

# Dephosphorization of Nigerian Agbaja Iron Ore by Hydrometallurgical Method

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**Abstract**—The research studied the dephosphorization of Nigerian Agbaja iron ore to enable its utilization in steel production. The ore contains 1.4 to 2.0% phosphorus which is beyond the acceptable limit of 0.08% for tradable steel and 0.045% for engineering applications. Beyond 0.045% phosphorus content, cold shortness is impacted to the steel. The digestion technique was adopted for the research using sulphuric acid ( $H_2SO_4$ ), hydrochloric acid (HCl) and citric acid ( $C_6H_8O_7$ ) separately or in various combinations.  $2^3$  full factorial design of experiment were used to determine the main factor effects, their interactions effects and optimization at different factor levels. The result showed that at levels of concentration of 1.0M, 20 minutes reaction time and 0.4mm particle size (d50), the degree of phosphorus removal was 96% for  $H_2SO_4$  and 94% for HCl with a reaction time of 30 minutes. The set target of 98% was reached with 1.0M acid concentration, 20 minutes reaction time and iron dissolution of 9.35mg/l using two acid mixtures while 99% dephosphorization was reached using 0.3M acid concentration, 50 minutes reaction time and 0.22 particle size using three mixtures.

**Index Terms**—dephosphorization, digestion technique, hydrometallurgy, iron ore.

## I. INTRODUCTION

Phosphorus removal remains a key area of research because of the detrimental effects on the mechanical properties of steel. If phosphorus content is not maintained within the acceptable limit, it will seriously degrade the quality of steel produced [1]. Phosphorus is primarily introduced to integrated steelmaking through blast furnace additions of iron ore, coke, alloys and recycled converter slag. R.K Upadhyay, S. Asokan and A.S Venkatesh [2] in their studies noted that phosphorus gets adsorbed in the iron ore by way of iron exchange mechanism in clay minerals and hydrated secondary iron oxide minerals. The conditions in iron making are unsuitable for the removal of phosphorus (because of the similarities of the standard free energies of formation of iron oxide and phosphorous pentoxide) which has subsequently led to the development of steelmaking practices to manage the removal of the impurity [3]. Nigeria is one of the richest countries of the world as far as mineral resources are concerned including iron ore [4]. The estimates of workable iron ore deposits stand in excess of 2.5billion tones and most of it belongs to hematite, hematite-

magnetite, hematite-goethite and siderite-goethite grades found around Itakpe in Kogi State Nigeria. Agbaja iron ore deposit is the largest in Nigeria, but its phosphorus content (1.4%-2.0%), low silicon modulus ( $SiO_2/Al_2O_3=0.89$ ) and fine texture constitute a major setback for its utilization in the blast furnace or direct reduction process [5]. Forsberg and Asolfesson; Cuj and Fang; Hang et al; He and Zhou[6-9] investigated dephosphorization with acid leaching. In their studies, the acid concentrations were very high and low phosphorus extraction were obtained. Jin Young-shi et al [10] investigated removal of phosphorus from Changde iron ore by chemical leaching using sodium hydroxide, sulphuric and citric acids separately and found sulphuric acid more effective among the three acids (91.61%). This investigation is aimed primarily at developing hydrometallurgical techniques for reducing phosphorus content in the largest proven Nigerian iron ore deposit with phosphorus content in the range of 1.4-2.0%. In this study, dephosphorization of Agbaja iron ore using three acids and in different combinations were investigated. The design of experiment for the valuation of interactive factorial effects on phosphorus removal was also investigated. It is noteworthy that high premium grade iron ores with reduced phosphorus content is fast depleting globally visa-avis intense industrial production activity. Therefore, there is an urgent need to develop new techniques of dephosphorizing high phosphorus iron ore deposits and particularly Agbaja iron ore deposit in Nigeria to a desirable limit.

