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A Kinetic Study of the Leaching of Iron and Manganese from a Nigerian Tantalite-columbite Ore

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Abstract: A kinetic study of the leaching of iron and manganese from powdered tantalite-columbite ore by Hydrochloric Acid (HCl) and Sulphuric Acid (H_2SO_4) solutions has been carried out. The effects of (a) particle size ranging from 63 to 250 μm (b) stirring speed ranging from 180 to 540 min^{-1} (c) acid concentration ranging from 4.0 to 10.0 M (d) temperature ranging from 30 to 90°C on the leaching of iron and manganese are reported. The leaching rates were significantly dependent on the particle size of the ore, stirring speed, temperature, concentration and the nature of the acids used. Within the first 120 min of leaching, iron and manganese were largely leached by HCl solution. After 120 min more iron was leached by H_2SO_4 solution. The observed effects of the operating variables on the leaching rates were consistent with the ash/product layer diffusion-controlled kinetic model: $1+2(1-a)-3(1-a)^{2/3}=k_2t$ The apparent activation energies for the leaching of iron and manganese were 14.50 and 39.99 KJ mol^{-1} for the leaching of iron by HCl and H_2SO_4, respectively. The corresponding values for manganese were 19.91 and 60.78 KJ mol^{-1}.

Key words: Leaching, hydrochloric acid, sulphuric acid, tantalite-columbite ore

INTRODUCTION

A good number of works have been reported on the hydrometallurgical leaching of iron and manganese from their ores using various leachants such as chloride media, mineral acids with or without oxidants[1-5]. Limited reports have, however, been published on the leaching of iron and manganese from tantalite-columbite ore. Hence, there is a lack of information on the leaching mechanism of these metals from tantalite-columbite ores in mineral acids. Tantalite-columbite or tantalite niobium ores are oxides of tantalum, niobium, iron and manganese, (Fe, Mn) $(Ta, Nb)_2O_6$[6].

Tantalite-columbite deposit is remarkable as it lies in a layer of loose alluvial sand, only about 1.5 m beneath the earth surface. It is ideal for low-cost mining using bulldozers, simple barrel washing and magnetic separation. Tantalite-columbite is mined primarily from pegmatite and their associated alluvial[7]. In the Nasarawa area in Nigeria, artisanal mining started in 1995 and a monthly production of 1000 kg was reported, although, production records are not maintained[8]. Within the last decade ore processors have made considerable progress in the processing of tantalum and niobium minerals using different methods such as pyrometallugy, chlorination or hydrometallurgy[9-11]. It has been observed during chlorination and carbochlorination of Low Grade Concentrate (LGC) and High Grade Concentrate (HGC) that while the tantalum and niobium products from LGC were contaminated with chloride compounds of manganese and iron, pure tantalum and niobium compounds can be obtained from HGC[11]. Therefore a knowledge of the kinetics of leaching of iron and manganese which are main components of tantalite-columbite, is essential for the production of HGC and hence pure tantalum and niobium compounds.

In the present study, a kinetic study of the leaching of iron and manganese from Awo tantalite-columbite ore obtained from Awo in Osun State of Nigeria was investigated.

MATERIALS AND METHODS

Material: A hard rock tantalite-columbite from Awo, Osun State, Nigeria, was used for all kinetic leaching processes. The chemical analysis of the ore is shown in Table 1. The hydrochloric and sulphuric acids used were reagent grades. They were purchased and used without further purification.

Equipment: A 250 mL three-necked round-bottomed pyrex flask equipped with a thermometer, a mechanical stirrer and a reflux condenser was used as the batch reactor. The reactor was placed on an electrical heating mantle with

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Table 1: Chemical analysis of the tantalite-columbite ore

Elements	Content (wt.%)
Ta	6.93±0.09
Nb	14.70±0.12
Fe	9.45±0.16
Mn	4.50±0.09
Sn	6.73±1.90
Ti	0.58±0.09
Co	0.08±0.00
Hf	0.09±0.00
Zn	0.04±0.01
W	0.19±0.04
Pb	0.04±0.01
Br	0.01±0.00
Rb	0.01±0.00
Th	0.01±0.00
Y	0.01±0.00
U	0.03±0.00
Zr	0.16±0.00

temperature control. The desired reaction temperature was maintained within ±1°C.

