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HYDROMETALLURGICAL PROCESS OF DEPHOSPHORIZATION OF AGBAJA IRON ORE

T.O. Chime

Department of Chemical Engineering, ESUT, Enugu, Nigeria

O.D. Onukwuli

Department of Chemical Engineering, NAU, Awka, Nigeria

A.J. Ujam

Department of Mechanical Engineering ESUT, Enugu, Nigeria

ABSTRACT

A study on the dephosphorization of Agbaja Iron Ore using hydrometallurgical process has been carried out. The central composite design of 2^3 *response was formulated and used to develop a model equation. The optimized result of the equation using Matlab shows that 97.97% degree of dephosphorization was obtained at 117 minutes leaching time, 0.2M leachant concentration and particle size of 30 microns. Iron loss during the hydrometallurgical leaching was less than 5%. It can be inferred that chemical leaching using HCl is attainable under the prevailing conditions of the experiment.*

Key Words: Hydrometallurgy, Dephosphorization, Iron loss, Surface response.

INTRODUCTION

Nigeria is one of the richest countries of the world as far as mineral resources are concerned, iron ore inclusive. The estimated workable iron deposits stand in excess of 2.5 billion tonnes most of which belong to hematite, magnetite, hematite-geothite and siderite-geothite. (Alafara *et al.*, 2005) Iron is the sixth most abundant element in the universe and the most abundant metal in the earth's crust after aluminum. However, Agbaja iron ore has an estimated reserve of over 1 billion tones (Alafara *et al.*, 2005). The utilization of Agbaja iron ore is hampered by its poor response to established industrial beneficiation techniques. This is as a result of fine grained texture of the Agbaja iron ore (Uwadiale and Whewel, 1988).

Its high phosphorus and low silicon modulus and fine texture also constitute a major problem for utilization in blast furnace or direct reduction process.

(Peixoto, 1991) investigated the affect 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 which converted to hematite and facilitated the dissolution of phosphorus in mineral acids. Without thermal treatment of the ore, hydrochloric acid was not effective. The higher the acid concentration of the leach solution, the higher the phosphorus extraction and the iron loss increased with increase in acid concentration. (Cheng *et al.*, 1999) 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 viability of acid leaching of iron ore in which apatite was the phosphorus containing minerals. It was found that the economy of leaching using hydrochloric acid depended very much on the extent to which the phosphorus can be recovered as phosphoric acid.

The iron ore contained phosphorus in the form of apatite. The optimum leaching time was found to exceed 10hours. Without the use of heat treatment, a 20% reduction in phosphorus content was achieved. With heat treatment a reduction of phosphorus to 40% was obtained (Matsuo *et al.*, 1980). (Chime, 2010) observed that at higher concentration of 16moles of HCl that the degree of dephosphorization increased substantially.

(Gooden *et al.*, 1974) investigated high phosphorus ore from the Pilbara region of Western Australia. Physical beneficiation methods failed as the phosphorus was in solid solution in goethite. Chemical dephosphorization methods for iron ore were reviewed and tested on the ore samples from the Pilbara region. Leaching without thermal treatment was found to be quite ineffective.

When phosphorus is disseminated in iron structure, possibly forming cryptocrystalline phosphates or solids, solutions with the iron oxide faces secondary mineralization, the beneficiation can only proceed by chemical routes (Kokal, 1990). CUj et al (Kokal *et al.*, 2003) investigated dephosphorization with acid leaching. In their studies, the acid concentrations were very high and low phosphorus extraction was obtained.

In this investigation the dephosphorization of Agbaja iron ore with high phosphorus content was carried out. Central composite design was also used to determine the surface response interactions between prevailing dephosphorization factors.

MATERIALS AND METHODS

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

Scrubbing Process

Scrubbing was carried out to remove argillaceous material from the raw iron ore. The iron ore was poured into a head pan and water was poured to a reasonable level. The ore was washed and the water was decanted. This was repeated for five times until clear water was observed. At this point 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 mixed thoroughly. After mixing, the argillaceous materials were removed leaving behind the iron ore. The residue was washed thoroughly and was sun dried for 24hours. Some quantities were sent for chemical analysis using atomic absorption spectrophotometer and X-ray fluorescence diffraction spectrometer.

Chemical Leaching Process

The dried scrubbed iron ore was further pulverized and sieved to obtain particle size of 10,20,40,60 and 80 microns. Analar grade of hydrochloric acid solutions of different moles of 0.2, 0.4, 0.8, 1.0, 2.0, 4.0, 8.0, 12.0 and 16.0 were prepared. 100grams of particle size of 10 microns of scrubbed iron ore was weighed and poured into a conical flask. 100ml of 0.2M of hydrochloric acid was then poured into the 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 period, 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, 4.0, 8.0, 12.0 and 16.0 moles and for the different particle sizes. The samples were sent for chemical analysis using atomic absorption spectrophotometer and X-ray fluorescence diffraction spectrometer.

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

Design of Experiment for Leaching

Statistically designed experiment was carried for the leaching treatment based on central composite design 2^3. The design matrix for the three variables, two levels and seventeen experimental runs and responses are shown below

Table-1. Experiment Range and Levels of Independent Variables

Independent variable	**Lower level** **-1**	**Base level** **0**	**Upper level** **+1**
X_1 time	5mins	60mins	**120mins**
X_2 Concentration	0.2M	8M	**16M**
X_3 Particle size	10Microns	40Microns	**80Microns**

