

Optimization of Process Conditions for the Dephosphorization of Iron Ore Using Sulphuric Acid

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Abstract– An investigation has been carried out in this study to optimize the process variables for the dephosphorization of an iron ore using sulphuric acid. A 2^3 full factorial of standard central composite design was used to develop a model. The model was optimized using MATLAB. The surface responses of the plots show that particle size, leaching time and sulphuric acid concentration interacted effectively to enhance the degree of dephosphorization. The results show that 99.87% of dephosphorization was obtained at optimum values of 120 minutes leaching time, 10 microns particle size and concentration of 0.2M. The iron loss during the chemical leaching was less than 4%. It is inferred that dephosphorization using sulphuric acid is feasible under the prevailing conditions.

Keywords– Dephosphorization, Surface Response, Optimization, Chemical Leaching and Central Composite Design

I. INTRODUCTION

Nigeria is one of the countries in the world endowed richly with mineral deposits. Among these mineral deposits is iron ore, located at Agbaja, Kogi State of Nigeria. The estimated proven reserve is about 1.3 billion tones. Agbaja iron ore is of low silicon module, fine texture and contains about 1.4-2.0% phosphorus. The high phosphorus content is the major set back in the use of Agbaja iron ore in the blast furnace or direct reduction process (Alafara et al 2005).

Chemical leaching of an iron ore involves the attack on the ore by hydrogen ions which act as reducing agents. The main function of these ions is to reduce the oxide ore to metallic or near metallic state depending on the concentration and nature of the chemical involved. During this process, some iron and other components of the iron ore dissolved in the solution.

Chang et al (1999) investigated dephosphorization of Western Australian iron ore using hydrometallurgical process. They used 0.1M, 0.3M and 0.5M of different low concentrations of H_2SO_4 for their work because the sample was roasted to a temperature of 1250°C before dephosphorization

Chang et al (1999) observed that the higher the concentration of the leach solution, the higher the phosphorus extraction and the iron loss increased with the increase of acid concentration. Surface adsorption theory can be used to explain the existence of phosphorus in goethite and the dephosphorization process. Forssberg and Adolfsson (1981) investigated the economic feasibility of acid leaching of iron ore in which apatite, $Ca_5(PO_4)_3(F,OH)$, was the phosphorus containing mineral. It was found that the economy of leaching

using acid leaching depended very much on the extent to which the phosphorus can be recovered as phosphoric acid.

Matsuo et al (1980) investigated the dephosphorization of iron ore using acid leaching. The iron ore contained phosphorus in the form of apatite, $Ca_5(PO_4)_3F$. The optimum leaching time was found to be 10 hours. Without the use of heat treatments a 20% reduction in the phosphorus was achieved. Peixoto (1991) studied the effects of heat treatment on the acid leaching of iron ore. When the ore contained phosphorus in solid solution in the goethite phase, it was found that thermal treatment of the ore at 1200°C caused structural re-arrangement of goethite which converted to hematite and facilitated the dissolution of phosphorus in mineral acids. The dephosphorization of high phosphorus ore from the Pilbara region of Western Australia was investigated by (Gooden et al, 1979). Using sulphuric acid, it was discovered that the quantity of iron leached was dependent on the solution concentration and independent of the leaching time. The minimum sulphuric acid concentration required to dissolve phosphorus was found to be 0.2M. The optimum leaching time was found to be between 0.1 and 0.5 hours. However, leaching at temperatures above 70°C was found to cause ferric phosphate to precipitate at much lower iron and phosphate concentrations than temperatures below 70°C, improving the ease of phosphorus recovery.

However, when phosphorus is disseminated in the iron structure, possibly forming crypto crystalline phosphates or solids solutions with the iron oxide phase (Secondary mineralization) the beneficiation can only proceed by chemical routes (Kokal, 1990, Kokal et al, 2003, Forssberg and Adolfsson, 1981).

The use of acid leaching for dephosphorization was investigated (Cuj and Fang 1998). In their studies, the acid concentrations were very high and low phosphorus extractions were obtained.

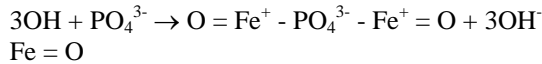
In this study, the dephosphorization of Agbaja iron ore using sulphuric acid at various leaching times, particle sizes and concentrations were investigated. Also 2^3 central composite designs were used to develop model equation which was to optimize the process variables using Matlab.

II. THEORY

Leaching Mechanism

A lot of theories have been propounded to explain the existence of phosphorus in goethite. Graham (1973) proposed

that elemental phosphorus existed in solid solution with goethite. Dukino (1997) has disagreed with this theory on the bases that interstitial solid solution is likely only if the substituting cation is of a similar or smaller size than the lattice bound cation and its charge is the same. The size and valency of phosphorus are not suitable for its existence in solid solution with goethite and it is considered unlikely that elemental phosphorus exist in solid solution with goethite. A more reasonable mechanism has been proposed by Babour (1973) and Morris (1973), involving surface adsorption. It has been suggested that, prior to the dehydration of ferri hydrate to goethite, a surface hydrate group is replaced by a phosphate ligand as shown in the equation below:



This theory is considered to be likely explanation of the existence of phosphorus in goethite. Dephosphorization can be explained by the theory. Roasting of the iron ore causes the goethite to dehydrate to hematite, liberating the phosphorus in an acid soluble compound.

III. MATERIALS AND METHODS

The Agbaja iron ore was crushed to liberation size of 100 microns using Tyler standard. The crushed iron ore was sent for chemical analysis using X-ray fluorescence spectrometer and atomic absorption spectrophotometer.

Desliming Process

Desliming was carried out to remove argillaceous materials from the raw iron ore. The iron ore was poured into a head pan and water was poured into a required level. The crushed iron ore was washed and water was decanted. This was repeated for five times until clear water was observed. At this stage 5g of sodium silicate and 25 drops of oleic acid were sprinkled and distributed uniformly throughout the ore. 20 liters of distilled water was also introduced into the pan and the content stirred thoroughly. After stirring, the argillaceous materials were removed leaving behind the iron ore. The residue was washed thoroughly and dried for 24 hours. Atomic absorption spectrophotometer and X-ray fluorescence diffraction spectrometer were used for the chemical analysis.

