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Reduction of Phosphorus Content of Koton-Karfe Iron Ore in Sulphuric Acid (H_2SO_4)

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ABSTRACT

The dissolving kinetics of iron ore in sulfuric acid solution were investigated. X-ray fluorescence (XRF) analysis was used to determine the ore's elemental and oxide contents as follows: Fe (40.715 %), Cu (0.00040 %), Mg (0.17 %), Mn (1.409 %), K (0.270 %), Ca (0.3266 %), and Zn (0.0331 %) were found in the iron ore. With increasing acid concentration, temperature, and reaction time, the dissolution rate increased. The best parameters for dissolving 69 % of the iron ore were found to be 1.0 M sulphuric acid, 55^0C dissolution temperature, 120 min dissolution time, and ore particle size of 0.15 to 0.3 mm. Film diffusion: $Xk_1t = XB$ was used to investigate the kinetics of the dissolution process. The results revealed that the Film diffusion layer was the rate-determining phase in the dissolution process, and that the reaction followed this mechanism. The apparent activation energy (Ea) and order of reaction, respectively, were found to be 11.1kJ/mol and roughly 0.3, indicating that the reaction is half order. The flame spectrophotometric analysis shows that the least phosphorus content of 0.0074% and highest phosphorus content of 0.0247% were achieved in this study. These are within the acceptable limit of 0.075 % phosphorus content required in industrial application of iron ore.

Keywords: Concentration, Dissolving kinetics, Iron ore, Phosphorus, Temperature

INTRODUCTION

Metallic iron may be economically produced from iron ore, which are rocks and minerals. Oxides are frequently abundant in the ores. Hematite (Fe_2O_3, 69.9% Fe), magnetite (Fe_3O_4, 72.4% Fe), siderite ($FeCO_3$, 48.2% Fe), goethite (FeO(OH), 62.9% Fe), and siderite ($FeCO_3$, 48.2% Fe) and limonite ($FeO(OH).n(H_2O)$, 55% Fe). (Baba *et al.*, 2005; Abdus-Salam *et al.*, 2018; Osama *et al.*, 2020). Natural ore or "straight shipping ore" refers to ore that has a high percentage of hematite (more than roughly 60% iron) and may be fed directly into blast furnaces to produce iron. Iron (Fe) is a valuable ferrous metal since it is largely utilized in the creation of steel, one of the most essential structural materials on the planet (Olade, 2020; Osama *et al.*, 2020; Nadezhda *et al.*, 2021)

Iron ore is utilized as a pigment or pigment formulation, in thermite, and as key adsorbents in anions adsorption. Because of their value as adsorbents and their abundance in nature, several iron oxides have gotten a lot of attention (Abdus-Salam *et al.*, 2018).

In the form of apatite or fluorapatite, iron ore with a high phosphorus level (>0.1% P) coexists with other minerals. Phosphorous is found on the edges of iron oxide mineral particles, embedded in quartz or carbonate minerals, and in trace amounts in the iron mineral grid (Xia *et al.*, 2011; Osama *et al.*, 2020).The 248 metric tons of iron ore deposit in Koton-karfe (Baba *et. al*, 2005) could make a significant contribution to Nigeria's economy if properly harnessed. The use of XRF analysis in this study has been able to identify the presence of phosphorous as a major setback to the industrial application of this iron ore for use in iron and steel production (Baba *et. al*, 2005; Fisher-white *et al.*, 2011). The dissolution kinetics was addressed in this study in order to understand the reaction mechanism between iron ore and mineral acid (H_2SO_4). Flame spectrophotometer was used to determine the phosphorus content in the leachate.

MATERIALS AND METHODS

Materials and Sample Collection

The iron ore used in this study was collected from Koton-karfe iron ore deposit in Kogi State, Nigeria. The ore was crushed with stainless steel hammer and ground to a particle size of 0.15 to 0.3 mm with the help of a stainless steel mortar and pestle. The H_2SO_4 used is of analytical grade and distilled water was also used.

