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Dissolution Kinetics of Columbite in Nitric Acid

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An investigation of the dissolution kinetics of a Nigerian columbite mineral ore sample in nitric acid media has been undertaken. The effects of acid concentration, process temperature, stirring rate and particle size on the dissolution rate were also investigated. Experimental results indicated that columbite dissolution was greatly influenced by hydrogen ion concentration and the leaching data fitted a diffusion model. Values of 15.100 kJ mol^{-1} and 9.42×10^{-5} min^{-1} were obtained for the activation energy and Arrhenius constant of columbite dissolution in nitric acid respectively and the order of reaction was 0.35.

Key Words: Columbite, Kinetics, Nitric acid, Activation energy and arrhenius constant.

INTRODUCTION

Columbite is the most widespread niobium mineral and makes for an important ore of the industrially useful metal. Columbite, also called niobite, niobite-tantalite and columbate (Fe, Mn, Mg) $(Nb, Ta)_2O_6$ (iron, manganese, magnesium, niobium, tantalum oxide), is a black mineral group that is an ore of niobium and tantalum. It has a submetallic luster and a high specific gravity and is a niobate of iron and manganese, containing tantalate of iron.

Nigeria's endowments in fluid and solid minerals are extensive. The country's mineral development in terms of prospecting and exploitation has been largely focused on its oil and gas industry. The solid minerals sector has been neglected. Examples of widely reported mineral deposits in Nigeria with strong international influence are niobium and tantalum bearing minerals and the major world deposits of columbite-tantalite minerals are located in Nigeria[1].

Columbite is taken exclusively as niobium mineral and niobium is used in superconducting magnets, commemorative coins, medical device, jewelleries, arc-tube seals, capacitors, optical lens, barometer, nuclear applications, superconducting RF cavities, electromagnetic radiation detector and it is used in nickel-, cobalt- and iron-based super-alloys, which are used in jet engines components, rocket sub-assemblies, heat resistant and combustion equipments[2].

The present investigation was therefore aimed at establishing the conditions for the leaching of a Nigerian columbite in nitric acid media.

Kinetic analysis: For this study, three shrinking core models were investigated on the result obtained on the effect of temperature. If the process is controlled by the reactant diffusion through the fluid surrounding the particle:

$$\frac{t_f}{t_f^*} = 1 - \left[\frac{r_c}{R}\right]^3 = X \quad (1)$$

where, t^*_f is the time required for the particle to react completely, r_c is the unreacted core radius at a given time and R is the initial particle radius. If the reaction is controlled by product layer diffusion, then:

$$\frac{t_d}{t_d^*} = 1 - 3\left[\frac{r_c}{R}\right]^2 + 2\left[\frac{r_c}{R}\right]^3 = 1 - 3(1-X)^{2/3} + 2(1-X) \quad (2)$$

where, similarly to equation 1, t^*_d is the time required for the particle to react completely. If the process is controlled by chemical reaction:

$$\frac{t_r}{t_r^*} = 1 - \left[\frac{r_c}{R}\right] = 1 - (1-X)^{1/3} \quad (3)$$

In hydrometallurgy the shrinking core models are applied to describe the shrinkage of ore particles during mineral leaching reactions, which are a central unit operation in the hydrometallurgical ores treatment[3]. To find out the mechanism controlling the shrinkage process, eqns. 4, 5 and 6 are used.

$$1-3(1-X)^{2/3} + 2(1-X) = k_d t \quad (4)$$

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

$$[1-(1-X)^{2/3} + 2(1-X)] + b[1- (1-X)^{1/3}] = k_m t \quad (6)$$

where, X is the fraction of columbite dissolved; t is contact time (s); k_r, k_d and k_m are the reaction rate constants.

Equation 4 is based on the diffusion controlled reaction and its slope corresponds to the apparent rate constant k_d. Equation 5 on the other hand is based on chemically controlled reaction and its slope gives the apparent rate constant k_r. Lastly, eqn. 6 is based on a mixed controlled reaction and apparent rate constant k_m.

