Model for Predictive Analysis of the Concentration of Dissolved Iron Relative to the Weight Input of Iron Oxide Ore and Leaching Temperature during Sulphuric Acid Leaching

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Abstract: Model for predictive analysis of the concentration of dissolved iron during leaching of iron oxide ore in sulphuric acid solution has been derived. The model %Fe = 0.987(μ/T) was found to predict %Fe dissolved with high degree of precision being dependent on the values of the leaching temperature and weight of iron oxide ore added. It was observed that the validity of the model is rooted in the expression %Fe = N(μ/T) where both sides of the relationship are correspondingly approximately equal. The positive or negative deviation of each of the model-predicted values of %Fe (dissolved) 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. [Nature and Science. 2009;7(3):41-47]. (ISSN: 1545-0740).

Keywords: Model, Predictive Analysis, Dissolved Iron, Sulphuric Acid, Iron Oxide Ore, Leaching Temperature.

1. Introduction

Several studies have been carried out to evaluate the use of different organic and inorganic acids for dissolution of iron. Dissolution of iron oxides and oxyhydroxides in hydrochloric and perchloric acids has been evaluated [1]. Lim-Nunez and Gilkes [2] evaluated the use of synthetic metal-containing goethite and haematite for similar work while Borghi et al. [3] studied the effect of EDTA and Fe(II) during the dissolution of magnetite. It has been reported [4] that goethite can be dissolved in several inorganic acids belonging to the families of the carboxylic and diphosphoric acids in the presence of reducing agents. The effectiveness of several organic acids (such as acetic, formic, citric, ascorbic acids etc.) used for dissolving iron from iron compounds has also been evaluated [5]. Oxalic acid was found to be the most promising because of its acid strength, good comlexing characteristics and high reducing power, compared to other organic acids. Using oxalic acid, the dissolved iron can be precipitated from the leach solution as ferrous oxalate, which can be re-processed to form pure haematite by calcinations [6]. Many researchers have studied the use of oxalic acid to dissolve iron oxide on a laboratory scale [7-13]. Lee et al [14] used 0.19-0.48M oxalic acid to dissolve hydrated iron oxide. Iron dissolution was found [14] to reach 90% for a 20% slurry within 60mins. using 0.19M oxalic for the finer fraction (< 150μm) containing 0.56% Fe_2O_3. The coarser fraction (>150μm) containing 1.06% Fe_2O_3 achieved a lower iron removal, reaching a steady state of only 78% after 1 h of leaching. Although the pH was not measured or controlled, it was expected that the liquor pH is < pH1 at the oxalic acid concentration range studied (0.19-0.48). Taxiarchou et al.[6] found that the maximum iron dissolution of only 40% is within 3 h at temperatures in the range 90-100^{0}C. At 0.5M oxalate and all temperatures (25, 60 and 80^{0}C) the dissolution of iron was faster at a lower pH in the range pH 1-5 studied. Biological processes for iron dissolution have been evaluated by several researchers based on the use of several micro organisms that were easily sourced and isolated. Mandal and Banerjee [15] recently presented their findings on the study of the use of Aspergillus niger and their cultural filtrates for dissolving iron present in iron compounds. It has been found that dissolution of iron oxide is via a photo-electro chemical reduction process, and involves a complicated mechanism of charge transfer between the predominant oxalate species, namely ferric oxalate $Fe(C_2O_4)_3^{3-}$, ferrous oxalate $Fe(C_2O_4)_2^{2-}$ acting also as an auto catalyst, and the oxalate ligand on the iron oxide surface [16].

Iron oxide dissolution in oxalic acid has been found to be very slow at temperatures within the range 25-60^{o}C, however, its rate increases rapidly above 90^{o}C [17]. The rate of the dissolution process also increases with increasing oxalate concentration at the constant pH values set within the optimum range of pH 2.5-3.0. The dissolution of fine pure haematite (Fe_2O_3) (105-140µm) was discovered to follow a diffusion-controlled shrinking core model at this optimum pH [17].