Table-2. Design Matrix and Responses

	X_1	X_2	X_3	Y_n(%) degree of dephosphorization
1	0	0	0	**96.81**
2	-1	-1	-1	**96.86**
3	+1	-1	-1	**97.39**
4	-1	+1	-1	**97.68**
5	+1	+1	-1	**95.94**
6	0	0	0	**96.81**
7	-1	-1	+1	**89.71**
8	+1	-1	+1	**95.94**
9	-1	+1	+1	**92.03**
10	+1	+1	+1	**96.81**
11	0	0	0	**96.81**
12	-1	0	0	**96.23**
13	+1	0	0	**97.10**
14	0	-1	0	**96.96**
15	0	+1	0	**97.54**
16	0	0	-1	**97.54**
17	0	0	+1	**94.20**

Developed Model Equation

$$y_n = 97.20 + 1.06x_1 + 0.30x_2 - 1.68x_3 - 0.45x_1x_2 + 1.54x_1x_3 + 0.49x_2x_3 - 0.59\,x_1^2 + 0.08\,x_2^2 - 1.39\,x_3^2$$

Optimization of Model Equation Using Matlab

```
function f = leaching1(x)
f = 97.2+1.06*x(1)+0.30*x(2)-1.68*x(3)-0.45*x(1)*x(2)+1.54*x(1)*x(3)+0.49*x(2)*x(3)-0.59*x(1)^2+0.08*x(2)^2-1.39*x(3)^2;
>> 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 =
0.9420
-1.0000
-0.2587
fval =
97.9719
exitflag =
5
```

```
output =
iterations: 10

funcCount: 55
stepsize: 1
algorithm: 'medium-scale: SQP, Quasi-Newton, line-search'
firstorderopt: 2.6703e-005
cgiterations: []
message: [1x172 char]
```

RESULTS AND DISCUSSION

Table-3. Chemical Composition of raw Agbaja Iron ore

Component	Average composition %
Fe	56.34
SiO_2	5.16
S	0.12
AL_2O_3	6.60
CaO	0.23
MgO	0.07
MnO	0.18
TiO_2	0.15
K_2O	0.04
P	0.79
H_2O	2.06

Table-4. Chemical Composition of scrubbed Agbaja Iron Ore

Component	Average composition%
Fe	56.90
SiO_2	5.02
S	0.05
AL_2O_3	5.20
CaO	0.21
MgO	0.03
MnO	0.17
TiO_2	0.25
K_2O	0.007
P	0.69
H_2O	2.81

Effects of Hcl Concentration on the Degree of Dephosphorization

Investigations of effects of acid concentration on dephosphorization of Agbaja Iron Ore are shown in figures 1,2,3,4,5.

Fig-1. Effect of HCl Concentration on the %degree of dephosphorization for 80 microns

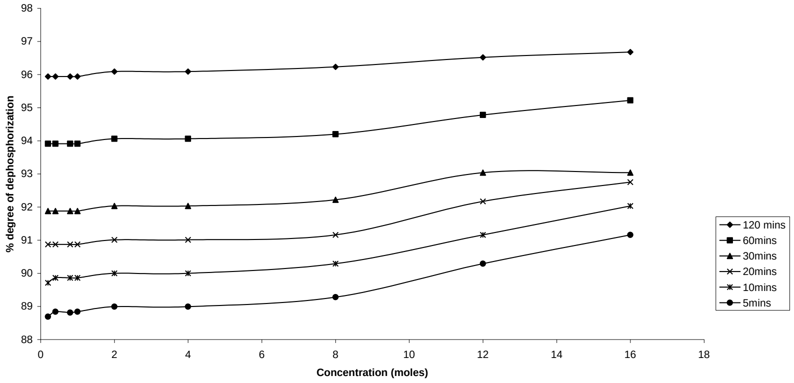


Fig-2. Effect of HCl Concentration on the %degree of dephosphorization for 60 Microns

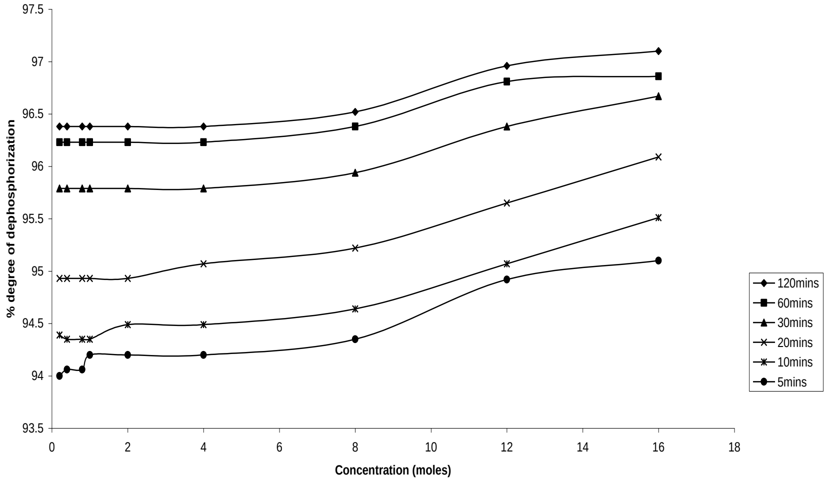


Fig-3. Effect of HCl Concentration on the %degree of dephosphorization for 40 microns

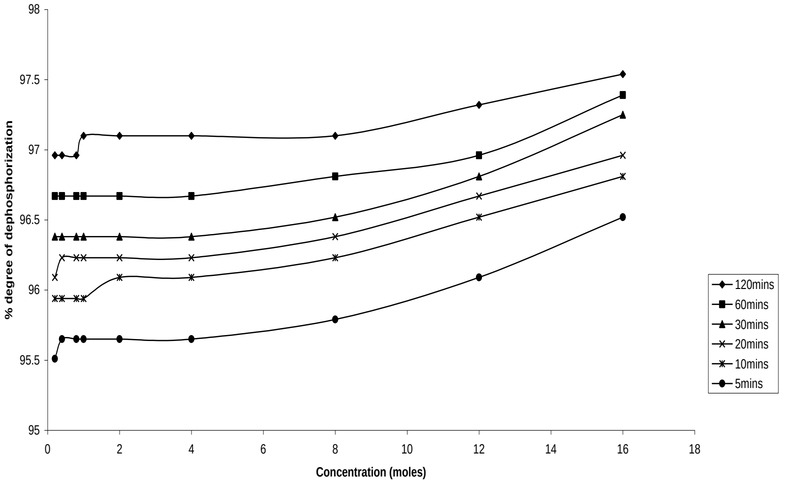


Fig-4. Effect of HCl Concentration on the %degree of dephosphorization for 20 microns