Procedure: For each run, 150 mL of the acid solution of predetermined molarity was charged into the reactor and heated to the required temperature. When the desired temperature was reached, tantalite-columbite (0.5 g) was added to the reactor with continuous stirring. Solution samples of 2 mL were pipetted through a fine frit at after 10 min and then 30 min. Subsequent sampling was done at 30 min intervals. The total time of leaching was 5 h. Iron and manganese were determined by atomic absorption spectrophotometer (Perkin-Elmer model 403).

RESULTS

Effect of stirring speed: The effect of string speed on the rate of leaching of iron and manganese was investigated using 6.0 M HCl solution with the < 63 µm size fraction of the tantalite-columbite at 70°C, at 180, 360 and 540 min^{-1}. The results in Fig. 1 show that leaching rates depends on the stirring speed as the amount of iron and manganese leached with time increase with increase in stirring speed.

Effect of particle size: The effect of particle size on the leaching of iron and manganese was investigated in 6.0 HCl solution at 70°C, using the three particle size fractions, 0 < diameter (µm) < 63, 63 < diameter (µm) < 171 and 171 < diameter (µm) < 250. The results as shown in Fig. 2 indicated that the rates of leaching of iron and manganese are inversely proportional to the average initial diameter of the particles.

Concentration effect: The effect of HCl and H_2SO_4 concentrations on the leaching of iron and manganese was investigated at 70°C using < 63 µm sized fraction of the tantalite-columbite and a stirring speed of 360 min^{-1}. The HCl and H_2SO_4 concentrations used are 4.0, 6.0, 8.0 and 10.0 M. The amount in milligrams of iron and manganese leached versus time plots for various HCl and H_2SO_4 concentrations are shown in Fig. 3 and 4. Concentration of the leachants has a significant effect on the leaching of iron and manganese from tantalite-columbite as the amount leached increases with increase in concentration.

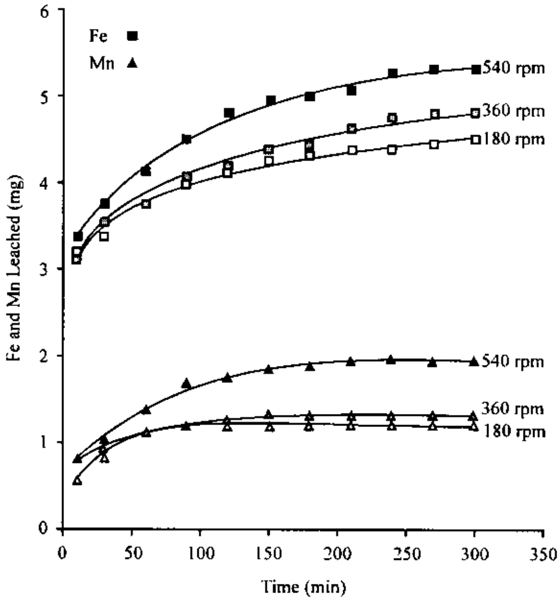

Fig. 1: Effect of stirring speed on the Leaching of Fe and Mn by 6.0 M HCl solution at 70°C and a particle size of <63 µm

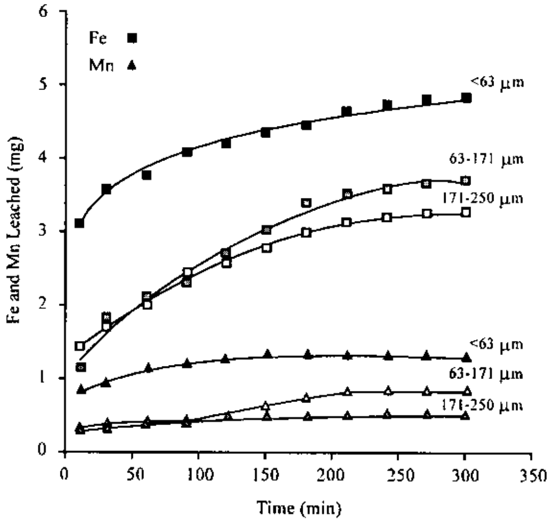

Fig. 2: Effect of particle size on the leaching of Fe and Mn by 6.0 M HCl solution at 70°C and a stirring speed of 360 rpm

