



INVESTIGATION OF DISSOLUTION KINETICS OF A NIGERIAN COLUMBITE IN HYDROFLUORIC ACID USING THE SHRINKING CORE MODEL

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ABSTRACT

A study of the kinetics of the dissolution of a Nigerian columbite in hydrofluoric acid has been examined and an investigation on the quantitative leaching of the mineral was also carried out. The effects of some parameters such as acid concentration, contact time and temperature were investigated. Elemental analysis of the ore was done using Particle-induced X-ray Emission (PIXE) spectroscopy with 2.5 MeV protons and this showed the major elements in the ore to be Si (8.82 %), Fe (10.74 %), Mn (4.72 %), Ta (6.80 %), Nb (28.90 %) and W(2.61%), with K, Ni, Zn, Sr and Y occurring in traces. Experimental results indicate that the dissolution rate is chemical reaction controlled, with reaction order of 0.57. Dissolution of over 90 % of the columbite was achieved in 5 h, using 20 M HF at 90 °C with 100 μm particle sizes. Activation energy, E_a of 15.70 KJ.mole⁻¹ was obtained for the process.

Keywords: columbite, tantalum, leaching, shrinking core model, PIXE

1. INTRODUCTION

Tantalite-columbite and tantalite concentrates are comprised of an isomorphous series of tantalite minerals which are chemically stable and have a general chemical formula of $(\text{Fe,Mn})(\text{Nb,Ta})_2\text{O}_5$. The concentrates have a variable composition with respect to iron, manganese, niobium and tantalum, but these generally have a combined niobium-tantalum content of about 50 to 60 percent [1]. The mineral is referred to as tantalite if it contains a higher proportion of FeTa_2O_6 (or MnTa_2O_6) than FeNb_2O_6 (or MnNb_2O_6) and is referred to as columbite, if otherwise. The ore in addition to the tantalite mineral contains other “non-tantalite” materials which accounts for the variable composition. Tantalite-columbite minerals are not readily attacked by most mineral acids, except hydrofluoric acid, or a mixture of hydrofluoric and other mineral acids such as sulphuric acid.

Niobium/tantalum bearing minerals are mined in Australia, Brazil, Canada, China, Nigeria, Ethiopia and Mozambique [2,3]. Columbite and various niobium-bearing minerals are widespread in the pan-African basement of Nigeria with the tantalite-columbite reserves spreads across ten states in comprising Niger, Nassarawa, Oyo, Kaduna, Kogi, Kwara, Gombe,

Zamfara, Ekiti and the Federal Capital Territory (FCT) [4, 5].

Several works have been carried out on the mineralogical and compositional characterisation of major tantalum bearing mineral deposits in the country [6 – 8]. These works revealed the extensive abundance of elemental tantalum in association with niobium. The mineralogical characterisation of tantalite from selected parts of Nigeria revealed that the niobium constituents in the deposits studied ranges from 20 % to 39 %, indicating that the deposits in Nigeria contain ores of economic value with respect to their niobium content and are amenable to hydrometallurgical processing [8].

The objective of this work is to study the leaching kinetics of Nigerian columbite in hydrofluoric acid under different conditions in order to facilitate the eventual recovery of the niobium values by solvent extraction.

2. THEORY

The Shrinking Core Model (SCM) was developed by Yagi and Kunii [9 – 11] originally for gas-solid combustion system, but has been successfully applied to non-combustion systems involving liquids and solids [12 – 14].

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The SCM is based on the following assumptions [13, 15]:

- The particles are spherical.
- During the process, the particle shrinks uniformly, thus, it maintains its spherical shape.
- In the absence of adequate information, the thickness of the layer around the core was assumed constant during the leaching process.
- The temperature remains constant during the process.

Considering the assumptions above, the rate of reaction per unit surface of the core can be related to the dissolution rate of the solute of interest is expressed as follows [15]:

$$R = -\frac{M}{S_e} \frac{dN}{dt} \tag{1}$$

where M and N are the molar mass of the solute and the amount (in moles) of the solute present in the solid, respectively and S_e is the surface area of the unreacted solid. Since the particles are assumed to be spherical, equation (1) can be written as:

$$R = -\frac{M}{(4\pi r_t^2)} \frac{d}{dt} \left(\frac{4\pi r_t^3 \rho}{3M} \right) \tag{2}$$

where ρ is the particle density and r_t is the radius of the unreacted solid at any time ($t > 0$), respectively.