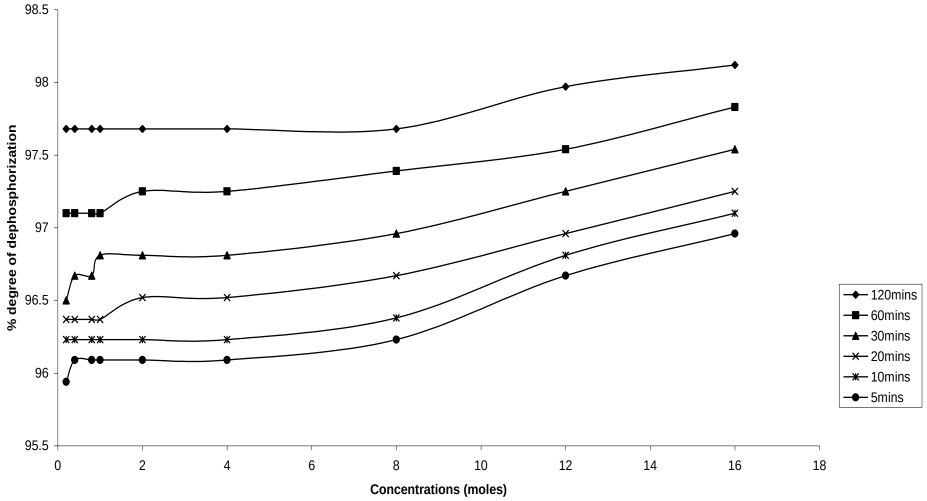
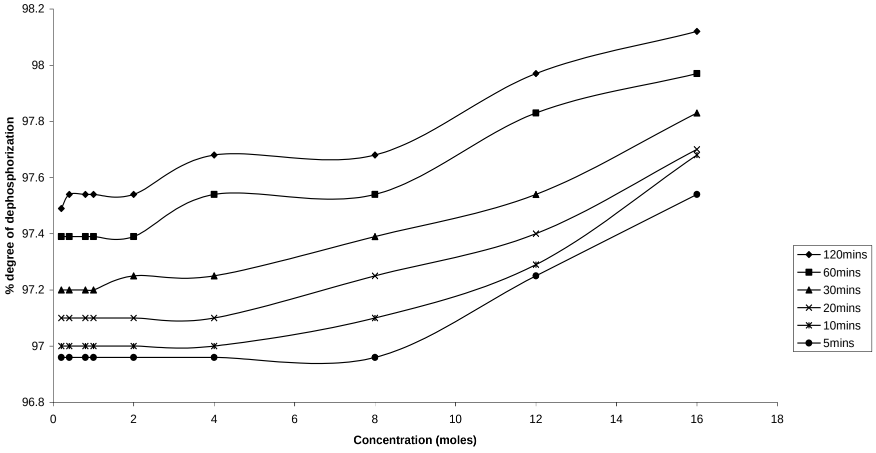


Fig-5. Effect of HCl Concentration on the %degree of dephosphorization for 10 microns



In figure 1, where particle size of 80 microns was used, the percentage degree of dephosphorization increases as concentration increases. For concentrations of 0.2M to 2M the increase was gradual due to the resistance of the gangue materials in the iron ore. As soon as the resistance was overcome the increase becomes more evident. It can be observed that 96.68% degree of dephosphorization was achieved at 120 minutes for concentration of 16 moles. For the same concentrations of 16moles, 91.16% degree of dephosphorization was obtained for 5 minutes leaching time. Similar trends were obtained for figures 2 to 5 for 10 minutes, 20 minutes, 30 minutes and 60 minutes. In figure 2 the percentage degree of dephosphorization was 95.5% for 16 moles at 5 minutes leaching time. At 120 minutes for 16 moles concentration, the percentage degree of dephosphorization was 97.10%. The percentage degree of dephosphorization was 97.54% for 120 minute using HCl concentration of 16moles and particles size of 40microns is shown in figure 3. It was observed that for concentrations of 2.0moles, 97.1% was obtained. This illustrates that as the concentration increases, the rate of phosphorus removal increases. Similar trends were also obtained in figures 4 and 5.

From the results it can be inferred that the rate of phosphorus removal is affected directly by the hydrogen ion (H^+) concentration. These are in accordance with the works on leaching of sphaletite (Dutrizac and MacDonald, 1983; Zuo *et al.*, 1984; Cuj and Fang, 1998)

Influence of Leaching Time on the Percentage Degree of Dephosphorization

Fig-6. Effect of leaching time on the %degree of dephosphorization for 80 microns using HCl

