

# Optimization of Process Parameters for the Dephosphorization of iron ore using Nitric Acid

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**Abstract** - An attempt has been made in this study to optimize the process variables for the dephosphorization of iron ore using nitric acid. Standard central composite design with  $2^3$  full factorial was used to develop the model. The model was optimized using Matlab. The surface responses of the plots show that concentration interacted effectively with leaching time and particle size. The result shows that 99.74% degree of dephosphorization was obtained at optimum values of 120 minutes, 2.0 Moles and 10 microns

**Keywords:** Optimization, Dephosphorization, Surface Response, Nitric acid.

## INTRODUCTION

The Nigeria's Agbaja iron ore reserve is estimated to be over 1.2 billion tones (Uwadielle, 1991). Iron ore resources are fast depleting as a result of a pressure originating from population and industrial development requirement.

However, there exist large stockpiles of low and lean grade ores to be mined, of which Agbaja iron ore is one of such ores. The ore is low grade because of the high phosphorus content (Chime et al, 2011).

Phosphorus, which is frequently found as one of the components of iron ore, is harmful in the production of iron and steel. High level of phosphorus in steel production will cause the steel produced to be brittle and can easily crack hence the need for its dephosphorization. Heat treatment and subsequent leaching is a way for up-grading high phosphorus iron ores (Field et al, 1968, Gooden et al, 1974; Muhammed and Zhang, 1989, Kokal, 1990; Aranjó et al, 1994; Cheng et al, 1999, Kokal et al, 2003).

Smelting process is effective for dispersion but with very high cost and it is still under fundamental research. For physical separation, comminution followed by wet magnetic separation or froth flotation is generally employed when the phosphatic gangue mineral appears as discrete inclusion in the iron body matrix (primary mineralization) (Kokal, 1990, Kokal et al, 2003; Fonesca et al, 1994).

Low phosphorus extraction, high grinding cost and iron loss are the major demerits of the method. Therefore, when phosphorus is disseminated in the iron structure, possibly forming cryptocrystalline phosphates or solid solutions with the iron oxide phases (secondary mineralization), the dephosphorization can only proceed by chemical routes using acid leaching (Kokal, 1990; Kokal et al, 2003; He and Zhou, 2000; Fang, 1998). The result of their studies showed that the acid concentrations were high and low phosphorus extractions were obtained.

In recent times, an increase in world steel production has increased the demand for iron ore with a consequent increase in price for this commodity, making hydrometallurgical phosphate removal critical (Kokal et al, 2003). Peioxoto, (1991) investigated the effect 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 a structural rearrangement of goethite and facilitated the dissolution of phosphorus in mineral acids. In this study nitric acid is used in the removal of phosphorus from Agbaja iron ore. Standard central composite design of  $2^3$  full factorial design was used to develop model equations using MATLAB.

## MATERIALS AND METHODS

Agbaja iron ore in this work was obtained from Agbaja in Kogi State, Nigeria. The raw ore was crushed in order to expose the surface for desliming process. Desliming was carried out to remove argillaceous material from the raw ore. 25kg raw ore was placed in a pan, 20 drops of oleic acid and 4g of sodium silicate were sprinkled and distributed evenly throughout the ore. 16 litres of distilled water was also introduced and the content mixed thoroughly. After mixing, the argillaceous materials were decanted leaving behind the iron ore. The residue was then washed thoroughly and sun dried for 24 hours. The raw and deslimed iron ore were then analyzed using x-ray fluorescence spectrometer. The dried deslimed iron ore was sieved to obtain particles sizes of 10microns, 20microns, 40microns, 60microns and 80microns. Nitric acid solutions of different moles of 0.2, 0.4, 0.8, 1.0, 2.0, 4.0 and 8.0 were

prepared. 100grams of particle size of 10microns of the deslimed iron ore was weighed and poured into a conical flask. 100ml of 0.2m nitric acid was poured into the conical flask containing the ore. The mixture was stirred properly to ensure homogeneity. The content was allowed to leach for 5mins, 10mins, 20mins, 30mins, 60mins and 120mins. At the end of each period, the solution was cooled and filtered. The residue was collected, washed to neutrality with distilled water, air dried and oven dried. The experiment was repeated for 0.4, 0.8, 1.0, 2.0, 4.0 and 8.0

moles and particles sizes of 20microns, 30microns, 40microns, 60microns, and 80microns. The samples were analyzed using x-ray fluorescence spectrometer.

*Design of Experiment for Dephosphorization*

Statistically designed experiment was carried out for the dephosphorization treatment based on 2<sup>3</sup> central composite design. The design matrix for the three variables, two levels and 17runs and responses were developed.

Table 1: Experiment range and levels of independent variables

Independent Variables	Lower Level	Base Level	Upper Level
	-1	0	+1
X <sub>1</sub> leaching time	5minutes	60minutes	120munites
X <sub>2</sub> Concentration	0.2M	4M	8M
X <sub>3</sub> Particle size	10microns	40microns	80microns

DEVELOPMENT OF STATISTICAL MULTIVARIABLE MODELS

The standard design of experiment is an efficient procedure for planning experiments so that data obtained can be analyzed to yield valid objective conclusions. Standard central composite design of 2<sup>3</sup> full factorial design was used. This design was constructed from 2<sup>m-t</sup> for cube portion, which is augmented with centre points and star points.

