Establishment of Dissolution Kinetics and Mechanism of Direct Leaching of Gagi Phosphate Rock in Hydrochloric Acid Solution

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Abstract

Hydrochloric acid leaching kinetics of Gagi phosphate rock assaying 36.1% P_2O_5, 4.3% Al_2O_5, and 3.9% SiO_2 was examined. The phosphate rock mineralogical characterization indicated that the major phase of the rock was Quartz (SiO_2) with calcium aluminum phosphate as the major phosphate ore. The effect of different optimization parameters such as lixiviant concentration, system temperature, ore particle size and stirring speed were investigated. At selective extracted duration of 2 h with standard leaching condition of -70 + 63µm, 80°C, 0.20 M HCl and 300 rpm stirring speed, more than 84% P_2O_5 could be achieved. The leaching process kinetic mechanism was found to be surface diffusion controlling mechanism. The calculated reaction order and activation energy was 0.789 and 42.31 kJ/mol respectively. In addition, a mathematical expression including the experimental parameter to represent the kinetic of this leaching process was proposed in the study.

1.0   Introduction

There is no alternative to phosphate rock as a raw material for phosphates in the production of fertilizers production for agriculture purposes [1-3]. Aside this aforementioned application, raw phosphate is also the main ingredient for many important industries with fertilizer industries consuming about 90% of global phosphate production yearly [4]. On annual basis, raw phosphate consumption is close to 150 million tons, and demand for raw phosphate is on the increase especially in countries like Nigeria that are investing in agricultural production to defend their food security [5] .

The composition of phosphate rock varies from one deposit to another. Based on this fact; phosphate rocks from different sources are expected to behave differently in acidulation processes. Most of the world's phosphate rocks primary composed of the hydroxylapartite group in association with a wide range of assorted silicate minerals [6,7]. However, more than 200 types of raw phosphate occur in nature with varying chemical and physical specifications [8,9]. Examples of raw phosphate that can be found in nature include flour-apatite ($Ca_{10}(PO_4)_6F_2$), Hydroxy-apatite ($Ca_{10}(PO_4)_6(OH_2)$), Datillite ($3Ca_3(PO_4)_2$ $CaCO_3$) and varsisate ($AlPO_4.2H_2O$) [10]. Grading of raw phosphate depends on the total phosphorous content and type of impurities and amount of impurities [11]. Phosphate is usually enriched on concentrated until the total phosphorous concentration becomes more than 65% calcium phosphate (BPL) or 30% phosphate pentoxide (P_2O_5) [3,6].

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Calcareous phosphate rocks of acidic nature have 10 direct uses and are rejected globally. Such rocks are not usually suitable for direct use in acidulation plants unless their tricalcium phosphate content is increased to 70% and above, using conventional methods like crushing, surging and dragging, or some other physical separation process which include washing and deshing. Other conventional beneficiation technique may also be applied, such as calcination, floatation and leaching acidulation for both siliceous and high carbonate phosphate rock [12-14]. Quite a number of techniques have been studied to treat the low-grade rocks, however, satisfactory beneficiary technology is yet to be developed on commercial scale to deal with the typical indigenous phosphate rocks [15, 16].

Hydrochloric acid (HCl) can be adopted for the manufacture of phosphoric acid. Phosphoric acid obtained from phosphate rock by this route is much purer than that produced by the sulphuric acid route. Consequently, in addition to the receiving phosphoric acid, there are other technical problems that need to be overcome in a plant using hydrochloric acid [15]. Special consideration needs to be given to the plant operation because of the chloride containing environment that must be prevented against corrosion of equipment. Dilute hydrochloric acid solution may be used to selectively leach out the calcareous materials from low-grade phosphate rock rather than the dissolution of apatite.

The purpose of this research work is to investigate the effect of different factors on the kinetics of the dissolution of Gagi phosphate rock in HCl solution. These is with a view to assessing the dissolution mechanism and establish an empirical equation relating the rate constant of phosphate rock leaching to particle size, system temperature as well as HCl concentration for the purpose of scaling up and process design for fertilizer industries utilization.

2.0   Materials and Methods

2.1   Collection and Preparation of Sample

The phosphate ore sample used in this study was obtained from Gagi Village (Latitude 13.04329° and Longitude 5.27916°) along the Eastern Bye-Pass Sokoto, Nigeria. The ore was crushed using hammer mill, ground with porcelain mortar and pestle and oven dried at 110°C for 2 h and then sieved using standard test sieve to obtain the desired particle size fractions (63μm, 75 μm and 84 μm).