The slope that gave the best correlation coefficient was chosen as the mechanism that controls the shrinkage process of columbite leaching in nitric acid media.

EXPERIMENTAL

Columbite sample used for this study was collected from a mining site in Daba-Lema, Edu Local Government of Kwara State. All reagents used were of analar grade and were all products of BDH. De-ionized water was used for all the analytical preparations

Leaching procedure: 0.5 g of columbite sample was leached in 100 mL of nitric acid. The fraction of columbite sample dissolved for each process was calculated by the expression:

$$X = M_r/M_i \text{ X } 100 \text{ \%} \quad (7)$$

where, $M_r = M_i - M_f$, M_i - initial mass of columbite before leaching, M_f - final mass of columbite after leaching, M_r - mass of columbite dissolved.

RESULTS AND DISCUSSION

Leaching studies

Effect of concentration: The effect of nitric acid concentration on columbite sample dissolution was studied over the concentration range of 0.1 M-8.0 M. The results obtained are as shown in Fig. 1.

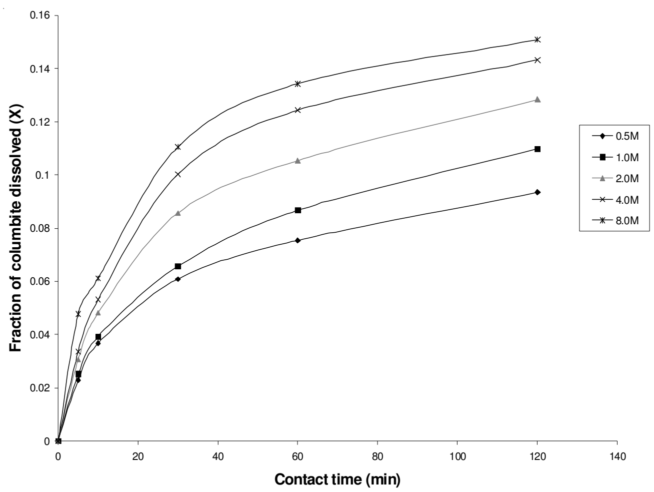

Fig. 1. Fraction of columbite dissolved (X) *versus* contact time (min) at different concentrations of HNO_3; Experimental conditions: Temperature = 55 ºC, mass of columbite used = 0.5 g, stirring rate = 200 rpm, particle size = < 0.15 mm.

It was observed from Fig. 1 that an increase in the concentration of nitric acid was accompanied with increase in the rate of columbite dissolution. The result also showed that 15.08 % columbite was dissolved by contacting columbite sample with 8.0 M HNO_3 at a temperature of 55 ºC and a contact time of 2 h.

Effect of temperature: The effect of temperature was studied over the temperature ranges of 28-80 ºC and investigated in different concentrations of nitric acid ranging from 0.5 M-8.0 M. The results obtained are presented in Fig. 2.

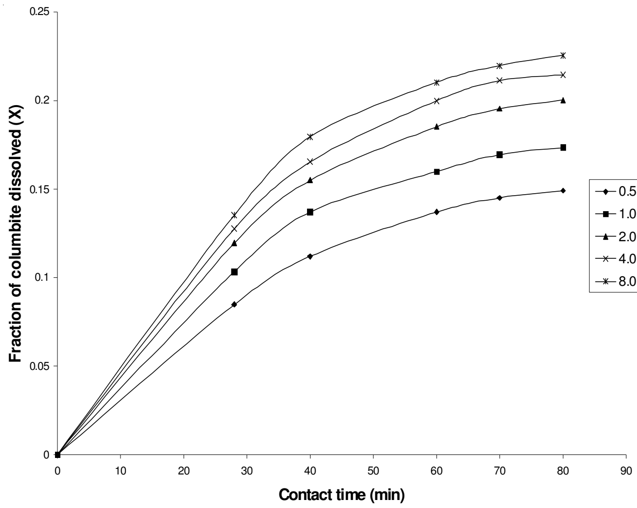

Fig. 2. Fraction of columbite dissolved (X) *versus* temperature (ºC) at different concentration of HNO_3; Experimental conditions: Mass of columbite used = 0.5 g, elapse time: 2 h, stirring rate = 200 rpm, particle size = < 0.15 mm.