If the progress of the reaction is unaffected by the presence of a product (or “ash”) layer, the reaction is said to be chemical reaction controlled. If the dissolution is assumed to be a first order reaction, (2) becomes [16]:

$$\frac{dN}{dt} = \omega \rho \frac{dr_c}{dt} = k'' C_A \tag{3}$$

where k'' and C_A are the mass transfer coefficient between fluid and particle, and the concentration of the reactant in the reacting fluid respectively. Solving (3) gives

$$t = \frac{\omega \rho r_i}{k'' C_A} \left[1 - \frac{r_t}{r_i} \right] \tag{4}$$

where r_i is the initial radius of the unreacted solid and ω is the mass fraction of the solute in the bulk solid. k'' is the first-order rate constant for the surface reaction.

Taking $k_r = \frac{k'' C_A}{\omega \rho r_i}$ where k_r is the “apparent” rate constant, (4) becomes [16]:

$$k_r t = 1 - (1 - X)^{\frac{1}{3}} \tag{5}$$

where X is the fractional conversion, and

$$1 - X = \frac{\text{mass of unreacted core at time } t}{\text{initial mass of particle}} = \frac{\frac{4}{3}\pi r_t^3 \rho}{\frac{4}{3}\pi r_i^3 \rho} = \left(\frac{r_t}{r_i} \right)^3 \tag{6}$$

It is noteworthy that the time required for complete conversion in this case is the reciprocal of the “apparent” rate constant [16].

In many cases, the rate-determining step is the resistance offered by the solid product or gangue layer. In this case, equation (1) is written as [16]:

$$-\frac{1}{S_e} \frac{dN}{dt} = \mathcal{D}_e \frac{dC_A}{dr} \tag{7}$$

where \mathcal{D}_e is the effective diffusivity.

Solving equation (7) gives the relation for the Shrinking Core Model with product layer controlling the reaction kinetics [16, 17]:

$$1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) = k_r t \tag{8}$$

$$\text{with } k_r = \frac{6\mathcal{D}_e C_A}{\omega \rho r_i^2}$$

3. EXPERIMENTAL

The columbite used for this investigation was sourced from Wambe-Nassarawa field in Nassarawa State of Nigeria. The elemental analysis of the columbite mineral was determined by particle induced X-ray emission (PIXE) analysis using 2.5 MeV protons from a 1.7 MV Tandem Accelerator. The charge and the current used in the analysis were 0.5 μC and 0.26 nA respectively and the spectrum obtained were analysed using the Gupixwin software, v 2.1.

Analar grade HF was used in this work and doubly distilled water was used in the preparation of all solutions. Due to the corrosive action of HF on glass, thick-walled polypropylene containers were used as reaction and storage vessels in this work.

The ore was milled to 100 μm using a Rocklabs ring mill. The dissolution was carried out using 5 g of the milled ore in HF concentrations varying from 5 – 20 mol.dm⁻³ at reaction temperatures and times ranging from 30 – 90 °C and 1 – 5 h respectively. The dissolution was carried out in well covered polypropylene bottles with 50 ml of the hydrofluoric acid solution used per batch. For experimental runs involving elevated temperatures, the heating was done using a thermostatic water bath. To ensure proper mixing of the reaction mixture, the reaction vessels were shaken at 5 min intervals. Considering the toxic nature of HF vapour, all experimental runs were carried out in a fume chamber.

At the end of each run, the mixture was filtered and the residue was washed using distilled water to get rid of residual HF, dried in an oven at 105°C for 3 h and weighed. The extent of dissolution was determined by the formula:

$$X = \frac{W_o - W_f}{W_o} \tag{9}$$

In (9), W_o is the initial mass of the sample, g, W_f is the final mass (or mass of residue), g, X is the mass fraction of ore dissolved. A plot of X against time for each acid concentration and temperature gives a picture of how these parameters affect the extent of ore dissolution and can be of use when developing a model which describes the dissolution process.

4. RESULTS AND DISCUSSION

4.1 Elemental Analysis

The PIXE spectrum shown in Fig. 1 shows the major constituents of the ore to be silicon (8.82 %), iron (10.74 %), tantalum (6.80 %), niobium (28.90 %), titanium (3.75%), tungsten (2.61 %) and manganese (4.72%), with, potassium, zirconium, vanadium, nickel, zinc, strontium, and ytterbium occurring in traces. The result of the elemental analysis is presented in Table 1. As shown in Table 1, the constituents do not add up to 100%. The reason for this is that the analytical technique used (that is, PIXE) is suited for elements with atomic numbers greater than 18. Components such as silica, alumina, and oxygen (from oxides) which are common to most mineral ores are usually not reported by this technique, and should account for the deficit observed here. In addition, the detector commonly used for PIXE is silicon based [19] and might not detect silica. Since there is no peak for silicon in Fig. 1, the “silicon” reported in Table 1 might be from the detector and not from the sample itself.

