other valuable economic metals in association. Um Bogma Formation, Gabal Allouga, Southwestern Sinai, Egypt is an example of the radioactive anomalies in the area that are associated with high carbonate (El Aassy et al., 1986; Mira & Aita, 2009). These authors stated that the Allouga localities are of good uranium potentiality and in which some U, Cu, V minerals, and REE are visible besides the famous Fe–Mn deposits in different concentrations.

Hydrometallurgically, several leaching studies for uranium and copper have previously been done by many authors. The type of leaching – acid or alkaline, relies upon the nature of the host rock, type of the present gangues, availability and cost of reagent, solubility of undesirable contaminates, and the later recovery process. Wherever, the host rock is acid consuming in nature, alkaline route is chartered upon to avert excessive acid exhaustion. Several studies of leaching have been accomplished upon comparable Um Bogma ore materials from different locations and comprising different rock facies.

Thus, some studies have also succeeded to leach Al, Cu, Zn, Co, Ni, and U beside several Mn minerals from a comparable ore materials using sulfuric acid (Abdel Fattah, 2003; Abdel Moneim, 2005; Amer, 1997; Amer, Mahdy, El Hazek, El Bayoumi, & Hassanein, 2000; El Hazek, Ahmed, El Kasaby, & Attia, 2008). In addition, El-Sheikh, Ali, Ghazala, Abdel Warith, and Salem (2015) have studied in detail the selective recovery of U and Cu from the raw material of carbonate-rich latosol ore material occurring at Abu Thor locality of southwestern (SW) Sinai mineralization by applying two successive alkaline leaching processes. Selective uranium leaching was performed using urea while copper was subsequently and relatively leached with mixed solutions of ammonium hydroxide and ammonium carbonate.

Presently, several new projects are sophisticated to recover uranium from carbonate deposits (Gillman, 2010; Lunt, Boshoff, Boylett, & El-Ansary, 2007; Sole, Cole, Feather, & Kotze, 2011). The advantages of the alkaline leaching process include higher selectivity, a lower corrosively than acid leaching and insoluble of desirable metals, such as iron and silica. Chung et al. (2010) explained a successful in the leaching of Polish sandstone ores by using the oxidative process for simulated nuclear fuel. The approximate complete extraction of uranium was attained in that case by Frackiewicz et al. (2012).

The chemistry of alkaline leaching of uranium ores with Na₂CO₃ and NaHCO₃ reagent combine was explained earlier by Merritt (1971). The U⁶⁺ complexes with CO₂⁻³ to form uranyl carbonate ions. On the base of pH of the leach solution, the ionic charge of the uranyl carbonate complex varies. While neutral complexes are preponderate at pH 5–6.5 the divalent species – [UO₂(CO₃)₃]²⁻ is present in between pH 6.5 and 7.6. In the pH range of 7.6–12, the main species is [UO₂(CO₃)₃]⁴⁻.

The lixiviant system, comprising NH₄HCO₃ along with H₂O₂, was found to be the most efficient for uranium from an arkosic type of sandstone (Khan, Shah, & Siddiq, 2012). Uranium was leached with 8%
NaOH and 18% Na₂CO₃ containing H₂O₂ from Triassic Peribaltic sandstones (Gajda et al., 2015).

Demerdash described the dissolution of uranium from a high-carbonate ore material using mixture of Na₂CO₃ and NaHCO₃. The mechanism of uranium leaching process was followed the shrinking core kinetic model (Demerdash, 2016).

Sreenivas and Rajan (2013) described the separation of uranium from alkaline carbonate leach liquors by resin-in-pulp process (PFA 4740 and 4783). The kinetics of dissolution of UO₂ using the lixiviant combination of Na₂CO₃–NaHCO₃–O₂ at elevated temperature and pressure was elaborated by Rao, Sreenivas, Vinjamur, and Suri (2016).

Some studies have been proceeded to monitor the effect of reagent concentration and temperature on the kinetic dissolution rate of uranium in alkaline solution. Smith, Peper, Douglas, Kate, and Finn (2009) concluded that the dissolution rate of uranium increases linearly over the temperature (15–60°C) in 1 M ammonium carbonate with 0.1 M hydrogen peroxide. This has been assured by Pierce, Icenhower, Serne, and Catalano (2005), who observed that the uranium dissolution rate in carbonate solution increased with rising temperature.

Explaining the oxidative dissolution of uranium in alkaline media, Clarens et al. (2005) observed that it increased with rising concentration of hydrogen peroxide. On the other hand, Grandstaff (1976) found that the rate of uranium dissolution in carbonate/bicarbonate media was directly proportional to hydrogen carbonate concentration. Thus, it can be proven that the temperature and reagents concentration has an influence on the dissolution rate of uranium in carbonate media (Robert & Melvin, 1981).

Alkaline leaching can be more effective for certain copper minerals, such as ores with great amounts of acid-consuming carbonate rocks, as the leaching process is much more selective (Warhurst & Noronha, 2005). The copper leaching behavior from natural chalcocite in alkaline Na₂EDTA solutions containing oxygen was described by Konishi, Katoh, and Asai (1991).

Ammonia has been widely applied as an effective leaching agent in numerous hydrometallurgical processes for many years due to its low cost, low toxicity, and ease of regeneration (Meng & Han, 1996).

It is worthy to mention herein that El-Sheikh, Ghazala, and Ibrahim (2012) have applied adipic acid as a non-conventional reagent for selective copper leaching followed by uranium bioleaching from the latosol of Abu Thor locality.