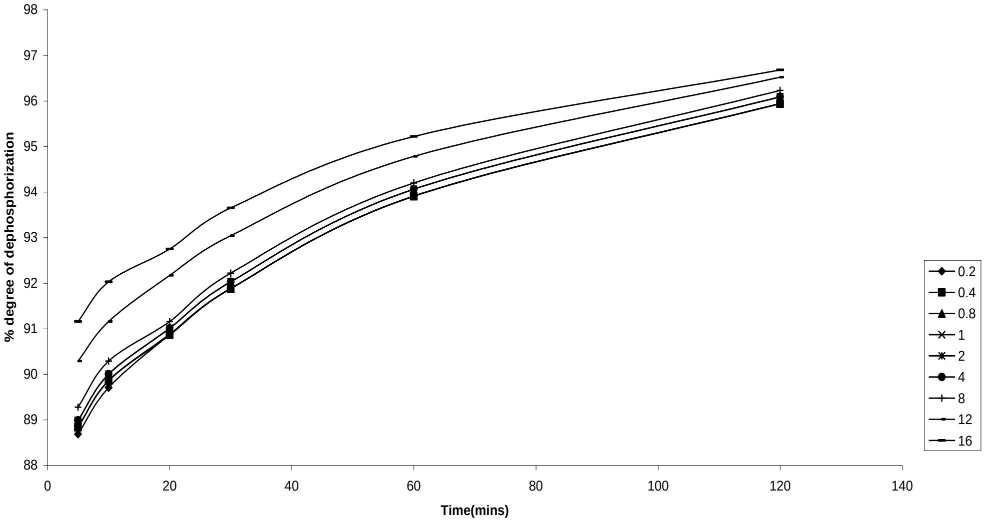


Fig-7. Effect of leaching time on the %degree of Dephosphorization for 60 microns using HCl

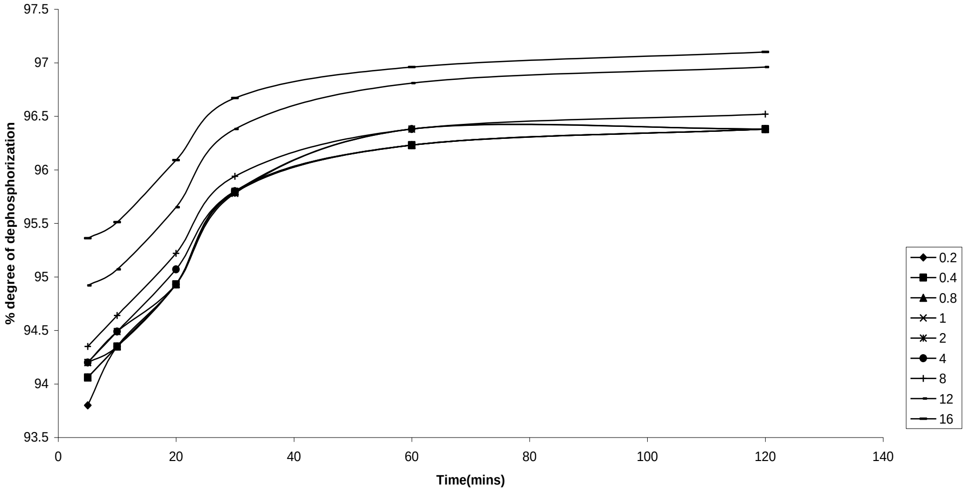


Fig-8. Effect of leaching time on the %degree of Dephosphorization for 40 microns using HCl

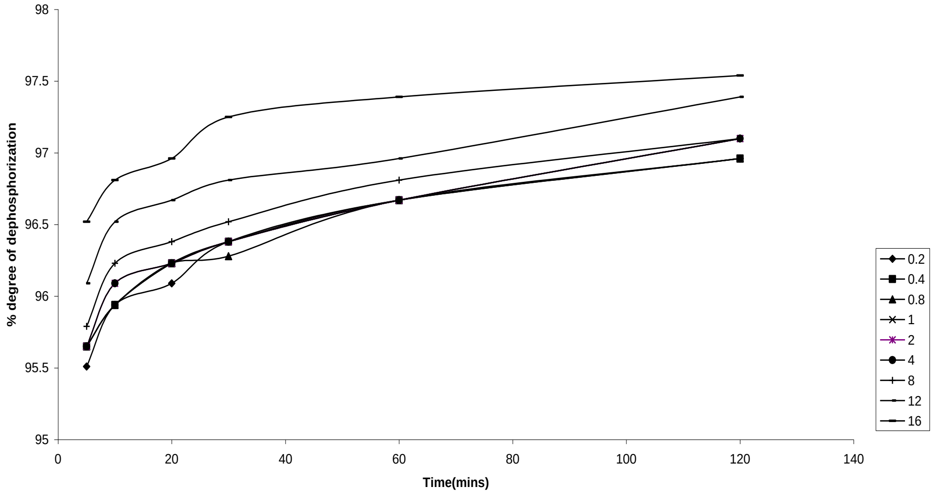


Fig.-9. Effect of leaching time on the %degree of Dephosphorization for 20 microns using HCl