2.2   Leaching investigations

Leaching experiments were performed in a 1 L glass reactor equipped with a mechanical stirrer, a reaction temperature control unit and a balk-cooler. For each experiment, 100 mL of aqueous hydrochloric acid solution of pre-determined molarity (0.05 - 0.25 M) and 1 g ore were mixed in the reactor vessel making 10 g/L bulk density. The contents of the reactor were initially heated with mild agitation during heating stage and on attaining the set temperature, the leaching duration start from this point. Sample was collected at an interval of 10, 15, 30, 60 and 120 min. after the desired reaction time, the leached slurry was immediately separated by filtration. The P_2O_5 content in the leached solution was determined by means of the vanadomolydo phosphoric acid colorimetric method [17, 18]. The dissolved fraction (α) of P_2O_5 was calculated using relation:

$$\alpha(P_2O_5) = \frac{Amount\ of\ P_2O_5\ in\ the\ filtrate}{Total\ amount\ of\ P_2O_5\ in\ the\ raw\ sample} \qquad (1)$$

The effect of hydrochloric acid (HCl) concentration on the extent of phosphate dissolution was studied in the HCl concentration range between 0.05 to 0.25 M at temperature 55°C, particle size -110+75 μm and 300 rpm stirring speed. Considering the temperature dependency, the effect of leaching temperature on phosphate leaching was studied in the temperature range 50 - 80 °C under standard condition of 0.25 M HCl, -110 +75 μm particle size and atmosphere pressure. To ascertain the effect of particle size on the rate of P_2O_5 dissolution, experiments were performed using three different size fractions in the range of -75+63 μm, -63+75 μm and -75+90 μm fractions.

2.3   Ore and Residues Characterization

The elemental analysis of the phosphate ore was carried out using ZEISS 142 ELS model Energy dispersive X-ray fluorescence (EDXRF). The ore mineralogical analyses of the phosphate ore and the leached residues were carried out using XRD (Rigaku RadBDMAX II) diffractometer, while morphological analysis was performed using a LEO-EVO 40 XVP model scanning electron microscope equipped with EDS facilities.

3.0   Results

3.1   Characterization of Ore

The result of elemental composition shows that the sample consist majorly of P_2O_5, Al_2O_3, SiO_2, CaO, Fe_2O_3 and V_2O_5, Cr_2O_3, MnO and SO_3 occurs from low to trace level. The elemental analysis of the phosphate ore by X-ray fluorescence is presented in Table 1.

Table 1: Chemical Composition of the Phosphate Ore

Compounds	Al_2O_3	SiO_2	SO_3	CaO	TiO_2	V_2O_5	Cr_2O_3	MnO	P_2O_5	Fe_2O_3	others
Concentrate Unit (%)	2.74	5.14	0.06	60.04	0.07	0.02	0.01	0.17	29.60	1.34	0.80

The X-ray diffraction patterns of the ore phosphate as presented in Fig.1 indicates that the sample contains mainly phosphate (P_2O_5), calcite (CaO), Quartz (SiO_2), hematite (Fe_2O_3) and Alumina(Al_2O_3).
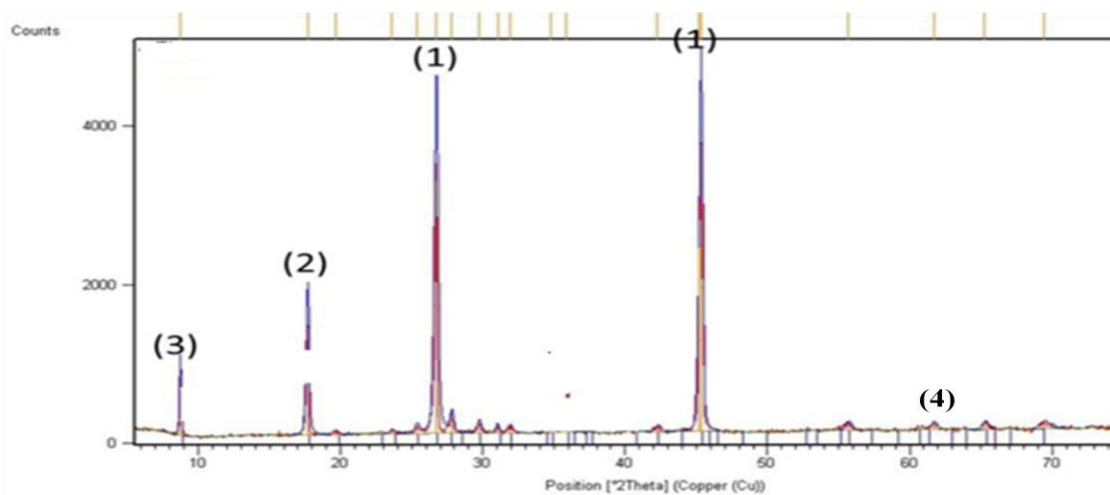

Figure 1: X-ray diffraction pattern of phosphate ore sample:(1) Phospate (P_2O_5) (2) Calcite (CaO) (3) Quartz (SiO_2) (4) Alumina (Al_2O_3).

