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Model for Predictive Analysis of the Leaching Solution Temperature Relative to the Final Solution pH during Oxalic Acid Leaching of Iron Oxide Ore

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Abstract

Model for predictive analysis of the solution temperature during leaching of iron oxide ore in oxalic acid solution has been derived. It was observed that the validity of the model is rooted in the expression $(\mathrm{In}T)^{1/2} = N(\mathrm{In}\gamma)$ where both sides of the expression are approximately equal to 2. The model; $T = \exp(1.0378\mathrm{In}\gamma)^2$ was found to depend on the value of the final pH of the leaching solution measured during the experiment. The respective deviation of the model-predicted temperature values from the corresponding experimental values was found to be less than 36% which is quite within the acceptable range of deviation limit of experimental results. [Researcher. 2009;1(3):1-7]. (ISSN: 1553-9865).

Keywords: Model, Leaching Solution Temperature, Solution pH Oxalic Acid, Iron Oxide Ore.

1. Introduction

Studies [1,2] have shown that at a temperature as low as 25°C, the presence of Fe^{2+} significantly enhances the leaching of iron extraction from silica sand. Air quickly oxidizes ferrous oxalate during dissolution, giving room for an induction period of a few hours unless a strong acidic environment (<pH 1) or an inert atmosphere is maintained. It has been found [3] that maintaining the high level of ferrous oxalate in the leach liquor using an inert gas enhance the reaction kinetics. It is believed that during this process, removal of phosphorus from the iron compound and subsequent dissolution of the phosphorus oxide formed were effected.

The optimum pH for dissolving iron oxide has been reported [4] to be is pH 2.5 – 3.0. The solution pH governs the distribution of various oxalate ions in the leach system. Below pH 1.5, oxalic acid exists mainly as $H_2C_2O_4$, whereas HC_2O_4 is the most predominant species at pH 2.5 – 3.0.

It has been found [5,6] that the final pH of leaching solution depend on the leaching time, initial pH for the leaching solution and the leaching temperature.

Models for computational analysis of the concentration of dissolved haematite and heat absorbed by oxalic acid solution during leaching of iron oxide ore have been derived [7]. These models are:

$$\%Fe_2O_3 = K(\gamma/\mu) \tag{1}$$

$$Q = K_C\,\mu \tag{2}$$

Where

$\%Fe_2O_3$ = Concentration of dissolved haematite in oxalic acid solution.
γ = Final pH of the leaching solution at time t at which $\%Fe_2O_3$ was obtained.
μ = Weight of iron oxide added into the oxalic acid leaching solution (g)
K = Constant of proportionality associated with haematite dissolution
K_C = Constant of proportionality associated with heat absorption
Q = Quantity of heat absorbed by oxalic acid solution during the leaching process (J)

Nwoye [7] found that optimization of the weight input of iron oxide ore could be achieved using the model; ($\%Fe_2O_3 = K(\gamma/\mu)$) by comparing the concentrations of dissolved haematite at different weights input of the iron oxide ore, with the view to identifying the optimum weight input of iron oxide ore that gives the maximum dissolution of Fe_2O_3. The model also indicates that the concentration of haematite dissolved during the leaching process is directly proportional to the final pH of the leaching solution and inversely proportional to the weight input of the iron oxide ore.

It was also found [7] that values of Q obtained from both the experiment and model ($Q = K_C\,\mu$) agree to the fact that leaching of iron oxide ore using oxalic acid solution is an endothermic process, hence the absorbed positive heat energy by the leaching solution. The quantity of heat energy absorbed by the oxalic acid solution during the leaching process (as calculated from the model; $Q = K_C \mu$) was found to be directly proportional to the weight input of the iron oxide ore. These results were obtained at initial pH 6.9, average grain size of 150µm and leaching temperature of 30^0C. The constants of proportionality K and K_C associated with the respective derived models were evaluated to be 0.0683 and 66.88 respectively.

Nwoye [8] derived a model for predicting the time for dissolution of pre-quantified concentration of phosphorus during leaching of iron oxide ore in oxalic acid solution as:

$$\tau = \text{Log}\left(\frac{\left(\frac{P^{1/4}}{1.8}\right)}{\text{LogT}}\right) \qquad (3)$$

Where

T= Leaching temperature (^{0}C) in the experiment [9], taken as specified leaching temperature (^{0}C) aiding the expected dissolution of phosphorus .