The figure showed that increase in temperature accelerates the reaction rate and this leads to increase in the amount of columbite dissolved. 22.54 % of columbite sample was dissolved in 8.0 M HNO_3 at a temperature of 80 ºC and a contact time of 2 h.

Effect of particle size: The result of the effect of particle size on the dissolution of columbite sample as investigated in 4.0 M HNO_3 is represented in Fig. 3.

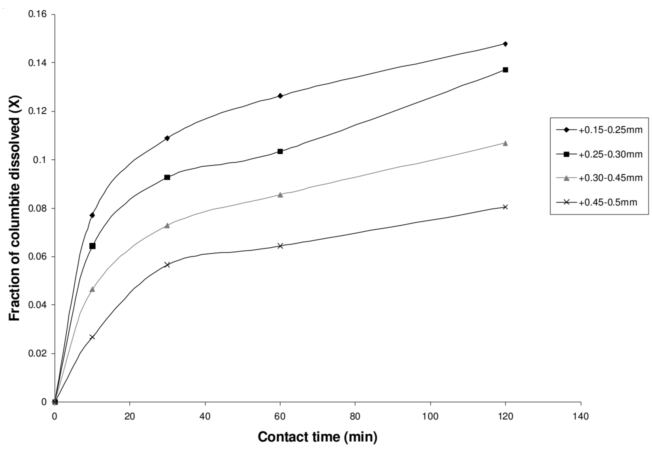

Fig. 3. Fraction of columbite dissolved *versus* contact time for different particle size fraction of columbite

A graph of the fraction of columbite dissolved *versus* contact time for the different particle size fraction as represented in Fig. 3, showed that the fraction with the smallest particle size (+ 0.15-0.25 mm) gave the highest percentage of columbite dissolution (14.78 %). This is due to the highest surface area of the smallest particle size fraction.

TABLE-1
k_r, k_d AND k_m AND CORRELATION COEFFICIENTS VALUE AT VARIOUS TEMPERATURES OF HNO_3 FOR COLUMBITE SAMPLE DISSOLUTION

Temperature (ºC)	Apparent rate constant (min^{-1})			Correlation coefficient (R^2)		
	k_{r2}	k_{d2}	k_{m2}	k_{r2}	k_{d2}	k_{m2}
28	4.44×10^{-4}	3.66×10^{-5}	4.79×10^{-4}	0.9269	0.9921	0.9330
40	4.94×10^{-4}	4.98×10^{-5}	5.40×10^{-4}	0.9066	0.9901	0.9142
60	5.77×10^{-4}	6.42×10^{-5}	6.38×10^{-4}	0.9136	0.9906	0.9222
70	6.27×10^{-4}	7.75×10^{-5}	6.98×10^{-4}	0.9165	0.9922	0.9253
80	6.54×10^{-4}	8.85×10^{-5}	7.33×10^{-4}	0.9041	0.9904	0.9136

Effect of stirring speed: The percentage of columbite dissolved (%) *versus* stirring rate (rpm) as investigated between 0 to 540 rpm is as shown in Fig. 4.

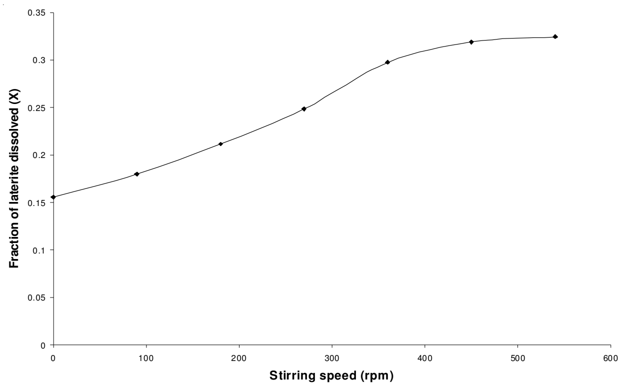

Fig. 4. Fraction of columbite dissolved (%) *versus* stirring rate (rpm)

The result showed that the amount of columbite dissolved increases with stirring speed between 0-360 rpm. The percentage dissolved appears to be practically constant afterwards. About 31.89 % of columbite was dissolved in 4 M HNO_3, at a temperature of 80 ºC, and a stirring speed of 360 rpm.