The morphology of the phosphate ore to ascertain its libration and arrangement of associated minerals is shown in Figure 2a; while the EDS of targeted point reveals phosporous (P) as major element (Figure 2b).
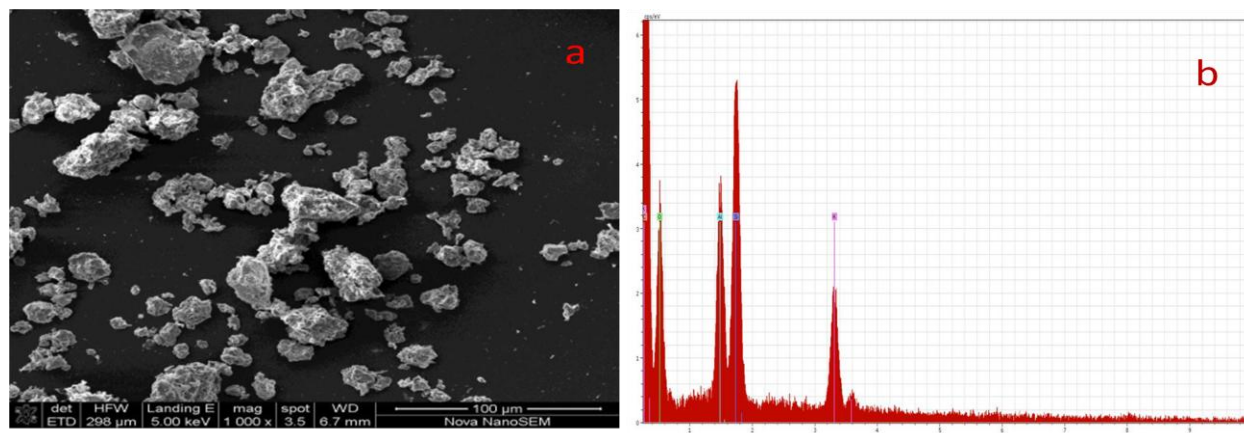

Figure 2: Micro structural image of phosphate ore (a) SEM image (b) EDS of targeted point on SEM image.

3.2   Effect of HCl Concentration

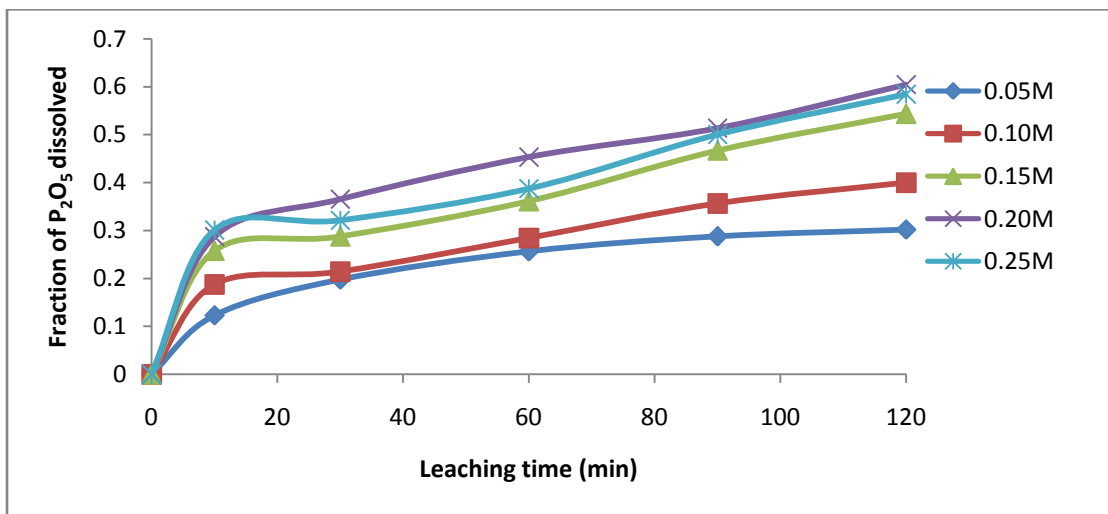Figure 3 shows dissolution data as a function of hydrochloric acid concentration at various times of leaching.

Figure 3: Effect of HCl concentration on P_2O_5 dissolution at 55°C, -110 + 75 μm particle size and 300 rpm.

From Figure 3, it can be seen that by increasing total HCl concentration from 0.05 to 0.25 mol/L, the P_2O_5 conversion fraction (α) increases from 23.7% to 61.70% in 2 h leaching time.