Chemical Leaching Process

The dried deslimed iron ore was further pulverized and sieved to obtain particle size of 10, 20, 40, 60 and 80 microns. Sulphuric acid solution of analar grade of different moles of 0.2, 0.4, 0.8, 1.0, 2.0 and 4.0 were prepared. 100grams of particle size of 10 microns of deslimed iron ore was weighed out and then poured into a conical flask. 100ml of 0.2M of sulphuric acid was then poured into a conical flask containing the iron ore. The mixture was stirred thoroughly to ensure homogeneity at 60°C. The content was allowed to leach for 10, 20, 30, 60 and 120 minutes. At the end of each leaching time, the solution was cooled and filtered. The residue was collected, washed to neutrality with distilled water, air dried and oven dried at 150°C for 24 hours. The experiment was

repeated for 0.4, 0.8, 1.0, 2.0 and 4.0 moles and for the different particle sizes. The samples were sent for chemical analysis using the same equipment.

$$\% \text{ Degree of Dephosphorization} = \frac{\text{As received value P(wt\%)} - \text{Final Value P(wt\%)}}{\text{As received P (wt\%)}} \times \frac{100}{1}$$

Development of Multivariable Model

Standard central composite design with 2^3 full factorial was used. This was constructed from $2m-t$ design for cube portion, which is augmented with center points and star points.

$$N = k^{m-t} + 2n + N_0 \quad \dots(1)$$

Where,

k = level of experiments = 2

m = Total number of variables (3: x_1, x_2, x_3)

t = The degree of fractionality, $t = 0$ for $m < 4$

N_0 = centre points added = 3

$N = 2^{3-0} + 2(3) + 3 = 17$ runs

The model equation for the experiment is proposed as:

$$\hat{Y}_n = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2$$

The coefficients were obtained using the following equations:

$$b_0 = a \sum_{u=1}^m y_u + p \sum_{j=1}^m \sum_{u=1}^N x_j^2 J_u Y_u \quad \dots(3)$$

$$b_1 = e \sum_{u=1}^N x_{1u} Y_u \quad \dots (4)$$

$$b_2 = e \sum_{u=1}^N x_{2u} Y_u \quad \dots (5)$$

$$b_3 = e \sum_{u=1}^N x_{3u} Y_u \quad \dots (6)$$

$$b_{12} = g \sum_{u=1}^N x_{1u} x_{2u} Y_u \quad \dots (7)$$

$$b_{13} = g \sum_{u=1}^N x_{1u} x_{3u} Y_u \quad \dots (8)$$

$$b_{23} = g \sum_{u=1}^N x_{2u} x_{3u} Y_u \quad \dots (9)$$

$$b_{11} = c \sum_{u=1}^N x_{1u}^2 Y_u + d \left[\sum_{u=1}^N x_{2u}^2 Y_u + \sum_{u=1}^N x_{3u}^2 Y_u \right] + P \sum_{u=1}^N Y_u \quad \dots(10)$$

$$b_{22} = c \sum_{u=1}^N x_{2u}^2 y_u + d \left[\sum_{u=1}^N x_{1u}^2 y_u + \sum_{u=1}^N x_{3u}^2 y_u \right] + P \sum_{u=1}^N y_u \dots(11)$$

$$b_{33} = c \sum_{u=1}^N x_{3u}^2 y_u + d \left[\sum_{u=1}^N x_{1u}^2 y_u + \sum_{u=1}^N x_{2u}^2 y_u \right] + P \sum_{u=1}^N y_u \dots(12)$$

Design of Experiment for Chemical Leaching

Statistically designed experiment for leaching treatment based on central Composite Design plan of 2³
 Number of variables = 3
 Number of star points = 6
 Number of center points = 3
 X₁ = leaching time (5 mins - 120mins)
 X₂ = concentration 0.2M - 4M
 X₃ = particle size (10 microns - 80microns)

Table 2.1: Experimental range and level of independent variables

Independent variables	Lower level	Base level	Upper level
	-1	0	+1
X ₁	5 mins	60 mins	120 mins
X ₂	0.2M	2M	4M
X ₃	10 microns	40 microns	80 microns

Design matrix and response

	X ₁	X ₂	X ₃	Y (P)%Dephosphorization
1	0	0	0	98.55
2	-1	-1	-1	99.28
3	+1	-1	-1	99.42
4	-1	+1	-1	99.57
5	+1	+1	-1	99.42
6	0	0	0	98.55
7	-1	-1	+1	98.55
8	+1	-1	+1	97.10
9	-1	+1	+1	98.55
10	+1	+1	+1	97.10
11	0	0	0	98.55
12	-1	0	0	98.55
13	+1	0	0	98.53
14	0	-1	0	98.55
15	0	+1	0	98.55
16	0	0	-1	99.57
17	0	0	+1	98.35

Developed model equation for dephosphorization

$$\hat{y}_u = 98.77 - 0.29x_1 - 0.74x_3 + 0.29x_3^2$$

Optimization program using Mat Lab
 Copy the program from computer

IV. RESULTS AND DISCUSSIONS

Table 3.1: Chemical composition of Agbaja iron ore before desliming

Components	Average composition (wt%)
Fe	56.00
SiO ₂	5.16
S	0.12
Al ₂ O ₃	6.60
CaO	0.23
MgO	0.07
MnO	0.18
TiO ₂	0.37
K ₂ O	0.04
P	0.80
H ₂ O	2.06

Table 3.2: Chemical composition of Agbaja ore iron after desliming

Component	Average composition (wt%)
Fe	52.34
SiO ₂	5.02
S	0.09
Al ₂ O ₃	5.20
CaO	0.21
MgO	0.03
TiO ₂	0.32
K ₂ O	0.007
P	0.79
H ₂ O	2.81

Table 3.1 shows the chemical composition of as received Agbaja iron ore. The iron content shows that if properly beneficiated and dephosphorized the iron ore can be used in steel making. The iron ore was abandoned because of its high phosphorus content shown in the Table 3.1

The chemical composition of the iron ore after desliming is shown in Table 3.2. The desliming process increased the degree of dephosphorization from 0.80% to 0.79% while the degree of beneficiation increased from 56% to 56.34%. This depicts that the desliming process removed deleterious materials like sand and dirt but contributed insignificantly to beneficiation and dephosphorization.

Influence of Acid Concentration on the Degree of Dephosphorization of the Iron Oxide

The influences of acid concentrations on the degree of dephosphorization of the iron oxide are shown in Fig. 1 – Fig. 5.

In Fig. 1 the percentage degree of dephosphorization was constant for all the concentrations for leaching time of 5 minutes. 98.55% of dephosphorization was achieved for 10, 30, 60 and 120 minutes for all the concentrations, for particle size of 60 microns.

Fig. 2 depicts that the percentage removal of phosphorus was constant for 5 minutes leaching time and 60 microns particle size. For 10 minutes, the phosphorus percentage removal was 98.55% for all the concentrations. In 20 and 30 minutes the same degree of removal was obtained for all the concentrations. 98.88% degree of dephosphorization was obtained for 60 minutes and 120 minutes.

The percentage degree of dephosphorization for 40 microns is shown in Fig. 3. This profile shows that for 5 and 10

minutes, the degree of phosphorus removal remained constant as the concentration increases. For 20, 30 and 60 minutes the percentage removal of phosphorus remained 98.84% as the concentration increases. Similar profile was obtained for 20 and 10 microns as shown in Fig. 5 and Fig. 4. The high

phosphorus removal is as a result of greater affinity of sulphuric acid to phosphorus and high redox potential during the dephosphorization. It can be inferred that in using sulphuric acid as leaching agent that increase in concentration does not necessarily mean increase in percentage removal.