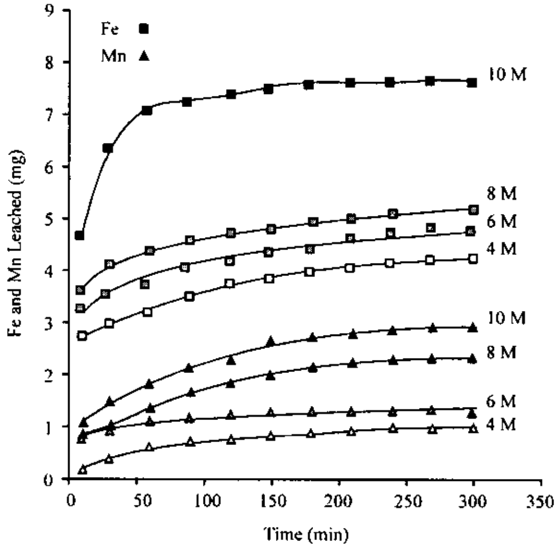

Fig. 3: Effect of HCl concentration on the leaching of Fe and Mn from the Tantalite-columbite ore at 70°C, a stirring speed of 360 rpm and a particle size of <63 μm

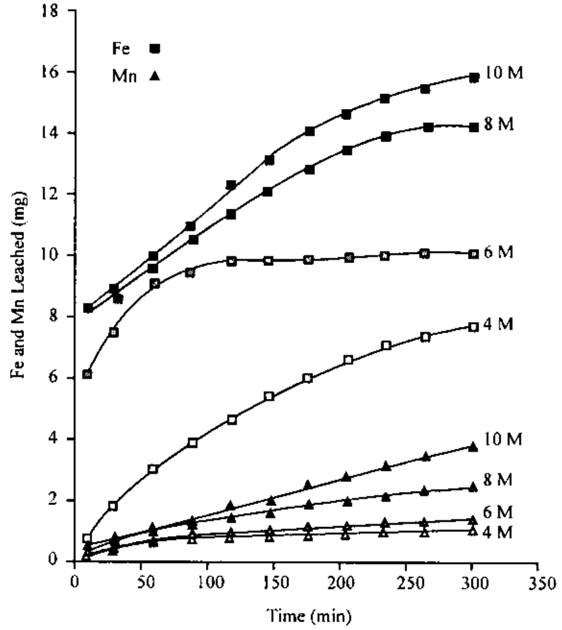

Fig. 4: Effect of H_2SO_4 concentration on the leaching of Fe and Mn from the Tantalite-columbite ore at 70°C, a stirring speed of 360 rpm and a particle size of <63 μm

Comparative effect of leachants: The effect of leachants (HCl and H_2SO_4) on the leaching of iron and manganese from the tantalite ore was investigated using 8.0 M HCl and 4.0 M H_2SO_4 at 70°C using the < 63 μm size fraction and stirring speed of 360 min^{-1}. It can be seen from the results in Fig. 5 that both metals were largely leached in HCl within the first 120 min of leaching. Beyond 120 min the leaching of iron was significantly more enhanced in H_2SO_4.

