ABSTRACT

A kinetic study of the leaching of Abu Rusheid ferrocolumbite concentrate sample in sulfuric acid media under atmospheric pressure has been investigated. The effects of reaction temperature, sulfuric acid concentration, stirring speed, particle size and solid/liquid mass ratio on the dissolution rate of ferrocolumbite were examined. It is found that the dissolution rate of ferrocolumbite significantly increases with increasing acid concentration, temperature, stirring speed and decreasing the particle size. By using 3M H₂SO₄ solution, about 89% of ferrocolumbite was dissolved within 140 minutes using < 0.053 mm particle size at a temperature of 75°C and a stirring speed of 360 rpm. The experimental data were well interpreted with a shrinking core model under diffusion control through the product layer, where the following rate equation was established:

\[1 + 2 (1 - X)^{2/3} \times \text{dt} = k_2 t\]

The result of the study indicated that the leaching data fitted a diffusion model. Values of 0.7993, 23.64 kJmol⁻¹ and 1.24 X 10⁻³ min⁻¹ were calculated as reaction order, activation energy and Arrhenius constant, respectively for the dissolution process.

INTRODUCTION

The sister elements niobium and tantalum belonging to Group V-B of the periodic table, are relatively very scarce in the earth’s crust. The order of abundance of niobium is around 24 ppm and of tantalum only 2 ppm. On account of their very close chemical similarity, the two elements invariably occur together in nature, predominantly in the form of an isomorphous series of oxide minerals, called columbites and tantalites depending on whether the concentration of niobium or tantalum is greater corresponding to the general formula \{FeMnO₁₂(NbTa)O₅\}. Columbite is a black mineral group which is an ore of both niobium and tantalum (Damodaran et al., 1969 & Mosheim, 2003). It contains a higher percentage of niobium as compared to tantalum and as a result it is taken exclusively as niobium mineral. Another important economic source particularly for niobium is the pyrochlore mineral which is essentially a complex niobate of calcium and sodium, containing fluorine (NaCaNb₂O₆F).

A survey of the pattern of utilization of niobium in industry indicates that around 85% is consumed in the form of ferro-niobium and ferro-tantalum-niobium which are used in production of alloys and stainless steels. Niobium, added as ferro-niobium to austenitic chromium-nickel stainless steels, acts as a stabilized...
stainless steel is extensively used in chemical and petroleum processing equipment, operating at high temperature in corrosive atmospheres, and also in steam turbine generating equipment and high temperature steam lines. From consideration of weld stability, very reliable corrosion resistance and low radiation pick-up, this steel is the popular material of construction for radio-chemical nuclear-fuel processing plants (Damodaran et al., 1969).

Niobium (Nb) and tantalum (Ta) are a key metal in the current electronics industry. It is primarily consumed for the manufacture of tantalum capacitors utilized in mobile phones, laptop computers, digital cameras, as well as automotive and medical electronic equipments (Mosheim, 2003).

The host rocks (cataclastic rocks) bearing columbite at Abu Rusheid area which is located at south Eastern Desert, Egypt (Fig.1) covering a total area of 3 km², occupy the core of the granitic pluton and composed of protomylonites, mylonites, ultramylonites and quartzite (Ibrahim et al., 2010), Fig.(1). The protomylonite and mylonite are richer in columbite than ultramylonite and quartzite. Columbite crystals are sometimes found up to 3 cm in length, and 0.5 cm in width. The average contents of Nb in the study area are about 500 ppm, with cut off grade 150 ppm and the absolute Nb content about 86000 tons above Wadi level (Ibrahim personal communication).

The aim of this study is to investigate the chemical kinetics of ferrocolumbite leaching from Abu Rusheid ore using sulfuric acid, as well as, to establish kinetic model dissolution.

EXPERIMENTAL

Ore Preparation

The following steps are carried out on Abu Rusheid columbite ore sample by physical processing (Ibrahim et al., 2013) as follows:

Crushing and grinding

Using jaw crushers followed by roll mill, the various mineral grains are liberated.

Wet–gravity tabling concentration

The comminuted raw ore sample must be deslimed to diminish the content of slimes (- 53 µ). It was noticed that when the slimes content was more than 10 % and in using an open circuit in the process of comminution, the process of shaking tabling is not efficient. Then, the deslimed fraction was directed to the wet gravity concentration circuit using the available industrial (Full-Size) shaking table, at the Nuclear Materials Authority.

High–tension electrostatic separation

This operation is carried out to obtain most of the conductor columbite, ilmenite and rutile minerals in addition to some varieties of micas in a deflected fraction.