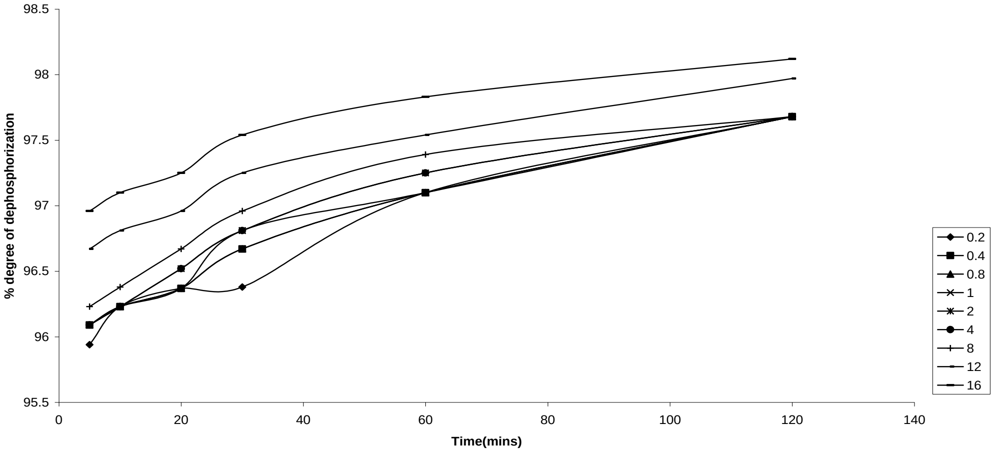
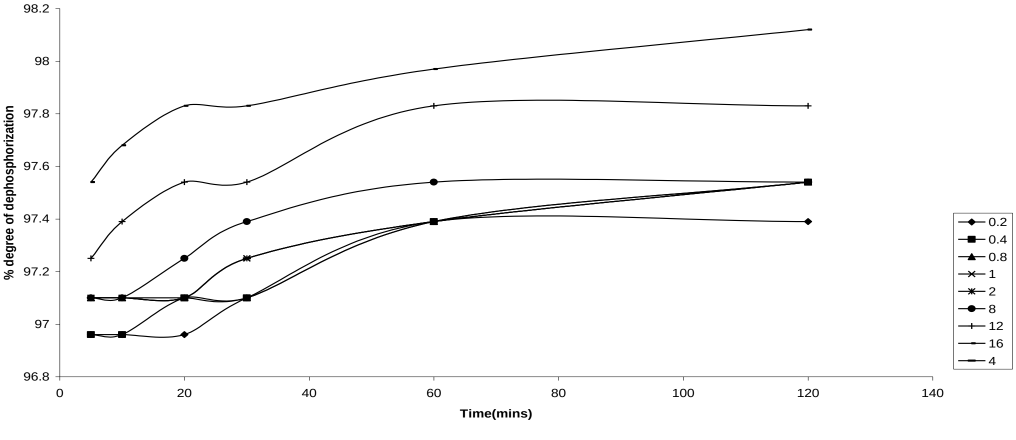


Fig-10. Effect of Leaching Time on the %degree of Dephosphorization for 10 Microns using HCl



In figure 6, the percentage degree of dephosphorization increases with increase in leaching time for particle size of 80microns. The least dephosphorization was obtained for 0.2M at the leaching time of 120minutes. The highest value of 96.68% dephosphorization was recorded for 16moles at the leaching time of 120minutes. Fig.7 shows that there was a sharp increase in degree of dephosphorization from 5 minutes to 30 minutes. After 30 minutes, the rate of removal remains fairly constant. The figure also shows that 97.15% dephosphorization was achieved at 120 minutes for 16M while at 5 minutes 95.36% was obtained.

It can also be observed in fig. 8 that there was noticeable increase in degree of removal from 5 minutes to 10 minutes. But from 10 minutes, the increase in percentage removal was gradual. At 120 minutes for concentration of 16moles the highest % removal of 97.54% was achieved.

Fig. 9 shows that percentage removal of phosphorus for concentrations of 0.2M, 0.4M, 0.8M, 1.0M, 2.0M, 4.0M and 8M was nearly the same while that of 12M and 16M were 97.9% and 98.12% respectively.

From 5-30minutes the increase in phosphorus removal was visible while from 30 minutes there was fairly increase in percentage degree of dephosphorization. At 60 minutes the percentage removal was nearly the same for concentrations of 0.2M, 0.4M, 0.8M, 1.0M, 2.0M and 8.0M as shown in fig.10.

It is observed from the foregoing statements that as the time increases the percentage degree of dephosphorization increases, showing that leaching time is directly proportional to the percentages of degree of dephosphorization.

Effects of particle size on the percentage removal of phosphorus.

Fig-11. Effect of particle size on the %degree of dephosphorization for 5mins using HCl

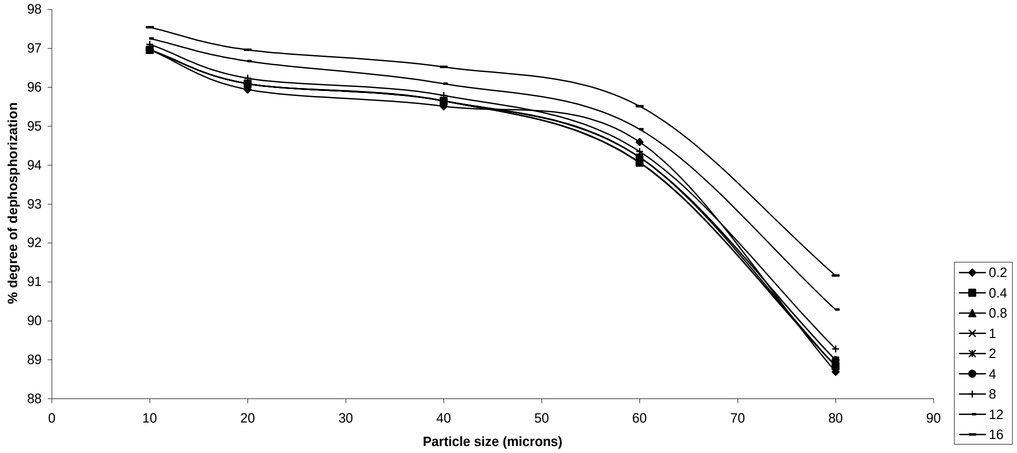


Fig-12. Effect of particle size on the %degree of dephosphorization for 10mins using HCl