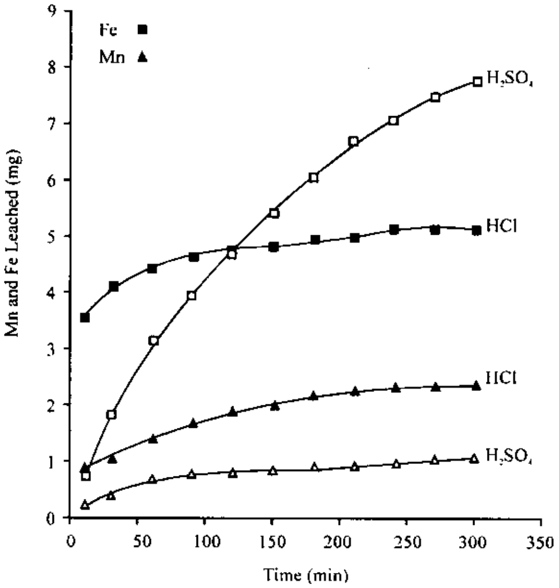

Fig. 5: Effect of hydrogen ion concentration, [H+], of the leachants on the leaching of Fe and Mn at 70°C, a stirring speed of 360 rpm and a particle size of <63 μm

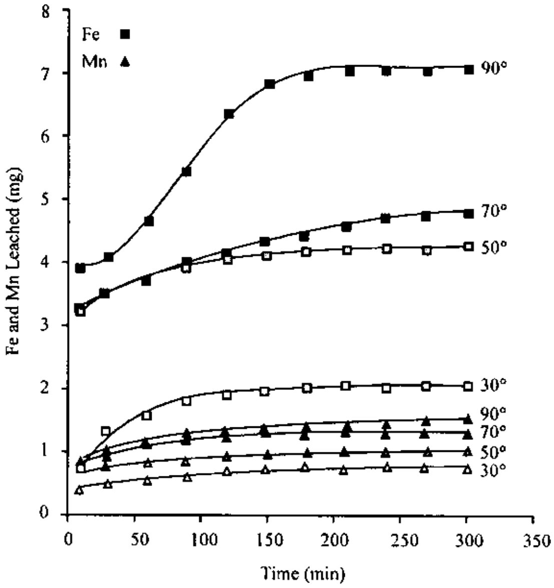

Fig. 6: Effect of temperature on the leaching of Fe and Mn by 6.0 M HCl solution at a stirring speed of 360 rpm and a particle size of <63 μm

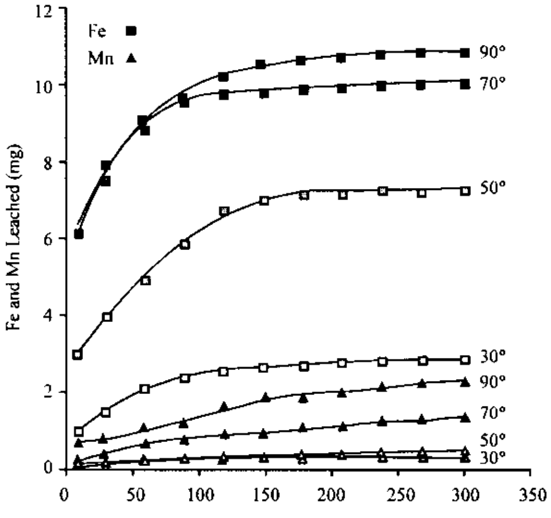

Fig. 7: Effect of temperature on the leaching of Fe and Mn by 6.0 M H_2SO_4 solution at a stirring speed of 360 rpm and a particle size of <63 µm

Effect of temperature: The effect of temperature on the leaching of iron and manganese was investigated using 6.0 M HCl and H_2SO_4 solutions at a stirring speed of 360 min^{-1} and < 63 µm size fraction at temperature of 30, 50, 70 and 90°C. The results in Fig. 6 and 7 show that leaching rate increases with increase in temperature with both metals being more strongly leached at 90°C.