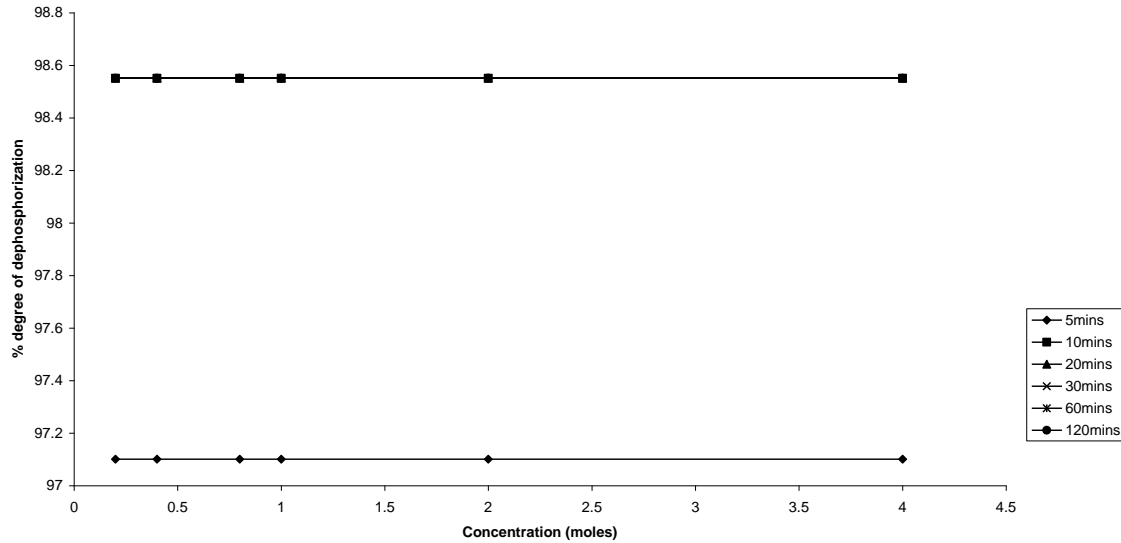


Fig. 1: Effect of H₂SO₄ Concentration on the degree of the dephosphorization for 80 microns

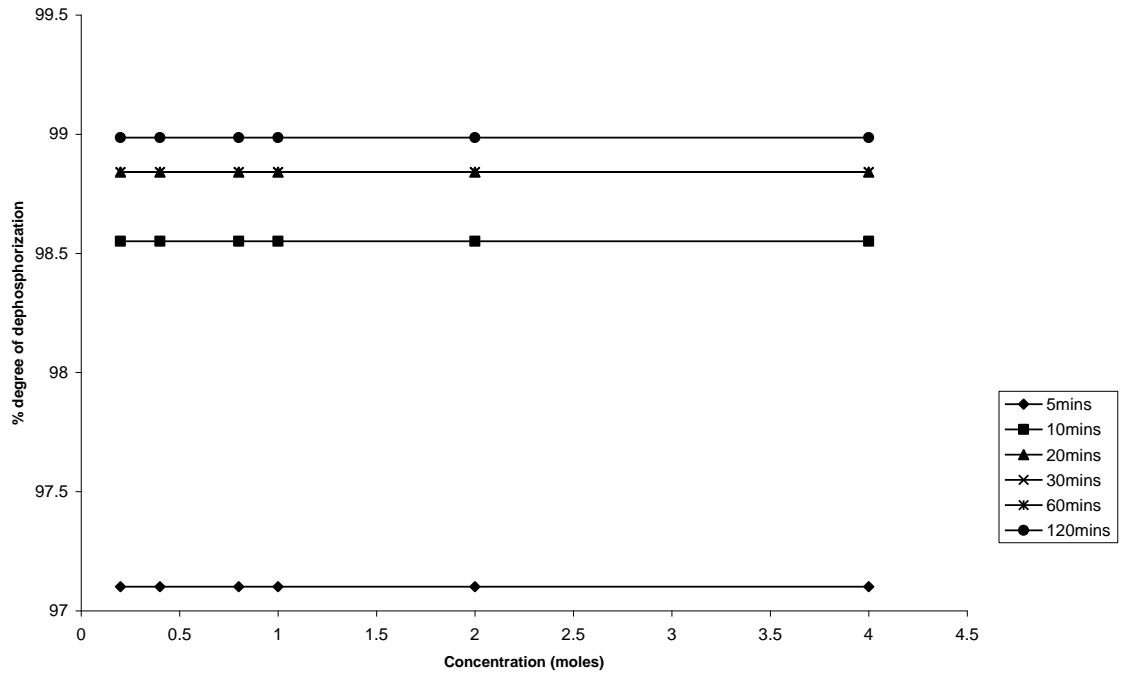


Fig. 2: Effect of H₂SO₄ Concentration on the degree of the dephosphorization for 60 microns

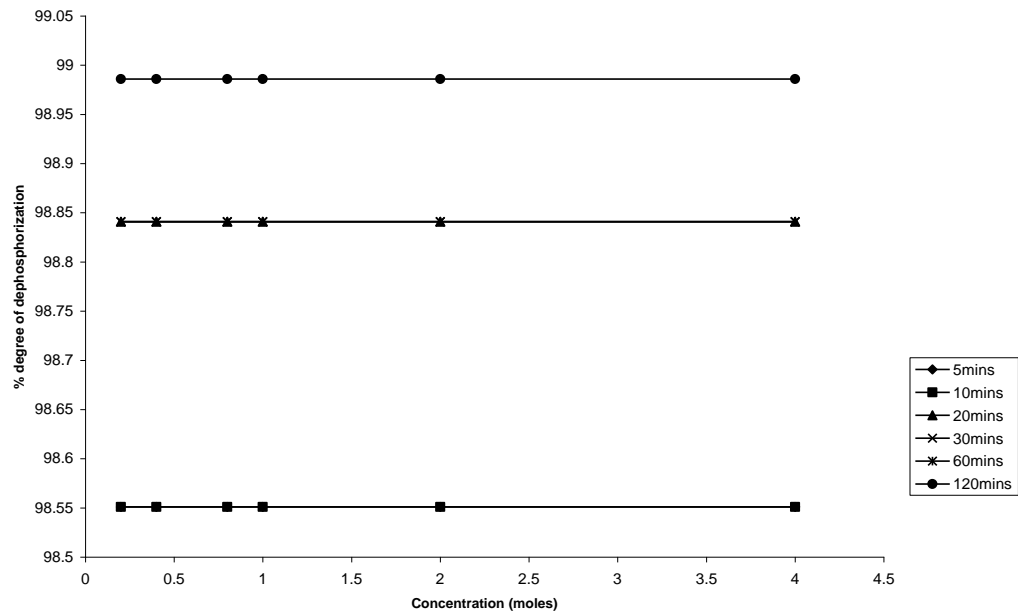


Fig. 3: Effect of H₂SO₄ Concentration on the degree of the dephosphorization for 40 microns