Table 1: Elemental composition of the columbite used

Element	Concentration (wt. %)
Si	8.83
K	0.04
Ca	0.10
Ti	3.75
Mn	4.72
Fe	10.74
Ni	0.003
Zn	0.03
Sr	0.009
Y	0.002
Zr	0.27
Nb	28.90
Sn	0.93
Ta	6.80
W	2.61
U	0.78

4.2 Effect of Acid Concentration

The results obtained as seen in Fig. 2, showed that the rate of dissolution is affected directly by the concentration of the acid. The rate of dissolution of the columbite was observed to increase with increasing HF concentration.

To determine the order of the dissolution, equations (4) and (6) were used to test the results obtained from the dissolution. The assumption is that the dissolution of the ore in hydrofluoric acid is either chemical reaction controlled or ash/products layer diffusion controlled.

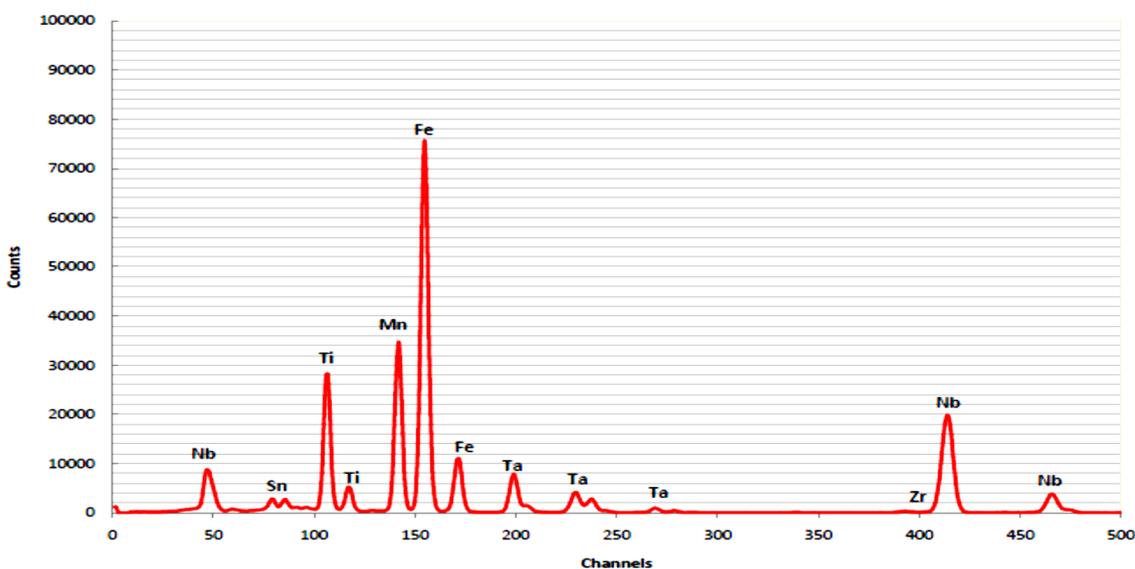


Figure 1: PIXE spectrum of the columbite showing the major elements present

Comparing the data obtained using 20 M hydrofluoric acid for the two models, the deviation from linearity is more pronounced for the ash layer diffusion model as shown in Table 2, indicating that the predominant rate controlling mechanism is chemical reaction. This result is comparable with what has been reported by various authors [15, 17, 18].

The results obtained from the dissolution showed that the dissolution followed the Shrinking Core Model (SCM) with chemical reaction as the rate controlling step as shown by the plots in Fig. 3. The apparent rate constants (k_r) obtained from Fig. 3 can be related to the acid concentration $[H^+]$ by the relation presented in equation (8):

$$k_r = a[H^+]^b \tag{10}$$

Where b is the order of the reaction and a is a constant which depends on the system under consideration. A plot of k_r against $[H^+]$ (Fig. 4) gave the order of the reaction to be 0.57, which is similar to the values reported in other works on similar systems [4, 17, 18].