High–intensity magnetic separation

Trying to differentiate between Nb-Ta bearing minerals, ilmenite and rutile present in the deflected conductor fraction (Ibrahim et al., 2010).

Materials/Analysis

The ferrocolumbite ore concentrate used in our study was obtained from a physical
concentration process upon Abu Rusheid Cataclastic rocks. The mineralogical purity of the concentrate was investigated using Philips PW 1830 X-ray diffraction unit with CuKα (1.54Å) radiation, generated at 40kVand 30mA which is presented in Table 1.

Table 1: Results of mineralogical identification

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Identified phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ferrocolumbite (Fe,Mn) (Nb, Ta)O₄</td>
</tr>
<tr>
<td>2</td>
<td>Phlogopitefluor KMg₃(Si₃AlO₄F)</td>
</tr>
</tbody>
</table>

The inductively coupled plasma-mass spectrophotometry (ICP-MS) was used for the elemental analysis of the ferrocolumbite mineral. Analur grade H₂SO₄ acid was used in this research work and distilled water was used for all the analytical preparations. The analysis results of ferrocolumbite (Fe, Mn) (Nb, Ta)O₄ for Nb, Ta and Fe upon ICP-Ms and Atomic absorption spectroscopy, is given in Table 2.

Table 2: Results of chemical analysis of ferrocolumbite ore by ICP- Ms & Atomic absorption spectroscopy

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Element</th>
<th>Results (units)</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ta</td>
<td>700</td>
<td>ICP-MS</td>
</tr>
<tr>
<td>2</td>
<td>Nb</td>
<td>7700</td>
<td>ICP-MS</td>
</tr>
<tr>
<td>3</td>
<td>Fe</td>
<td>9640</td>
<td>Atomic absorption spectroscopy</td>
</tr>
</tbody>
</table>

Kinetic Studies

For this study, three shrinking core models (Ayanda et al., 2012; Dicinoski et al., 2000 & Adekola et al., 2010) were investigated upon the results obtained from the effect of temperature.

Effect of concentration

The effect of concentration on ferrocolumbite sample dissolution is studied over the concentration range of 1M- 8.0M. One gram of ferrocolumbite of particle size <0.053 mm is dissolved at different concentration of sulfuric acid with contact time 140 min at a temperature of 75 and stirring speed 360 rpm. It is observed that an increase in the concentration of sulfuric acid was accompanied with an increase in the rate of ferrocolumbite dissolution i.e the rate of ferrocolumbite dissolution was affected directly by hydrogen ion[H⁺] concentration (Fig.2). This agrees with several reported work on acid dissolution of solid mineral ores (Olanipekun, 1999 & 2000; Antonijevi et al., 2004 & Gulfen et al., 2006).

Effect of temperature

The effect of temperature is studied over a temperature range of 25 – 1250°C for a re-

RESULTS AND DISCUSSION

Leaching Studies

Effect of concentration

The solution was investigated in a 500ml glass reactor equipped with a magnetic stirrer. The reactor is filled with sulfuric acid solution which was heated to the desired temperature (Ibrahim et al., 2013). One gram of ferrocolumbite sample is leached in 100 ml of sulfuric acid. The fraction of ferrocolumbite sample dissolved for each process was calculated by the expression (Kimball et al., 2010 & baba et al., 2010):

\[ x = \left( \frac{M_f}{M_0} \right) \times 100 \quad \text{..................................(1)} \]

Where \( M_f \) is the mass of ferrocolumbite after leaching, \( M_0 \) is the mass of ferrocolumbite.

Kinetic Studies

The effect of temperature is studied over a temperature range of 25 – 1250°C for a re-
Fig. 2: Fraction of ferrocolumbite dissolved (x) versus time (t) at different concentrations (Mass of ferrocolumbite used 1.0, elapsed time: 140 min. stirring rate 360 rpm, particle size <0.053 mm at 75 °C)

action time of 60 min and investigated upon 1.0g ferrocolumbite of particle size <0.053 mm with 5.0 M sulfuric acid concentration at a stirring speed 360 rpm.

The results obtained on Fig. (3) revealed that the increase in temperature from 25 to 125°C accelerates the reaction rate and this leads to an increase in the amount of ferrocolumbite dissolved.