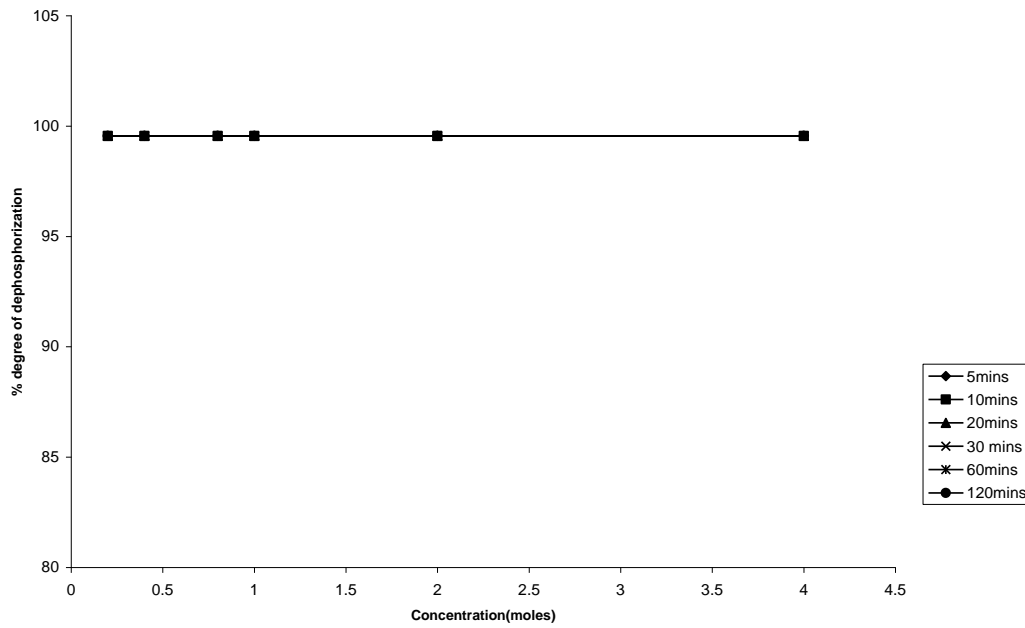


Fig. 4: Effect of H₂SO₄ Concentration on the degree of the dephosphorization for 20 microns

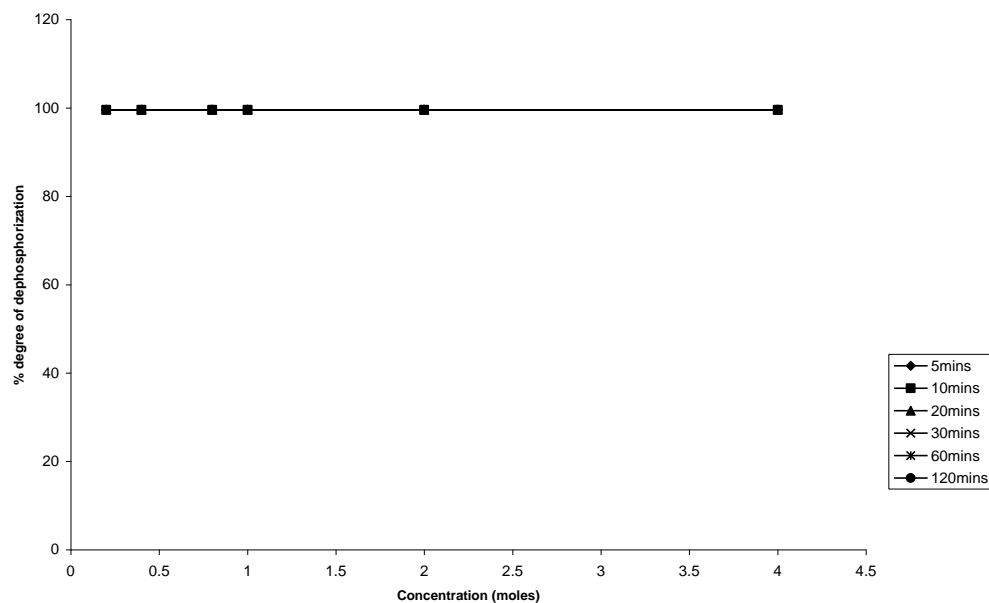


Fig. 5: Effect of H₂SO₄ Concentration on the degree of the dephosphorization for 10 microns

Effect of Leaching Time on the Percentage Degree of Dephosphorization

The effects of leaching time on the removal of phosphorus from the iron ore is depicted in Fig. 6 – Fig. 10.

In Fig. 6 there were significant removal of phosphorus between 5 and 10 minutes. Immediately after 10 minutes the percentage removal remained fairly constant. The least value of 97.10% removal was achieved at 5 minutes while the highest value of 98.96% was obtained for 120 minutes at concentration of 4M.

It is inferred also that the rate of iron ore dissolution is directly proportional to the concentration of hydrogen ion (H⁺). This reflected the reports recently published on separate studies involving the leaching of sulphidic minerals including

iron ore (Anthonijevi et al, 2004; Baba et al, 2005 and Baba 2002).

In Fig. 7 a similar trend is presented as in Fig. 6.

Between 5 minutes and 10 minutes a constant value of 98.55% was obtained as depicted in Fig. 8 from leaching time of 10 minutes to 20 minutes, there was a significant increase in percentage degree of dephosphorization. The highest value of 98.98% was obtained at 120 minutes for all the concentrations.

Fig. 9 and Fig. 10 have similar profile. The percentage degree of dephosphorization remained fairly constant in both figures. The highest value of removal of phosphorus in these figures was attributed to the large surface area of the iron ore.