Taxiarchour et al [18] 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 Fe_2O_3) at pH 1. He stated that even at 90^0C, 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% Fe_2O_3). The iron oxide concentration in the leach is equivalent to 0.058g/L $Fe_{2}O_{3.}$

The speciation of Fe(III) oxalate and Fe(II) oxalate has been found [19] to be governed by pH and total oxalate concentration. For a having pH › 2.5 and an oxalate concentration higher than 0.1M, the most predominant Fe(III) complex ion existing is $Fe(C_2O_4)_3^{3-}$. At these conditions, (pH › 2.5 and an oxalate concentration higher than 0.1M) the predominant Fe(II) complex species is $Fe(C_2O_4)_2^{2-}$.

Nwoye [20] derived a model for quantitative analysis of dissolved iron in oxalic acid solution in relation to the final pH of the solution during leaching of iron oxide ore;

$$\gamma = 0.5\left(\frac{K_1[\%Fe_2O_3]+K_2[\%Fe]}{[\%Fe][\%Fe_2O_3]}\right) \qquad (1)$$

where

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

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

The values of the dissolution constants compared with those of % Fe and % Fe_2O_3 from the experiment [20] indicate clearly that the constants K_1 and K_2 are numerical equivalence of the chemical resistance to the dissolution of Fe and Fe_2O_3 (respectively) in oxalic acid solution. It was found that $K_1 \approx 2K_2$ indicating twice chemical resistance to the dissolution Fe compare to that of Fe_2O_3. This expression agreed with the higher percentage of Fe_2O_3 dissolved compared to that of the corresponding Fe.The model also predicted the final pH of the leaching solution when the concentrations of Fe and Fe_2O_3 dissolved (at a temperature of 30^0C and average ore grain size; 150µm) are known.

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 [21]. These models are:

$$\%Fe_2O_3 = K(\gamma/\mu) \qquad (2)$$

$$Q = K_C\,\mu \qquad (3)$$

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 [21] 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 [21] 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 [21].

Model for predictive analysis of the quantity of heat absorbed by oxalic acid solution during leaching of iron oxide ore has been derived [22]. It was observed that the validity of the model is rooted in the expression $(InQ)/N = \sqrt{T}$ where both sides of the relationship are correspondingly almost equal. The model was found to depend on the value of the final solution temperature measured during the experiment. The respective deviation of the model-predicted Q values from the corresponding experimental values was found to be less than 21% which is quite within the acceptable range of deviation limit of experimental results. The positive values of heat absorbed as obtained from experiment and model were found to agree and indicate that the leaching process is endothermic in nature.

Nwoye [23] 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:

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

Where

T= Leaching temperature (^{0}C) in the experiment [23], 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 [23].

P = Concentration of dissolved phosphorus (mg/Kg) in the experiment [23], 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 [23], 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^{0}C) for its validity. It was found [23] that the time for dissolution of any given concentration of phosphorus decreases with increase in the leaching temperature (up to 70^{0}C), at initial pH 5.5 and average grain size of 150µm. The model (formulated at conditions; leaching temperature of 25^{0}C, 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.

It has been found [24, 25] that the final pH of the leaching solution depend on the leaching time, initial pH for the leaching solution and the leaching temperature.

Model has been derived [26] for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution. The model is expressed as;

$$P = \left(\frac{150.5}{\mu\alpha} \right) \qquad (5)$$

Where

P = Concentration of phosphorus removed during the leaching process (mg/Kg)

(µ) = Weight input of iron oxide ore (g)

(α) = Final pH of the leaching solution at the time t when P is evaluated

150.5 = (pH coefficient for phosphorus dissolution in oxalic acid solution during the process) determined in the experiment [26].

The model [26] predicted the concentration of phosphorus removed, with high degree of precision being dependent on the final pH of the leaching solution and weight input of the iron oxide ore. It also shows that the concentration of phosphorus removed (at a temperature of 25^{0}C, average ore grain size; 150µm and initial leaching solution pH 5.5) is inversely proportional to the product of the final pH of the leaching solution and the weight input of the iron oxide ore.