2<sup>3</sup> full factorial design

$$N = k^{m-t} + 2m + N_0$$

Where, N = Number of runs

K = level of experiment = 2

m = total number of variables (3) x<sub>1</sub>, x<sub>2</sub>, x<sub>3</sub>

t = the degree of fractionality t = 0 for m<4

N<sub>0</sub> = centre points added = 3

$$\therefore N = 2^{3-0} + 2^3 \times 3 + 3 = 17 \text{ runs}$$

The model equations for the experiment is proposed as

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

Table 2: Design matrix and response

	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	Y(P)% dephosphriazation
1	0	0	0	95.65
2	-1	-1	-1	97.10
3	+1	-1	-1	98.55
4	-1	+1	-1	98.55
5	+1	+1	-1	98.55
6	0	0	0	95.65
7	-1	-1	+1	89.86
8	+1	-1	+1	97.10
9	-1	+1	+1	92.75
10	+1	+1	+1	97.10
11	0	0	0	95.65
12	-1	0	0	95.65
13	+1	0	0	98.55
14	0	-1	0	97.10
15	0	+1	0	96.65
16	0	0	-1	98.55
17	0	0	+1	95.65

Developed model equations for dephosphorization

$$Y = 96.97 + 1.59x_1 + 0.48x_2 - 1.58x_3 - 0.92x_1x_2 + 0.88x_1x_3 + 0.56x_2x_3 - 0.61x_1^2 - 0.85x_1^2 + 0.88x_3^2$$

Optimization of model equation using MATLAB

DEPHOSPHORIZATION OF AGBAJA IRON ORE USING HNO<sub>3</sub>

```
>> A=[1 1 1];
>> b=[3];
>> lb=[-1;-1;-1];
>> ub=[1;1;1];
>> x0=[0;0;0];
>> [x,fval,exitflag,output]=fmincon(@leaching1,x0,A,b,[],[],lb,ub)
x =
    1.0000
   -0.5882
   -1.0000
fval =
    99.7441
exitflag =
     5
output =
    iterations: 3
    funcCount: 19
    stepsize: 1
    algorithm: 'medium-scale: SQP, Quasi-Newton, line-search'
    firstorderopt: 3.8147e-006
    cgiterations: []
    message: [1x172 char]
```

RESULTS AND DISCUSSION

Table 3: X-ray fluorescence chemical analysis of the Agbaja iron ore before desliming

Component	% Average Composition
Fe	56.34
SiO <sub>2</sub>	5.16
S	0.12
Al <sub>2</sub> O <sub>3</sub>	6.60
Ca 0	0.23
Mg 0	0.07
Mn 0	0.18
TiO <sub>2</sub>	0.15
K <sub>2</sub> O	0.04
P	0.79
H <sub>2</sub> O	2.06

Table 4: x-ray Fluorescence chemical analysis of Agbaja iron ore after desliming.

Component	% Average Composition
Fe	5.69
SiO <sub>2</sub>	5.02
S	0.05
Al <sub>2</sub> O <sub>3</sub>	5.20
Ca0	0.21
Mg0	0.03
Mn0	0.17
TiO <sub>2</sub>	0.25
K <sub>2</sub> O	0.007
P	0.69
H <sub>2</sub> O	2.81

The result in table 1 shows that the iron content of Agbaja iron ore is high and if the iron ore is properly beneficiated and dephosphorized can be used in steel making (Chime et al, 2011).

In table 2, the chemical analysis of the deslimed iron ore is shown. The effect of desliming is not significant though it

increased the iron content from 56.3% to 56.9% (Chime et al, 2011). It can also be observed that 0.13% removal of phosphorus was achieved. From the foregoing, it can be inferred that desliming helps in the removal of argillaceous materials like sand and dirt but does not contribute significantly to beneficiation and dephosphorization.

EFFECT OF NITRIC ACID CONCENTRATIONS ON THE PERCENTAGE DEGREE OF DEPHOSPHORIZATION

The effects of nitric acid concentration on the percentage degree of dephosphorization are represented in figures (1-5)

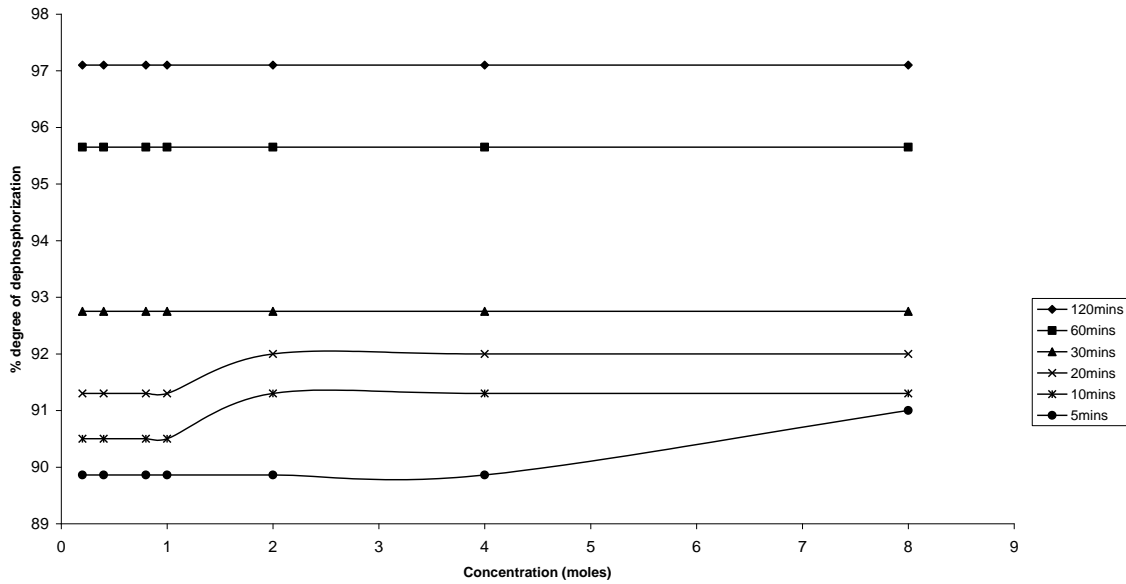


Figure 1: Effect of nitric acid concentrations on the % degree of dephosphorization for 80microns.

From figure 1 it can be observed that between 0.2M and 1.0M, the percentage removal remained constant because the reaction is just being initiated. From 1.0M to 2.2M, there was a slight increase in the percentage phosphorus removal. The percentage degree of dephosphorization

remained fairly constant between 2.0M and 8.0M. The highest percentage removal was 97.50 for 8.0M at particle size of 80microns. The least value was 97.10% for 8.0M at the same particle size.

