# **Predictability of Removed Phosphorus Concentration during** Microbial Leaching of Iron Oxide Ore Using Acidithiobacillus **Ferrooxidans (ATF)**

E. M. Ameh<sup>1</sup>, A. O. Agbo<sup>1</sup>, S. E. Ede<sup>1</sup>, C. A. Mgbachi<sup>2</sup>, S. I. Neife<sup>3</sup>, I. D. Adiele<sup>4</sup> and E. E. Nnuka<sup>5</sup>

<sup>1</sup>Department of Metallurgical and Materials Engineering, Enugu State University of Science & Technology, Enugu, Nigeria

<sup>2</sup>Department of Computer Science Engineering, Enugu State University of Science & Technology, Enugu, Nigeria

<sup>3</sup>Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka, Nigeria

<sup>4</sup>Projects Development Institute (PRODA), Enugu, Nigeria

<sup>5</sup>Department of Metallurgical and Materials Engineering, Nnamdi Azikiwe University, Awka, Nigeria ebere.monica@vahoo.com

Abstract: Predictability of removed phosphorus concentration was carried out based on multi-factorial influence of pH, resident time and as-beneficiated phosphorus content of the iron ore during microbial leaching with Acidithiobacillus Ferrooxidans. The model was expressed as;  $P_R = 0.00429^3 - 0.0718 \theta^2 + 0.3297 \theta - 0.001 \theta + 0.01 \gamma - 0.0903$ 

The validity of the multi-factorial model was found to be rooted on the expression  $P_R + 0.001 \text{f} - 0.01 \gamma +$  $0.0903 = 0.00429^3 - 0.07189^2 + 0.3297$  9 where both sides of the expression are correspondingly approximately equal. Statistical analysis of removed phosphorus concentration for each value of the bioleaching solution pH as obtained from experiment and derived model-predicted results show standard errors of 0.1031 and 0.1010% respectively. Furthermore, removed phosphorus concentration per unit solution pH as obtained from experiment and derived model-predicted results were 0.005 and 0.006 % respectively. The maximum deviation of model-predicted removed phosphorus concentration (from experimental result) was less 8%. This translates into a derived model confidence level of above 92%.

Keywords: Analysis, Phosphorus Removal, Acidithiobacillus Ferrooxidans, Agbaja Iron Ore.

#### I. Introduction

The unavoidable need for intensive reduction of phosphorus present in iron ore as a preventive measure against abrupt steel structural failures has necessitated a lot of researches. The objectives of these researches are geared towards actualization of the production of iron and steel materials that can withstand high stress and strain without possibly failing in service due to brittleness.

Researches [1-6] have been carried out to remove phosphorus from steel during steel making. In all these works, low treatment temperature and high oxygen activity were revealed as the only essential and unavoidable process conditions which can enhance the rate of dephosphorization. Decomposition of CaCO<sub>3</sub> and high activity of produced CaO; a slag forming material is required for enhancement of the dephosphorization process with the phosphorus forming part of the slag.

It has been reported [7] that the removal of phosphorus from iron can be achieved only by oxidation during steel making, under a basic slag.

Past studies [8] have shown that phosphorus can be removed through leaching of the iron ore in oxalic acid solution. The work culminated in a model formulation for predicting the concentration of phosphorus removed during the leaching process. The model is expressed as;

$$P = 150.5/\mu\alpha \tag{1}$$

It was found to predict the removed phosphorus concentration, with utmost dependence on the final pH of the leaching solution and weight input of the iron oxide ore. The model indicates that the concentration of phosphorus removed is inversely proportional to the product of the weight input of the iron oxide ore and the final pH of the leaching solution. Process conditions considered during the formulation of the model [8] include: leaching temperature of 25°C, initial solution pH 5.5 and average ore grain size; 150µm).

Research [9] has revealed successful evaluations of phosphorus removal using biological processes based on the use of several types of fungi and bacteria. Recently, Aspergillus niger and their cultural filtrates were used for removing phosphorus from Agbaja (Nigeria) iron oxide ore. The results of this work [9] show

that phosphorus removal efficiencies at the end of the 49 days of the leaching process are 81, 63 and 68% for 5, 100 and 250 mesh grain sizes respectively.

The aim of this work is to predict the concentration of phosphorus removed based on multi-factorial influence of initial bioleaching solution pH during microbial leaching of iron oxide ore using acidithiobacillus ferrooxidans. The essence of this work is to ascertain the level of dephosphorization achievable at different initial bioleaching solution pH where all other input process parameters are kept constant.