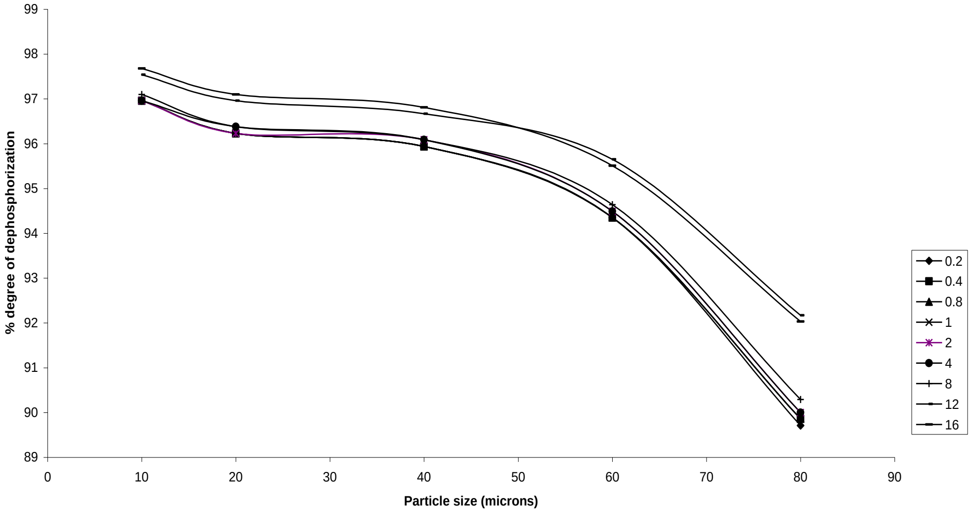


Fig-13. Effect of particle size on the %degree of dephosphorization for 20mins using HCl

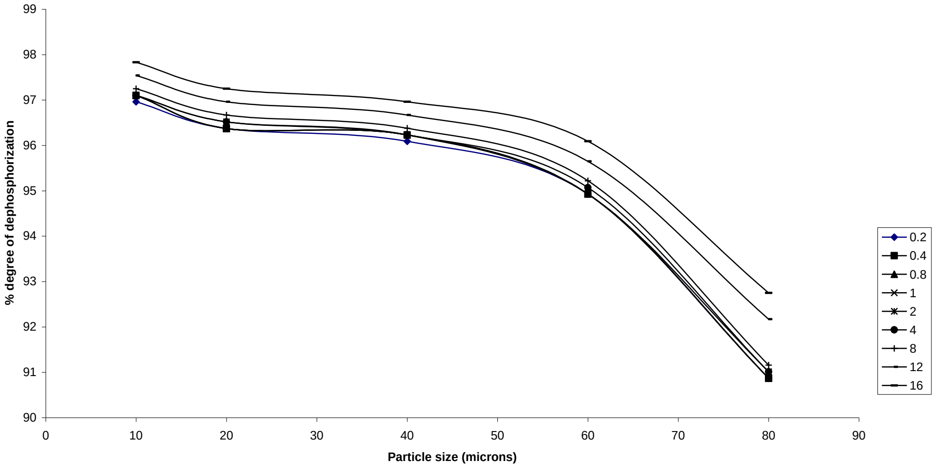


Fig-14. Effect of particle size on the %degree of dephosphorization for 30mins using HCl

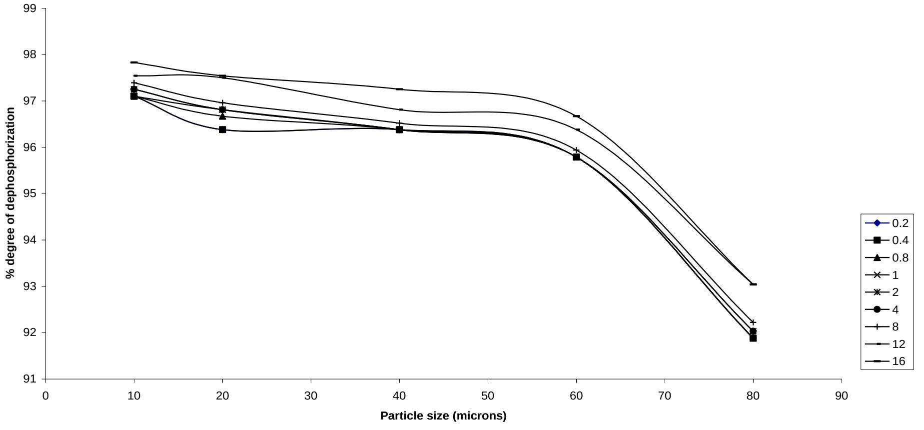


Fig-15. Effect of particle size on the %degree of dephosphorization for 60mins using HCl

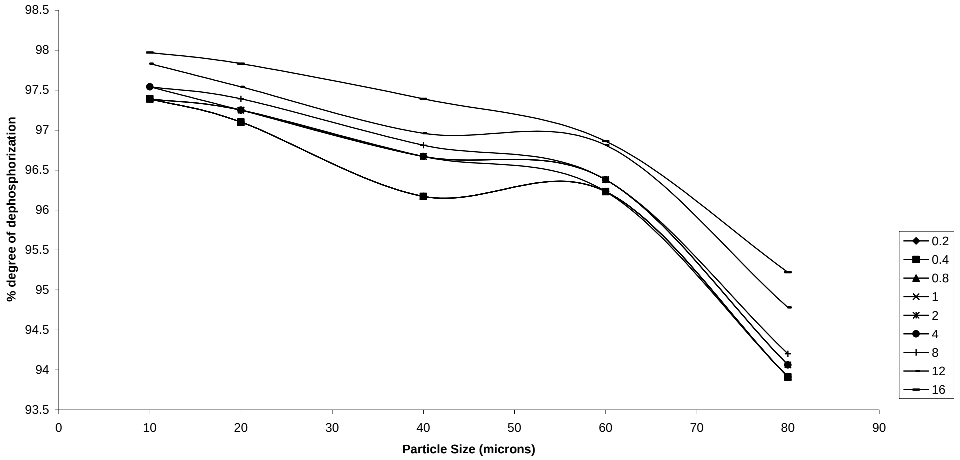
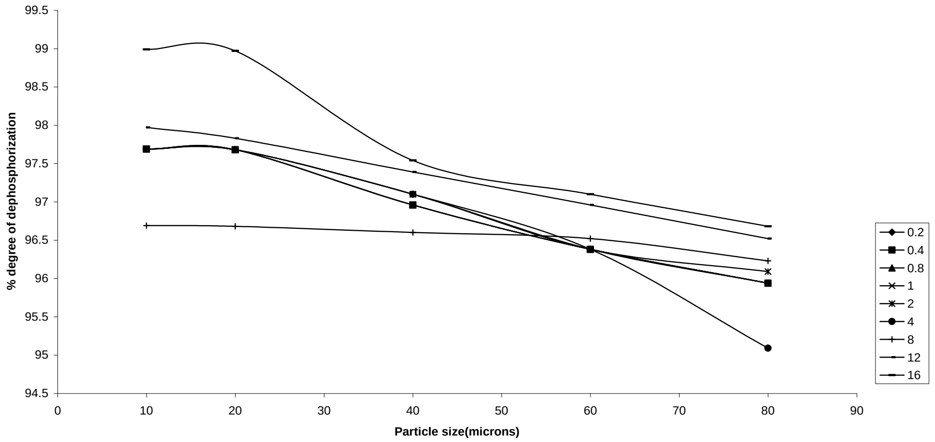