3.3   Effect of Reaction Temperature

Figure 4 shows the temperature dependency of phosphate dissolution on phosphate ore. As depicted in the figure, increasing the leaching temperature significantly increases the leaching rate. The P_2O_5 conversion after 2 h increased from 29% to 84.3% by increasing temperature from 50°C to 80°C.
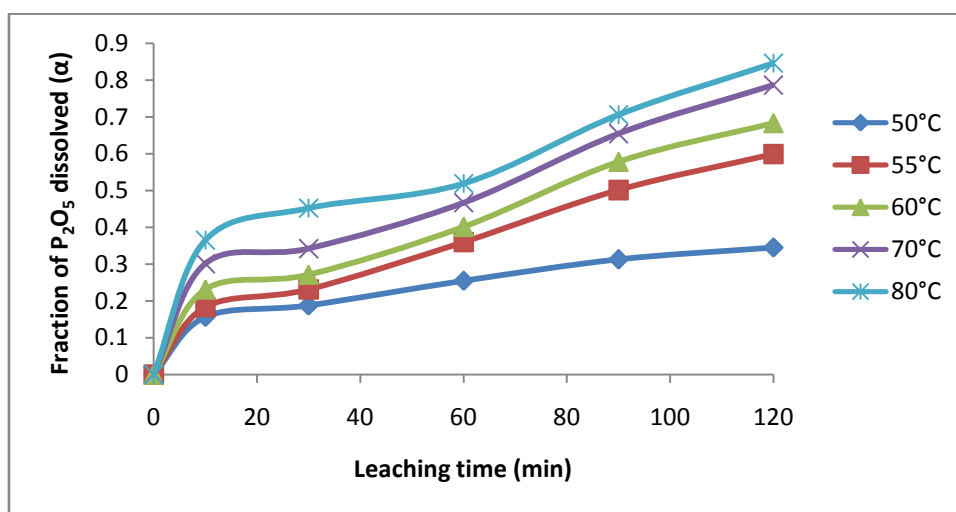

Figure 4: Effect of reaction temperature on leaching rate (HCl concentration = 0.2 M, particle sizes = -110+75μm).

3.4   Effect of Particle Size

The effect of surface area of the ore as a function of phosphate ore dissolution was well presented in the dissolution profile as shown in Figure 5.
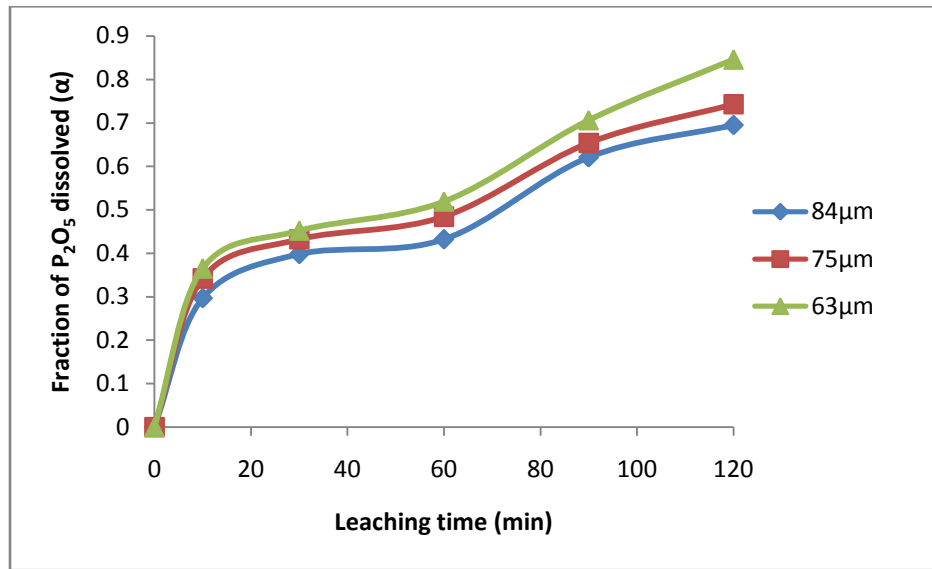

Figure 5: Effect of particle size on P_2O_5 dissolution rate

As seen in Figure 5, the rate of P_2O_5 dissolution increased sharply as the size of the ore particle reduced. Above 80% P_2O_5 dissolution was achieved with -75+63μm particle size conversely, 53.3% P_2O_5 was obtained with -90+83μm size.