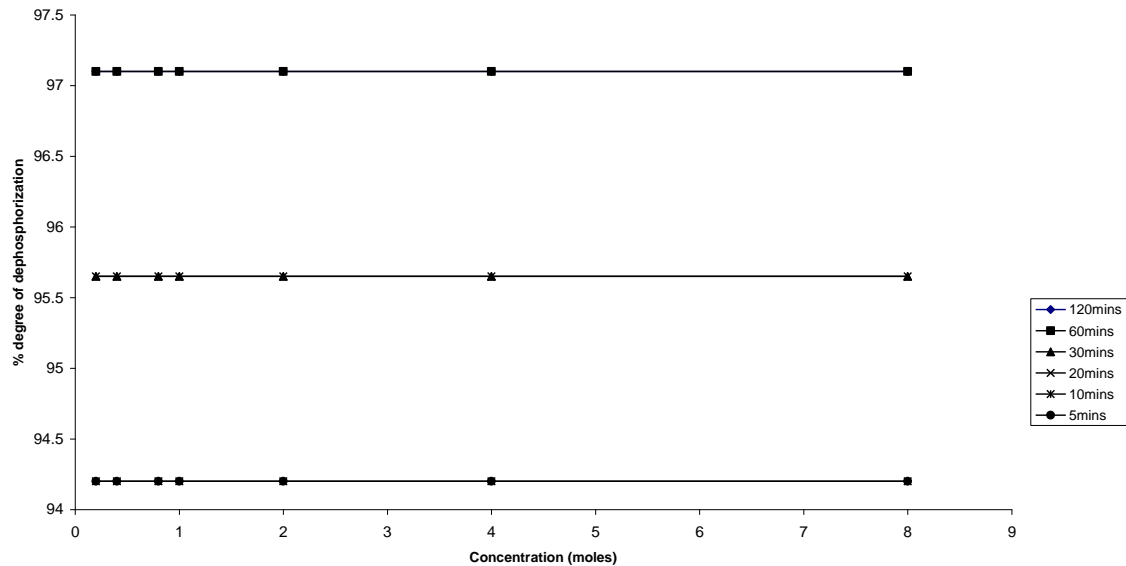


Figure 2: Effect of nitric acid concentrations on % degree of dephosphorization for 60microns.

In figure 2, the percentage degree of dephosphorization was fairly constant between 0.2M and 1.0M. But between 1.0M and 2.0M there was a slight increase in percentage

removal of phosphorus from 2.0M to 8.0M, the removal of phosphorous remained constant.

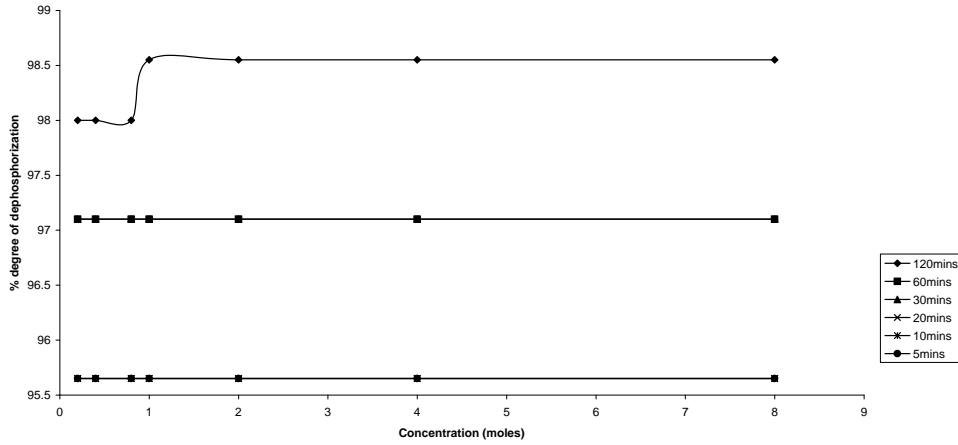


Figure 3: Effect of nitric acid concentrations on percentage degree of dephosphorization for 40microns.

The percentage degree of dephosphorization remained constant between 0.2M and 0.8M, there was a significant increased between 0.8M and 1.0M while between 1.0M to 8.0M, the percentage removal remained constant. The

highest percentage removal was obtained at 98.55% for 8.0moles and leaching time of 120minutes as shown in figure 3.

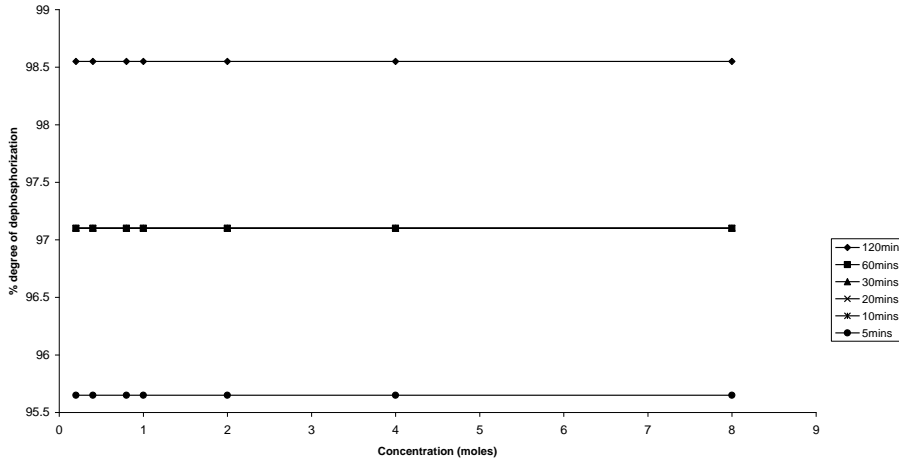


Figure 4: Effect of nitric acid concentration of the percentage degree of dephosphorization for 20minutes.