With respect to copper dissolution, many workers, including Habashi (1983), Alguacil (1999), El-Sheikh et al. (2012), and El-Sheikh et al. (2015), have studied the leaching potentiality of copper by using ammonium hydroxide with or without other ammonium reagents as indicated from the following reaction:

\[
2\text{CuCO}_3 \cdot \text{Cu(OH)}_2 + 12\text{NH}_3 \rightarrow 3\left[\text{Cu(NH}_3\text{)}_4\right]^2+ + 2\text{CO}_3^{2-} + 4\text{OH}^- \quad \text{Azurite}
\]

This work relates to the selection of carbonate system for leaching uranium and copper and their recovery from dolostone material, Gabal Allouga, at upper member of Bogma formation Southwestern Sinai, Egypt in a manner to avert excessive acid exhaustion due to the occurrence of a relatively high content of carbonate minerals. This is due to the fact that the carbonate content of these ore materials is generally very high as it exceeds 50–60%. For this purpose, a technological sample of this material assaying 1.2% Cu and 0.15% U has been collected. Kinetic information of dissolution in alkaline media is another concern. The work then shifted to explain the potentiality of recovery of both metal values successively.

2. Experimental

2.1. Ore characterization

2.1.1. Chemical characterization of dolostone, Gabal Allouga ore material

The working dolostone ore sample was provided from variably mineralized lenses that occur at upper member of Um Bogma formation. The working dolostone ore sample was provided from variably mineralized lenses that occur at upper member of Um Bogma formation. The technological sample was collected from upper member layer of up to 2 m thickness blended and representative samples of them were properly prepared by crushing, grinding to ~60 mesh size and quartering. The major element oxides besides the economic metal values in working dolostone sample were analyzed using the rapid silicate analytical procedure (Shapiro & Brannock, 1962). Special sample portions were used for the determination of the weight loss at various temperatures to estimate the loss of ignition.

2.1.2. Mineralogical investigation of dolostone, Gabal Allouga ore material

To explain the mineralogical composition of dolostone, Gabal Allouga ore material, heavy liquid separation procedure was applied using bromoform (sp. gr.2.85). The obtained heavy mineral fractions were investigated under the binocular microscope and some picked mineral grains were analyzed by X-ray diffraction technique (XRD). A Philips X-ray generator model PW1140/90 fitted with a diffractometer model PW1050/80 was used. The X-ray tube used was a Cu-target model PW2233/30 fitted with a Ni-filter and was operated at 40 kV and 20 mA.
In the meantime, the environmental scanning electron microscope (ESEM-EXL30 Philips type) coupled with an energy dispersive X-ray analyzer (EDX unit system) was also used to identify the obtained products.

2.2. Leaching procedure

Leaching process was applied upon two dolostone samples namely; roasted sample and un-roasted sample or raw ore material. The former was subjected to roasting at 540°C to eliminate all organic matter as a means of physical beneficiation. The latter sample was subjected to leaching process without any physical beneficiation. Several leaching experiments for both uranium and copper have actually been performed using carbonate system to optimize the relevant leaching factors upon both samples roasted and un-roasted. In these experiments, a suitable weight of the working Cu/U ore ground to −60 mesh size was mixed with a suitable volume of carbonate system of various concentrations. The slurry was then agitated for a fixed time at a certain temperature after which the treated slurry was filtered and the residue left behind was thoroughly washed and both were analyzed.

The leaching efficiency of metal was determined according to the following equation:

\[
\text{Leaching efficiency} \% = \left( \frac{\text{concentration of metal in the leaching solution}}{\text{Total, initial input, concentration of metal}} \right) \times 100
\]

2.3. Recovery procedures

For the preparation of pure copper and uranium products, a proper leach liquor of 5 l was prepared using 1 kg of technological sample. From the latter, uranium was first recovered through the anion exchanger IRA 400. The pH of the resin effluent was then adjusted to pH 5.5 whereby the product of the blue crystals of copper hydroxide was obtained.

2.4. Analytical procedures

The control analysis of uranium (VI) in the different solution streams has been performed fluorometrically by laser fluorimeter ‘UA-3’ [Uranium Analyzer (Scintrex, Canada)]. On the other hand, various metal ions, including V, Cu, Ni, Zn, Pb were determined by using atomic absorption spectrometer (Unicam 969, England) (Ward, Nakagawa, Harms, & Van Sickle, 1969) and X-ray fluorescence technique (XRF) using Philips Unique II unit with automatic sample changer PW 1510 (30 position), connected to a computer system using X-40 program for spectrometry. Meanwhile, REEs was spectrophotometrically determined by using the chromogenic reagent, Arsenazo-III (Marczenko, 1986). In the meantime, the purity of the final precipitate of the U and Cu has qualitatively been determined using ESEM-EDX analysis.