## II. Materials And Methods

Agbaja (Nigeria) iron ore concentrate used for this work was obtained from Nigeria Metallurgical Development Centre (NMDC) Jos. The concentrate was dried in air (under atmospheric condition) and used in the as-received condition. Five samples of constant weight quantity of the dried iron ore concentrate of particle size 0.25 mesh size were each added to a culture of ATF in a conical flask and the mixtures (each with pH 1.0) allowed to react for 10 weeks at a temperature of  $25^{\circ}$ C after which the mixtures were filtered and the concentration of removed phosphorus determined using atomic absorption spectrometer (AAS). The average of the removed phosphorus concentration determined in each experiment set was taken as the precise result. The experiment was repeated with different initial bioleaching solution pHs; 2, 4, 7 and 9 and the corresponding phosphorus removal also determined using AAS. Details of the experimental procedures and process conditions prevailing during the biooxidation process are as reported in the previous work [10].

### **Model Formulation**

Experimental data obtained from the highlighted research work were used for the model derivation. Computational analysis of these data shown in Table 1, gave rise to Table 3 which indicate that;

$$P_{R} + S_{e} \vartheta - K\gamma + S \approx N\vartheta^{3} - N_{e} \vartheta^{2} + K_{e} \vartheta$$
<sup>(2)</sup>

Introducing the values of S<sub>e</sub>, K, S, N, N<sub>e</sub>, and K<sub>e</sub> into equation (2)

$$P_{\rm R} + 0.001 \$ - 0.01 \gamma + 0.0903 = 0.0042 \$^3 - 0.0718 \$^2 + 0.3297 \$$$
(3)

$$P_{\rm R} = 0.00429^3 - 0.07189^2 + 0.32979 - 0.0018 + 0.01\gamma - 0.0903$$
(4)

Where

 $P_R$  = Conc. of removed phosphorus (%)

 $(\gamma)$  = As- beneficiated phosphorus content of the ore (%)

 $(\mathcal{X}) =$ Leaching time (weeks)

- $(\vartheta)$  = Initial bioleaching solution pH
- $S_e = 0.001$ , K = 0.01, S = 0.0903, N = 0.0042,  $N_e = 0.0718$  and  $K_e = 0.3297$  are equalizing constant (determined using C-NIKBRAN [11])

Table 1: Variation of removed phosphorus concentration with initial bioleaching solution pH [10]

(γ)	pH	$P_{R}(\%)$
0.9	1	0.16
0.9	2	0.34
0.9	4	0.33
0.9	7	0.15
0.9	9	0.12

### **Boundary and Initial Condition**

Consider iron ore (in a furnace) mixed with a culture of ATF. The atmosphere was not contaminated i.e (free of unwanted gases and dusts). Initially, atmospheric levels of oxygen are assumed just before the reaction between the ore and the microbes. Mass of iron oxide ore: (50g), particle size: 0.25 mesh size, treatment time: 10 weeks, constant treatment temperature:  $25^{\circ}$ C, range of initial bioleaching solution pH used; 1.0-9.0.

The boundary conditions are: oxygen atmosphere at the top and bottom of the ore particles interacting with the microbes. At the bottom of the particles, a zero gradient for the gas scalar are assumed and also for the gas phase at the top of the particles. The reduced iron is stationary. The sides of the particles are taken to be symmetries.

# III. Results And Discussions

The result of the chemical analysis carried out on the beneficiated iron ore concentrate is presented in Table 2. The table shows that the percentage of phosphorus present in the as-beneficiated ore is 0.9%.

Table 2: Result of chemical analysis of iron ore used [10]						
Element/Compound	Fe	Р	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>		
Unit (%)			5.30	11.0		
	78.6	0.90				

#### **Model Validation**

The validity of the model is strongly rooted in equation (3) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 3 also agrees with equation (3) following the values of  $P_R + 0.001$  s - 0.01 $\gamma$  + 0.0903 and 0.0042 $\vartheta^3$  - 0.0718  $\vartheta^2$  + 0.3297  $\vartheta$  evaluated from the experimental results in Table 1.

Table 3: Variation of  $P_{R}$  + 0.001§ - 0.01 $\gamma$  + 0.0903 with 0.0042 $\vartheta$ <sup>3</sup> - 0.0718 $\vartheta$ <sup>2</sup> + 0.3297 $\vartheta$ 

$P_R + 0.001$ s - 0.01 $\gamma$ + 0.0903	$0.0042\vartheta^3 - 0.0718\vartheta^2 + 0.3297\vartheta$
0.2513	0.2621
0.4313	0.4058
0.4213	0.4388
0.2413	0.2303
0.2113	0.2133

Furthermore, the derived model was validated by comparing the removed phosphorus concentration predicted by the model and that obtained from the experiment. This was done using various evaluative techniques such as computational, statistical, graphical and deviational analysis.