N= 1.8 (Dissolution coefficient of phosphorus in oxalic acid solution during leaching of iron oxide ore) determined in the experiment [9].

P = Concentration of dissolved phosphorus (mg/Kg) in the experiment [9], taken as pre-quantified concentration of phosphorus expected to dissolve after a leaching time t (mg/Kg) in the model.

τ = Leaching time (sec.) in the experiment [9], taken as time for dissolution of the pre-quantified concentration of phosphorus (hrs) in the model.

The model was found to depend on a range of specified leaching temperatures (45-70^0C) for its validity. It was found [9] that the time for dissolution of any given concentration of phosphorus decreases with increase in the leaching temperature (up to 70^0C), at initial pH 5.5 and average grain size of 150µm.

Nwoye et al. [10] also formulated a model for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution. 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 [10] include: leaching temperature of 25^0C, initial solution pH 5.5 and average ore grain size; 150µm).

Biological processes for phosphorus removal have also been evaluated based on the use of several types of fungi, some being oxalic acid producing. Anyakwo and Obot [11] recently presented their results of a study on the use of Aspergillus niger and their cultural filtrates for removing phosphorus from Agbaja (Nigeria) iron oxide ore. The results of this work [11] 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.

An attempt has been made in the past [12] to leach Itakpe iron oxide ore using oxalic acid solution in order to determine the maximum concentration of phosphorus that is removable. Results of chemical analysis of the ore indicate that the percentage of phosphorus in the ore is about 1.18%, which from all indication is quite high and likely to affect adversely the mechanical properties of the steel involved; hence the need for dephosphorization. It was reported [12] that phosphorus can be removed from iron oxide ore through a process associated with hydrometallurgy. Phosphorus was removed at a temperature of 25^0C and initial solution pH 2.5, leading to the dissolution of the phosphorus oxide formed. This involved using acid leaching process to remove phosphorus from the iron oxide ore in readiness for steel making process.

Nwoye et al [13] derived a model for predicting the concentration of dissolved iron during leaching of iron oxide ore in sulphuric acid solution. The model is stated as;

$$\%\text{Fe} = 0.35(\alpha/T)^3 \qquad (4)$$

Where

T = Solution temperature at the time t, when the concentration of dissolved iron is evaluated. (^{0}C)

0.35= (pH coefficient for iron dissolution in sulphuric acid solution during the leaching process) determined in the experiment [13].

α = Final pH of the leaching solution at the time t, when the concentration of dissolved iron is evaluated.

The model (formulated at conditions; leaching temperature of 25^0C, initial solution pH 5.0 and average grain size; 150µm) is dependent of the final pH and temperature of the leaching solution. The model shows that the concentration of iron dissolved during the leaching process is directly proportional to the third power of the ratio of final leaching and temperature.

Nwoye [14] derived a model for evaluating the final pH of the leaching solution during leaching of iron oxide ore in oxalic acid solution. The model evaluates the pH value as the sum of two parts, involving the % concentrations of Fe and Fe_2O_3 dissolved. The model can be expressed as;

$$\gamma = 0.5\left(\frac{K_1}{\%Fe} + \frac{K_2}{\%Fe_2O_3}\right) \qquad (5)$$

Where

K_1 and K_2 = dissolution constants of Fe and Fe_2O_3 respectively.

γ = final pH of leaching solution (after time t).

It was also found that the model [14] could predict the concentration of Fe or Fe_2O_3 dissolved in the oxalic acid solution at a particular final solution pH by taking Fe or Fe_2O_3 as the subject formular. The prevailing process conditions under which the model works include: leaching time of 30mins., constant leaching temperature of 30°C, average ore grain size; 150µm and 0.1M oxalic acid.

Nwoye [15] has reported that the heat absorbed by oxalic acid solution during leaching of iron oxide ore can be predicted using the model he derived which works under the process condition; initial pH 6.9, average ore grain size; 150µm and leaching temperature; 30^0C. The model [15] can be stated as

$$Q = K_N\left(\frac{\gamma}{\%Fe_2O_3}\right) \qquad (6)$$

Where

Q = Quantity of heat absorbed by oxalic acid solution during the leaching process. (J)

γ = Final pH of the leaching solution (at time t).

$\%Fe_2O_3$= Concentration of haematite dissolved in oxalic acid solution during the leaching process.