Sample Characterization

X-ray fluorescence (XRF) analysis was carried out on the ore sample at Faculty of Natural and Agricultural Sciences at Umaru Musa Yar'adua University Katsina, Nigeria in order to determine the elemental and oxide composition of the iron ore.

Dissolution Study of Iron Ore

A 500 cm^3 clean beaker was used as a reactor, 100 cm^3 of acid solution was measured and poured into it. It was then placed on a thermostatically controlled heating plate and allowed to attain the dissolution temperature. The dissolution temperature was varied from 40 to 80°C, the acid concentration was varied from 0.2 to 1.0 M, and the dissolving period was adjusted from 20 to 120 minutes. The weight of 1g of the iron ore was added to a conical flask with steady stirring, and at the end of the reaction time, the contents of the flask were filtered through Whatman filter paper. The residue was dried in the oven at temperature of 100 ^oC for 60 minutes and it was weighed and recorded, the dissolved fraction was estimated using equation 1. Other experimental runs were carried out using the same approach. The leachates were subjected to Flame spectrophotometric analysis using Vanado-molybdate method described by Stanislawa *et al.* (2018) in order to determine the phosphorus content, the analysis was carried out in Soil Science Department, Prince Abubakar Audu University, Anyigba, Kogi State, Nigeria.

$$\text{Fractions of dissolved ore} = \frac{Initial\ Mass\ of\ ore\ - Final\ Mass\ of\ ore)}{Initial\ Mass\ of\ ore} \quad (1)$$

RESULTS AND DISCUSSION

Chemical Analysis

Table 1 displays the results of the XRF analysis. Fe (40.72 %), Si (4.202 %), Al (3.93 %), Mn (1.41 %), and P (1.26 %) are the principal elements identified in the sample; other elements are present in minor amounts. The high presence of Fe in this study confirms the iron ore, however the 40.72 % of Fe in this study is below the 66.4 % of Fe reported for natural goethite by Abdus-Salam *et al.* (2018). The 1.26 % phosphorus present in Koton-karfe iron ore is higher than the acceptable specification of the approximately 0.075 % phosphorus content of iron ore in Australia (Fisher-white *et al.,* 2011), hence there is need for phosphorus removal in Koton-karfe iron before it can meet industrial requirement.

Table 1: XRF of Koton-karfe Iron Ore

Element	(%)	Element	(%)
Fe	40.715	V	0.0688
Si	4.202	As	0.0066
Al	3.928	Pb	0.00087
Mg	0.17	Ga	0.00022
P	1.2595	Ni	0.00116
S	0.051	Cl	0.36
Ti	0.1039	Zr	LOD
Mn	1.409	Ta	0.004
Ca	0.3266	W	0.109
K	0.027	Sr	LOD
Cu	0.0004	Ce	0.1006
Zn	0.0331	Y	0.00157
Cr	0.0037		

LOD: Detection Limit

Table 2: XRF Results of oxide Composition of Iron ore Sourced from Koton-Karfe in Kogi State, Nigeria.

Oxide	(%)	Oxide	(%)
Fe_2O_3	58.212	ZnO	0.0412
SiO_2	8.99	Cr_2O_3	0.0054
Al_2O_3	7.442	V_2O_5	0.1228
MgO	0.28	As_2O_3	0.0088
P_2O_5	2.886	PbO	0.00094
SO_3	0.1275	Ga_2O	0.0003
TiO_2	0.1733	NiO	0.00148
MnO	1.82	Cl	0.36
CaO	0.457	Ta_2O_5	0.0049
K_2O	0.0325	WO_3	0.137
CuO	0.0005	CeO_2	0.124

The results of the oxide composition of the iron ore are presented in Table 2. The main oxide composition of the ore are Fe_2O_3 (58.2 %), SiO_2 (8.99 %), Al_2O (7.44 %), P_2O_5 (2.89 %) and MnO (1.8 %).The high presence of Fe_2O_3 (58.2 %) is a further confirmation of the iron ore and is in agreement with the 48.20 – 55.63% reported for iron ore deposit at Iyuku in Edo State by Irabor and Okolo (2010).