Fig. 3: Fraction of ferrocolumbite dissolved (x) versus time (t) at different temperatures (Mass of ferrocolumbite used 1.0g, elapsed time:60 min. stirring rate 360 rpm, particle size <0.053 mm at 5.0 M H₂SO₄)

Effect of particle size

An important factor to be studied is the effect of particle size, and particles of different size of ferrocolumbite representing samples of 1.0g. Each is investigated in 5.0M sulfuric acid in a series of leaching experiments while the other conditions are kept constant at a contact time120 minutes, stirring speed 360 rpm and a reaction temperature 75 °C. The results are summarized on Fig.(4). From this figure it can be seen that the particle size plays an important role in the leaching process. As a result, the fraction with the smallest particle size used (<0.053mm) gave the highest percentage of ferrocolumbite dissolution. This is due to the highest surface area of the smallest particle size fraction; the conversion rates are inversely correlated with average initial diameter of the particles.

Effect of stirring speed

The percentage of ferrocolumbite dissolved versus the stirring rate (rpm) is investigated between 0 – 600 rpm as shown on Fig. (5). One gram of ferrocolumbite of particle size <0.053 mm is dissolved in 5.0 M H₂SO₄ at a temperature of 75°C, and contact time140

Fig. 4: Fraction of ferrocolumbite dissolved (x) versus time (t) at different grain size (Mass of ferrocolumbite used 1.0g, elapsed time:120 min. stirring rate 360 rpm, 5.0 M H₂SO₄ at 75 °C)

Fig. 5: Fraction of ferrocolumbite dissolved (x) versus time (t) at different RPM (Mass of ferrocolumbite used 1.0g, elapsed time:140 min. 5.0 M H₂SO₄, particle size <0.053 mm at 75 °C)
min. The results showed that the amount of ferrocolumbite dissolved increases with the increase of the stirring speed from 250 to 600 rpm.

**Effect of solid/liquid ratio**

The percentage of ferrocolumbite dissolved versus solid/liquid ratio is investigated between 0.5gm/100ml to 3gm/100ml. One gram of ferrocolumbite of particle size <0.053 mm is dissolved at 5.0 M sulfuric acid with contact time 120 min, at a temperature of 75° C and stirring speed 360 rpm. The results obtained are shown on Fig. (6). The results showed that the amount of ferrocolumbite dissolved increases with increasing time between 0–60 min. The percentage dissolved appears to be practically constant afterwards.

![Fraction of Ferrocolumbite dissolved(x) versus time (t) at different solid/liquid ratios (5.0 M H₂SO₄, elapsed time :120 min. stirring rate 360 rpm, particle size <0.053 mm at 75 °C)](image)

**Kinetics of Dissolution**

The dissolution of mineral from ore takes place through the following stages (Demerdash, 2010):

1. Diffusion of reactant through the diffusion layer
2. Adsorption of the reactant on the solid
3. Chemical reaction between the reactant and the solid
4. Desorption of the product from the solid
5. Diffusion of the product through the diffusion layer

Any of these may be rate controlling depending on its relative speed to the others. Understanding the mechanism of a leaching system is the main objective of this study. Leaching of mineral particle may be described by a number of reaction models already proposed in the literature. Consequently, the dissolution rates of the ferrocolumbite ore were analyzed with the shrinking core models, under the assumption that the ore is a homogenous spherical solid phase. For this study and for better understanding of the leaching mechanism, two established Kinetic models were used (Levenspiel, 1999), as expressed by the following equations:

\[
1 - (1 - X)^{1/3} = k_1 t \quad \text{......................(1)}
\]

\[
1 + 2 (1 - X) - 3 (1 - X)^{2/3} = k_2 t \quad \text{......(2)}
\]

Where \( k_c \) is the first-order rate constant (min⁻¹), \( M \) is the molecular weight of the solid reactant (kg/mol), \( C_A \) is the acid concentration (mol/m³), \( D \) is the diffusion coefficient (m²/min), \( d \) is the density of the particle (kg/m³), \( r \) is the initial radius of the particle (m), \( X \) is the fraction of ferrocolumbite ore dissolved at time \( t \) (min), \( k_1 \) (min⁻¹) and \( k_2 \) (min⁻¹) are the overall rate constants and \( u \) is the stoichiometric coefficient.

The first equation is applicable to chemically controlled processes and the second equation referred to the diffusion controlled processes through the porous product layer. The slope which gives the best correlation coefficient is chosen as the model that fit perfectly with the ferrocolumbite dissolution.