DISCUSSION

Leaching profiles: The results of the effects of acid concentration on the removal of iron and manganese as presented in Fig. 3 and 4 showed that acid concentrations have significant effect on the leaching. In the two solvent systems, it was observed that the rate of leaching increases with increase in acid concentration. Iron and manganese were leached best by hydrochloric acid within the first 120 mins of leaching. The observed enhanced of leaching of iron by sulphuric acid after 120 min was due to the fact that H_2SO_4 is initially less than 100% dissociated (second proton not as readily released as the first proton).

$$H_2SO_4 \rightarrow HSO_4- + H^+ \tag{1}$$

$$HSO_4^- \rightarrow SO_4^{2-} + H^+ \tag{2}$$

It takes time for H^+ from reaction (2) to accumulate. Hence as the reaction progresses more ion is leached by H_2SO_4.

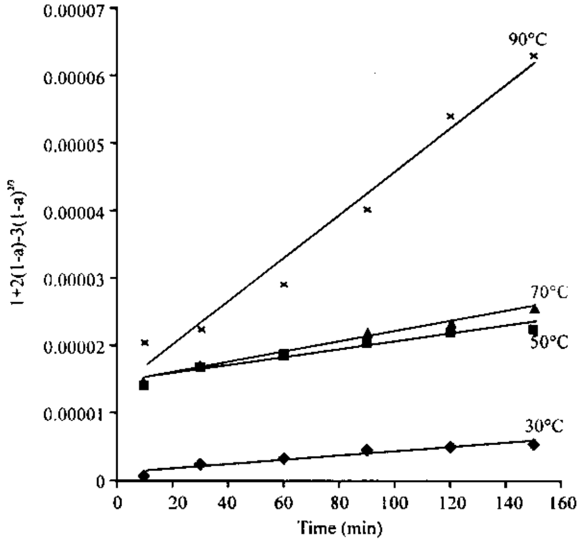

Fig. 8: Graph of $1+2(1-a)-3(1-a)^{2/3}$ against time for the leaching of Fe by HCl solution

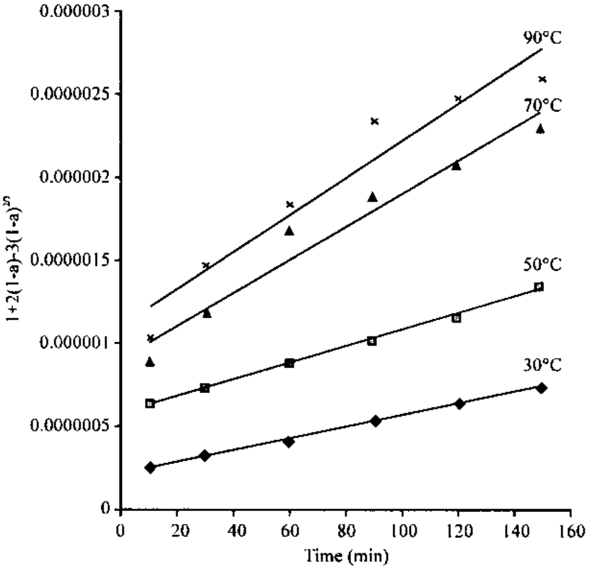

Fig. 9: Graph of $1+2(1-a)-3(1-a)^{2/3}$ against time for the leaching of Mn by HCl solution

Kinetic models: The leaching rates of iron and manganese were analysed with the shrinking core model for reaction control under the assumption that the ore is a homogeneous spherical solid phase[12]. Two previously established models were used, expressed by the following equations:

$$1+(1-a)^{1/3}=k_1t \tag{3}$$

$$1+2(1-a)-3(1-a)^{2/3}=k_2t \tag{4}$$

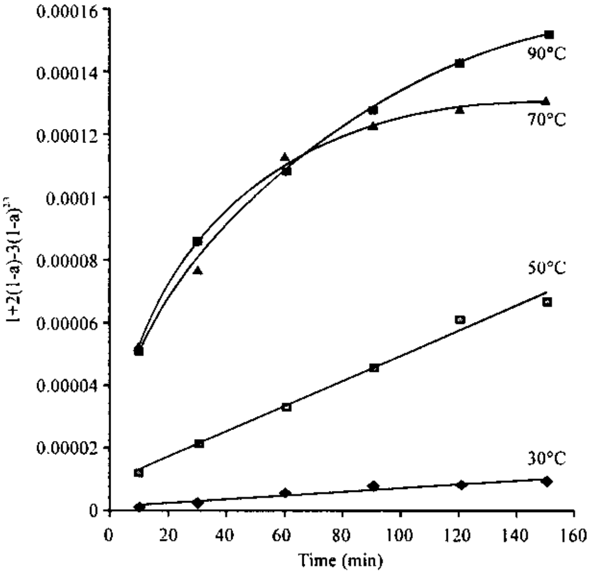

Fig. 10: Graph of $1+2(1-a)-3(1-a)^{2/3}$ against time for the leaching of Fe by H_2SO_4 solution

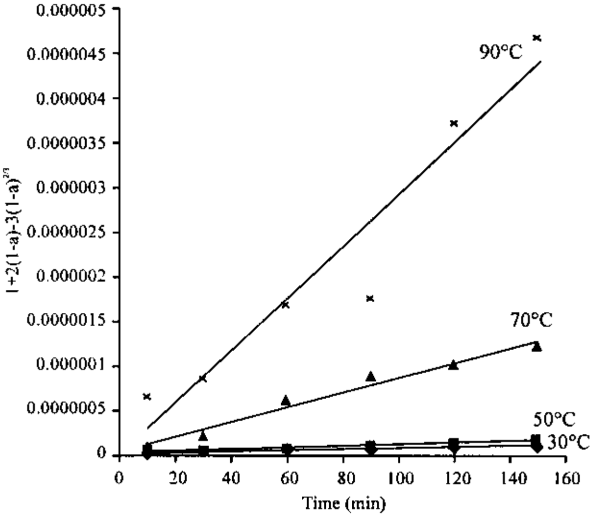

Fig. 11: Graph of $1+2(1-a)-3(1-a)^{2/3}$ against time for the leaching of Mn by H_2SO_4 solution

where, 'a' is the fraction reacted at time t (min), k_1 (m min^{-1}) and k_2 (m^2 min^{-1}) are the overall rate constants. Equation (3) is applicable to chemically controlled processes and equation (4) to diffusion controlled processes through the porous product layer.

The diffusion controlled kinetic model fits the use of hydrochloric acid and sulphuric acid for both iron and manganese at the temperature range covered except for the leaching of iron by H_2SO_4 solution where deviation was observed at higher temperatures 70 and 90°C, (Fig. 10). At these temperatures (70 and 90°C) thermal motion is greater and diffusion may not significantly be rate determining.

