Open System Analysis of Bioextracted Iron during Leaching of Iron Oxide Ore using Acidithiobacillus Ferroxidans

E. M. Ameh¹, I. D. Adiele², C. A. Mgbachi³, S. I. Neife⁴, S. E. Ede¹, A. O. Agbo¹ and E. E. Nnuka⁵

¹Department of Metallurgical and Materials Engineering, Enugu State University of Science & Technology, Enugu, Nigeria
²Projects Development Institute (PRODA), Enugu, Nigeria
³Department of Computer Science Engineering, Enugu State University of Science & Technology, Enugu, Nigeria
⁴Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka, Nigeria
⁵Department of Metallurgical and Materials Engineering, Nnamdi Azikiwe University, Awka, Nigeria

Abstract: This paper presents an open system analysis of bioextracted iron during leaching of iron oxide ore using acidithiobacillus ferroxidans. The analysis showed prediction of the concentration of bioextracted iron at varying initial bioleaching solution pH and as-beneficiated Fe content of the ore. An empirical model was derived, validated and used as a tool for the analysis. The validity of the polynomial model expressed as:

\[ \zeta = 0.0077\varphi - 0.1618\varphi^2 + 0.9345 + 0.0002\varphi + 0.0931 \]

was found to be rooted on the core expression \[ \zeta = 0.0002\varphi - 0.0931 = 0.0077\varphi - 0.1618\varphi^2 + 0.9345 \] where both sides of the expression are correspondingly approximately equal. Statistical analysis of the extracted iron concentration as obtained from experiment and derived model for each value of the initial bioleaching solution pH used shows standard errors of 0.3917 and 0.3780 respectively. Extracted iron concentrations per unit initial bioleaching solution pH as obtained from experiment and derived model are 0.0917 and 0.0784 %. Deviation analysis indicates that the maximum deviation of the model-predicted iron extraction (from experimental results) was less than 11%, implying a confidence level above 89%.

Keywords: Open system Analysis, Iron Bioextraction, Iron Ore Leaching, Acidithiobacillus Ferroxidans.

I. Introduction

Extraction of metal from its ore through hydrometallurgy has been widely recognized and accepted to be significantly environmentally friendly. Intensive researches are unavoidably necessary to review this potentiality and also explore ways of improving on hydrometallurgical techniques that would ensure optimum results.

The dissolution of iron oxide is believed to take place via a photo-electro chemical reduction process, involving a complicated mechanism of charge transfer between the predominant oxalate species, namely ferric oxalate \( \text{Fe}(	ext{C}_2	ext{O}_4)^{3-} \), ferrous oxalate \( \text{Fe}(	ext{C}_2	ext{O}_4)^{2-} \) acting also as an auto catalyst, and the oxalate ligand on the iron oxide surface [1]. The dissolution of iron oxides in oxalic acid was found to be very slow at temperatures within the range 25-60°C, but its rate increases rapidly above 90°C [2]. The dissolution rate also increases with increasing oxalate concentration at the constant pH values set within the optimum range of pH 2.5-3.0. At this optimum pH, the dissolution of fine pure haematite \( \text{Fe}_2\text{O}_3 \) (105-140μm) follows a diffusion-controlled shrinking core model [2]. Taxiarchour et al [3] reported that it took close to 40h to dissolve 80% of pure haematite slurry (97% purity, 0.022% w/v or 0.21% g/L \( \text{Fe}_2\text{O}_3 \)) at pH 1. He stated that even at 900°C, it required close to 10h to achieve 95% dissolution of iron of the slurry at pH 1. They also dissolved iron using 0.1-0.5M oxalic acid (pH1.5) to dissolve iron from a 20% w/v slurry (83% of particle size in the range 0.18-0.35mm, containing 0.029% \( \text{Fe}_2\text{O}_3 \)). The iron oxide concentration in the leach is equivalent to 0.058g/L Fe2O3.