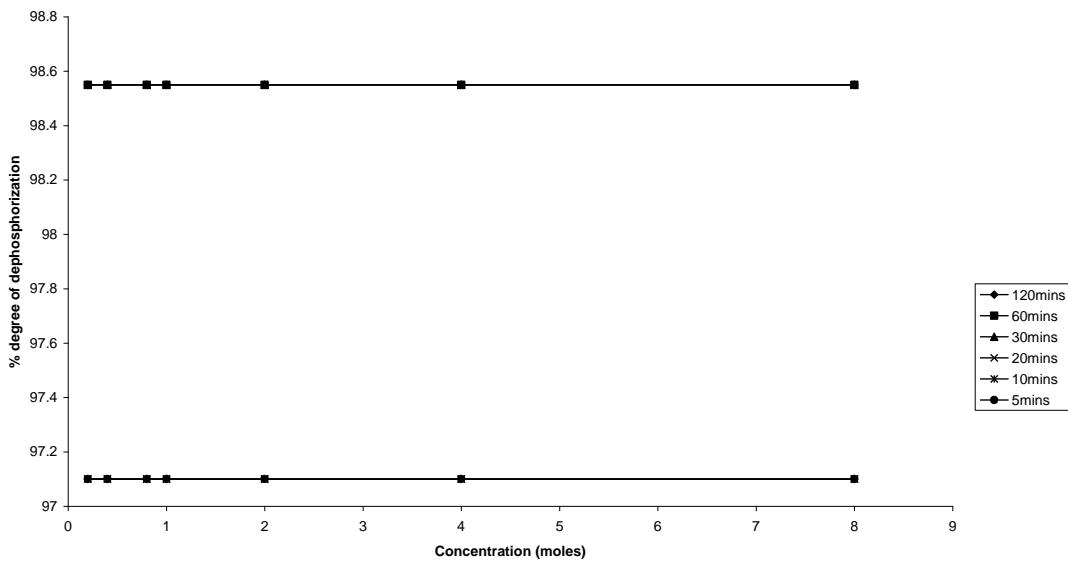


Figure 5: Effective of nitric acid concentration in the percentage removal of phosphorus for 10minutes.

Figure 4 and 5 show similar trend.

As the concentration of nitric acid increase, the percentage degree of dephosphorization remained constant. It is also noteworthy that fairly constant values were obtained initially showing that the initial dissolution rate is independent of the acid concentration (Zang et al, 1989).

#### EFFECT OF LEACHING TIME ON THE PERCENTAGE DEGREE OF DEPHOSPHORIZATION

Leaching time effects on the percentage degree of dephosphorization are depicted in figures 6-10. The percentage degree of dephosphorization increases with increase in leaching time as shown in figure 6. Between 5minutes and 60minutes, there was significant increase in percentage removal of phosphorus. There was slight increase in degree of dephosphorization between 60minutes and 120minutes.

In figure 7, it can be observed that between 5 minutes and 10minutes there was constant percentage removal of phosphorus. As the leaching time increases from 10minutes to 20minutes, there was an average increase of 1% while an average increase of 2% was recorded between 30minutes and 60minutes. A fairly constant result was achieved between 30minutes and 120minutes. From 5minutes to 20minutes a constant degree of dephosphorization was achieved as shown in figure 8. The average increase in percentage phosphorus removal was 4% between 20minutes and 30minutes.

Figure 9 shows that between 5minutes and 20minutes there was a significant increase in the percentage removal of phosphorus. Fairly constant value were obtained in figure 10 and the highest value of 98.55% was achieved. This shows that as the leaching time increases the percentage degree of dephosphorization increases.

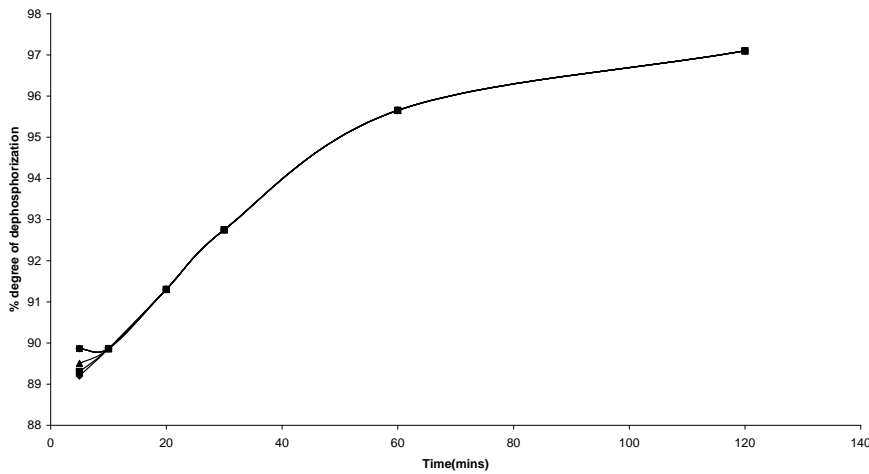


Figure 6: Effect of leaching time on the % degree of dephosphorization for 80microns

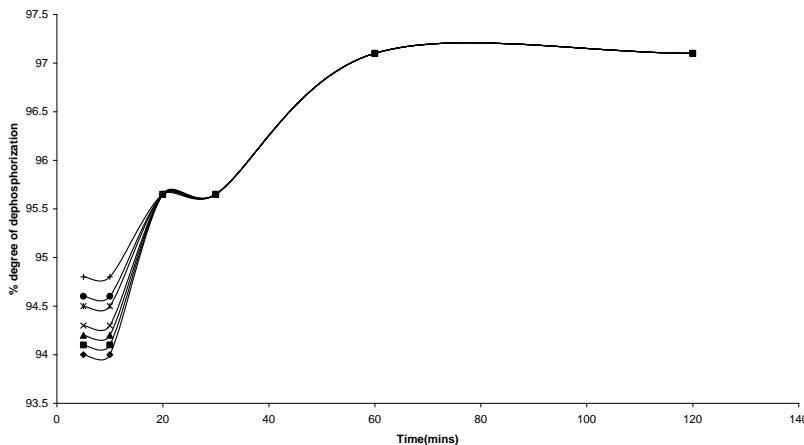


Fig.4.72: Effect of leaching time on the %degree of dephosphorization for 60microns

Figure 7: Effect of leaching time on the % degree of dephosphorization for 60microns