Kinetics of dissolution: The rate constant values k_r, k_d and k_m calculated from eqns. (4), (5) and (6) respectively and their correspondng correlation coefficients are given in Table-1.

The values of the correlation coefficients indicated that the dissolution rate of columbite in nitric acid is diffusion controlled. The application of the diffusion kinetic model is shown in Fig. 5.

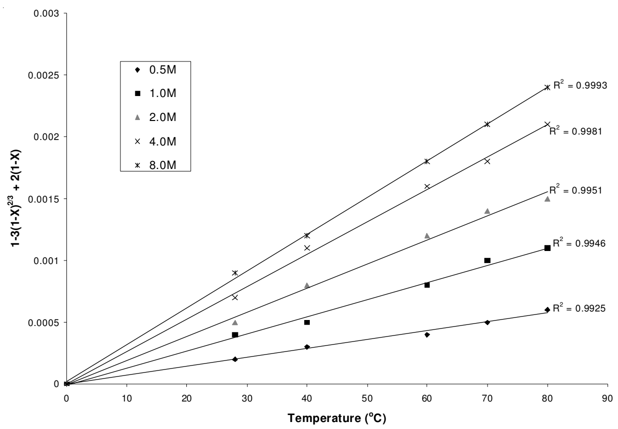

Fig. 5. Plot of $1-3(1-X)^{2/3}+ 2(1-X)$ *versus* contact time at various temperatures of HNO_3

Activation energy: This model was chosen for further studies. Table-2 shows the values for the apparent rate constants and ln of the apparent rate constants for HNO_3 at various temperatures and the Arrhenius plot is illustrated in Fig. 6.

TABLE-2
RATE CONSTANTS FOR HNO_3 AT VARIOUS TEMPERATURES

T(ºC)	1/T (K^{-1})	k_{d2}	$\ln k_{d2}$
28	3.32×10^{-3}	3.66×10^{-5}	-10.22
40	3.19×10^{-3}	4.98×10^{-5}	-9.91
60	3.00×10^{-3}	6.42×10^{-5}	-9.65
70	2.92×10^{-3}	7.75×10^{-5}	-9.47
80	2.83×10^{-3}	8.85×10^{-5}	-9.33

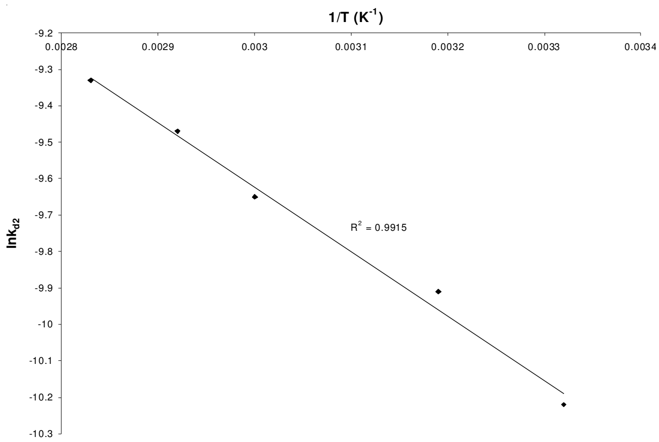

Fig. 6. Plot of ln k_{d2} *versus* 1/T (K^{-1})

From the slope of Fig. 6, using eqn. 5, the activation energy (E_a) for the dissolution of columbite in HNO_3 is 15.100 kJ mol^{-1}.

$$\ln k = \ln A + \frac{E_a}{R}\frac{1}{T} \quad (5)$$

Arrhenius constant: The extrapolation of Fig. 6 to the y-axis (Fig. 7) gave a value of -9.27 min^{-1}, which is equivalent to ln A in eqn. 5. The Arrhenius constant (A) for the columbite dissolution in HNO_3 is 9.42×10^{-5} min^{-1}.