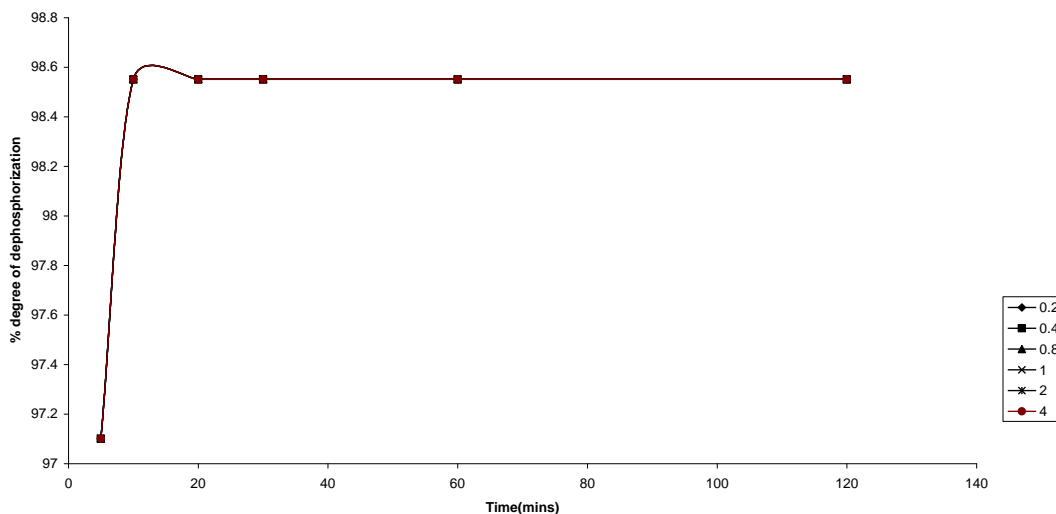


Fig. 6: Influence of leaching time on the % degree of dephosphorization for 80 microns using H₂SO₄

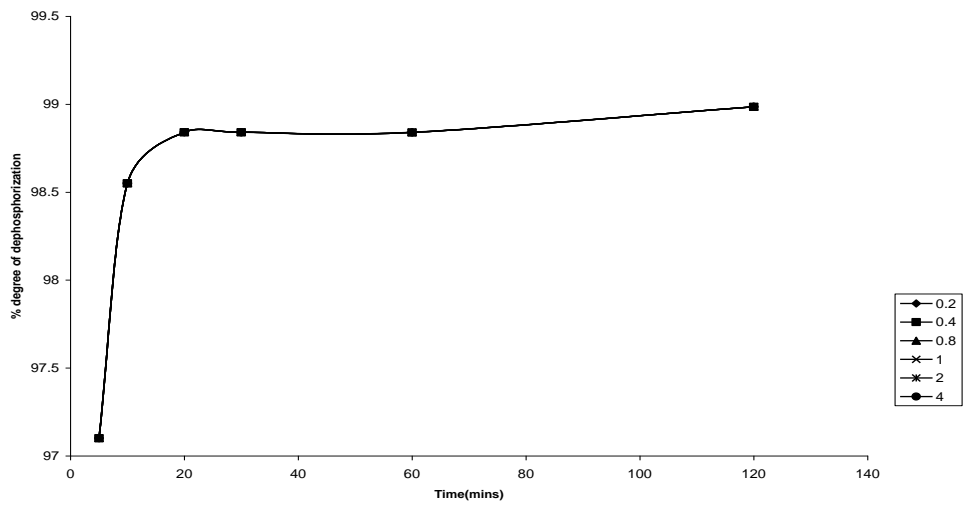


Fig. 7: Influence of leaching time on the %degree of dephosphorization for 60 microns using H₂SO₄

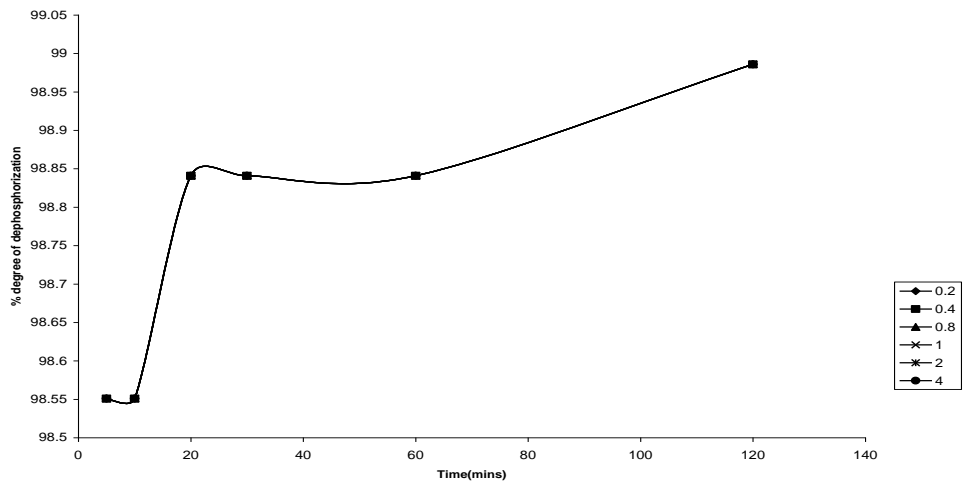


Fig. 8: Influence of leaching time on the %degree of dephosphorization for 40 microns using H₂SO₄

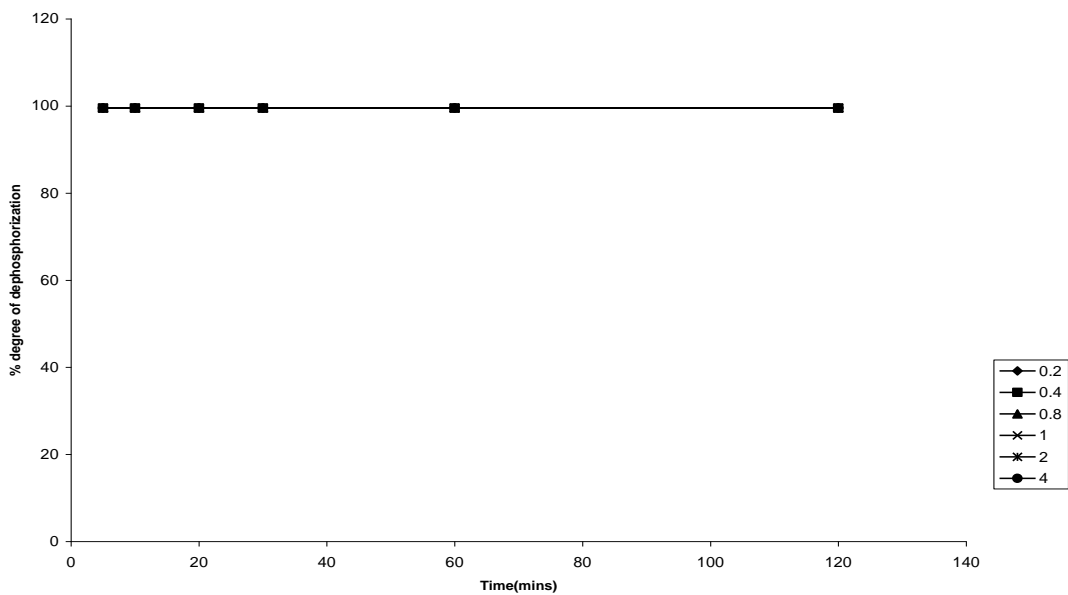


Fig. 9: Influence of leaching time on the %degree of dephosphorization for 20 microns using H₂SO₄