K_N = 4.57(Haematite dissolution constant in oxalic acid solution) determined in the experiment [15].

Nwoye [15] carried out further work on the model using the same process conditions and observed that on re-arranging the model as;

$$\%Fe_2O_3 = K_N\left(\frac{\gamma}{Q}\right) \qquad (7)$$

the concentrations of haematite predicted deviated very insignificantly from the corresponding experimental values. In this case, the value of Q was calculated by considering the specific heat capacity of oxalic acid. Values of heat absorbed by the oxalic acid solution during the leaching of iron oxide ore as predicted by the model [15] agree with the experimental values that the leaching process is endothermic. This is because all the predicted values of the heat absorbed by the oxalic acid solution were positive. The model shows that the quantity of heat absorbed by oxalic acid solution during the leaching process is directly proportional to the final pH of the solution and inversely proportional to the concentration of haematite dissolved.

Model for evaluation of the concentration of dissolved phosphorus (relative to the final pH of the leaching solution) during leaching of iron oxide ore in oxalic acid solution has been derived [16]. It was observed that the validity of the model is rooted in the relationship $\ln P = N/\alpha$ where both sides of the expression are approximately equal to 4. The model; $P = e^{(12.25/\alpha)}$ is dependent on the value of the final pH of the leaching solution which varies with leaching time. In all, the positive or negative deviation of the model-predicted phosphorus concentration from its corresponding value obtained from the experiment was found to be less than 22%.

Temperature measured at the reaction sites gives an idea of whether the reaction is speeding up or stopping especially when it is measured consistently.

It has been reported [17] that the temperature of a reaction system plays the major role in controlling the rate of the reaction.

Past report [18] has shown that measurement of the temperature of a reaction system consistently shows whether the reaction involved is endothermic or exothermic.

Nwoye [19] derived a model for the computational analysis of the solution temperature during leaching of iron oxide ore in hydrochloric acid solution. The model is expressed as:

$$T = e^{(8.9055/\gamma)} \qquad (8)$$

where

T= Solution temperature during leaching of iron oxide ore using hydrochloric acid.(^{0}C)

N= 8.9055(pH coefficient for hydrochloric acid solution during leaching of iron oxide ore) determined in the experiment [19].

γ = Final pH of the leaching solution at the time t when the solution temperature is evaluated.

The model is dependent on the value of the final pH of the leaching solution which was found to also depend on the concentration of iron dissolved in the acid. The prevailed process conditions on which the validity of the model depended on include: initial pH 2.5, leaching time; 30 minutes, leaching temperature; 25°C, average ore grain size; 150µm and hydrochloric acid concentration at 0.1mol/litre.

The aim of this work is to derive a model for predictive analysis of the leaching solution temperature relative to the final pH of the solution during leaching of Itakpe (Nigerian) iron oxide ore in oxalic acid solution.

2. Model

The solid phase (ore) is assumed to be stationary, contains the un-leached iron remaining in the ore. Hydrogen ions from the oxalic acid attack the ore within the liquid phase in the presence of oxygen.

2.1 Model Formulation

Experimental data obtained from research work [20] carried out at SynchroWell Research Laboratory, Enugu were used for this work.

Results of the experiment as presented in report [20] and used for the model formulation are as shown in Table 1.

Computational analysis of the experimental data [20] shown in Table 1, gave rise to Table 2 which indicate that;

$$(\mathrm{In}T)^{1/2} = N(\mathrm{In}\gamma) \quad \text{(approximately)} \tag{9}$$

$$\mathrm{In}T = (N\mathrm{In}\gamma)^2 \tag{10}$$

$$T = \exp(N\mathrm{In}\gamma)^2 \tag{11}$$

Introducing the value of N into equation (11)

$$T = \exp(1.0378\mathrm{In}\gamma)^2 \tag{12}$$

where

T= Solution temperature during leaching of iron oxide ore using oxalic acid (^{0}C)

N=1.0378 (pH coefficient for oxalic acid solution during leaching of iron oxide ore) determined in the experiment[20].

γ = Final pH of the leaching solution at the time t when the solution temperature is evaluated.

Equation (12) is the derived model.