The speciation of Fe(III) oxalate and Fe(II) oxalate has been found [4] to be governed by pH and total oxalate concentration. For a having pH \( \geq 2.5 \) and an oxalate concentration higher than 0.1M, the predominant Fe(III) complex ion existing is \( \text{Fe}_6\text{C}_6\text{O}_{14}^{6+} \). At these conditions, (pH \( > 2.5 \) and an oxalate concentration higher than 0.1M) the predominant Fe(II) complex species is \( \text{Fe}_4\text{C}_4\text{O}_{12}^{2+} \).

Lee et al. [5] reported that the leaching of 3g/L pure haematite (98.2% purity, 105-140μm size range) using 0.048-0.48M oxalic acid at 80-1000°C passed through a maximum peak at pH 2.5. Dissolution of haematite was found [5] to be slower than magnetite \( \text{Fe}_3\text{O}_4 \) and other hydrated iron oxide such as goethite \( \alpha\text{-FeOOH} \), lapidochrosite \( \gamma\text{-FeOOH} \) and iron hydroxide \( \text{Fe(OH)}_3 \).

The presence of \( \text{Fe}^{3+} \) was found to significantly enhance the leaching of iron extraction from silica sand at a temperature even as low as 25°C [3]. Ferrous oxalate however is oxidized quickly by air during the dissolution and in general an induction period of a few hours was observed to exist unless a strong acidic
environment (<pH 1) or an inert atmosphere is maintained. Maintaining the high level of ferrous oxalate in the leach liquor using an inert gas, was found [3] to enhance the reaction kinetics. Intensive researches have been conducted on the dissolution of goethite in several inorganic acids belonging to the families of the carboxylic and diphosphoric acids in the presence of reducing agents. Analysis of results generated from these extraction processes has been carried using various derived models which functioned as tools. A model for the evaluation of the concentrations of dissolved iron (relative to the final solution pH and temperature) during leaching of iron oxide ore in sulphuric acid solution has been derived [6]. The model

\[
\%Fe = 0.35(\alpha/T)^3
\]  

(1)

Depended on the values of the final pH and temperature of the leaching solution which varied with leaching time. The positive and negative deviations of the model-predicting values of %Fe (dissolved) from those of the experimental values were found to be within the range of acceptable deviation limit for experimental results.

Calculations of the concentrations of leached iron during leaching of iron oxide ore in sulphuric acid solution has been achieved through application of a model [7]. The model is expressed as

\[
\%Fe = e^{-2.0421(lnT)}
\]  

(2)

The predicted concentrations of leached Fe were observed to be very close to the values obtained from the experiment. The model shows that the concentrations of leached Fe were dependent on the values of the final leaching solution temperature measured during the leaching process. It was observed that the validity of the model is rooted in the expression ln(%Fe) = N(InT) where both sides of the expression are correspondingly approximately equal.

A model was successfully derived for predictive analysis of the concentrations of dissolved iron during leaching of iron oxide ore in sulphuric acid solution [8]. The model expressed as

\[
\%Fe = 0.987(\mu/T)
\]  

(3)

Was able to predict the concentrations of dissolved Fe with a high degree of precision. It was observed that the model was dependent on the values of the leaching temperature and weight of iron oxide ore added. The validity of the model was found to be rooted in the expression %Fe = N(\mu/T) where both sides of the relationship are correspondingly approximately equal. The maximum deviation of the model-predicted concentration of dissolved Fe from those of the experimental values was found to be less than 19% which is quite within the acceptable range of deviation limit for experimental results, hence depicting the usefulness of the model as a tool for predictive analysis of the dissolved iron during the process.

The aim of this work is to take an open system analysis of bioextracted iron during leaching of iron oxide ore using Acidithiobacillus ferrooxidans. The essence of this work is to predict the concentration of Fe bioextraction 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 2 weeks at a temperature of 25°C after which the mixtures were filtered and the concentration of bioextracted Fe determined using atomic absorption spectrometer (AAS). The average of the bioextracted Fe 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 bioextracted Fe also determined using AAS. Details of the experimental procedures and process conditions prevailing during the biooxidation process are as reported in the previous work [9].