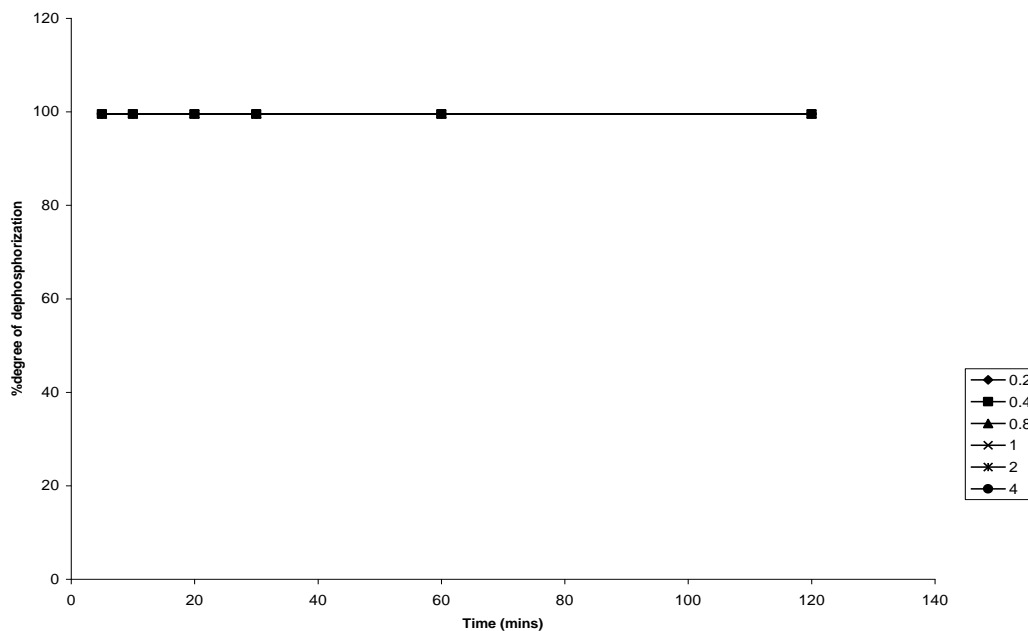


Fig. 10: Influence of leaching time on the % degree of dephosphorization for 10microns using H₂SO₄

Effect of Particle Size on Percentage Degree of Dephosphorization

The particle size effects on the percentage degree of dephosphorization are represented in Fig. 11 – Fig. 16. The percentage removal was fairly constant between 10 microns and 20 microns in fig 11. Between 20 microns and 60 microns there was significant degree in percentage removal of phosphorus.

In Fig. 12, a fairly constant value was achieved between 10 microns and 20 microns. From 20 to 40 microns, there was a significant drop in percentage removal of phosphorus. A fairly constant removal was achieved between 40 and 80 microns.

Fig. 13 – Fig. 16 have similar behavior in their relationships and their profiles are of the same trend as in Fig. 11 and Fig. 12.

The result above is in line with the work of (Cheng et al, 1999). In their work 66.66% removal was achieved using particle size of 0.15mm, 5 hours leaching time and 0.1M acid concentration. It can be inferred that the smaller the particle size, the greater the surface area exposed for chemical reaction and the greater the percentage removal of phosphorus. In other words, the dissolution rates are inversely proportional to average diameter of the particle.

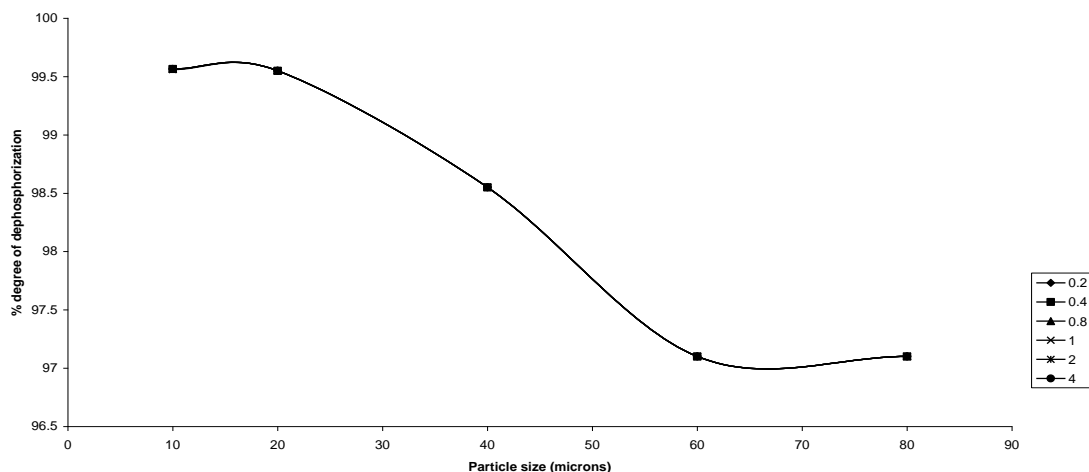


Fig. 11: Influence of particle size on the % degree of dephosphorization for 5mins using H₂SO₄

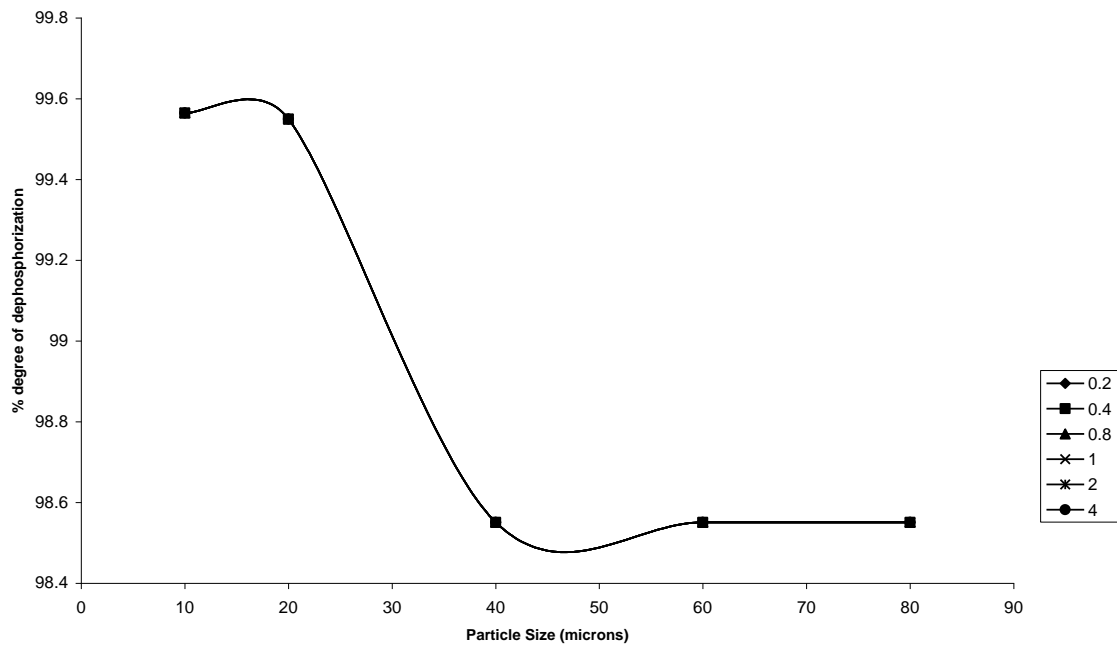


Fig. 12: Influence of particle size on the %degree of dephosphorization for 10mins using H₂SO₄