3.5   Characterization of Leach Residues

The XRD and SEM patterns of a typical leach residue with > 90% P_2O_5 recovery are presented in Figure 6 and Figure 7 respectively. It was observed that P_2O_5 peaks disappeared while Al_2O_3 and CaO peaks appeared as a result of phosphate oxidation in chloride media. As expected, the silica peaks remain nearly unaltered. The micro-structural morphology of the residues by SEM as shown in Figure 7a and b clearly show the morphological features of alumina (Al_2O_3) and calcite (CaO).
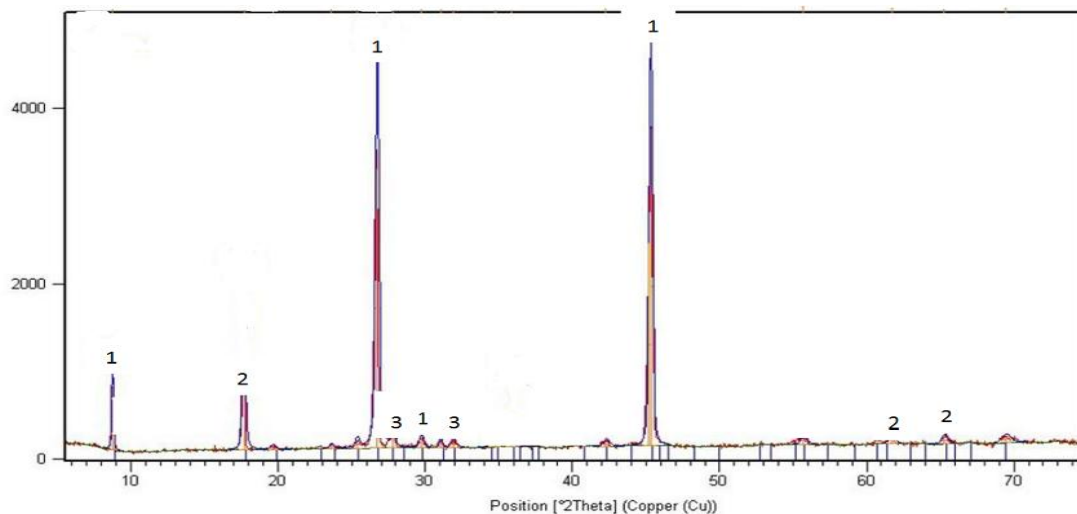

Figure 6: XRD spectral of residues after leaching: (1) Silica (SiO_2) (2) Alumina (Al_2O_3) (3) Calcite (CaO)
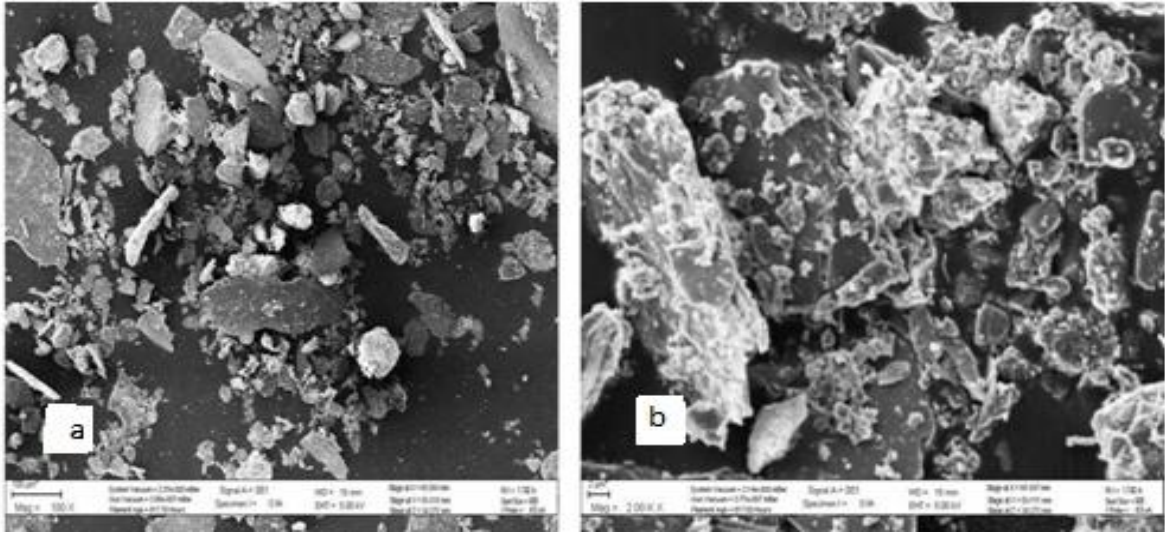
Figure 7: SEM images of leach phosphate ore (a) optimal concentration (b) optimal temperature