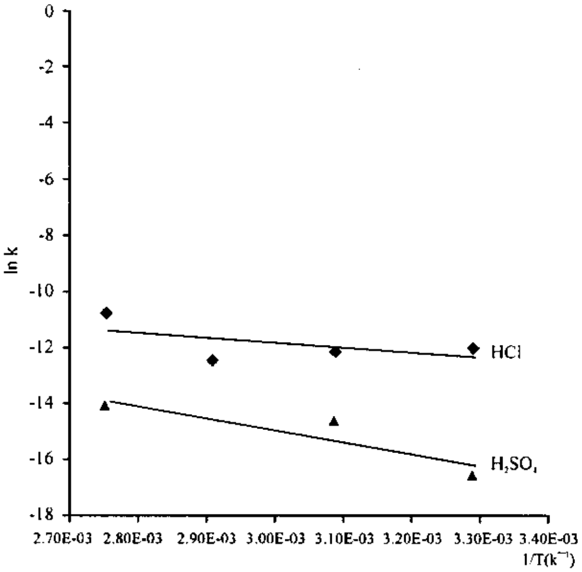

Fig. 12: Arrhenius plot for the leaching of Fe by HCl and H_2SO_4 solutions

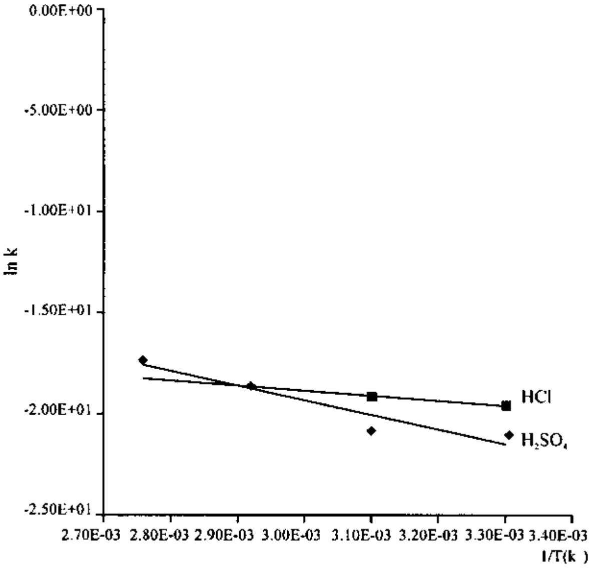

Fig. 13: Arrhenius plot for the leaching of Mn by HCl and H_2SO_4 solutions

For oxidizing acid like H_2SO_4 the validity of diffusion controlled model may be influenced by formation of metal oxides. It is known that iron (II) oxide, FeO and manganese (II) oxide, MnO, present in the tantalite-columbite matrix in the solid in solution[13]. During

Table 2: Activation energy values for the leaching of iron and manganese by HCl and H_2SO_4 solutions

Leachant	Ea for the leaching of Fe (KJ mol^{-1})	Ea for the leaching of Mn (KJ mol^{-1})
HCl	14.50	19.91
H_2SO_4	34.99	60.78

phase transformation, solid/solution, it is presumed that iron and manganese oxides are separated out of the tantalite-columbite matrix, but are still surrounded by newly formed Fe_2O_3 (hematite) and Mn_2O_3 layer (products of oxidation of FeO and MnO). Therefore, during leaching the rate of removal of both metals, Fe and Mn is controlled by diffusion through the Fe_2O_3 and Mn_2O_3 layers.

Estimation of activation energies: The reaction between the overall rate constant and temperature from equation (4) may be expressed by the Arrhenius equation, $k=Ae^{-Ea/RT}$ where, k is the overall rate constant ($m^2 min^{-1}$), Ea is the activation energy (J mol^{-1}), R is the universal gas constant (8.314 KJ^{-1}), T is the reaction temperature (k) and A is the preexponential factor (m^2 min^{-}). Rate constants for different temperatures were calculated from the plots in Fig. 8-11 and the Arrheniun plots of ln k vs T^{-1} are as shown in Fig. 12 and 13 for iron and manganese respectively. The estimated activation energies from these plots are as stated in Table 2.

The relatively low values of activation energies (< 20 KJ mol^{-1}) for the leaching of iron and manganese by hydrochloric acid are clearly indicative of a diffusion and not chemically-controlled mechanism[14]. However, the relatively high values of activation energies (34.99 and 60.78 KJ mol^{-1}) for the leaching by sulphuric acid are not an indication that the leaching is by chemical control since the best way to predict the leaching mechanism of a reaction is through the kinetic model plots.

CONCLUSION

The following conclusions can be drawn from this study;

1. Both temperature and concentration of hydrochloric and sulphuric acids, particle size of the ore and stirring speed have a significant effect on the rate of leaching of iron and manganese from the tantalite-columbite ore.
2. The shrinking core model for spherical particles is applicable to the leaching process which is controlled by diffusion of iron (II) and manganese (II) through the porous product layer.
3. Over an extended leaching time, the leaching with hydrochloric acid was observed to approach saturation while the leaching with sulphuric acid yielded a higher concentration of the metals beyond 120 min of the leaching time. This, however, may not necessarily recommend sulphuric acid as better leachant than hydrochloric acid, giving the recoverability and low activation energy features exhibited by hydrochloric acid, which makes for less heat transfer in the reactor design.
4. The tantalite-columbite ore contains tantalum, niobium, iron, manganese and tin as major elements.

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