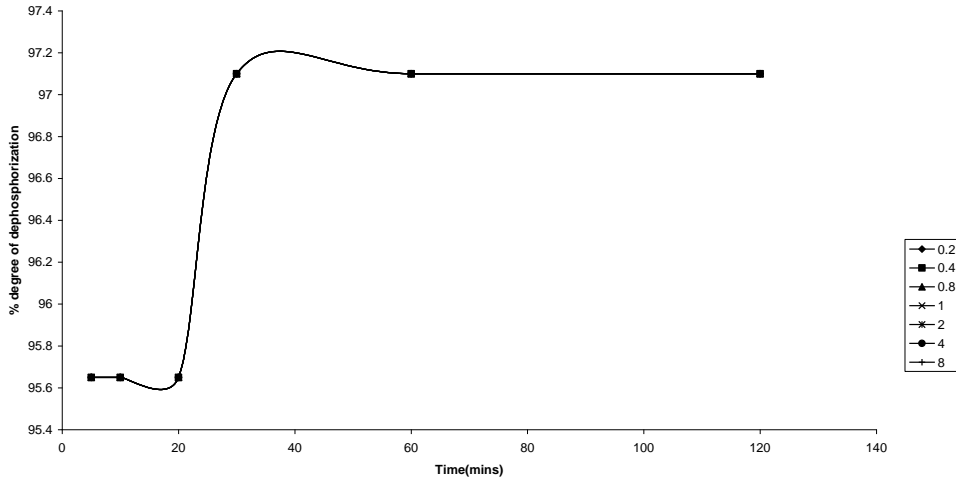


Figure 8: Effect of leaching time on the % degree of dephosphorization for 40microns

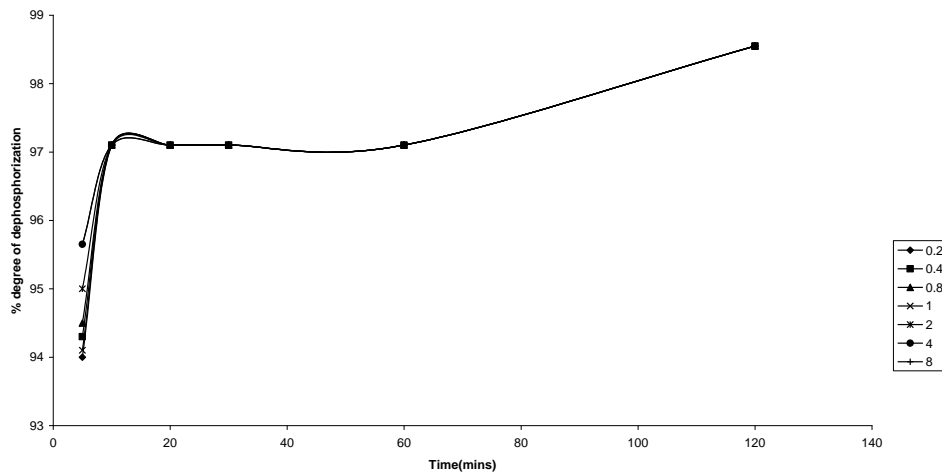


Figure 9: Effect of leaching time on the % degree of dephosphorization for 20microns

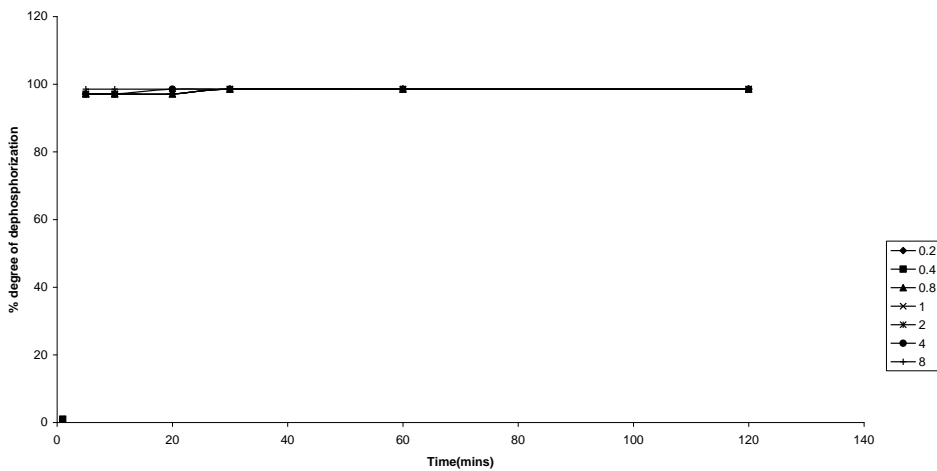


Figure 10: Effect of leaching time on the % degree of dephosphorization for 10microns

### EFFECT OF PARTICLE SIZE ON THE PERCENTAGE DEGREE OF DEPHOSPHORIZATION

The effects of particle size on the percentage degree of dephosphorization are shown in figure 11-16. In figure 11, the percentage degree of dephosphorization increases as the particle diameter decreases. From 10microns to 60microns,

there was significant reduction of phosphorus. The percentage removal of phosphorus was small from 60microns to 80microns because of size of the particles.

An average percentage removal of 2% was obtained from 60microns to 80microns as shown in figure 12. Between

10microns and 20microns there was slight decrease in the quantity of phosphorus removed. There was a steady decrease on the percentage removal of phosphorus as shown in figure 13.

Figure 14 shows that as the particle size increases from 10microns to 40microns there was a decrease in percentage removal of phosphorus.

The percentage removal in figure 15 shows that the highest value obtained was 98.55% at optimum conditions. There

was a gradual decrease of percentage of dephosphorization from 10microns to 80microns showing that particle size has an effect on the quantity of phosphorus removed.

As the particle increases from 10microns to 20microns, there was an average percentage removal of 1.5%. From 40microns, there was a steady decrease of quantity of phosphorus removed as shown in fig.16. It can be observed from the forgoing analysis that the less the particle size the greater is the quantity of phosphorus removed.