3.6   *Kinetic Analysis of the Leaching Experiment*

Kinetic profile linearity of leaching process as a function of time using chemical control model is presented in Figure 8. From the slopes of the straight lines (Figure 8), the apparent rate constants k were evaluated for different concentrations. The reaction order was determined by plotting ln k versus ln [HCl] (Figure 9). According to Figure 9, the reaction order of hydrochloric acid leaching of phosphate ore with respect to H^+ concentration equals.
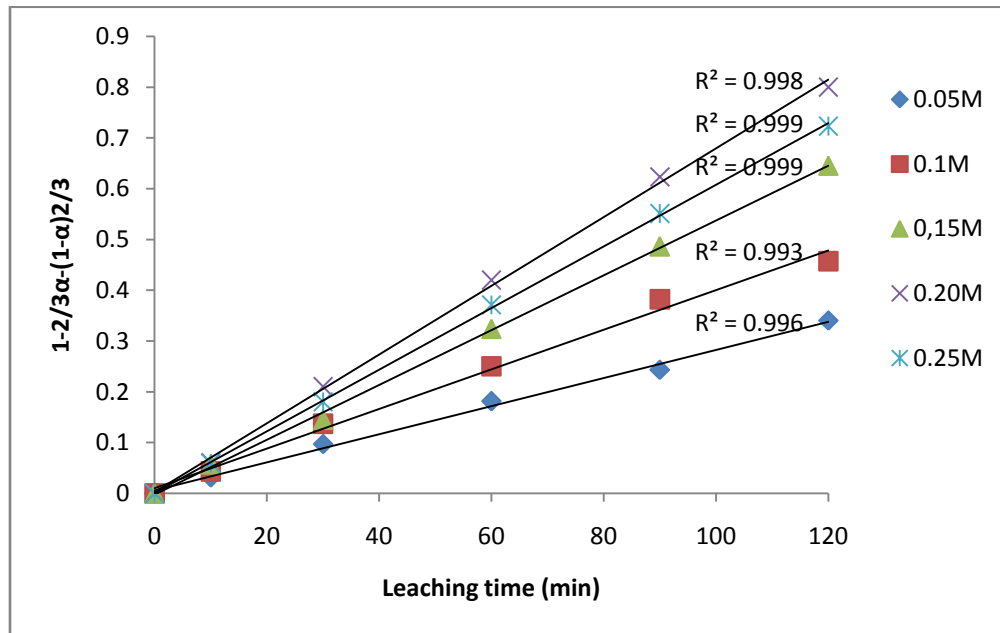

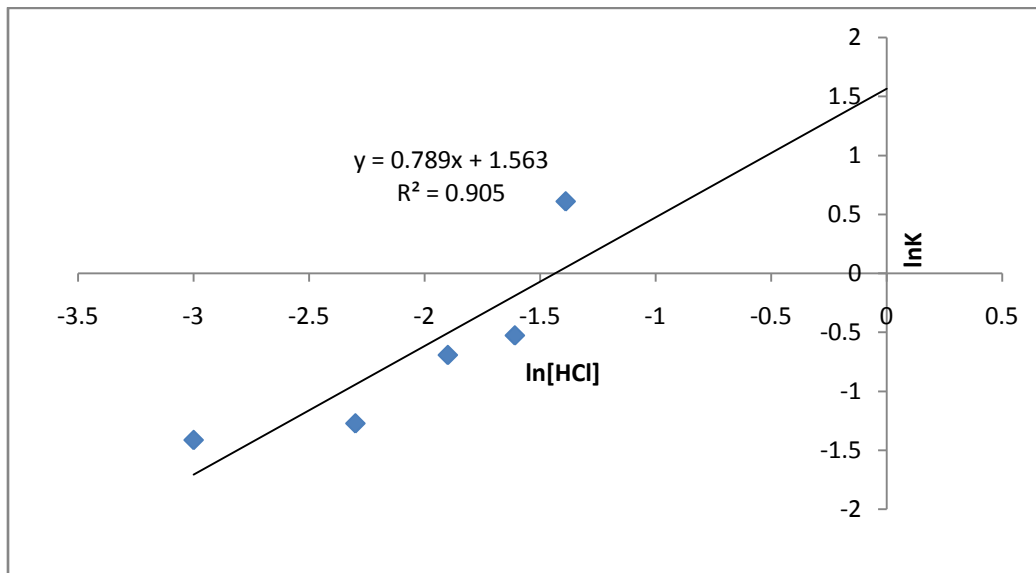**Figure 8: Plot 1-2/3α-(1-α)$^{2/3}$ versus leaching time**