4.3 Effect of temperature

From Figures 2 and 3, it can be deduced that the dissolution of columbite in hydrofluoric acid is predominantly chemical reactions controlled, with the apparent rate constants k_r shown in Table 3. The dissolution model in mathematical form can be written as shown below:

$$1 - (1 - X)^{\frac{1}{3}} = k_o \exp\left(\frac{E_a}{RT}\right) \cdot t \tag{11}$$

Where

$$k_r = k_o \exp\left(\frac{E_a}{RT}\right) \tag{12}$$

R is the universal gas constant in KJ.mol^{-1} , E_a is the activation energy and T is the temperature in Kelvins. Equation (10) can be written in logarithmic form:

$$\ln k_r = \ln k_o + \left(\frac{E_a}{R}\right) \cdot \frac{1}{T} \tag{13}$$

From the plot of $\ln k_r$ against $\frac{1}{T}$ for columbite dissolution using 20 M HF (Fig. 5), the activation energy E_a was found to be 15.7 KJ.mol^{-1}

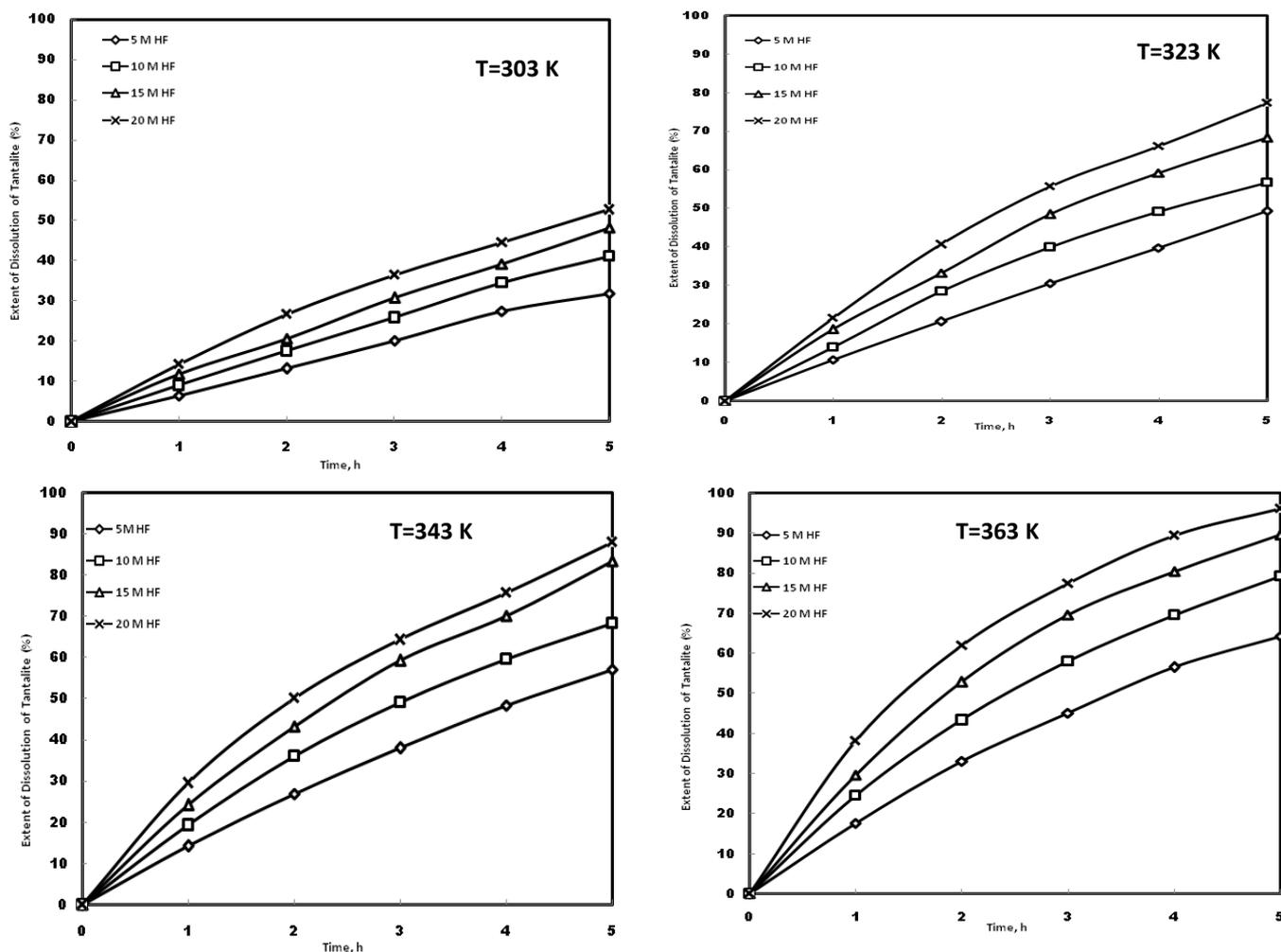


Figure 2: Extent of dissolution of columbite at various temperatures and acid concentrations