Table 1: Variation of Weight input of ore with final solution pH and temperature. [20]

µ (g)	(γ)	T (^{0}C)
10	6.90	41.00
14	6.87	48.00
18	6.85	48.40
22	6.90	54.40
26	6.90	55.10
30	6.92	55.00
34	6.91	53.60
38	6.91	55.00
42	6.91	54.30

Where µ = Mass of iron oxide ore used for the leaching process (g).

Table 2: Variation of $(\mathrm{InT})^{1/2}$ with $(\mathrm{NIn}\gamma)$

$(\mathrm{InT})^{1/2}$	$(\mathrm{NIn}\gamma)$
1.9271	2.0045
1.9675	2.0000
1.9696	1.9970
1.9991	2.0045
2.0023	2.0045
2.0018	2.0075
1.9954	2.0060
2.0018	2.0060
1.9986	2.0060

3. Boundary and Initial Condition

Consider iron ore in cylindrical flask 30cm high containing leaching solution of oxalic acid. The leaching solution is stationary i.e (non-flowing). The flask is assumed to be initially free of attached bacteria. Initially, atmospheric levels of oxygen are assumed. Varying weights (10-42g) of iron oxide ore were used as outlined in Table 1. The initial pH of leaching solution; 6.5 and leaching time; 30 minutes were used. A constant leaching temperature of 25°C was used. Ore grain size; 150µm, volume of leaching solution; 0.1 litre and oxalic acid concentration; 0.1mol/litre were used.. These and other process conditions are as stated in the experimental technique [20].

The boundary conditions are: atmospheric levels of oxygen (since the cylinder was open at the top) at the top and bottom of the ore particles in the liquid and gas phases respectively. At the bottom of the particles, a zero gradient for the liquid scalar are assumed and also for the gas phase at the top of the particles. The leaching solution is stationary. The sides of the particles are taken to be symmetries.

4. Model Validation

The formulated model was validated by direct analysis and comparism of T values predicted by model and the corresponding experimental T values for equality or near equality.

Analysis and comparison between these T values reveal deviations of model-predicted T values from the corresponding experimental values. This is believed to be due to the fact that the surface properties of the ore and the physiochemical interactions between the ore and leaching solution which were found to have played vital roles during the leaching process [20] were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted T values to those obtained from the experiment (Table 3).

Deviation (Dv) (%) of model-predicted T values from the corresponding experimental T values is given by

$$Dv = \frac{Tp - Te}{Te} \times 100 \qquad (13)$$

Where Tp = Predicted T values from model

Te = Experimental data

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

$$Cf = -Dv \qquad (14)$$

Therefore

$$Cf = -100\left(\frac{Tp - Te}{Te}\right) \qquad (15)$$

Introduction of the corresponding values of Cf from equation (15) into the model gives exactly the corresponding experimental T value [20].

5. Results and Discussion

The derived model is equation (12). A comparison of the values of T from the experiment and those from the model shows very minimum positive deviation hence depicting the reliability and validity of the model. This is shown in Table 3. The respective positive deviations observed is less than 36% which is quite within the acceptable range of deviation of experimental results. The validity of the model is believed to be rooted on equation (9) where both sides of the equation are approximately equal to 2. Table 2 also agrees with equation (9) following the values of $(\text{InT})^{1/2}$ and $(\text{NIn}\gamma)$ evaluated from Table1.

Table 3: Comparison between leaching solution temperature as predicted by model and as obtained from experiment [20].

T_{exp}	T_M	Dv (%)	Cf (%)
41.00	55.60	+35.61	-35.61
48.00	54.60	+13.75	-13.75
48.40	53.94	+11.45	-11.45
54.40	55.60	+2.21	-2.21
55.10	55.60	+0.91	-0.91
55.00	56.27	+2.31	-2.31
53.60	55.93	+4.35	-4.35
55.00	55.93	+1.69	-1.69
54.30	55.93	+3.00	-3.00

Where

T_{exp} = T values from experiment [20]

T_M = T values predicted by model.

6. Conclusion

The model predicts the leaching solution temperature relative to the final solution pH during oxalic acid leaching of Itakpe iron oxide ore. The validity of the model is believed to be rooted on equation (9) where both sides of the equation are approximately equal to 2. The respective deviations of the model-predicted T values from the corresponding experimental T values are all positive and less than 36% which is quite within the acceptable range of deviation limit of experimental results.

Further works should incorporate more process parameters into the model with the aim of reducing the deviations of the model temperature values from those of the experiment.

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