3. Results and discussion

3.1. Ore characteristics

3.1.1. Chemical composition

As previously mentioned, the collected sample of the working dolostone, Gabal Allouga, Southwestern Sinai, Egypt was first subjected to a complete chemical analysis (Tables 1 and 2). From the latter, it is clearly evident that SiO₂ is relatively low in the rock where its assay is less than 8.83% while Al₂O₃ attaining 3.80%, also presence of about 2.50% Fe₂O₃. On the other hand, the dolostone ore materials is also characterized by a relatively high CaO and MgO contents reaching about 22.30 and 16% respectively, which reflects the relatively high attaining dolostone mineral content. As a matter of fact, the presence of such high carbonate content about 41% has been behind the choice of carbonate system leaching of both uranium and copper in order to avert excessive exhaustion of sulfuric acid in classical leaching procedures. On the other hand uranium, copper, rare earth elements, and vanadium were found in relatively reasonable grades, 0.15%, 1.20%, 0.15%, and 0.06%, respectively.

| Constituent | SiO₂ | Al₂O₃ | Fe₂O₃** | CaO | MgO | Na₂O | K₂O | TiO₂ | P₂O₅ | LOI* | Total |
|-------------|------|-------|---------|-----|-----|------|-----|------|------|------|-------|
| Oxide, %    | 10.83 | 3.80  | 2.50    | 22.30 | 16.00 | 0.57 | 0.24 | 0.41 | 0.50 | 41.00 | 98.15 |

*Total loss in ignition at 1000°C.
** Total iron.

| Constituent | Cu  | REEs | U   | V   | Ni  | Zn  | Pb  |
|-------------|-----|------|-----|-----|-----|-----|-----|
| Concentration (%) | 1.2000 | 0.1500 | 0.01500 | 0.06 | 0.0193 | 0.0055 | 0.0076 |
3.1.2. Mineralogical study
The ore sample was identified mineralogically using X-Ray Diffraction and Photography as shown in Figures 1 and 2. The obtained results from the mineralogical study revealed that the study ore material consists mainly of Ankerite \([\text{Ca}(\text{Fe,Mg,Mn})(\text{CO}_3)_2]\), Azurite \([\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2]\), Quartz \([\text{SiO}_4]\), Malachite \([\text{Cu}_2\text{CO}_3(\text{OH})_2]\), Chalcocite \([\text{Cu}_2\text{S}]\), Hematite \([\text{Fe}_2\text{O}_3]\), and Hematitized pyrite. Furthermore, the raw material under consideration shows no specific minerals for either rare earth elements, uranium or vanadium. This is probably due to their adsorption upon minerals of the study ore material.

3.2. Results of alkaline leaching of uranium and copper from roasted and unroasted dolostone sample
The collected technological sample has been subjected to several alkaline leaching experiments for uranium and copper from raw dolostone sample and roasted dolostone sample. To optimize alkaline processing for the recovery of both metal values several series of leaching experiments have first been performed. All experiments were run on roasted and non-roasted (raw ore material).

Figure 1. X-ray diffraction of the powdered selected sample. Diffraction data from ASTM card nos. 12–88, 70–1576, 1–649, and 46–1409 for Ankerite, Azurite, and Quartz, respectively (Ank = Ankerite, Az = Azurite, and Qz = Quartz).

Figure 2. Photography of some minerals associated with the input raw material: (1) Malachite, (2) Chalcocite, (3) Hematitized pyrite, and (4) Azurite.
3.2.1. Results of alkaline leaching of uranium and copper from roasted dolostone sample

3.2.1.1. Material characteristics. The chemical analysis of the major constituent of the working technological roasted ore sample is given in Tables 3 and 4. From the latter, it is obviously evident that besides a loss on ignition of up to 2.45% indicating a loss of organic matter content, the working ore material assays 18.32% of silica, 37.70% and 26.80% of CaO and MgO, respectively.

Another part of the working representative roasted raw sample was subjected to X-ray fluorescence analysis for several trace elements using a Philips X-ray unit (Table 4). These analyses have revealed the presence of interesting values of Cu, REEs, U, V, Ni, Zn, and Pb; namely 1.90%, 0.24%, 0.10%, 0.03%, 90 ppm, and 120 ppm, respectively.

3.2.1.2. Effect of different alkaline reagents. The effect of different alkaline leaching reagents whether single or in combination, upon copper and uranium leaching efficiencies has probably been studied. In these experiments, the other leaching factors were fixed at 90 min agitation time, 60°C leaching temperature, and 1/3 solid–liquid (S/L) ratio and the concentration of the leaching agents is 150 g/L. The obtained leaching efficiencies of either copper or uranium are given in Table 5. From the later, it is indicate that a mixture of 3:1 Na$_2$CO$_3$ and (NH$_4$)$_2$HCO$_3$ is the best leaching reagent which a achieved a 95% leaching for both metal values. This behavior is agreed with that reported by previous investigators (El-Sheikh et al., 2012).

3.2.1.3. Effect of 3:1 Na$_2$CO$_3$/(NH$_4$)$_2$HCO$_3$ concentration. The effect of mixed 3:1 of Na$_2$CO$_3$/((NH$_4$)$_2$HCO$_3$) HCO$_3$ concentration upon Cu and U leaching efficiencies from the roasted sample was studied between 50 and 150 g/l, while the other leaching conditions were fixed at −60 mesh size, 90 min agitation time, 60°C leaching temperature, and 1/3 solid–liquid (S/L) ratio. The leaching efficiencies of both copper and uranium are given in Figure 3(a), and indicated that the best concentration is 100 g/l for copper and uranium leaching. By using these conditions, the leaching efficiency of copper has attained 95% with a uranium dissolution efficiency of 94%. Higher concentrations of the mentioned mixture did not markedly affect the copper or the uranium leaching efficiency.

3.2.1.4. Effect of time. The effect of leaching time upon Cu and U leaching efficiencies from roasted sample was studied in the range from 30 to 120 min. while the other leaching conditions were fixed at 100 g/l concentration of 3:1 mixed Na$_2$CO$_3$/((NH$_4$)$_2$HCO$_3$, −60 mesh size ore fines, a leaching temperature of 60°C, and using a solid/liquid ratio of 1/3. The obtained data shown in Figure 3(b) revealed that a high copper leaching efficiency of 95% and 96% occurs within the experiment of 90 and 120 min, respectively, associated with about 94% uranium leaching efficiency for both time experiment. Thus, it can be concluded that 90 min can indeed be considered as an optimum value.