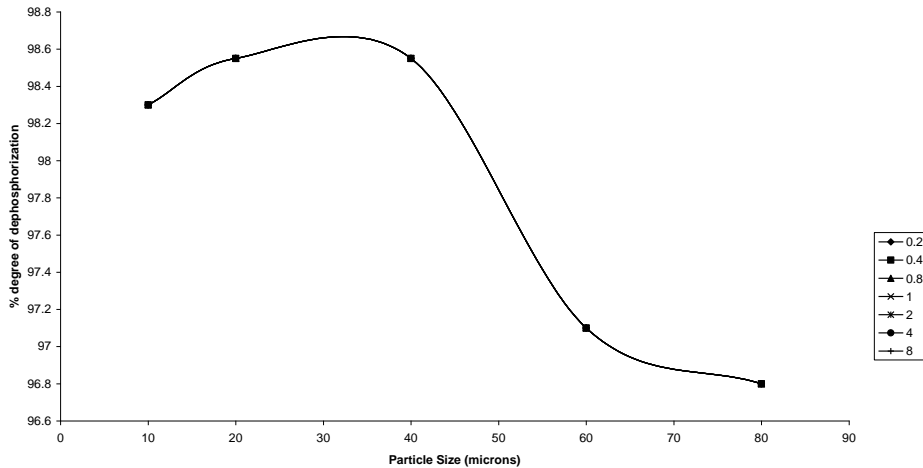


Figure 11: Effect of Particle size on %degree of dephosphorization for 120mins

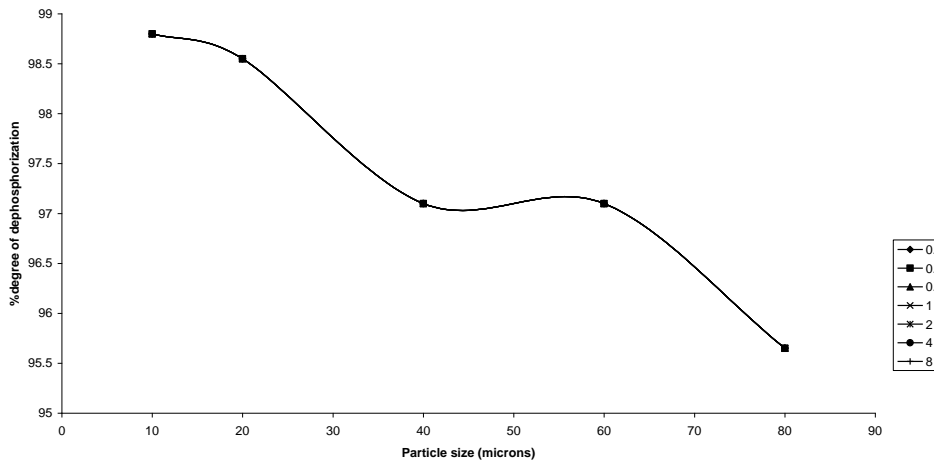


Figure 12: Effect of Particle size on %degree of dephosphorization for 80mins



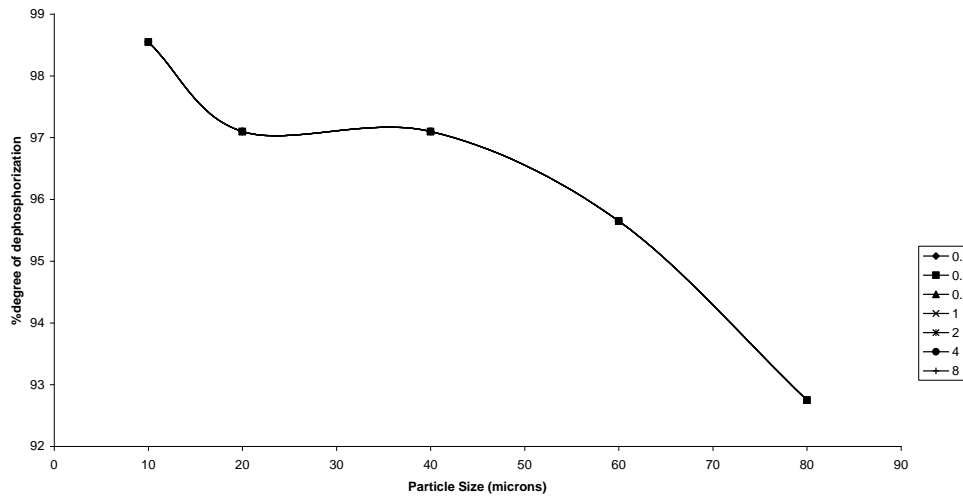


Figure 13: Effect of Particle size on %degree of dephosphorization for 30mins

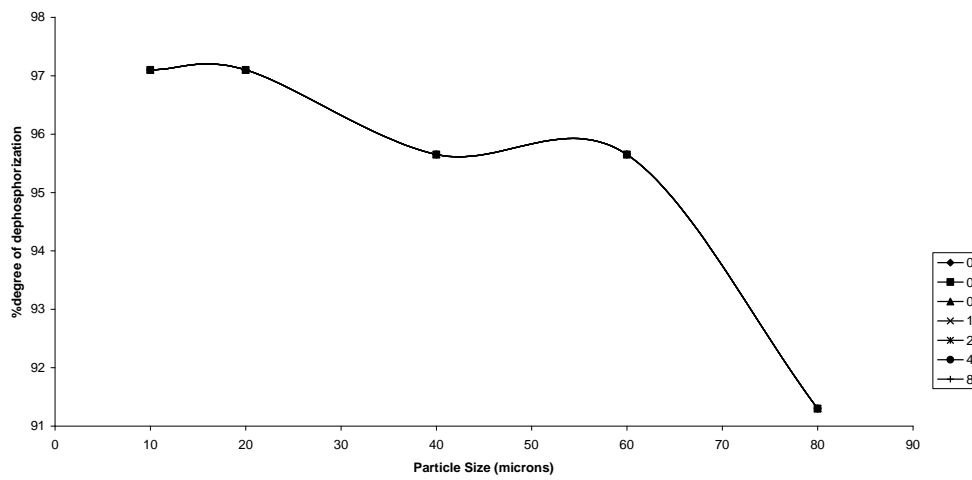


Figure 14: Effect of Particle size on %degree of dephosphorization for 20mins

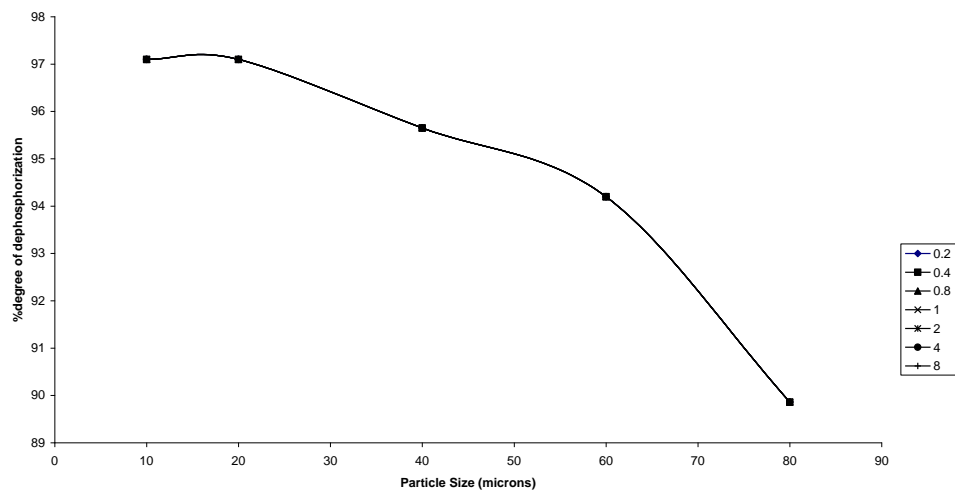


Figure 15: Effect of Particle size on %degree of dephosphorization for 10mins

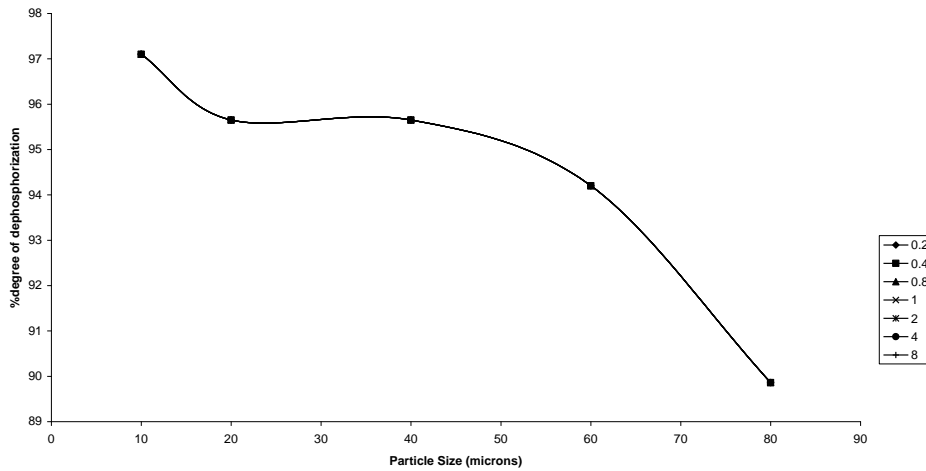


Figure 16: Effect of Particle size on %degree of dephosphorization for 5mins

### INTERACTION EFFECTS AND SURFACE RESPONSES

The design matrix is shown in table 2. The parameters  $x_1$ (leaching time),  $x_2$ (concentration) and  $x_3$ (particle size) were chosen as independent variables while the percentage degree of dephosphorization is the output response. The analysis is based on