Fig-16. Effect of particle size on the %degree of dephosphorization for 120mins using HCl



In figure 11, the percentage degree of dephosphorization decreases slightly from particle size of 10microns to 60 microns. But from 60 microns there was a sharp decrease, implying that the surface area has decreased and consequently less surface area is available for reaction. For particle size of 10microns at 16M concentration, the percentage removal of phosphorus was 97.45% while for 80 microns the percentage degree dephosphorization was 91.16% for leaching time of 5 minutes.

It can be observed that from 10microns to 20 microns there was a slight decrease of phosphorus removal while from 20microns to 40 microns there was fairly constant removal of phosphorus. From 40 microns to 60 microns there was a significant decrease until 60 microns where the rate of removal became steep as shown in fig. 12. In figure 13, there was a sharp decrease in percentage removal of phosphorus from particle size of 60 microns to 80 microns. For the particle size of 80 microns, the percentage removal of phosphorus was 92.75% while for 10microns the percentage degree of removal was 97.83% for concentration of 16M at leaching times of 20minutes. Fig 14 shows that the percentage degree of dephosphorization for 10microns was 97.83% and that of 80microns was 93.04% for 16M concentration at leaching time of 30 minutes. Between 10microns and 60microns the rate of removal of phosphorus was fairly constant but from 60microns particle size, the rate of percentage degree of dephosphorization decreased because of decreased surface area due to increased particle size as shown in fig. 15. Figure 16 follows similar trends as the other figures.

Interaction effects and Surface Responses

The design matrix is shown in table 2.1. The parameters: x_1(time), x_2(concentration) and x_3 (particle size) were chosen as independent variables while percentage degree of dephosphorization is the output response. The analysis is based on how the percentage degree of dephosphorization is influenced by independent variables in order to study the combined effects of these factors. Experiments were performed at different combination of the parameters using statistically designed experiments. The determination of polynomial coefficients was followed by statistical analysis (G-test, F-test, T-test) to develop a model that is adequate, significant and homogeneous **[7]**

Fig-17. Percentage removal of phosphorus using HCl (Time and Concentration variables).

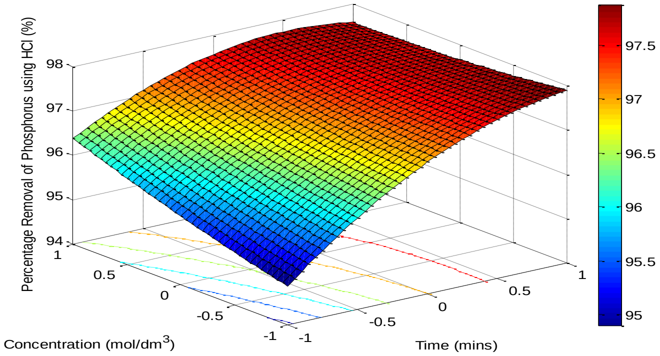


Fig-18. Percentage removal of phosphorus using HCl (time and particle variable)

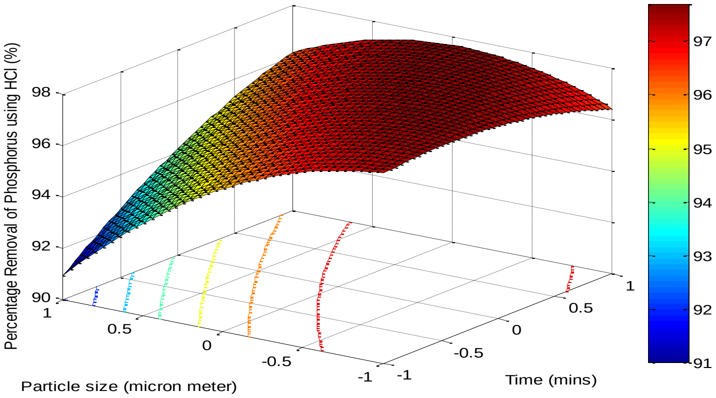
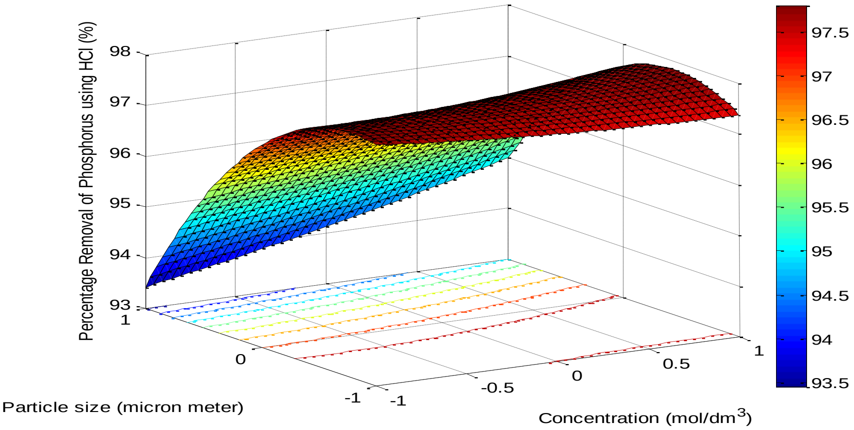


Fig-19. Percentage removal of phosphorus using HCl (particle size and concentration).