#### **Computational Analysis**

Computational analysis of the experimental and model-predicted removed phosphorus concentration was carried out to ascertain the degree of validity of the derived model. This was done by comparing phosphorus removal per unit initial bioleaching solution pH valuated from model-predicted results with those from actual experimental results

*Removed phosphorus concentration per unit initial bioleaching solution pH*  $P_R^P(\%)$  was calculated from the equation;

 $P_{R}^{P} = P_{R} / \vartheta$ (5)

Therefore, a plot of the concentration of phosphorus removed against initial bioleaching solution pH as in Fig. 1 using experimental results in Table 1, gives a slope, S at points (1, 0.16) and (9, 0.12) following their substitution into the mathematical expression;

$P_R^P = \Delta P_R / \Delta \vartheta$	(6)
Equation (6) is detailed as	
$\mathbf{P}_{\mathbf{R}}^{P} = \mathbf{P}_{\mathbf{R}2} - \mathbf{P}_{\mathbf{R}1} / \vartheta_2 - \vartheta_1$	(7)

Where

 $\Delta P_R$  = Change in removed phosphorus concentrations of  $P_{R2}$ ,  $P_{R1}$  at two values of the initial bioleaching solution pH  $\vartheta_2$ ,  $\vartheta_1$ . Considering the points (1, 0.16) and (9, 0.12) for ( $\vartheta_1$ ,  $P_{R1}$ ) and ( $\vartheta_2$ ,  $P_{R2}$ ) respectively, and substituting them into equation (7), gives the slope as - 0.005 % mm<sup>-1</sup> which is the removed phosphorus concentration per unit initial bioleaching solution pH during the actual leaching process.



Fig. 1: Coefficient of determination between concentration of removed phosphorus and initial bioleaching solution pH as obtained from the experiment [10]

Similarly a plot of the concentration of removed phosphorus against initial bioleaching solution pH (as in Fig. 2) using derived model-predicted results gives a slope: - 0.006 % on substituting the points (1, 0.1708) and (9, 0.122) for ( $\vartheta_1$ ,  $P_{R1}$ ) and ( $\vartheta_2$ ,  $P_{R2}$ ) respectively into equation (7). This is the model-predicted removed phosphorus concentration per unit initial bioleaching solution pH.

It is very pertinent to state that the actual removed phosphorus concentration per unit initial bioleaching solution pH (as obtained from experiment and derived model) was just the magnitude of the signed value. The associated sign preceding these values signifies that the associated slope tilted to negative plane. Based on the foregoing, removed phosphorus concentration per unit initial bioleaching solution pH as obtained from experiment and derived model were 0.005 and 0.006 % respectively.



Fig. 2: Coefficient of determination between concentration of removed phosphorus and initial bioleaching solution pH as obtained from derived model

A comparison of this set of values for removed phosphorus concentration (per unit initial bioleaching solution pH ) also shows proximate agreement and a high degree of validity of the derived model.

# **Statistical Analysis**

The standard errors (STEYX) in predicting the removed phosphorus concentration (using results from experiment and derived model) for each value of the initial bioleaching solution pH are 0.1031 and 0.1010% respectively. The standard error was evaluated using Microsoft Excel version 2003.

Considering the coefficient of determination  $R^2$  from Figs. 1 and 2, the correlations between removed phosphorus concentration and initial bioleaching solution pH as obtained from experiment and derived model predicted results, was calculated using the equation;

$$\mathbf{R} = \sqrt{\mathbf{R}^2} \tag{8}$$

The evaluations show correlations 0.9867 and 1.0000 respectively. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from actual experiment.

# **Graphical Analysis**

Comparative graphical analysis of Fig. 3 shows very close alignment of the curves from modelpredicted removed phosphorus concentration (MoD) and that of the experiment (ExD). The degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted phosphorus removed concentration.



Fig. 3: Comparison of the concentrations of removed phosphorus (relative to initial bioleaching solution pH ) as obtained from experiment [10] and derived model

# **Deviational Analysis**

Analysis of removed phosphorus concentrations from the experiment and derived model revealed deviations on the part of the model-predicted values relative to values obtained from the experiment. This is attributed to the fact that the surface properties of the iron ore and the physiochemical interactions between the ore and the microbes (ATF) which were found to have played vital roles during the process were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted removed phosphorus concentration to those of the corresponding experimental values.

Deviation (Dn) of model-predicted removed phosphorus concentration from that of the experiment is given by

$$Dn = \left( \frac{P_V - E_V}{E_V} \right) x \quad 100$$

Cr

Where

Pv = Removed phosphorus concentration as predicted by derived model Ev = Removed phosphorus concentration as obtained from experiment

Correction factor (Cr) is the negative of the deviation i.e

(10)

(9)

(11)

Therefore

$$Cr = - \left( \frac{P_V - E_V}{E_V} \right) \times 100$$

Introduction of the corresponding values of Cr from equation (11) into the derived model gives exactly the removed phosphorus concentration as obtained from experiment.