3.2.1.5. Effect of solid/liquid ratio. It has not been achievable to study the effect of the solid/liquid ratio upon copper and uranium leaching efficiencies from the roasted working sample Cu/U mineralization. This has been due to the nature of the clay component in the latter that has resulted in almost total absorption of the solution at the S/L ratios of 1/1 and 1/2. Thus, a S/L ratio of 1/3 to 1/6 leaching experiments were conducted and a mixed reagent concentration of 100 g/l of 3:1 Na$_2$CO$_3$/((NH$_4$)$_2$HCO$_3$ for 90 min agitation time at 60°C as leaching temperature, it was found that the leaching efficiency of both metal values at S/L ratio of 1/3 have attained 95% for Cu and leaching of about 94% for uranium. So the S/L ratio of 1/3 is considered as a suitable S/L ratio (Figure 3(c)).

3.2.1.6. Effect of temperature. Five alkaline leaching experiments have been performed to investigate
the effect of leaching temperature upon copper and uranium leaching efficiencies from the roasted working sample in the range from room (about 25°C) up to 70°C. In these experiments, the other leaching parameters were fixed at −60 mesh size ore material, 3:1 mixed Na₂CO₃/(NH₄) HCO₃ of 100 g/l concentration for 90 min dissolution time and using S/L ratio of 1/3. The results are given in Figure 3(d), in comparison to that obtained at 60°C actually reveal the importance of temperature to obtain a high leaching efficiency of copper and uranium. Working at room temperature under the mentioned conditions did not leach more than 78% of copper while that of uranium amounted to 71%. Increasing the leaching temperature to 50°C has increased the leaching efficiency of copper and uranium to 90% and 88%, respectively. Also, its further increase to 60°C increased the Cu leaching efficiency to 95% while that of uranium increased to 94% and after which there has been no increase in the leaching efficiencies at 70°C. It can thus be mentioned that an optimum leaching temperature of copper and uranium under the above mentioned conditions would be 60°C.

From the above studied leaching factors of the roasted dolostone Cu/U mineralization of Gabal Allouga, Southwestern Sinai, Egypt, it can be concluded that the optimum leaching conditions for dissolving about 95% of Cu and about 94% of U would be summarized as follows: −60 mesh, 100 g/l of 3:1 mixed Na₂CO₃/(NH₄) HCO₃, 90 min leaching time, 1/3 solid/liquid ratio at 60°C.

3.2.2. Results of alkaline leaching of uranium and copper from raw dolostone sample without roasted

The collected technological sample has been subjected to several alkaline leaching experiments for uranium and copper using alkaline solution. To optimize alkaline processing for the recovery of both metal values several series of leaching experiments have first been performed.

3.2.2.1. Effect of different alkaline reagents. The effect of different alkaline leaching reagents whether single or in combination, upon copper and uranium
leaching efficiencies has probably been studied. In these experiments, the other leaching factors were fixed at 180 min agitation time, 80°C leaching temperature and 1/5 solid–liquid (S/L) ratio and the concentration of the leaching agents is 200 g/L. The obtained leaching efficiencies of both copper and uranium are given in Table 6. From the later, it is indicate that a mixture of 3:1 Na₂CO₃ and (NH₄)HCO₃ is the best leaching reagent that achieved a complete leaching for both metal values. This behavior is agreed with that reported by previous investigators (El-Sheikh et al., 2012).

### Table 6. Effect of different alkaline reagents upon Cu and U leaching efficiencies of the working dolostone technological ore materials without roasted.

| Reagents                                      | Leaching efficiency, % |
|-----------------------------------------------|------------------------|
| NH₄OH                                         | 90                     |
| Na₂CO₃ + Na HCO₃ (3:1)                        | 54                     |
| (NH₄)₂CO₃ + (NH₄)HCO₃(3:1)                    | 100                    |
| (NH₄)₂CO₃ + Na HCO₃                          | 82                     |
| Na₂CO₃ + (NH₄)HCO₃(3:1)                       | 99                     |

3.2.2.2. Effect of carbonate mixture concentration. The effect of carbonate mixture (3Na₂CO₃ + NH₄HCO₃) concentration on the leaching efficiency of Cu and U from the studied ore sample was explained. The carbonate mixture concentrations were varied from 50 to 200 g/l; temperature of solution was maintained upon the level of 80°C, 1:5 solid/liquid ratio, and 180 min. The obtained result was plotted in Figure 4(a). From the obtained data, it is obvious that the solubility of both uranium and copper was increased with increasing the carbonate mixture concentration from 50 to 200 g/l. As the carbonate mixture concentration increased from 50 to 150 g/l, the uranium leaching efficiency increased from 54% to 93.75%, while the Cu leaching efficiency increased from 60.5% to 97%. However, by increasing the carbonate mixture concentration above 150 g/l, lead to slightly increase in the U and Cu leaching efficiencies, while the carbonate mixture consumption was increased which means that more undesirable impurities were dissolved, that leads to serious defects in the purity of the final uranium product (Eliwa, 2009). Accordingly,
3.2.2.3. Effect of time. In a trial to improve the leaching conditions, another experimental leaching series was performed from 1 to 4 h leaching time. In these experiments, the leaching conditions were kept fixed at 150 g/l carbonate mixture in a solid/liquid ratio of 1:5 at 80°C. From the results shown in Figure 4(b), it was ascertained that at only one hour leaching time, the obtained efficiencies of U and Cu has achieved only 64.5% and 67.9%, respectively. However, maximum leaching efficiency of U and Cu was established during 180 min. It attained about 93.75% and 97% for U and Cu, respectively. Thus, it can be concluded that 180 min leaching time would be adequate to leaching process.