how the percentage degree of dephosphorization is affected by the independent variables in order to study the combined effects of these parameters. Statistically designed experiments were performed at different combinations of the parameters. The determination of polynomial coefficients were followed by statistical analysis (G-test, F-test, T-test) to develop a

model that is adequate, significant and homogeneous (Obiorah et al, 2011).

The corresponding interactive surface response plot presented in figure 17 shows that leaching time has greater effects than concentration. In figure 18, particle size has greater effect on the percentage removal than the leaching time. Concentration has greater influence on the degree of dephosphorization than particle as depicted in figure 19. The result shows that the three variables interacted effectively to enhance the phosphorus removal.

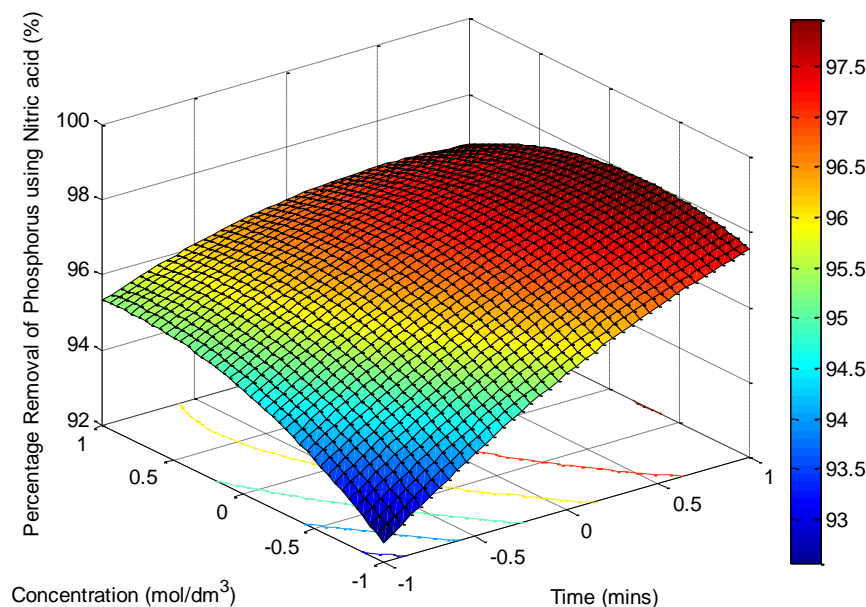


Figure 17: Percentage removal of phosphorus using  $\text{HNO}_3$  (time and concentration as a variables).