**Application of the obtained data upon the shrinking core model**

a- Chemically controlled process:

\[
1 - (1 - X)^{1/3} = \frac{M k_c C_A}{dr} t \quad \text{.................(1)}
\]

\[
1 - 2 (1 - X)^{2/3} = k_2 t \quad \text{..................(2)}
\]

By applying the obtained data of ferrocolumbite dissolution at different temperatures upon the chemically controlled equation, the following Fig. (7) has been obtained.
Fig. 8: Plot of $1+2 \times (1- X)^{1/3}$ versus contact time at various temperatures (Mass of ferrocolumbite used 1.0 g, 5.0 M H$_2$SO$_4$ (100 ml), stirring rate 360 rpm, particle size <0.053 mm)

The $k_1$ and the correlation coefficient values at various temperatures of the ferrocolumbite sample dissolution are represented in Table (3).

b- Diffusion controlled process:

$$\ln(1-x) = \frac{2}{3} \ln (1-x) - \frac{2}{3} x - \frac{2}{3} x^{2/3} = k_2 t$$

By applying the obtained data of ferrocolumbite dissolution at different temperatures upon the diffusion controlled equation are illustrated on Fig. (8)

Table 3: The value of $k_1$ and the correlation coefficient at various temperatures

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Apparent rate constant (min$^{-1}$) ($k_1$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$8.15 \times 10^{-4}$</td>
<td>0.938</td>
</tr>
<tr>
<td>50</td>
<td>$1.24 \times 10^{-4}$</td>
<td>0.927</td>
</tr>
<tr>
<td>75</td>
<td>$1.15 \times 10^{-4}$</td>
<td>0.86</td>
</tr>
<tr>
<td>100</td>
<td>$2.32 \times 10^{-4}$</td>
<td>0.837</td>
</tr>
<tr>
<td>125</td>
<td>$2.85 \times 10^{-4}$</td>
<td>0.836</td>
</tr>
</tbody>
</table>

The $K_2$ and the correlation coefficient values at various temperatures of ferrocolumbite sample dissolution are represented in Table (4). From these results and the high correlation coefficient obtained in the case of diffusion controlled process, we can suggest that the main dissolution process for ferrocolumbite is controlled by diffusion through the outer layer.

Table 4: The value of $K_2$ and the correlation coefficient at various temperatures

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Apparent rate constant (min$^{-1}$) ($k_2$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$4.73 \times 10^{-5}$</td>
<td>0.984</td>
</tr>
<tr>
<td>50</td>
<td>$7.34 \times 10^{-5}$</td>
<td>0.985</td>
</tr>
<tr>
<td>75</td>
<td>$2.20 \times 10^{-5}$</td>
<td>0.993</td>
</tr>
<tr>
<td>100</td>
<td>$4.65 \times 10^{-5}$</td>
<td>0.994</td>
</tr>
<tr>
<td>125</td>
<td>$7.0 \times 10^{-5}$</td>
<td>0.996</td>
</tr>
</tbody>
</table>

Activation energy of the dissolution process

The apparent rate constants, $k_1$ derived from the slopes of the lines in Fig. (8) were used to obtain the Arrhenius relation which indicated below $1nK=1nA-\frac{Ea}{RT}$

From which the energy of activation, $E_a$ of 23.6 kJ mol$^{-1}$ was calculated for the dissolution process. Since the diffusion-controlled reaction shows a proportional increase in rate with increasing agitation speed and typically have an activation energy $\leq$ 25 kJ mol$^{-1}$, so the calculated activation energy from Fig. (9) suggests a diffusion controlled process for ferrocolumbite dissolution in sulfuric acid.
The results of recent studies showed that some diffusion controlled reactions could have unusually high activation energy. For instance, the activation energy for the diffusion controlled dissolution of titanium and iron from ilmenite in hydrochloric acid solution are reported as 48.9 and 53.7 kJ mol\(^{-1}\) (Tsuchida et al., 1982), and that from a Nigerian ilmenite in hydrochloric acid solution were also reported as 62.4 - 67.1 kJ mol\(^{-1}\) (Olanipekun, 1999). Similarly, the activation energy for the diffusion controlled hydrochloric acid leaching of iron from bauxite varied from 62 to 79 kJ mol\(^{-1}\) for different particle size fractions (Paspaliaris & tsolakis, 1987).

On closer examination, it appears that the rate controlling mechanism of heterogeneous dissolution reactions is sometimes better predicted from plots of the kinetic equations than from the activation energy values.

**Order of reaction**

The order of reaction from the slope of ferrocolumbite dissolution in the sulfuric acid with respect to \([H^+]\) was 0.7993. The following Table (5) shows the values for the apparent rate constants for the hydrogen ion concentration while Fig. (10) shows the plot of \(\ln k_d\) versus \(\ln[H^+]\) for sulfuric acid concentrations.