## II. EXPERIMENTAL PROCEDURE

The bulk of Agbaja iron ore from Kogi state Nigeria, used in this study was obtained from the National Metallurgical Development Centre, Jos, Plateau State Nigeria. The chemical analysis was performed using atomic absorption spectrometer machine (AAS). Particle size analysis and weighing was done followed by digestion of Agbaja iron using hydrochloric acid (HCl), Sulphuric acid ( $H_2SO_4$ ) and citric acid ( $C_6H_8O_7$ ). From the particle size distribution carried out 0.4mm of Agbaja iron ore was selected where the phase composition most concentrated. 20g of 0.8mm and 0.4mm of untreated Agbaja ore were weighed out, washed with ordinary water and dried at 105°C. This served as control sample. At first, leaching with the acids were carried out separately and then simultaneously. 20g of Agbaja iron ore was weighed out from the 0.4mm particle size using a triple beam balance and the process was repeated for the eight different concentrations (1M, 0.8M, 0.7M, 0.6M, 0.5M, 0.4M, 0.3M and 0.2M) of leachants. Each concentration was kept in a beaker and 20ml of acid was admixed in the beaker containing the samples and stirred vigorously, each concentration was labelled according to the type of acid it contained, particle size and concentration of the acid on the single leaching process. The same procedure

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also held for double leaching except that each acid constituted 10ml of the 20ml of the solution. The pH of the solution was recorded with a pocket pH meter immediately after the introduction of the acid to the ore and after one hour for three hours interval. Temperature of 60°C was maintained for the samples for the last hour of incubation, using thermo electric heater. Filtration was done using filter papers labeled according to the type of acids, particle size and concentration of the acid. Ordinary water was used to rinse the ore at least three times to make sure the leachants were totally removed from the residue, the residues were dried in an oven at a temperature of 105°C for 20 minutes. The residues were reweighed and recorded and stored in dry containers for further analysis.

### III. RESULTS AND DISCUSSION

Atomic absorption spectroscopy (AAS) revealed the chemical composition of Agbaja iron ore as shown in Table 1. Since the phosphorus contained in the iron ore concentrate is in non-sulphidic phase (quartz, various carbonates and silicates) the contaminant may be solubilized by a process of complexation, using a range of inorganic or organic acids. This is in agreement with the findings of Rawlings 2005 [11]. It could be seen in the Table II that phosphorus retained in residue decreased as both molar concentration and particle size increased while reaction time decreased. The minimum amount of phosphorus in filtrate was achieved at concentration of 1.0M reaction time of 20mins and particle size of 0.4mm. This value corresponds to dephosphorization degree of 96%. Fig. 1 is a plot showing the relationship between Fe and P in filtrate (in percentage) and the molar concentrations of sulphuric acid. From the figure it could be seen that there was a strong interaction between the variables, it also shows that the  $R^2$  values for iron and phosphorus in filtrate as 0.941 and 0.969 showing the adequacy of the model. In Table III, the minimum amount of phosphorus 0.11% was reached at concentration of 1.0m reaction time of 30mins and particle size of about 0.4m. Also, iron loss during the leaching process reached 6.01mg/l at concentration of 0.2m, reaction time of 60 minutes and particle size of about 0.2mm. The pH change of the solution reached its minimum value at concentration of 1.0M, reaction time of 30minutes and particle size of about 0.4mm. Table IV shows the minimum value of phosphorus retained in filtrate is 0.08% (which corresponds to the degree of dephosphorization of 96%) is attained at 1.0M, 20mins of reaction time and 0.4mm particle size, while both minimum iron loss of 9.35mg/l and minimum pH change of 0.1 are reached at the same value of concentration, reaction time and particle size. Fig. 2 is also a plot showing the relationship between Fe and P in filtrate (in percentage) and the molar concentrations of the mixture of sulphuric and hydrochloric acids. From the figure it could be seen that there was a strong interaction between the variables, it also shows the  $R^2$  values for iron and phosphorus in filtrate as 0.941 and 0.969 showing the adequacy of the model. It could be deduced from Table V that minimum amount of phosphorus retained in residue is 0.02% which corresponds to dephosphorization degree of about 99% attained at 0.3M concentration, 50minutes reaction time, and 0.22 particle size respectively. Also, iron loss of minimum value of 10.31mg/l was reached at corresponding values of 0.7M concentration, 38 minutes and

0.35mm particle size range, while the pH change of solution reached its minimum at about 1.0M concentration, 20 minutes reaction time and 0.40m particle size range. In Table VI It could be seen that as the molar concentration of  $H_2SO_4$ , HCl and  $C_6H_8O_7$  increased, the percentage phosphorus in filtrate decreased while that of iron increased. Fig. 3 is a plot of Fe and P in filtrate and molar concentrations of the three acid mixtures showing a remarkable increase in Fe content with increase in molar concentrations of the three acid mixture. This indicates that there was a significant reduction of phosphorus in the filtrate, this strong interaction revealed that though the concentration was not up to 1.0M but has the most profound effect on the dephosphorization of Agbaja iron ore as the  $R^2$  value is 1.