Figure 9: ln k versus ln [HCl] for reaction order determination

To the established data in Figure 5, the chemical reaction rate limiting step was applied as shown in Figure 10. From the slope of the straight lines in Figure 10, Arrhenius equation $K=Ae^{-Ea/RT}$ was used to plot ln k versus (I/T) for each temperature and the activation energy was calculated from the slope $- E_a/RT$ and established to be 42.31 kJ/mol (Figure 11). The obtained activation energy value further supports chemical control mechanism model.
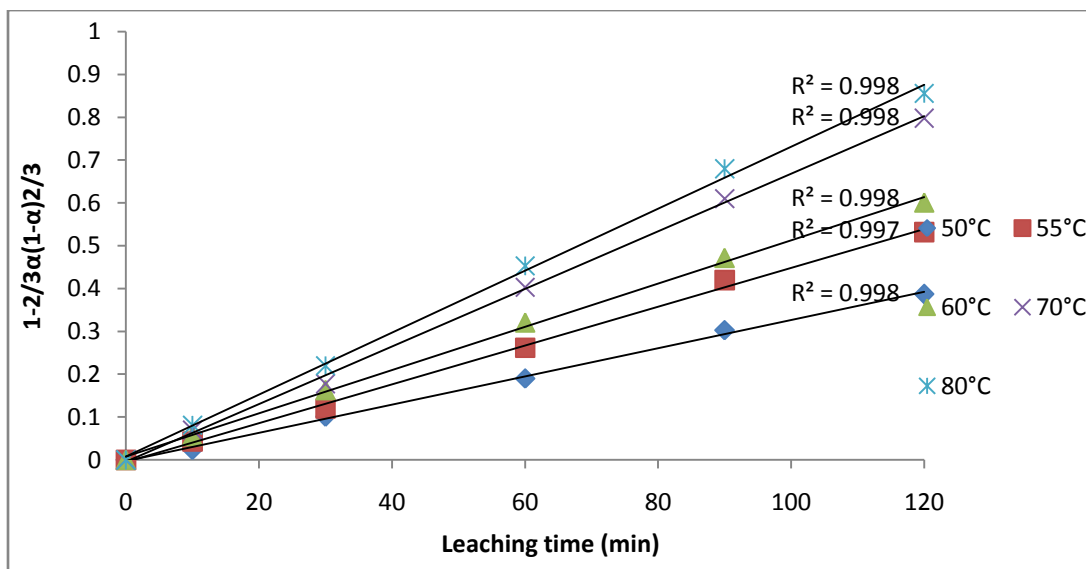

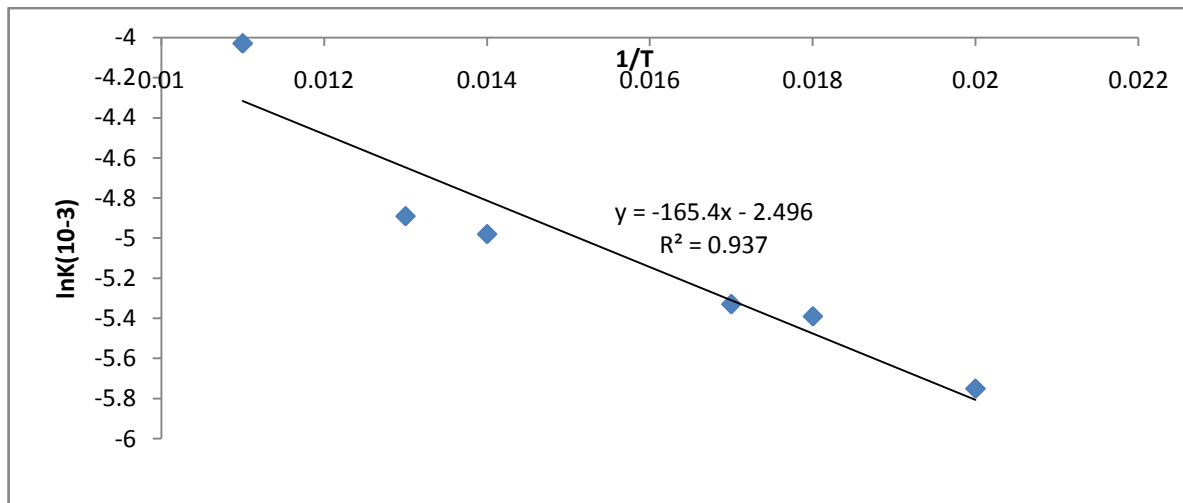**Figure 10: Plot of 1-2/3α - (1-α)$^{2/3}$ versus leaching time**

Figure 11: Plot of ln k versus 1/T

4.0   Discussion

During examination of the leaching kinetics of different ores in various leachates, variables such as reaction temperature, solution concentration, solid-liquid ratio, particles size and agitation speed are generally chosen as experimental parameters. All the data obtained during this exercise are statistically plotted as a function of conversion faction versus reaction time, and the kinetic analysis is performed by using heterogeneous reaction models. In any leaching studies, the dissolution rate generally increases with an increase in lixiviant concentration of rate controlling step, reaction temperature, particle size and agitation speed are often more important parameters. Therefore, the effects of reaction temperature particle size and lixiviant concentration on phosphate dissolution were investigated using optimal values from agitation speed and solid to liquid ratio initially established.

Various parameters such as concentration of lixiviants, system temperature and ore particle diameter were optimized to system scaling up process. The hydrochloric acid concentration of 0.20M was selected for further optimizations to compare their dissolution efficiencies (Fig. 3). It can be seen that P_2O_5 dissolution was very fast with HCl. It attained 33% at first 10 minutes and reach 65% at 120 min. This increase may be attributed to the increase of the H^+ ion in the solution [19]. Therefore, 0.20 M HCl is the choice acid concentration for leaching of Gagi phosphate ore. As shown in Fig. 4, there is a sharp increase in the dissolution rate while the system temperature was increased. The P_2O_5 conversion fraction (α) increase from 65% to 85% which indicates that temperature has a significant effect on the P_2O_5 fraction (α). The temperature beyond $80^{\circ}C$ was not exceeded to prevent further loss of the lixiviant due to evaporation process [20, 21]. The dissolution rate as a function of particle diameter is inversely proportional (Fig. 5), the reason for this could be due to the increase in the interfacial area of reaction as the solid particles become smaller [22, 23].