Fig. 4: Variation of model-predicted removed phosphorus concentration with associated deviation from experimental results (relative to initial bioleaching solution pH)

Fig. 4 shows that the maximum deviation of the model-predicted removed phosphorus concentration from the corresponding experimental values is less than 8%. The figure shows that the least and highest magnitudes of deviation of the model-predicted removed phosphorus concentration (from the corresponding experimental values) are + 1.67 and - 7.5 % which corresponds to removed phosphorus concentrations: 0.122 and 0.3145 %, as well as initial bioleaching solution pH: 9 and 2 respectively.



Fig. 5: Variation of model-predicted removed phosphorus concentration with associated correction factor (relative to initial bioleaching solution pH)

Comparative analysis of Figs. 4 and 5 indicates that the orientation of the curve in Fig. 5 is opposite that of the deviation of model-predicted removed phosphorus concentration (Fig. 4). This is because correction factor is the negative of the deviation as shown in equations (10) and (11). It is believed that the correction factor takes care of the effects of surface properties of the iron ore and the physiochemical interactions between the iron ore and microbes which have played vital roles during the process, but were not considered during the model formulation. Fig. 5 indicates that the least and highest magnitudes of correction factor to the model-predicted removed phosphorus concentration are -1.67 and +7.5 % which corresponds to removed phosphorus concentrations: 0.122 and 0.3145 %, as well as initial bioleaching solution pH: 9 and 2 respectively.

It is important to state that the deviation of model predicted results from that of the experiment is just the magnitude of the value. The associated sign preceding the value signifies that the deviation is a deficit (negative sign) or surplus (positive sign).

# IV. Conclusions

Predictability of removed phosphorus concentration was carried out based on multi-factorial influence of pH, resident time and as-beneficiated phosphorus content of the iron ore during microbial leaching with Acidithiobacillus Ferrooxidans. The validity of the multi-factorial model was rooted on the expression  $P_R + 0.001$  -  $0.01\gamma + 0.0903 = 0.00429^3 - 0.07189^2 + 0.32979$  where both sides of the expression are correspondingly approximately equal. Statistical analysis of removed phosphorus concentration for each value of the bioleaching solution pH as obtained from experiment and derived model-predicted results show standard errors of 0.1031 and 0.1010% respectively. Furthermore, removed phosphorus concentration per unit solution pH as obtained from experiment and derived model-predicted results were 0.005 and 0.006 % respectively. The maximum deviation of model-predicted removed phosphorus concentration (from experimental result) was less 8%. This translates into a derived model confidence level of above 92%.

#### References

- [1] Turkdogan, E.T., Pearson, J. (1953) J. Iron and Steel Inst., 221, pp. 393-401.
- [2] Decker, A., Sevrin, R., Scimar, R. (1962) Open Hearth Proceedings, 45, pp. 421-456.
- [3] Duke, D. A., Ramstad, H. F., Meyer, H. W. (1962) Open Hearth Proceedings, vol 45, pp.81-98.
- [4] Kootz, T., Neuhaus, H. (1961) Stahl u. Eisen, 81, pp. 1810-1815.
- [5] Kootz, K., Behrens, K., Maas, H., Baumgarten, P. (1965) Stahl u. Eisen, 85, pp 857-865.
- [6] Edneral, F. P. (1979) Electrometallurgy of Steel and Ferro-alloys, MIR Publisher, 5th edition Moscow. pp 30-239.
- [7] Zea, Y. K. (1945) J. Iron and Steel Inst., 151, pp. 459-504.
- [8] Nwoye, C. I., Agu, P. C., Mark, U., Ikele, U. S., Mbuka, I. E., and Anyakwo, C. N. (2008) Model for Predicting Phosphorus Removal in Relation to Weight of Iron Oxide Ore and pH during Leaching with Oxalic Acid. Inter. J. Nat. Appl. Sc., 4(3): 292-298.
   [9] A. L. C. N. (2008) Physical Acid. Inter. J. Nat. Appl. Sc., 4(3): 292-298.

[9] Anyakwo, C. N., and Obot, O.W., (2008). Phosphorus Removal from Nigeria's Agbaja Iron Ore by Aspergillus niger, Inter. Res. J. Eng. Sc. Tech. 5(1):54-58.

- [10] Ameh, E. M. (2013). Dephosphorization of Agbaja Iron Ore By Sintering And Bioleaching Processes. Ph.D Thesis, Nnamdi Azikiwe University Awka, Anambra State, Nigeria.
- [11] Nwoye, C. I. (2008). C-NIKBRAN; Data Analytical Memory.