### IV CONCLUSION

The hydrometallurgical option of dephosphorizing Agabja iron deposit to various levels has been carried out successfully.

- (1) Sulphuric acid at concentration of 1.0M and reaction time of 20mins and particle size range of 0.40 reduced phosphorus to 0.07% with a corresponding increase in Fe in the filtrate to 75.1%
- (2) Hydrochloric acid of 1.0M concentration and reaction time of 30minutes and particle size of 0.4mm range achieved a relatively poor 0.09% phosphorous reduction.
- (3) The use of two acid mixtures of  $H_2SO_4$  and HCl at concentrations of 1.0M and Reaction time of 20mins and particle size range of 0.4mm reduced the phosphorus in the ore to level of 0.04%. This could be ascribed to more cations present in solution as a result of high dissociation and ionization constant. The effect of using 3 acid mixtures, sulphuric, hydrochloric and citric acids achieved outstanding level of 0.02%P reduction at 0.3M concentration, 50 minutes reaction time and particle size range of 0.22mm.

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**Table I**  
MAJOR ELEMENTAL COMPOSITION OF AGBAJA IRON ORE DEPOSIT.

| Major Elements | Fe    | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | TiO <sub>2</sub> | MnO  | P <sub>2</sub> O <sub>5</sub> | S    |
|----------------|-------|------------------|--------------------------------|------|------|------------------|------|-------------------------------|------|
| Mass (%)       | 47.37 | 10.25            | 11.35                          | 0.88 | 0.22 | 0.31             | 0.15 | 1.60                          | 0.07 |

**Table II**  
EFFECT OF H<sub>2</sub>SO<sub>4</sub> ON DEPHOSPHORIZATION OF AGBAJA IRON ORE

| Conc. (m) | Reaction time (min) | Particle Size (mm) | P in Filtrate (%) | Fe in Filtrate (%) |
|-----------|---------------------|--------------------|-------------------|--------------------|
| X1        | X2                  | X3                 | Y1                | Y2                 |
| 0.2       | 60                  | 0.20               | 0.77              | 38.6               |
| 0.3       | 50                  | 0.22               | 0.66              | 43.4               |
| 0.4       | 55                  | 0.24               | 0.55              | 48.1               |
| 0.5       | 40                  | 0.30               | 0.44              | 49.1               |
| 0.6       | 33                  | 0.33               | 0.33              | 52.4               |
| 0.7       | 30                  | 0.36               | 0.22              | 53.4               |
| 0.8       | 25                  | 0.38               | 0.11              | 67.2               |
| 1.0       | 20                  | 0.40               | 0.07              | 71.5               |