Effect of Acid Concentration

The effect of varying concentrations and time on the leaching of iron ore was studied using sulphuric acid and a time interval of 20 minutes. The leaching was done at 55°C with 360 rpm agitation. The acid concentration was raised from 0.2 M to 1.0 M at the same contact time, as shown in Figure 1. This implies that as the acid concentration is increased, the number of ions responsible for the dissolution of the iron ore increases thereby forcing more molecules of the iron ore to dissolve. The optimum dissolution of 69 % of the iron ore was achieved at acid concentration of 1.0 M. However, Baba *et al.* (2015) reported 92 % iron dissolution from a non-phosphorus iron ore in 12 M hydrochloric acid at temperature of 80 ^{o}C and 120 Minutes dissolution time.

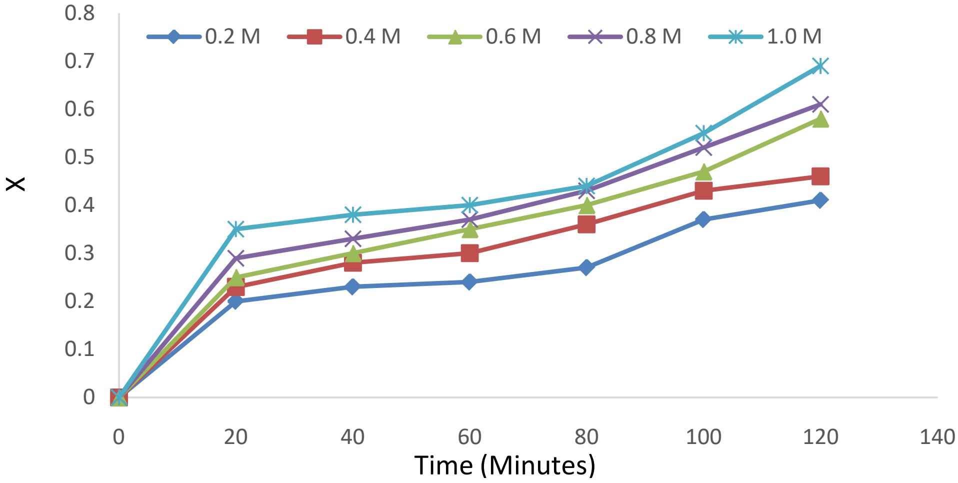

Figure 1: Plot of fraction of iron ore dissolved at different concentrations against time

Effect of Dissolution Temperature

Figure 2 depicts the effect of temperature fluctuation on iron ore leaching. The effect of temperature change was investigated at temperatures ranging from 40 to 80°C, with each increment of 10°C. The period was adjusted from 20 to 120 minutes at 20 minute intervals, while the concentration of 1.0 M sulphuric acid and the agitation speed of 360 rpm remained constant. The leaching fraction increases as the dissolution temperature and time rise, according to the data. This means that as the temperature rises, the reactant molecules obtain more kinetic energy, resulting in more effective collisions and an increase in the dissolution fraction. This is consistent with the findings of Xia *et al.* (2011), who found that as temperature rises, the proportions of iron ore that dissolve increases.