3.2.2.4. Effect of solid/liquid ratio. Working with 150 g/l carbonate mixture, another five leaching experiments were performed using the solid/liquid ratios 1:3, 1:4, 1:5, and 1:6 for 180 min at 80°C. From the obtained results shown in Figure 4(c), it was concluded that the leaching efficiencies of both studied metals have been lowered at 1:3 solid/liquid ratio. The obtained leaching yield at S/L ratio 1:3 for U and Cu was achieved only 78.6% and 82.4% as compared to 93.75% and 97% at a solid/liquid ratio 1:5, respectively. Increasing the carbonate mixture amount by applying the pulp ratio of 1:6 did not improve the leaching efficiency of studied elements but increase the undesirable impurities. From the previous observations, it is suggested to use 1:5 solid/liquid ratio because it gives a good leaching efficiency of U and Cu.

3.2.2.5. Effect of temperature. Five leaching experiments were carried out at room temperature, 50, 70, 80, and 85°C under the optimum conditions previously studied as S/L of 1/5 and contact time of 180 min. The resultant leaching efficiencies are shown in Figure 4(d). It indicates that the temperature has a critical role in leaching process. For example, working at room temperature the obtained leaching yield for U and Cu was achieved only 49% and 50.4% and by increasing temperature from 50 to 85°C the leaching efficiency of U and Cu was increased from 70.5% to 99% for uranium and from 76.6% to 99.9% for Cu, respectively. On the other hand, increasing the temperature enhances the solubility of the undesirable impurities, such as sulfides, arsenide, silicates, chlorites, clays, and phosphates (Merritt, 1971). Therefore, it can be concluded that 80°C leaching temperature would be adequate and considered optimum for high leaching of both metal values U and Cu.

From the above studied leaching factors of the working dolostone Cu/ U mineralization of Gabal Allouga, Southwestern Sinai, Egypt, it can be concluded that the optimum leaching conditions for dissolving about 97% of Cu and about 93.75% of U would be summarized as follows: −60 mesh, 150g/l of 3:1 mixed Na₂CO₃/(NH₄)H CO₃, 180 min leaching time, 1/5 solid/liquid ratio at 80°C.

Under the optimum conditions, it was possible to realize a dissolution efficiency of about 95% and 97% for Cu and uranium achieved 94% and 93.75% for roasted and un-roasted raw sample respectively. The leaching process for un-roasted sample has been preferred for economic point of view.

3.3. Kinetic leaching results of uranium and copper from dolostone ore sample

In order to establish the kinetic and thermodynamics terms and the rate-controlling step for the leaching of uranium from sandy dolostone rock using carbonate mixture, the experimental data can be analyzed according to the heterogeneous reaction models (Levenspiel, 1999; Ray, 1993).

The dissolution rates of uranium and copper were analyzed with the shrinking core model for reaction control under the assumption that the ore is a homogeneous spherical solid phase (Habashi, 1980). For the dissolution kinetics, two established kinetic models were used, expressed by the following equations:

\[ 1 - 1 - X^{1/3} = M.K_{C_{A}}.C_{A}.t/d.r = k_1t \]  
\[ 1 - 2/3(X) - (1 - X)^{3/2} = 6u.M.D. C_{A}.t/ dr^2 = k_2t \]  

where \( k_1 \) is the first-order rate constant (m/s), \( M \) is the molecular weight of the solid reactant (kg/mol), \( C_{A} \) is the acid concentration (mol/m³), \( D \) is the diffusion coefficient (m²/s), \( d \) is the density of the particle (kg/m³), \( r \) is the initial radius of the particle (m), \( X \) is the fraction reacted at time \( t \) (s), \( k_1 \) (m/s) and \( k_2 \) (m²/s) are the overall rate constants, and \( u \) is the stoichiometric coefficient. Eq. (4) is conducted to chemically controlled processes and Eq. (5) to diffusion controlled processes (Ray, 1993). Examination of plots of the above kinetic equations as a function of time showed that Eq. (5) gives perfectly straight lines (from 0 to 90 min)

3.3.1. Effect of temperature for the leaching of uranium and copper

The temperature effect was examined in the range of 25–100°C under the conditions of 150 g/l carbonate mixture and 1:5 solid/liquid ratio from 0 to 180 min. The results shown in Figure 5(a,b) indicate that the temperature has great effect on the leaching efficiency of uranium and copper.
The relationship between \( [1−2/3(X−(1−X) 2/3)] \) values and leaching time for uranium and copper at various temperatures are given in Figure 5(c,d), regression analysis shows all \( R \) squares for the equations at the five temperatures are greater than 0.98 (coefficient of determination, denoted \( R^2 \), it indicates how well data points fit a line). 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 and copper from sandy dolostone is diffusion controlled through the 'product' layer. Since, from the above discussion it is inferred that the insoluble oxide minerals (hematite, quartz, etc.) associated with uranium play the role of the 'product' layer. It seen that the leaching reaction is under kinetic control at temperature of 25°C and above.