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;
ρ - Σε S - S ≈ Nρ³ - K ρ² + Nε ρ

Introducing the values of Σε, S, N, K and Nε, into equation (4)

\[ \zeta - 0.0002 \rho - 0.0931 = 0.00779³ - 0.1618 \rho² + 0.9345 \rho \]

where

\[ \zeta = 0.00779³ - 0.1618 \rho² + 0.9345 \rho + 0.0002 \rho + 0.0931 \]

Table 1: Variation of removed phosphorus concentration with initial bioleaching solution pH [9]

<table>
<thead>
<tr>
<th>ζ</th>
<th>pH</th>
<th>ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.9</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>45.9</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>45.9</td>
<td>4</td>
<td>1.7</td>
</tr>
<tr>
<td>45.9</td>
<td>7</td>
<td>1.3</td>
</tr>
<tr>
<td>45.9</td>
<td>9</td>
<td>1.1</td>
</tr>
<tr>
<td>45.9</td>
<td>13</td>
<td>1.9</td>
</tr>
</tbody>
</table>

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: 2 weeks, constant treatment temperature: 25°C, range of initial bioleaching solution pH used; 1.0 – 13.

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

Model Validation

The validity of the model is strongly rooted in equation (5) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 3 also agrees with equation (5) following the values of ζ - 0.0002ρ - 0.0931 and 0.0077ρ³ - 0.1618 ρ² + 0.9345ρ evaluated from the experimental results in Table 1.

Table 3: Variation of ζ - 0.0002ρ - 0.0931 with 0.0077ρ³ - 0.1618 ρ² + 0.9345ρ

<table>
<thead>
<tr>
<th>ζ - 0.0002ρ - 0.0931</th>
<th>0.0077ρ³ - 0.1618 ρ² + 0.9345ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6978</td>
<td>0.7804</td>
</tr>
<tr>
<td>1.3978</td>
<td>1.2834</td>
</tr>
<tr>
<td>1.5978</td>
<td>1.6420</td>
</tr>
<tr>
<td>1.1978</td>
<td>1.2544</td>
</tr>
</tbody>
</table>

Furthermore, the derived model was validated by comparing the bioextracted Fe 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 bioextracted Fe concentration was carried out to ascertain the degree of validity of the derived model. This was done by comparing bioextracted Fe per unit initial bioleaching solution pH valuated from model-predicted results with those from actual experimental results.
Bioextracted Fe concentration per unit initial bioleaching solution pH $\zeta_p$ (%) was calculated from the equation;

$$\zeta_p = \frac{\zeta}{\vartheta}$$  \hspace{1cm} (7)

Therefore, a plot of the concentration of bioextracted Fe against initial bioleaching solution pH as in Fig. 1 using experimental results in Table 1, gives a slope, $S$ at points (1, 0.8) and (13, 1.9) following their substitution into the mathematical expression;

$$\zeta_p = \frac{\Delta\zeta}{\Delta\vartheta}$$ \hspace{1cm} (8)

Equation (8) is detailed as

$$\zeta_p = \frac{\zeta_2 - \zeta_1}{\vartheta_2 - \vartheta_1}$$ \hspace{1cm} (9)

Where

$\Delta\zeta = \text{Change in bioextracted Fe concentrations of } \zeta_2, \zeta_1$ at two values of the initial bioleaching solution pH $\vartheta_2, \vartheta_1$. Considering the points (1, 0.8) and (13, 1.9) for $(\vartheta_1, \zeta_1)$ and $(\vartheta_2, \zeta_2)$ respectively, and substituting them into equation (9), gives the slope as 0.0917 % which is the bioextracted Fe concentration per unit initial bioleaching solution pH during the actual leaching process.