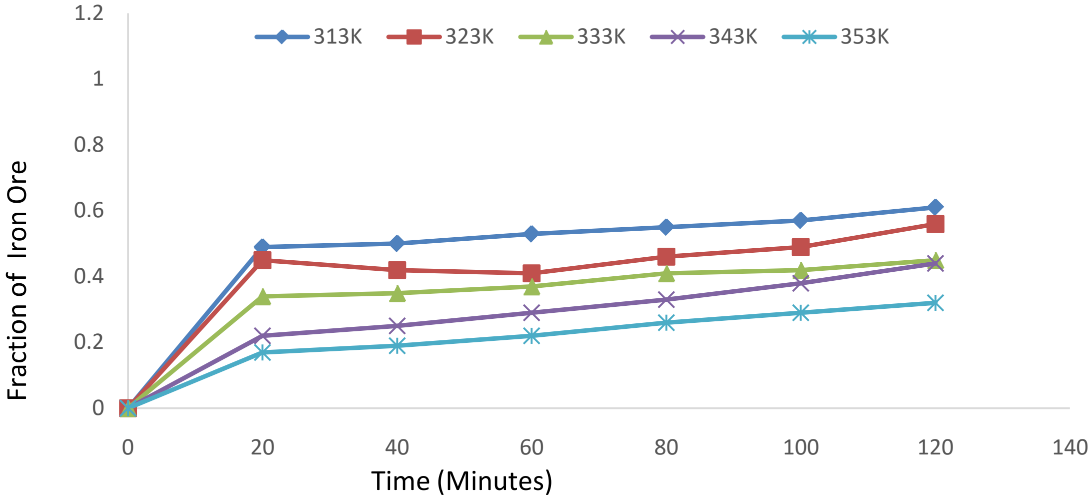

Figure 2: Plot of Fractions of Dissolved Iron Ore at Different Temperatures against Time

Kinetic Studies

The experimental data in Figures 1 and 2 were fitted into the Shrinking core model (2 - 4) to obtain the kinetic theory parameters directing the dissolving of Iron ore in sulfuric acid solution. According to the reduction core concept, one of the following phases can influence the reaction rate of a heterogeneous process.

Film diffusion control: $X = k_1t$ (2)

Surface chemical reactions control: $1–(1–X)^{1/3} = k_2t$ (3)

Product layer diffusion control: $1 + 2(1 – X) – 3(1 – X)^{2/3} = k_3t$ (4)

Where X is the fraction of iron ore reacted, t is the reaction time and k_1, K_2, k_3 are the rate constants, respectively, which were calculated from equations (2), (3) and (4) respectively (Are *et al.*, 2021).