The corresponding interacting surface response plots are shown in figure 17 – 19 for dephosphorization. Figure 17 shows the interaction effect of concentration and time. This plot shows that time responded more to leaching than concentration. The optimum is indicated on the dark red colour. Figure 18 shows the surface response of the percentage removal of phosphorus for time and particle size as variables. The particle size responded more to dephosphorization than time. The surface response plots for percentage removal of phosphorus for particle size and concentration is depicted in figure 19. The particle size responded more to hydrometallurgical leaching than concentration. It is pertinent to observe that the value of output responses are linked to the intensity of the colour of surface plots. The plots provided avenue to observe the surface area of the curve within which the process can perform at optimal level based on the effects of the interaction of the variables under consideration .

Fig-20. Percentage loss of Iron using HCl (Time and Concentration as variables)

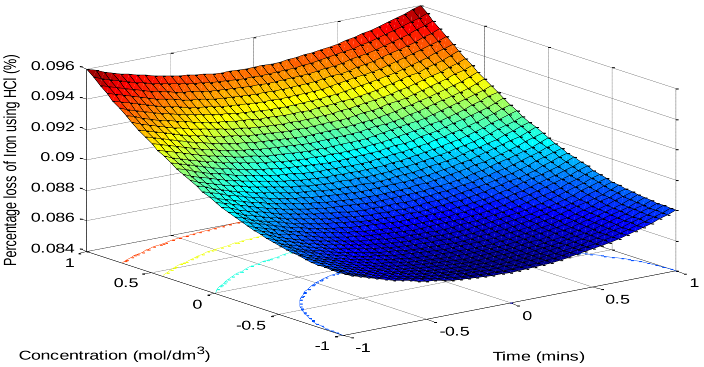
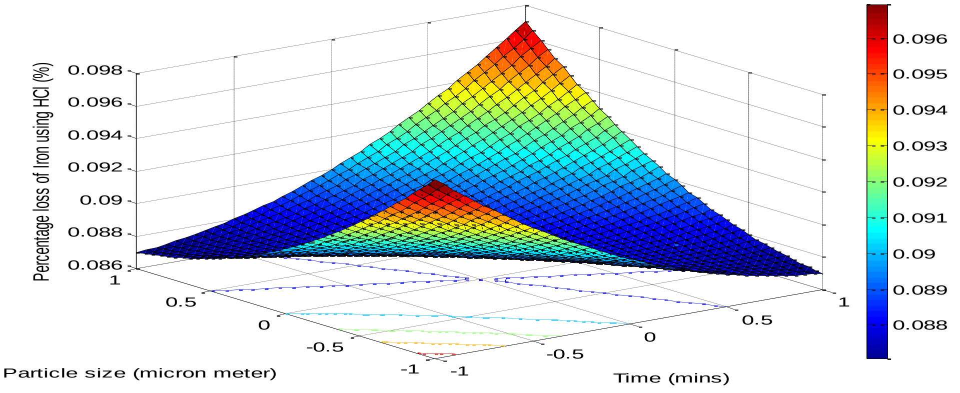


Figure 20 shows that concentration affected percentage iron loss more than time variable. The interaction affected the rate of beneficiation positively.

Fig-21. Percentage loss of Iron using HCl (Time and particle size as variables)



It is shown in figure 21 that the particle size has greater influence in loss of iron than time variable. The darkest blue colour indicates the position of optimum values. This interaction affected the degree of beneficiation positively

Fig-22. Percentage loss of Iron using HCl (Concentration and particle size as variables)

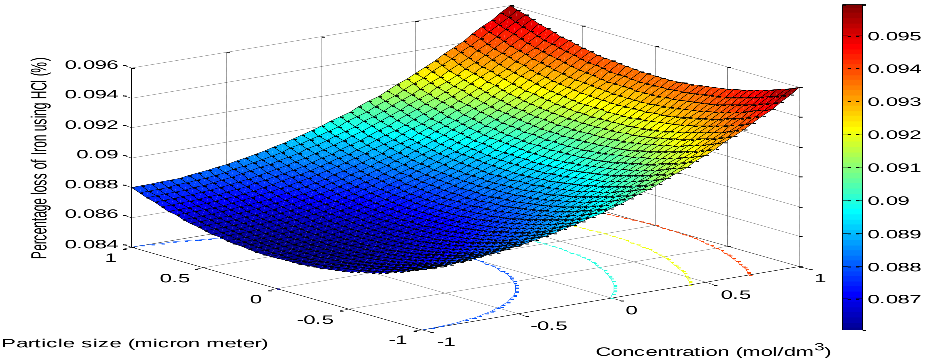


Figure 22 depicts that in the interaction concentration has greater effect in the loss of iron during dephosphorization. It is observed that the time and concentration affected the loss of iron in the dephosphorization of the iron ore.

CONCLUSION

The hydrometallurgical removal of phosphorus from Agbaja iron ore was successfully carried out using hydrochloric acid. The surface response plots show that the measured parameters interacted effectively and subsequently affected degree of dephosphorization positively. On optimization of the developed model equation 97.97% degree of dephosphorization was obtained.

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