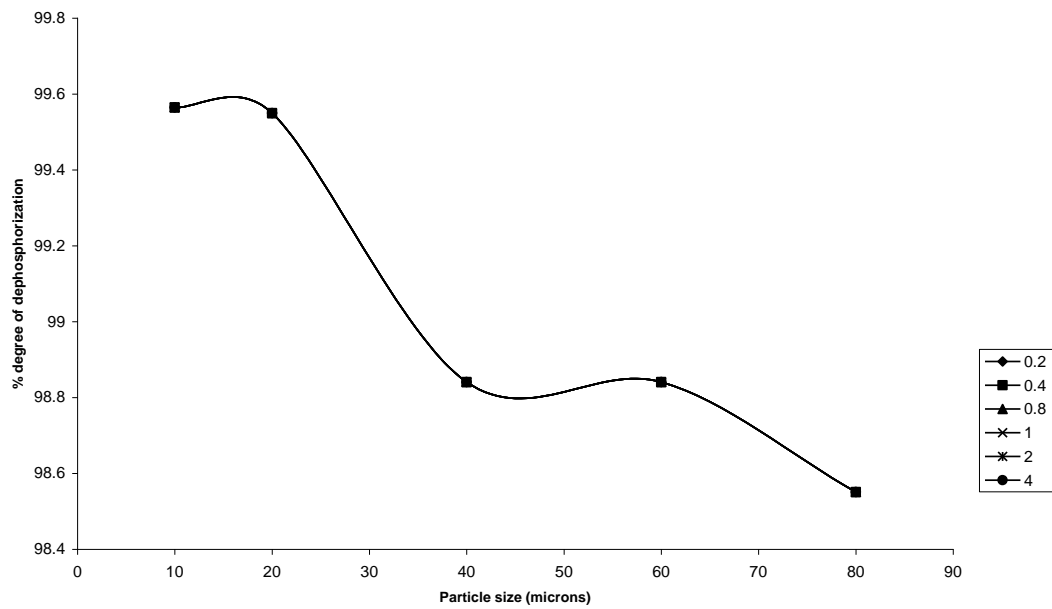


Fig. 13: Influence of particle size on the %degree of dephosphorization for 20mins using H₂SO₄

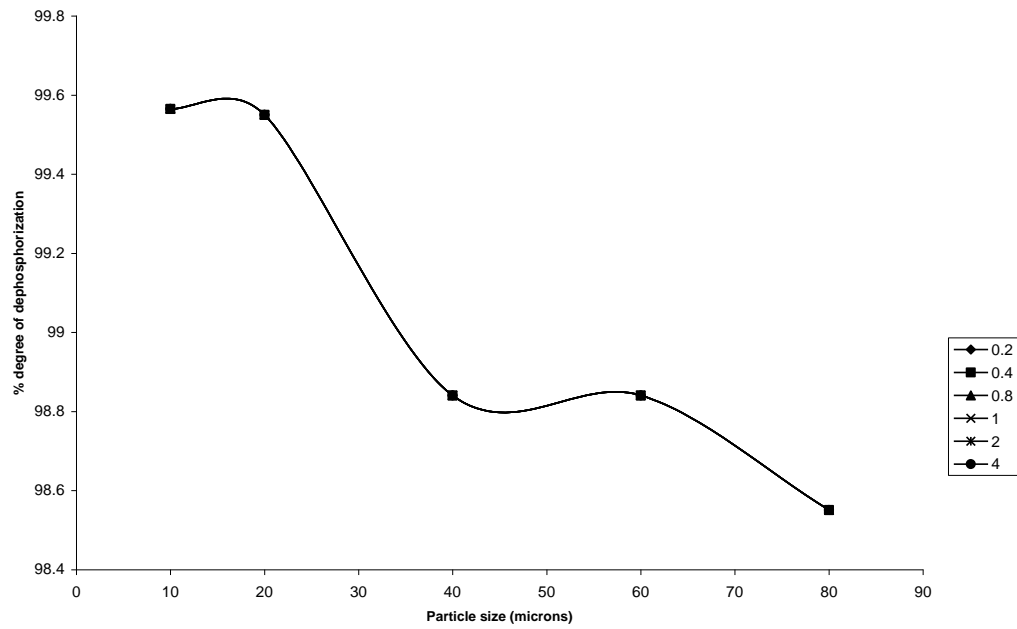


Fig. 14: Influence of particle size on the %degree of dephosphorization for 30mins using H₂SO₄

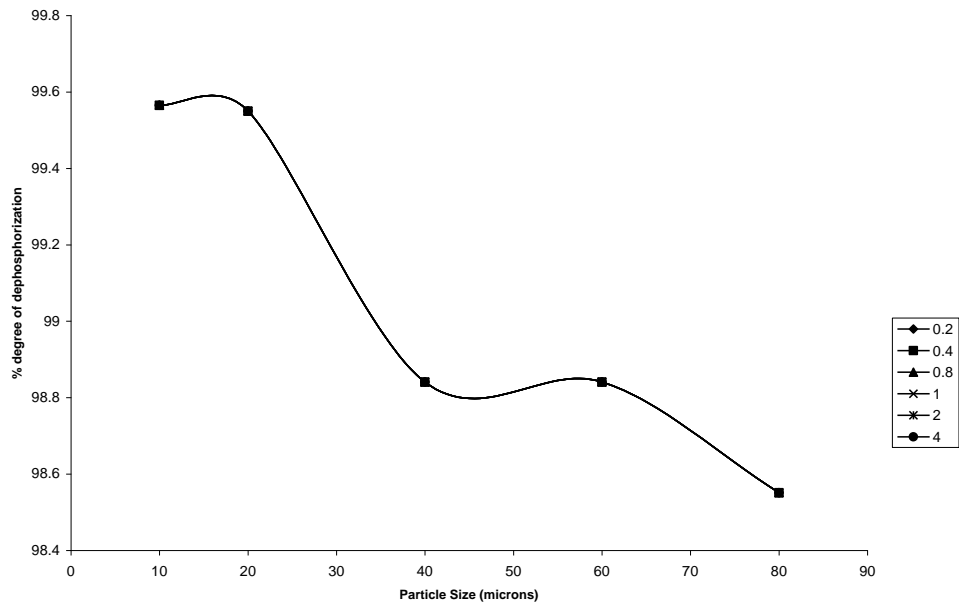


Fig. 15: Influence of particle size on the %degree of dephosphorization for 60mins using H₂SO₄