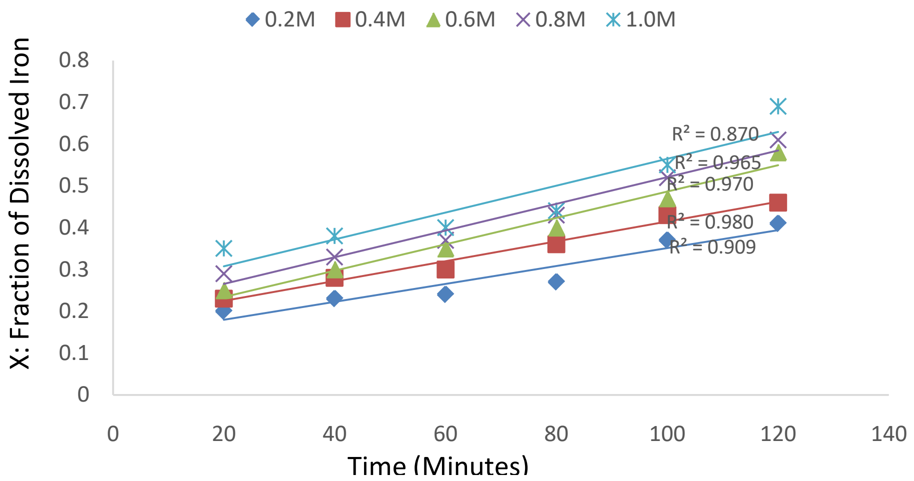

Figure 3: Plot of X agains reaction time at various H_2SO_4 concentrations

Table 3: Dissolution Rate Constants of Iron Ore in H_2SO_4

Process Parameters	Kinetic Equation					
	$X = k_1t$ (Film diffusion control)		$1+2(1-X)-3(1-X)^{2/3} = k_2t$ (Product layer control)		$1-(1-X)^{1/3} = k_3t$ (Chemical reaction control)	
	$k_1 \times 10^{-3}$	R^2	$k_2 \times 10^{-3}$	R^2	$k_3 \times 10^{-3}$	R^2
Concentration (M)						
0.2	2.14	0.9097	5.6	0.901	9.3	0.786
0.4	2.37	0.9809	7.4	0 .972	1.06	0.913
0.6	3.16	0.9706	1.243	0.921 0.931	1.513	0.941
0.8	3.19	0.9659	1.41	0.83	1.58	0.907
1	3.21	0.8705	1.77		1.75	0.876
Average	2.814	**0.9395**	2.555	**0.911**	3.041	**0.8846**
Temperature (K)						
313	2.27	0.995	2.85	0.959	7.18	0.99
323	3.07	0.99	6.3	0 .943	1.45	0.987
333	2.8	0.997	4.15	0.965 0.629	4.58	0.993
343	3.21	0.995	5.81	0.9659	6	0.996
353	3.64	0.99	7.21	0.8705	1.75	0.989
Average		**0.9934**				**0.991**

The constant and correlation coefficients of the various concentrations from film diffusion control (Figure 3) and that of temperatures together with the other models are shown in Table 3. Film diffusion controls > ash product layer control surface > chemical reaction were the orders followed in the differentiation of data based on the linear regression coefficient (R^2) values in Table 3 for different kinetic model equations. As a result, the film diffusion control kinetic equation (Equation 2) has the best agreement with the current kinetic processes in general. The experimental findings in this work fit the film diffusion control very well, and hence is the rate-determining step.

Activation Energy

The Arrhenius equation gives the activation energy, which is the lowest energy required for a reaction to occur. The link between temperature, activation energy, and the rate constant is depicted by equation 5. The Arrhenius equation, which is represented by the expression, describes the relationship between the rate constant Kd and the temperature.

$$Kd = A\exp^{(Ea/RT)} \quad (5)$$

Where A is the frequency factor and Ea is the apparent activation energy.

The rate constants were determined using the slopes from the graph in Figure 4. An Arrhenius graph of lnk vs 1/T (K^{-1}) was plotted to calculate the activation energy for the dissolution of the iron ore in the H_2SO_4 system. An Arrhenius plot was created, and the activation energy was also determined from the slope of the graph (Figure 4) using Equation (6).

$$K = \ln A – Ea/RT \quad (6)$$

This is equivalent to $y = mx + c$(7)and therefore the slope from the graph of lnk vs 1/T (K^{-1}) is equivalent to Ea/R, which means Ea = slope × R.

Slop = -1334.93K, R = 8.3145 $Jmol^{-1}k^{-1}$

Ea = -(-1334.93) K x8.3145 J/mol k =11099.94 $Jmol^{-1}k^{-1}$.

According to Figure 4, the slope is -1334.93, and the apparent activation energy is 11.1kJ/mol, which is within the range of activation energy for the film layer diffusion controlled mechanism.

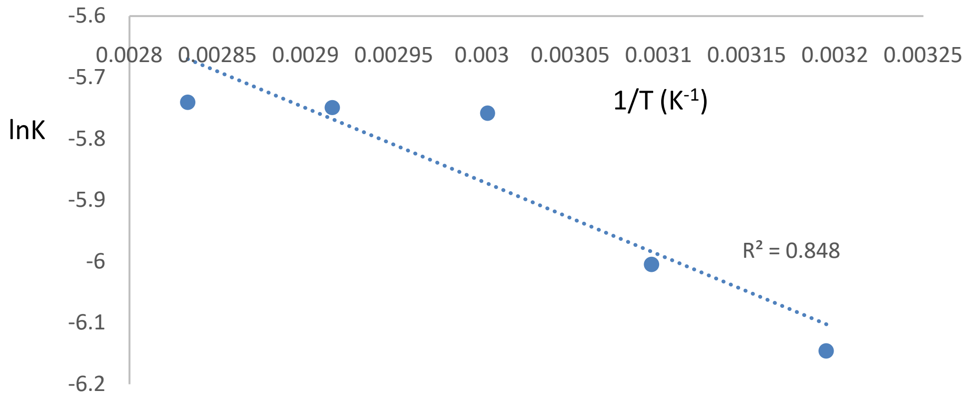

Figure 4 Plot of 1/T (K^{-1}) Against lnk.