Figure 5. Effect of temperature for the leaching kinetics of uranium and copper. (a) Effect of temperature on leaching rate of uranium. (b) Effect of temperature on leaching rate of copper. (c) Relationship between \([1−2/3(X−(1−X) 2/3)]\) and leaching time for uranium leaching at various temperature. (d) Relationship between \([1−2/3(X−(1−X) 2/3)]\) and leaching time for copper leaching at various temperature.

Figure 6. Arrhenius plot for uranium and copper leaching at 150 g/l carbonate mixture. (a) uranium; (b) copper.
The apparent activation energy of uranium and copper leaching was determined based on the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{R}T$$  \hspace{1cm} (6)

Where $k$ is a reaction rate constant, $A$ is the frequency factor, $E_a$ is the apparent activation energy, and $R$ is the gas constant.

The plotting of $\ln k$ versus $1/T$ data for the five temperatures are graphed in Figure 6(a,b). The regression analysis showed that the linear relationship is also significant. The apparent activation energy ($E_a$) was, hence, determined by the Arrhenius equation to be 27 kJ/mol for uranium and 27.37 kJ/mol for copper. The reported diffusion controlled dissolution process in this study may be due to secondary precipitation derived from the dissolution process (such as carbonate or hydroxide precipitation), which can coat the surface, can form a diffusive barrier, and have implications for the longevity and mobilization of studied metal values. So, it may be responsible for increasing temperature and this is agree with that reported earlier (Cerrato et al., 2012; Ibrahim, Lasheen, Hassib, & Helal, 2013).

### 3.3.2. Effect of carbonate mixture concentration for uranium and copper leaching

The effect of carbonate mixture concentration was studied in the range of 50–200 g/l under the conditions of 1:5 solid/liquid ratio and 80°C. The leaching results are illustrated in Figure 7(a,b). The corresponding results of values against time at various concentrations are integrated in Figure 7(c,d). It can be seen that increase in carbonate mixture concentration causes a distinct increase in the leaching rate of uranium and copper. An initial carbonate mixture concentration of 30% is necessary to obtain a high dissolution rate of uranium and copper.

In order to obtain the reaction order of carbonate mixture, the log–log results of the rate constants versus the concentration of carbonate mixture are shown in Figure 8(a,b). The slope of the line, or the reaction order of carbonate mixture, is found to be 1.4 for uranium and 1.24 for copper. Hence, the leaching rate of uranium and copper strongly depends on the carbonate mixture concentration.

![Figure 7](image-url) Effect of carbonate mixture concentration for the leaching kinetics of uranium and copper. (a) Effect of carbonate concentration on leaching rate of uranium. (b) Effect of carbonate concentration on leaching rate of copper. (c) Relationship between $[1-2/3(\frac{x}{1-x})^{2/3}]$ and leaching time for uranium leaching at various concentration of carbonate. (d) Relationship between $[1-2/3(\frac{x}{1-x})^{2/3}]$ and leaching time for copper leaching at various concentration of carbonate.

![Figure 8](image-url)
3.4. Recovery of uranium and copper from carbonate leach solution

For the recovery of copper and uranium from the carbonate leach liquor of the working sandy dolostone technological sample, proper 5 L leach liquor was prepared from 1 kg of the working ore sample using the above mentioned determined optimum leaching conditions (150 g/l carbonate mixture, 180 min, 80°C, and 1:5 ratio). Chemical analysis of Cu and U in this liquor was found to attain 2.32 Cu g/l and only 0.28 g U/l, respectively, within leaching efficiency of for 93.75% U and 97% for Cu. Analysis of leach liquor revealed the following composition, as shown in Table 7).

Table 7. Composition of carbonate leach liquor.

| Element | Conc. (g/l) |
|---------|------------|
| U       | 0.281      |
| Cu      | 2.32       |
| Ca      | 0.200      |
| Mg      | 0.070      |
| V       | N.D        |
| REEs    | N.D        |
| Na      | 150        |
| K       | 0.0165     |

* N.D: Not Detected.

From this composition, the recovery of Cu and U was planned firstly by removing of uranium from leach carbonate solution using anion exchanger resin followed by separating and recovery of Cu using precipitation technique as follow:

3.4.1. Recovery of uranium from carbonate leach liquor

Amberlite IR400 was used for adsorption and elution process of uranyl tri-carbonate complex from the obtained carbonate leach liquor.

Accordingly, a resin sample of Amberlite IR400 measuring 22.77 ml wet settled resin (w s r) was packed over a glass wool plug in a Pyrex glass column of 0.5 cm radius. The prepared 5000 ml carbonate leach liquor was adjusted to pH of 9.5 and then subjected to adsorption by passing through the prepared resin bed at a contact time of about 30 min equivalent to a flow rate of about 0.3 ml/min. Under the applied working conditions, it was found that the obtained uranium saturation has approximately amounted to 58.12 g/l w s r, which represents about 94.2% of the theoretical capacity of the working resin (61.7g/l).

Figure 8. Relationship between rate constant and total carbonate mixture concentration at 80°C, and 1:5 solid/liquid ratio. (a) Uranium; (b) copper.

Table 7. Composition of carbonate leach liquor.

| Element | Conc. (g/l) |
|---------|------------|
| U       | 0.281      |
| Cu      | 2.32       |
| Ca      | 0.200      |
| Mg      | 0.070      |
| V       | N.D        |
| REEs    | N.D        |
| Na      | 150        |
| K       | 0.0165     |

* N.D: Not Detected.