The main focus of this study is the basic understanding of the mechanism of phosphate dissolution kinetics from the calcareous phosphate rock of a Nigerian origin in chloride medium. However, act of leaching is a liquid-solid heterogeneous reaction that follows; the following reaction system in succession (1) Diffusion of fluid reactants from bulk liquid to fluid film (2) Diffusion of reactants across the fluid film to the particle surface (3) Diffusion of reactant across the product layer to the unreacted core (4) Reaction on the reacted core surface between fluid reactant and solid [17, 18]. The integrated rate equations derived from each step mentioned above from shrinking core model have been described in detailed in the literature [19-21]. To establish the kinetic parameters and the rate controlling step of the dissolution of phosphate ore in hydrochloric solution, the data provided by the leaching test were analyzed based on the shrinking core model using the integrated rate equations (2), (3) and (4).

$$\alpha = k_f t^{\;2/3} \tag{2}$$
$$1 - 2/3\, \alpha\, (1-\alpha)^{\,2/3} = k_d t \tag{3}$$
$$1 - 2/3\, \alpha\, (1-\alpha)^{\,1/3} = k_s t \tag{4}$$

Among the kinetic models applied to all the leaching data, it was established that equation (4) (the diffusion through the product layer) was more appropriate for the kinetics of the leaching of P_2O_5 from calcium phosphate ore in hydrochloric acid. By using the expression in equation (4), the apparent rate constants (k) were determined for each parameter. In order to determine the apparent rate constant, the left hand side of equation (3) was plotted versus the reaction time for each experimental parameter. The slopes of the straight line obtained were considered to be the rate constant. When the shrinking core model in which rate step is the chemical reaction, equation (4) was applied to the data obtained with leaching of phosphate ore (Figure 3) and good linear fits were obtained.

To establish the dissolution of Gagi phosphate rocks in hydrochloric acid, the shrinking core model (SCM) was adopted. In this case, the solid reactant were considered to be non-porous and being surrounded at initial point by a fluid film through which mass transfer occur between the solid particle and bulk of the solid [15, 24]. The overall leaching process may be controlled by chloride chemical reactions or by mass diffusion transfer, which can be described by expression equations 2-4. Equation 2 gave best fit plots with coefficient of determination (R^2) more than 0.907. From Figure10, the estimated reaction order 0.789 apparently supports the diffusion rate controlling mechanism. This was later supported by calculating the specific apparent activation energy of the main reaction from the Arrhenius plots of natural logarithm of reaction rate (ln k) against the reciprocal of absolute temperature (I/T) Fig. (11). Generally, the activation energy (E_a) of a diffusion controlled process is generally below 40 kJ/mol^{-1}, while for a chemically controlled process this value is usually greater than 40 kJ/mol^{-1} [25]. However, the calculated value of the activation energy obtained in the present study is above 40 kJ/mol; which supports that leaching is controlled by surface chemical mechanism. The high in E_a could be as a result of 2-stage mechanism which involves diffusion and surface chemical concurrent. Consequently, a mathematical expression including the experimental parameter to represent the kinetic of this leaching process was given as follows:

$$1- \frac{2}{3}\alpha - (1-\alpha)^{2/3} = 0.65[HCl]^{0.789} [PS]^{0.85} e^{\frac{-4321}{RT}}t \tag{5}$$

Finally, after leaching of phosphate ore, the residues emanating from filtration process was characterized by XRD and SEM. It was observed that all the peaks representing P_2O_5 reduced drastically as a result of leaching process, given rise to Al_2O_3 and CaO peaks. The surface morphology of the residues showed an eroded surface of the mineral phase, which may be as a result of leaching process using hydrochloric acid. At this point, it can be concluded that in the leaching step, P_2O_5 extraction has a peak value while aluminum and calcium extraction slow all the while.

5.0   Conclusion

Based on the results achieved in this study, it can be concluded that hydrochloric acid was able to dissolve the phosphate ore after 120 minutes using acid concentration of 0.20 at 80°C to reach dissolution efficiency. Depending on the nature of the acid solution, the combination of aggressive character of anions which is in reality a beneficial effect in leaching process and the acidic character of H^+ seems to play an important role on the acceleration of P_2O_5 dissolution rate. The plot of apparent rate constant versus inverse of absolute temperature evaluated that gave (42.3±1.73) kJ/mol further support the surface reaction rate controlling mechanism as the appropriate model to describe the reaction of P_2O_5 in hydrochloric acid solution.

6.0   Acknowledgement

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