Table 2: comparison of the rate constants and correlation fit for both models considered for 20 M HF

Temperature, T (K)	Apparent rate constants (k_r , h ⁻¹)		Correlation coefficients (R ²)	
	Chemical reaction controlled	Ash/product diffusion controlled	Chemical reaction controlled	Ash/product diffusion controlled
303	0.045	0.009	0.995	0.914
323	0.077	0.012	0.998	0.922
343	0.098	0.022	0.995	0.942
363	0.132	0.040	0.997	0.975

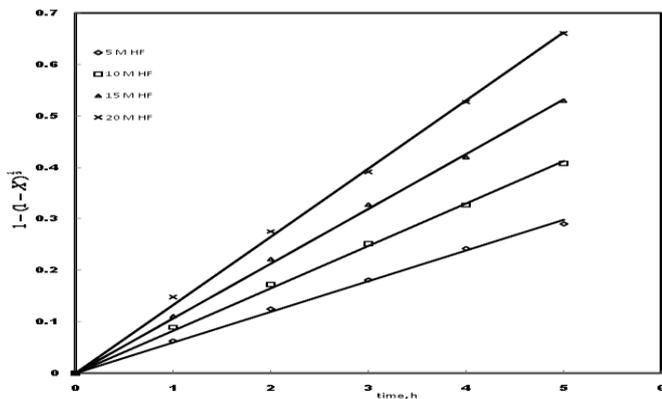


Figure 3: Plot of $1 - (1 - X)^{1/3}$ against contact time at 363 K

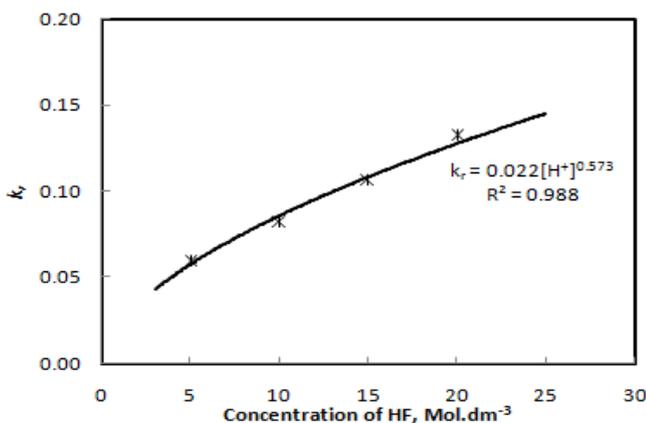


Figure 4: Plot of k_r against acid concentration at 363 K

Table 3: Variations in apparent rate constants with temperature

Temperature, T (K)	k_r values for dissolution in 20 M HF, h ⁻¹
303	0.045
323	0.077
343	0.093
363	0.132

The pre-exponential term k_0 varies for each dissolution system and for 20 M HF, equation (11) can be written in the form

$$1 - (1 - X)^{1/3} = (6.68 \times 10^{-3}) \exp\left(\frac{15700}{RT}\right) \quad (14)$$

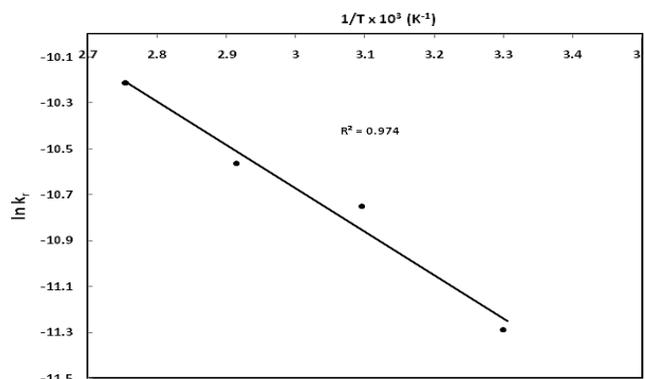


Figure 5: Arrhenius plot for columbite dissolution in 20 M HF

5. CONCLUSIONS

In this study, the dissolution kinetics of columbite in hydrofluoric acid was examined. The results showed that the reaction rate increases with acid concentration and reaction temperature. The dissolution kinetics was found to be governed by the shrinking core model with chemical reaction as the rate-controlling mechanism. The reaction order with respect to $[H^+]$ was found to be 0.57 and a value of 15.70KJ.mol⁻¹ was obtained as activation energy (E_a), for the dissolution process.

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