Figure 9. ESEM-EDX analysis of ammonium diuranate precipitated from Amb.I.R.A. 400 eluated at pH 5.5.
The loaded uranium was then eluted from the resin using 1 M NaCl with 0.25M Na$_2$CO$_3$ (El-Sheikh et al., 2012). An eluate volume of 140 ml was collected at the end of elution process indicating elution efficiency of about 97%. From the obtained eluate, uranium was precipitated by NH$_4$OH as ammonium diuranate at pH 5.5. The product was subjected to analysis using ESEM-EDX (Figure 9). Chemically, it has about 80% U$_3$O$_8$ after calcination at 850°C.

### 3.4.2. Copper recovery

From the uranium effluent liquor, blue copper hydroxide crystals have been obtained by adjusting its pH to 5.5 using proper dilute hydrochloric acid. The

![Diagram](image.png)

**Figure 10.** ESEM-EDX analysis of the prepared copper oxide product.

**Figure 11.** A tentative flowsheet for the recovery of U and Cu from sandy dolostone, Gabal Allouga, Southwestern Sinai, Egypt.
obtained crystals have been calcined and the obtained oxide has been subjected to ESEM-EDX analysis (Figure 10). Chemically, it has about 98% CuO.

4. Conclusions

A copper–uranium in dolostone Cu/ U mineralization of upper Um Bogma Formation at Gabal Allouga, Southwestern Sinai, Egypt has been studied for the recovery of both metal values. For this purpose, two samples were subjected to alkaline leaching roasted and un-roasted. The leaching process for un-roasted sample has been preferred for economic point of view. The relevant factors of alkaline leaching of a technological sample of this material were studied using a mixture of 150 g Na₂CO₃/[NH₄] HCO₃ solution. Under the most favorable conditions of contact time of 180 min at 80°C and S/L of 1/5 the leaching efficiency dissolving about 93.75% for U and about 97% for Cu. Recovery of the leached metal values was performed using ion exchange for the former and direct precipitation for the latter. Thus, it has been suitable to formulate the tentative flow sheet shown in Figure 11 for processing dolostone technological material for recovering of U and Cu.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

Abdel Fattah, N. A. (2003). Uranium extraction from gibbsite-bearing sediments and some other economic elements by using solvents and organic compounds (Abu Zeneima Area, Sinai, Egypt) (M.Sc. Thesis). Fac. Sc., Zagazig Univ., Egypt.

Abdel Moneim, A. (2005). Uranium extraction from Abu Zeneima Sedimentary Ore Material, Sinai, Egypt (Ph.D. Thesis). Fac. Sc., El- Mansoura Univ., Egypt.

Alguacil, F. J. (1999). Recovery of copper from ammoniacal/ammonium carbonate medium by LIX 973N. Hydrometallurgy, 52, 55–61.

Amer, T. E. (1997). Geochemistry and extraction of U, Cu and Mn from the ore materials of the uraniferous Paleozoic sedimentary rock, West Central Sinai, Egypt (Ph. D. Thesis) Fac. Sc., Cairo Univ., Cairo.

Amer, T. E., Mahdy, M. A., El Hazek, N. T., El Bayoumi, R., & Hassanein, S. (2000, September 9–15). Application of acid pugging and ferric salts leaching on West Central Sinai uraniferous silstone. 30th Annual Hydrometallurgical Conference, Proceedings of an International Symposium Processing Metallurgy of Uranium, Saskatchewan, Canada.

Cerrato, M., Barrows, C., Blue, L., Pacheco, J., Bargar, J., & Giammar, D. (2012). Effect of Ca²⁺ and Zn²⁺ on UO₂ dissolution rates. Environmental Science & Technology, 46, 27–31.

Chung, D., Seo, H., Lee, J., Yang, H., Lee, R., & Kim, K. (2010). Oxidative leaching of uranium from SIMFUEL using Na₂CO₃–H₂O₂ solution. Journal of Radioanalytical and Nuclear Chemistry, 284, 123–129.

Clarens, F., de Pablo, J., Casa, I., Gimenez, J., Rovira, M., Merino, J., . . . Martinez, A. (2005). The oxidative dissolution of unirradiated UO₂ by hydrogen peroxide as a function of pH. Journal of Nuclear Materials, 345, 225–231.

Demerdash, M. (2016). Alkaline leaching of uranium from high carbonate rock material with stress on kinetic studies, Southwestern Sinai, Egypt. Isotope and Radiation Research, 48, 97–118. Retrieved from https://inis.iaea.org/search/search.aspx?orig_q=RN:48040896

El Aassy, I., Botros, N. H., Abdel Razik, A., El Shamy, A. S., Ibrahim, S. K., Sherif, H. Y., . . . Moufhei, A. A. (1986). Report on proving of some radioactive occurrences in west central Sinai (International Report). Cairo, Egypt: N.M.A.

El Hazek, M. N., Ahmed, F. Y., El Kasaby, M. A., & Attia, R. M. (2008). A sulfuric acid leaching of polymetallic Abu Zeneima gibbsite-shale. Hydrometallurgy, 90, 34–39.

Eliaa, A. (2009). Recovery of niobium as a by-product fromGattar V mineralization (M.Sc. Thesis). Zagazig University, Egypt.