Fig. 1: Coefficient of determination between bioextracted Fe concentration and initial bioleaching solution pH as obtained from experiment [9]

Similarly a plot of the concentration of bioextracted Fe against ore particle size (as in Fig. 2) using derived model-predicted results gives a slope: 0.0784 % on substituting the points (1, 0.8826) and (13, 1.8234) for $(\vartheta_1, \zeta_1)$ and $(\vartheta_2, \zeta_2)$ respectively into equation (9). This is the model-predicted bioextracted Fe concentration per unit initial bioleaching solution pH.

Fig. 2: Coefficient of determination between bioextracted Fe concentration and initial bioleaching solution pH as obtained from derived
Statistical Analysis

The standard errors (STEYX) in predicting the bioextracted Fe concentration (using results from experiment and derived model) for each value of the initial bioleaching solution pH are 0.3917 and 0.3780 % 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 bioextracted Fe concentration and initial bioleaching solution pH as obtained from experiment and derived model predicted results, was calculated using the equation:

$$R = \sqrt{R^2}$$  \hspace{1cm} (10)

The evaluations show correlations 0.9817 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 model-predicted bioextracted Fe 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 bioextracted Fe concentration.

Deviational Analysis

Analysis of bioextracted Fe 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 bioextracted Fe concentration to those of the corresponding experimental values.

Deviation ($D_n$) of model-predicted bioextracted Fe concentration from that of the experiment is given by

$$D_n = \frac{P_v - E_v}{E_v} \times 100$$  \hspace{1cm} (11)

Where

$P_v$ = bioextracted Fe concentration as predicted by derived model

$E_v$ = bioextracted Fe concentration as obtained from experiment

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

$$C_r = -D_n$$  \hspace{1cm} (12)

Therefore
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\[ Cr = \left( \frac{Ev - Ex}{Ev} \right) \times 100 \]  

(13)

Introduction of the corresponding values of \( Cr \) from equation (13) into the derived model gives exactly the extracted iron concentration as obtained from experiment.

![Graph showing variation of model-predicted bioextracted Fe concentration with associated deviation from experimental results (relative to initial bioleaching solution pH)](image)

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

Fig. 4 shows that the maximum deviation of the model-predicted bioextracted Fe concentration from the corresponding experimental values is less than 11%. The figure shows that the least and highest magnitudes of deviation of the model-predicted bioextracted Fe concentration (from the corresponding experimental values) are + 2.6 and + 10.33 % which corresponds to bioextracted Fe concentrations: 1.7442 and 0.8826 %, as well as initial bioleaching solution pH: 4 and 1 respectively.

![Graph showing variation of model-predicted bioextracted Fe concentration with associated correction factor (relative to initial bioleaching solution pH)](image)

Fig. 5: Variation of model-predicted bioextracted Fe 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 bioextracted Fe concentration (Fig. 4). This is because correction factor is the negative of the deviation as shown in equations (12) and (13). 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 bioextracted Fe concentration are – 2.6 and – 10.33 % which corresponds to bioextracted Fe concentrations: 1.7442 and 0.8826 %, as well as initial bioleaching solution pH: 4 and 1 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).
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IV. Conclusions

Open system analysis of bioextracted iron was carried out during leaching of iron oxide ore using acidithiobacillus ferrooxidans. The analysis showed prediction of the concentration of bioextracted iron at varying initial bioleaching solution pH and as-beneficiated Fe content of the ore. An empirical model was derived, validated and used as a tool for the analysis. The validity of the polynomial model was rooted on the core expression $\zeta - 0.00024 - 0.0931 = 0.00770^2 - 0.1618 \vartheta^2 + 0.9345 \vartheta$ where both sides of the expression are correspondingly approximately equal. Statistical analysis of the extracted iron concentration as obtained from experiment and derived model for each value of the initial bioleaching solution pH used shows standard errors of 0.3917 and 0.3780 respectively. Extracted iron concentrations per unit initial bioleaching solution pH as obtained from experiment and derived model are 0.0917 and 0.0784 % Deviational analysis indicates that the maximum deviation of the model-predicted iron extraction (from experimental results) was less than 11%, implying a confidence level above 89%.

References