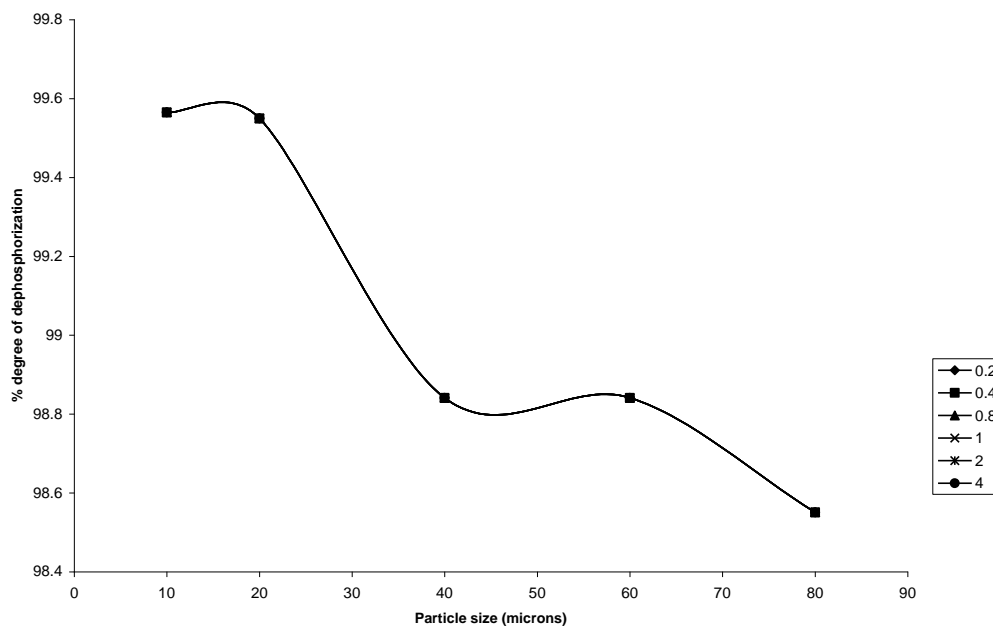


Fig. 16: Influence of particle size on the %degree of dephosphorization for 120mins using H₂SO₄

Interaction of the Variables and Surface Response

A 2³ full factorial design incorporating standard central composite design was employed in this study. The design matrix is depicted in Table 2.2.

The parameters: Leaching time (x₁), concentration (x₂) and particle size (x₃) were chosen as independent variables at two levels while the percentage degree of dephosphorization is the output response. The interaction is hinged on how the dependent output variable is influenced by the independent variables x₁, x₂ and x₃.

Upon the determination of polynomial coefficients, statistical analysis (G-Test, F-Test, T-Test) were performed to

develop a model that is adequate, significant and homogeneous (Chime, 2010).

The surface response plots for the interaction are shown in Fig. 17 and Fig. 18. The Fig. 17 represents the surface response for percentage removal of phosphorus for time and particle size as variables and the optimum is located on the dark red portion of the surface. Time responded more effectively than particle size in dephosphorization in Fig. 18. The Fig. 18 depicts surface response for iron loss for time and particle size as interactive variables. Particle size interacted more positively than time.

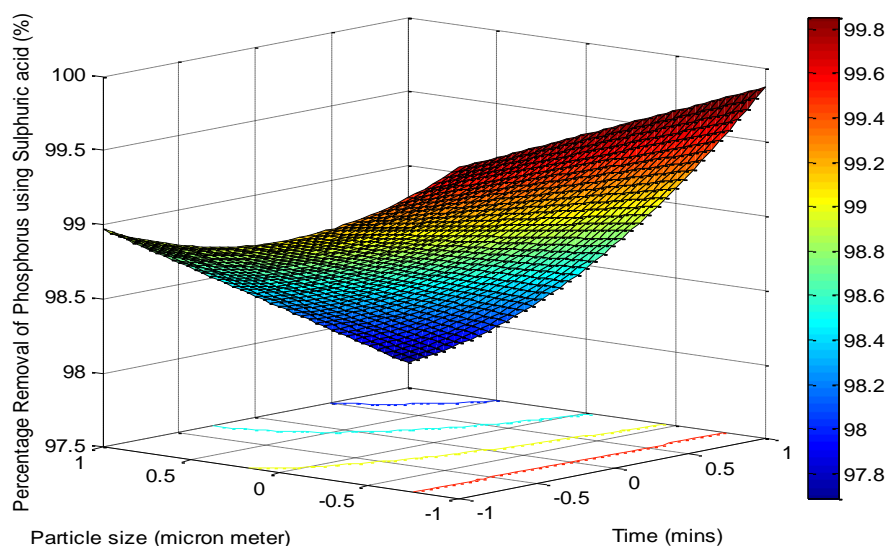


Fig. 17: Percentage removal of phosphorus using H₂SO₄ (Particle Size and Time)

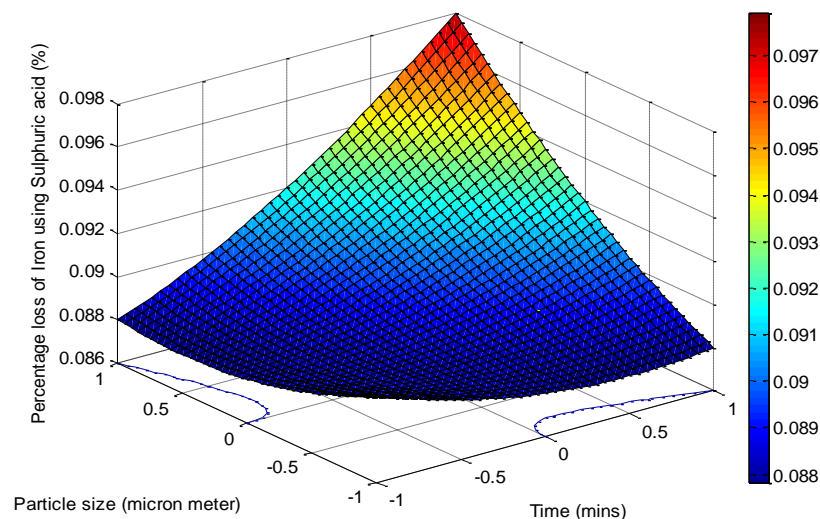


Fig. 18: Percentage Loss of Iron using H_2SO_4 (Particle Size and Time)

V. CONCLUSION

The dephosphorization of Agbaja Iron Ore was successfully carried out using sulphuric acid. The model equation developed was optimized using MATLAB and 99.87% degree of dephosphorization was obtained. The surface response plots show that the measured variables interacted with each other effectively and subsequently influenced the degree of removal of phosphorus positively. The iron loss during phosphorus metallurgical process was less than 4%.

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