El Sheikh, E. M., Ali, S., Ghazala, R., Abdel Warith, A., & Salem, F. (2015). Leaching characteristic of uranium and copper from their mineralization in the carbonate rich latisol of Abo Thor locality, SW Sinai, Egypt. Isotope and Radiation Research, 47, 231–246. Retrieved from https://inis.iaea.org/search/search.aspx?orig_q=RN:47091625

El Sheikh, E. M., Ghazala, A. R., & Ibrahim, H. A. (2012). Recovery of copper and uranium via alkaline leaching of their high carbonate mineralization at Abu Thor Locality, Southwestern Sinai, Egypt. Sedimentology of Egypt, 20, 55–61. Retrieved from https://www.researchgate.net/publication/318861217

Frackiewicz, K., Kiegiel, K., Herdzik-Konecko, I., Chajdak, E., Zakrewska-Trznaadel, G., Wolkowicz, S., . . . Bartosiewicz, I. (2012). Extraction of uranium from low-grade Polish ores: Dictyonemisshales and sandstones. Nukleonika, 57, 451–459. Retrieved from http://www.nukleonika.pl/www/abstrc/vol57_2012/v57n4p451.htm

Gajda, D., Kiegiel, K., Koltuniewicz, G., Chajdak, E., Bartosiewicz, I., & Wolkowicz, S. (2015). Mineralogy and uranium leaching of ores from Triassic Peribaltic sandstones. Journal of Radioanalytical and Nuclear Chemistry, 303, 521–529.

Gillman, A. (2010, May 11). Developing uranium projects three continents. 2010 Australia Uranium Summit, Perth, Australia.

Grandstaff, D. (1976). Akinetic study of the dissolution of uraninite. Economic Geology, 71, 1493–1506.

Habashi, F. (1980). Principles of extractive metallurgy. In General principles (Vol. 1, pp. 111–252). New York: Gordon and Breach.

Habashi, F. (1983). Trends in the hydrometallurgical treatment of copper oxides ores. Arab Mining Journal, 4, 46.

Ibrahim, M., Lasheen, T., Hassib, H., & Helal, A. (2013). Oxidative leaching kinetics of U(IV) deposit under acidic oxidizing conditions. Journal of Environmental Chemical Engineering, 1, 1194–1198.

Khan, Y., Shah, S., & Siddiq, M. (2012). Selection of lixiviant system for the alkaline in-situ leaching of uranium from an arkosic type of sandstone and measuring the dissolution behaviour of some metals and non-metals. Journal-Chemical Society of Pakistan, 34, 826–840. Retrieved from https://www.researchgate.net/publication/259146189_Selection

Konishi, Y., Katoh, M., & Asai, S. (1991). Leaching kinetics of copper from natural chalcocite in alkaline Na₄EDTA solutions. Metallurgical Transactions B, 228, 295–303.

Levenspiel, O. (1999). Chemical reaction engineering (pp. 664). New York: John Wiley & Sons.
Lunt, D., Boshoff, P., Boylett, M., & El-Ansary, Z. (2007). Uranium extraction: The key process drivers. *The Journal of Southern African Institute of Mining and Metallurgy*, 107, 419–426. http://hdl.handle.net/10520/AJAI0038223X_3280

Marczenko, Z. (1986). *Spectrophotometric determination of elements*. New York: John Wiley and Sons.

Meng, X., & Han, K. (1996). The principle and application of ammonia leaching of metals – A review. *Mineral Processing and Extractive Metallurgy Review*, 16, 23–61.

Merritt, R. (1971). *The Extractive Metallurgy of Uranium*. Boulder, Colorado: Colorado School of Mines, Johnson Publishing Co..

Mira, H. I., & Aita, S. K. (2009). Remobilization of uranium and copper through karstification processes; A case study in Abu Thor locality, Um Bogma region, West Central Sinai, Egypt. *Annals of the Geological Survey of Egypt*, 31, 21–42. Retrieved from https://trove.nla.gov.au/version/13318587

Pierce, E., Icenhower, J., Serne, R., & Catalano, J. (2005). Experimental determination of UO₂ dissolution kinetics: Effects of solution saturation state and pH. *Journal of Nuclear Materials*, 345, 206–218.

Rao, K., Sreenivas, K., Vinjamur, M., & Suri, A. (2016). Kinetics of alkaline leaching of UO₂ and FeS₂ in co-existing system. *Transactions of the Indian Institute of Metals*, 69, 23–31.

Ray, H. (1993). *Kinetics of Metallurgical Reactions* (pp. 1–75). New Delhi: InOxford& IBHC.

Robert, C., & Melvin, J. (1981). *CRC Handbook of Chemistry and Physics* (pp. B–75). London: CRC Press Inc.

Shapiro, L., & Brannock, N. W. (1962). Rapid analysis of silicate, carbonate and phosphate rocks. *United States Geological Survey Bulletin*, 174, 65.

Smith, S., Peper, S., Douglas, M., Kate, I., & Finn, E. (2009). Dissolution of uranium under alkaline oxidizing conditions. *Journal of Radioanalytical and Nuclear Chemistry*, 282, 617–621.

Sole, K. C., Cole, P. M., Feather, A. M., & Kotze, M. H. (2011). Solvent extraction and ion exchange applications in Africa’s resurging uranium industry. A review. *Solvent Extraction and Ion Exchange*, 29, 868–869.

Sreenivas, T., & Rajan, K. (2013). Studies on the separation of dissolved uranium from alkaline carbonate leach slurries by resin-in-pulp process. *Separation and Purification Technology*, 112, 54–60.

Ward, F., Nakagawa, H., Harms, T., & Van Sickle, G. (1969). *Atomic-absorption methods of analysis useful in geochemical exploration* (U.S. Geological Survey Bulletin No. 1289), p. 45.

Warhurst, A., & Noronha, L. (2005). Mining, mineral processing, and extractive metallurgy: An overview of the technologies and their impact on the physical environment. In *Environmental policy in mining: Corporate strategy and planning for closure* (pp. 33–56). Boca Raton, FL: CRC Press.