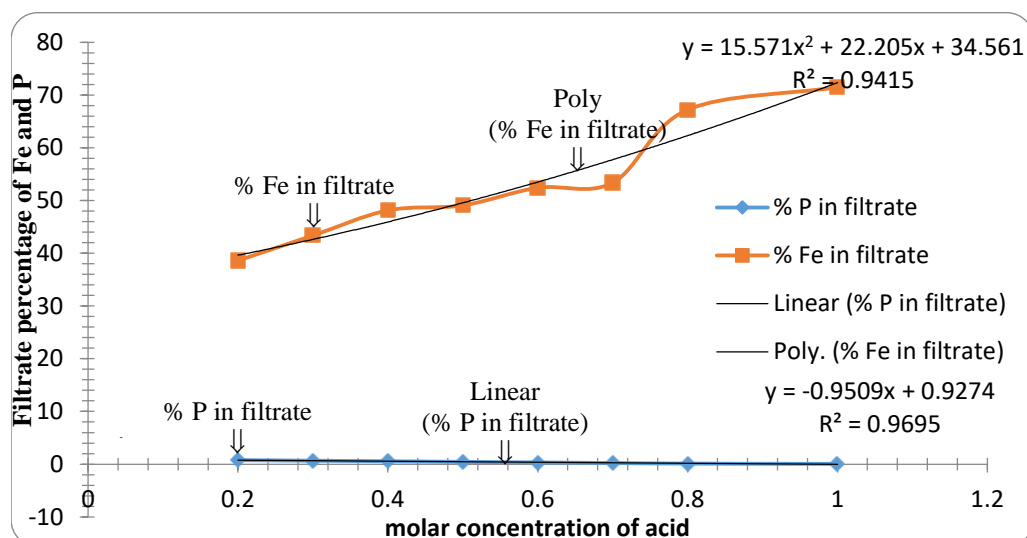


Fig.1. Dependence of filtrate percentage on molar concentration of sulphuric acid.

**Table III**  
EFFECT OF HCL ON DEPHOSPHORIZATION

| Conc. (M) | Reaction time (Min) | Particle Size (mm) | P in Filtrate (%) | Fe in Filtrate (%) | pH Change of Solution |
|-----------|---------------------|--------------------|-------------------|--------------------|-----------------------|
| $X_1$     | $X_2$               | $X_3$              | $Y_1$             | $Y_2$              | $Y_3$                 |
| 0.2       | 60                  | 0.20               | 0.88              | 29.10              | 0.6                   |
| 0.3       | 50                  | 0.22               | 0.77              | 33.36              | 0.6                   |
| 0.4       | 45                  | 0.24               | 0.66              | 38.12              | 0.5                   |
| 0.5       | 40                  | 0.30               | 0.55              | 43.36              | 0.4                   |
| 0.6       | 35                  | 0.33               | 0.44              | 45.26              | 0.4                   |
| 0.7       | 33                  | 0.36               | 0.33              | 46.70              | 0.3                   |
| 0.8       | 32                  | 0.38               | 0.22              | 48.12              | 0.2                   |
| 1.0       | 30                  | 0.40               | 0.11              | 53.84              | 0.1                   |

**Table IV**  
EFFECT OF TWO ACID MIXTURES HCL AND H<sub>2</sub>SO<sub>4</sub> ON DEPHOSPHORIZATION

| Conc. (M) | Reaction time (Min) | Particle Size (mm) | P in Filtrate (%) | Fe in Filtrate (%) | pH Change of Solution |
|-----------|---------------------|--------------------|-------------------|--------------------|-----------------------|
| $X_1$     | $X_2$               | $X_3$              | $Y_1$             | $Y_2$              | $Y_3$                 |
| 0.2       | 60                  | 0.20               | 0.66              | 36.12              | 0.4                   |
| 0.3       | 50                  | 0.22               | 0.01              | 43.36              | 0.4                   |
| 0.4       | 40                  | 0.24               | 0.55              | 45.26              | 0.3                   |
| 0.5       | 35                  | 0.30               | 0.44              | 46.70              | 0.3                   |
| 0.6       | 30                  | 0.33               | 0.33              | 48.12              | 0.2                   |
| 0.7       | 28                  | 0.35               | 0.22              | 51.46              | 0.2                   |
| 0.8       | 25                  | 0.38               | 0.09              | 59.56              | 0.1                   |
| 1.0       | 20                  | 0.40               | 0.08              | 71.48              | 0.1                   |