Table 5: Values for the apparent rate constant for the hydrogen ion concentration

<table>
<thead>
<tr>
<th>([H^+])</th>
<th>(\ln[H^+])</th>
<th>(k_d)</th>
<th>(\ln k_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1.95e-4</td>
<td>-5.54</td>
</tr>
<tr>
<td>3</td>
<td>1.1</td>
<td>9.20e-3</td>
<td>-4.69</td>
</tr>
<tr>
<td>5</td>
<td>1.61</td>
<td>0.015</td>
<td>-4.20</td>
</tr>
<tr>
<td>8</td>
<td>2.08</td>
<td>0.045</td>
<td>-3.91</td>
</tr>
</tbody>
</table>

**CONCLUSION**

In the present study, the dissolution of ferrocolumbite in sulfuric acid is studied. It is found that the rate of ferrocolumbite dissolution increases with acid concentration, temperature, stirring speed and decreases with particle size. The dissolution of ferrocolumbite in sulfuric acid is found to be controlled by the shrinking core model for a diffusion-controlled process. Values of 23.6 kJ mol\(^{-1}\) and 1.24 X 10\(^{-3}\) min\(^{-1}\) are obtained for the activation energy and Arrhenius constant of ferrocolumbite dissolution in sulfuric acid respectively; and the order of reaction was 0.7993.

**Nomenclature**

- \(A\) : is the frequency factor in min\(^{-1}\)
- \(E_a\): Activation energy (kJ/mol)
- \(k\) : Reaction rate constant (min\(^{-1}\))
- \(k_1, k_2\) : apparent reaction rate constants
- \(L/S\) : Liquid to Solid ratio
- \(M\) : mole/liter; \(t\) : Time (min); \(T\) : Recorded temperature
- \(r\) : Initial radius of the solid particle
- \(R\) : Universal gas constant, 8.314 J mol\(^{-1}\) K\(^{-1}\)
- rpm: Revolutions per minute
- \(R^2\) : Coefficient of determination (a statistical value)
- \(\alpha\) : Fraction of uranium ore concentrate reacted at contact time
- \(\mu_m\) : Micro meter

**REFERENCES**


دراسات لديناميكية عملية إذابة مركوزات الفيروكولومبайте باستخدام حامض الكبريت من صخور أبو رشيد التهشيرية - جنوب الصحراء الشرقية - مصر

دعاة إبراهيم زكي، غادة محمد محمود، محمد العرادي، محمد الأحمدي

يتعرض هذا البحث لدراسة ديناميكية عملية إذابة مركوزات الفيروكولومبائه باستخدام حامض الكبريت من صخور أبو رشيد التهشيرية - جنوب الصحراء الشرقية - مصر. تمت دراسة تأثير العوامل المختلفة مثل وقت عملية إذابة الفيروكولومبائه حتى 140 دقيقة، وتركيز حامض الكبريت من 1 إلى 5 جزيء، ونسبة إضافة المحاليل السائلة لرواسب الصلب تتراوح من 1/01 إلى 5/01، ودرجة حرارة التفاعل تتراوح من 52 إلى 521 درجة مئوية، وكذلك سرعة التقليل الميكانيكية من 25 إلى 60 دورة في الدقيقة، وذلك من أجل تحسين العوامل المختلفة للعملية لتحقيق أقصى قدر في إذابة الفيروكولومبائه. وقد أظهرت النتائج التجريبية أن مقدار ذوبان الفيروكولومبائه يزداد مع زيادة تركيز الحامض، وزيادة درجة الحرارة، وثقل حجم الجسيمات، وقد تحققت أقصى نسبة إذابة الفيروكولومبائه قدراً حوالي 89% بعد 45 دقيقة من التفاعل بين الحامض وال الخام، باستخدام حمض الهيدروكلوريك بتركيز 3 جرام جزئي ونسبة 3 جرام لكل 100 مللي إضافة المواد الصلبة لرواسب المحاليل باستخدام حجم الجسيمات 0.05 ملمتر عند 75% منوية مع سرعة التقليل الميكانيكية 360 لفة في الدقيقة، و التي (shrinking core model) وفرت تلك النتائج التجريبية بواسطة النماذج الأساسية مع ما يسمى به - يتم التفاعل بها عن طريق الانتشار من خلال طبق Platania المنتج، و أيضاً باستخدام عداددت أرهبيس، ثم تقييم طاقة التنشيط لتفاعل عملية إذابة الفيروكولومبائه، والتي قدرا بـ 412 كيلوجول لكل جرام جزئي بالإضافة إلى تقييم رتبة التفاعل والتي قدرت بـ 0.897.