ORDER OF REACTION

By plotting (Figure 5) the natural logarithm of apparent reaction rate constants calculated from the slope of Figure 2 against the natural logarithm of the concentration, the influence of acid concentration on the kinetics of iron ore dissolving in sulphuric acid was investigated.

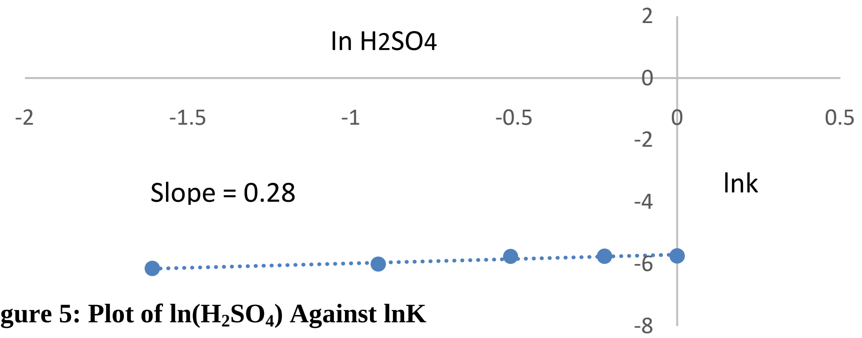

Figure 5: Plot of ln(H_2SO_4) Against lnK

Figure 5 shows that the order of reaction is equal to the slope of the plot and is 0.28. As a result, the reaction order for dissolving iron ore in H_2SO_4 solution is 0.3. This shows that the reaction is half-order.

Determination of Phosphorous Content using Flame Spectrophotometric Analysis

Based on the dissolution study of the iron ore, the phosphorus content at 20 and 120 minutes of dissolution were determined using flame spectrophotometer and the result presented in Table 4. XRF analysis (Table 1) shows that the initial amount of phosphorous (1.2595 %)present in the ore sample is much higher compared to that of the leachate (Table 4). The study has been able to leached significant amount of the iron ore with phosphorus content within the acceptable limit of 0.075 % (Fisher-white *et al.*, 2011).

Table 4: Spectrophotometric Analysis of some Selected Leachate

S/N	Concentration (M) at 55°**C**	Time (Min)	Dissolution Efficiency (%)	P (%)
1	0.2	20	20	0.0074
2	0.2	120	41	0.0121
3	0.4	20	23	0.0075
4	0.4	120	46	0.0182
5	0.6	20	25	0.004
6	0.6	120	58	0.0184
7	0.8	20	35	0.0093
8	0.8	120	61	0.00975
9	1	20	35	0.0079
10	1	120	69	0.0151
	Temperature (^{0}C) at 1 M			
11	40	20	33	0.0248
12	40	120	46	0.0167
13	50	20	22	0.00875
14	50	120	44	0.0151
15	60	20	33	0.022
16	60	120	45	0.0257
17	70	20	19	0.0075
18	70	120	36	0.0203
19	80	20	28	0.0241
20	80	120	49	0.0247

CONCLUSION

The amount of elemental iron content of the Koton-karfe ore sample obtained in this study is 40.715 % Fe, oxide is 58.212 % Fe_2O_3 with the 1.2595 % phosphorous. Acid concentration has a beneficial impact on the efficiency of leaching. At a temperature of 55°C, acid concentration of 1.0 M, an agitation speed of 360 rpm, and a leaching time of 120 minutes, a higher leaching efficiency of 69 % with 0.0151 % phosphorus content was recorded. The reaction rate was half order in relation to the concentration of hydrogen ions [H+], and the activation energy was 11.1kJ/mol. The film diffusion method was used to leach iron ore in H_2SO_4.

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