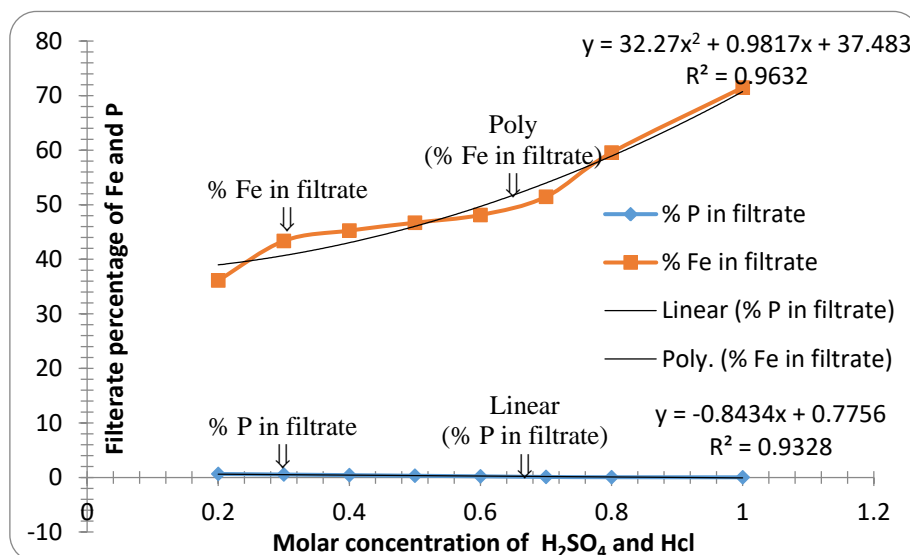


Fig. 2. Dependence of filtrate percentage on molar concentration of two acid mixtures of  $H_2SO_4$  and  $HCl$

Table V

EFFECT OF THREE ACID MIXTURES ( $H_2SO_4$ ,  $HCl$  AND  $C_6H_8O_7$ ) ON DEPHOSPHORIZATION

| Conc. (M) | Reaction time (Min) | Particle Size (mm) | P in Filtrate (%) | Fe in Filtrate (%) | pH Change of Solution |
|-----------|---------------------|--------------------|-------------------|--------------------|-----------------------|
| $X_1$     | $X_2$               | $X_3$              | $Y_1$             | $Y_2$              | $Y_3$                 |
| 0.2       | 60                  | 0.20               | 0.66              | 57.2               | 0.6                   |
| 0.3       | 50                  | 0.22               | 0.02              | 72.4               | 0.5                   |
| 0.4       | 40                  | 0.24               | 0.55              | 71.5               | 0.5                   |
| 0.5       | 35                  | 0.30               | 0.44              | 90.6               | 0.4                   |
| 0.6       | 30                  | 0.33               | 0.33              | 52.4               | 0.3                   |
| 0.7       | 38                  | 0.35               | 0.22              | 50.6               | 0.3                   |
| 0.8       | 25                  | 0.38               | 0.09              | 51.5               | 0.2                   |
| 1.0       | 20                  | 0.40               | 0.08              | 71.5               | 0.1                   |

Table VI

OPTIMUM DEPHOSPHORIZATION MODEL DATA OF AGBAJA IRON ORE USING 3 ACID ON MIXTURES

| Molar Conc. Of Acid (m) | % Phosphorus in Filtrate | % Iron in Filtrate |
|-------------------------|--------------------------|--------------------|
| 0.2                     | 0.66                     | 57.2               |
| 0.3                     | 0.02                     | 72.4               |
| 0.4                     | 0.55                     | 71.5               |
| 0.5                     | 0.44                     | 90.6               |

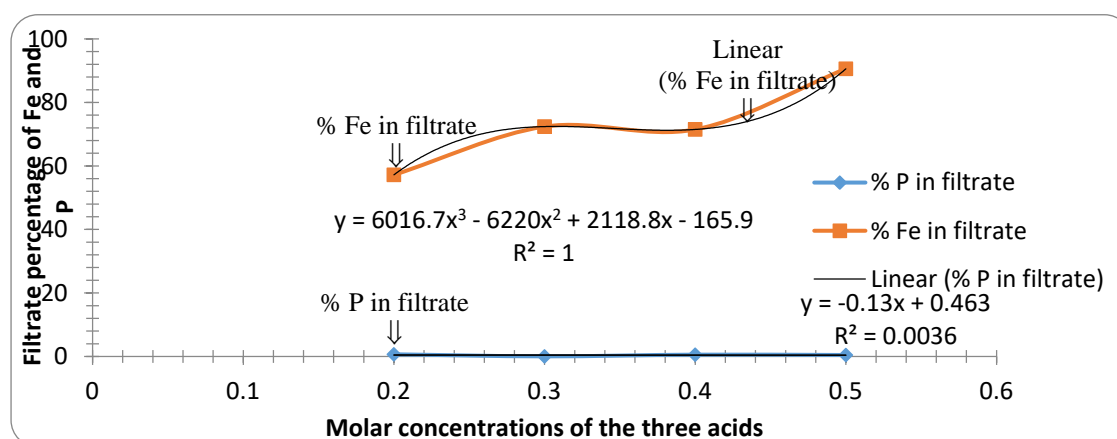


Fig. 3. Dependence of filtrate percentage on molar concentrate using 3 acid in mixtures.