Order of reaction: Table-3 shows the values for the apparent rate constants for the hydrogen ion concentration while Fig. 8 shows the plot of $\ln k_{d2}$ *versus* ln [H^+] for nitric acid concentrations.

TABLE-3
RATE CONSTANTS FOR HNO_3 AT VARIOUS CONCENTRATIONS

[H^+]	ln[H^+]	k_{d2}	$\ln k_{d2}$
0.5	-6.93×10^{-1}	8.19×10^{-6}	-11.71
1.0	0	1.16×10^{-5}	-11.36
2.0	6.73×10^{-1}	1.59×10^{-5}	-11.05
4.0	1.39	1.99×10^{-5}	-10.82
8.0	2.08	2.12×10^{-5}	-10.76

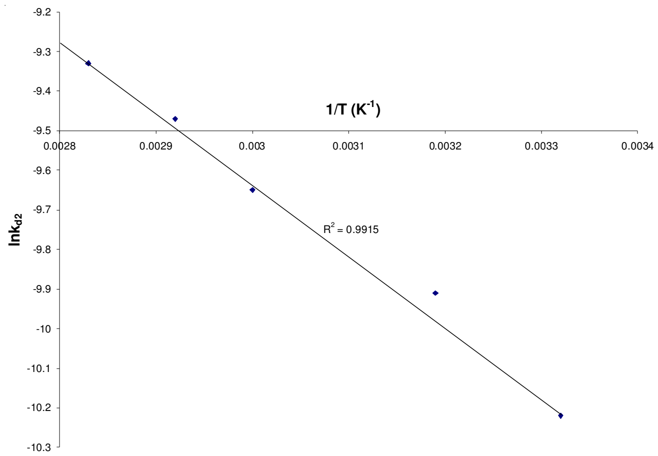

Fig. 7. Extrapolation of the plot of ln k_{d2} *versus* 1/T (K^{-1})

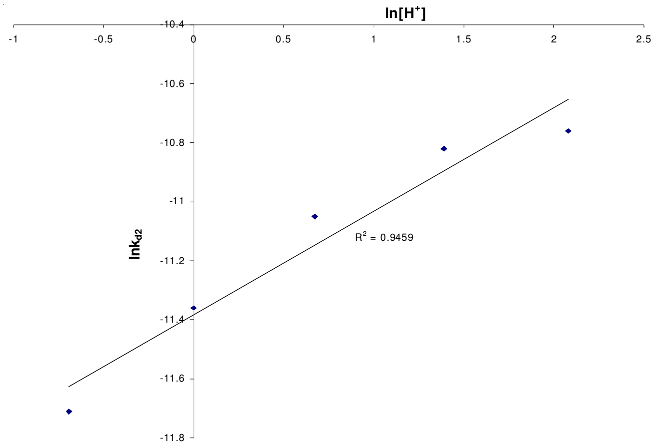

Fig. 8. Plot of ln k_{d2} *versus* ln[H^+]

The order of reaction from the slope for columbite dissolution in nitric acid with respect to [H^+] was 0.35.

Conclusion

In the present study, the dissolution of columbite in nitric acid was studied. It was found that the rate of columbite dissolution increases with acid concentration, temperature, stirring speed and decreases with particle size. The dissolution of columbite was found to be controlled by the shrinking core model for a diffusion-controlled process. Values of 15.100 kJ mol^{-1} and 9.42×10^{-5} min^{-1} were obtained for the activation energy and Arrhenius constant of columbite dissolution in nitric acid respectively and the order of reaction was 0.35.

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