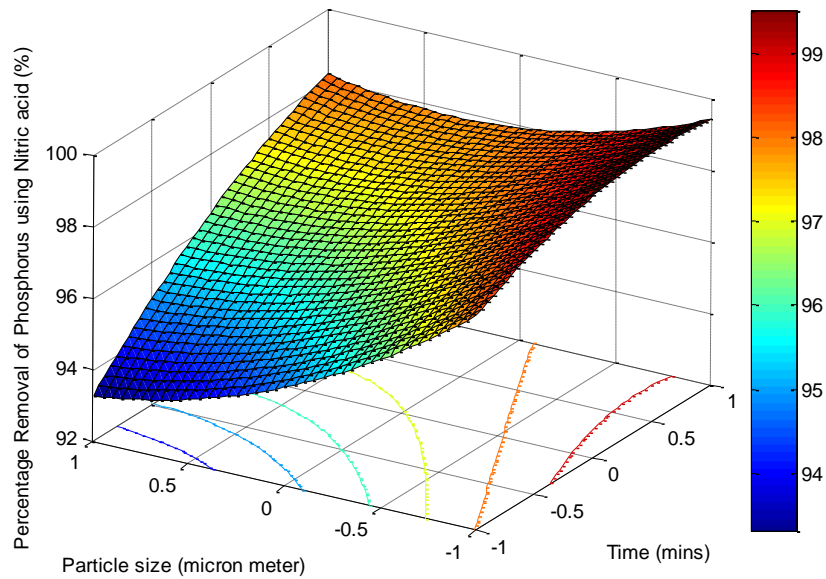


Figure 18: Percentage removal of phosphorus using HNO<sub>3</sub> (time and particle size are variables)

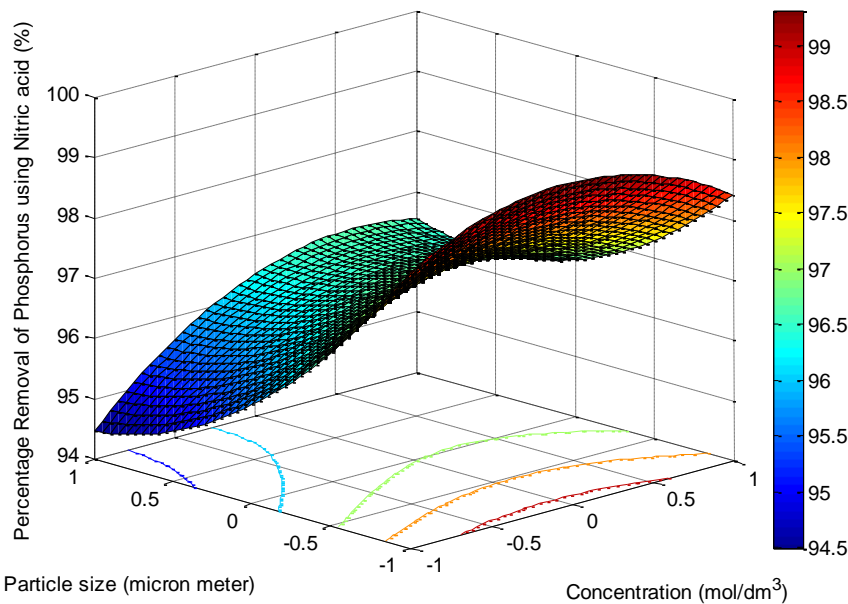


Figure 19: Percentage removal of phosphorus using HNO<sub>3</sub> (concentration and particle size as variables)

### CONCLUSION

The phosphorus removal was found to be feasible using nitric acid. The model developed was significant, adequate and homogeneous. The optimum percentage degree of dephosphorization was 97.74%. The surface responses show that the various process variables interacted effectively.

### REFERENCES

[1] Araujo, A; Fonseca, D. and Souza, C.(1994). Hydrometallurgical routes for reduction of phosphorus in iron ore. In: Wilkomirsky, I; Sanchez, M. and Hecker, C. Eds. A solution memorial volume, vol III, chemical metallurgy. In meeting of the southern hemisphere on mineral Technology, Universidad de Concepcion Chile. 83-92

[2] Cheng, C; Mirsa, V; Clough, J. and Mum, R. (1999) Dephosphorization of Western Australia iron ore by hydrometallurgical process. Mineral Engineering 12, 1083 – 1092  
[3] Chime, T.O. (2011). Biodephosphorization of iron ore using Acidothiobacillus Ferroacidans. New York Science Journal 1 – 6  
[4] Chime, T.O. Onukwuli, O.D and Menkiti, M.C(2011). Biodephosphorization of iron ore using Acidothiobacillus Feroxidoms, New York Science Journal 4(1) 1-6  
[5] Field, I, Franklin, T. and Lampkin, M.(1968) Process for removing phosphorus from iron ores. Us patent No.3, 402, 041.  
[6] Gooden, J. Waller, W. and Allen, R.(1974). ADEMPHOS – a chemical process for decomposition of iron ore. Proceedings of the National Chemical Engineering

- Conference, process industries in Australia – impact and growth sinters paradise. Queensland, Australia 38-49
- [7] Kokal, H.R.(1990) The origin of phosphorus in iron making raw materials and methods of removal. A review in proceedings of the 63<sup>rd</sup> Annual meeting. The Minnesota section AIME and 51<sup>st</sup> Annual mining symposium, Duluth Minnesota 225 -258
- [8] Kokal, H.R; Sirigh, M.P. and Naydyonov,V. (2003) Removal of phosphorus from Lisa kovsky iron ore by roast leach process. Hydrometallurgy proceeding of the 5<sup>th</sup> international symposium, vol 2 Vancouver B. C. Canada. The minerals, metals and minerals society (TMS) Warrandale PA 15086 USA 1517 – 1530.
- [9] Muhammed, M. and Zhan, Y. (1989). A hydrometallurgical process for the dephosphorization of iron ore. Hydrometallurgical 21, 277-292.
- [10] Obiorah, S.M.O; Menkiti, M.C. and Nnuka, E.E (2011). Beneficiation processing of Agbaja iron ore by chemical leaching technique New York Science Journal 4(5) 22 – 27.
- [11] Uwadielle, G.G.O.O.(1991) Electrolytic coagulation and selective flocculation of Agbaja iron ore. Elsevier Science Publishing Co. Inc pp 301 – 411
- [12] Zang, V.U and Muhammed, M. (1989). The removal of phosphorus from iron ore by leaching with nitric acid Hydrometallurgy, 21, 255 – 275