Nwoye [27] derived a model for predictive analysis of the concentration of phosphorus removed (relative to the initial and final pH of the leaching solution) during leaching of iron oxide ore in sulphuric acid solution. It was observed that the validity of the model is rooted in the mathematical expression; $(P/N)^{1/3} = (e^{\gamma/\alpha})$ where both sides of the relationship are almost equal. The model; $P = 4.25(e^{\gamma/\alpha})^3$ shows that the concentration of phosphorus removed is dependent on the values of the initial and final pH of the leaching solution. 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 29%.

Nwoye et al. [28] 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;

$$\%Fe = 0.35(\alpha/T)^3 \qquad (6)$$

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 [28].

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

The aim of this work is to derive a model for predictive analysis of the concentration of dissolved iron relative to the ore weight input and leaching temperature during leaching of Agbaja (Nigeria) iron oxide ore in sulphuric 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 sulphuric acid attack the ore within the liquid phase in the presence of oxygen.

2.1 Model Formulation

Experimental data obtained from research work [29] carried out at SynchroWell Research Laboratory, Enugu were used for this work.

Results of the experiment as presented in report [29] and used for the model formulation are as shown in Table 1.

Computational analysis of the experimental data [29] shown in Table 1, gave rise to Table 2 which indicate that;

$$\%Fe = N(\mu/T) \quad \text{(approximately)} \qquad (7)$$

Introducing the value of N into equation (7)

$$\%Fe = 0.987(\mu/T) \qquad (8)$$

where

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

N=0.987(Temperature coefficient for iron dissolution in sulphuric acid solution during leaching of iron oxide ore) determined in the experiment [29].

μ= Weight of iron oxide ore added during the leaching process. (g)

Equation (2) is the derived model.

Table1: Variation of leaching temperature with dissolved iron.[29]

T (^{0}C)	%Fe
55	0.0734
57	0.0725
60	0.0556
65	0.0554
68	0.0552
70	0.0551

Table 2: Variation of %Fe with N(μ/T)

%Fe	N(μ/T)
0.0734	0.0718
0.0725	0.0693
0.0556	0.0658
0.0554	0.0607
0.0552	0.0580
0.0551	0.0564

3. Boundary Conditions

Consider iron ore in cylindrical flask 30cm high containing leaching solution of sulphuric 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. Weight of iron oxide ore used; 4g, initial pH of leaching solution; 6.7 and leaching time; 30 minutes were used. Range of leaching temperatures used; 55-70^{o}C. Ore grain size; 150µm, volume of leaching solution; 0.1 litre and sulphuric acid concentration; 0.1mol/litre was used. These and other process conditions are as stated in the experimental technique [29].

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 %Fe values from model data and those from the experimental data for equality or near equality.

Analysis and comparison between these data reveal deviations of model data from experimental data. 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 [29] were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model data to that of the experimental values.

Deviation (Dv) (%) of model %Fe values from experimental %Fe values is given by

$$Dv = \frac{Dp - DE}{DE} \times 100 \qquad (10)$$

Where

Dp = Predicted %Fe values from model

DE = Experimental %Fe values

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

$$Cf = -Dv \qquad (11)$$

Therefore

$$Cf = -\left(\frac{Dp - DE}{DE}\right) \times 100 \qquad (12)$$

Introduction of the corresponding values of Cf from equation (12) into the model gives exactly the corresponding experimental %Fe values [29].

5. Results and Discussion

The derived model is equation (2). A comparison of the values of %Fe from the experimental data and those from the model shows very minimum positive and negative deviations less than 19% which is quite within the acceptable deviation limit of experimental results, hence depicting the reliability and validity of the model. This is shown in Table 3. The validity of the model is believed to be rooted on equation (1) where both sides of the equation are correspondingly approximately equal. Table 2 also agrees with equation (1) following the values of %Fe and N (µ/T) evaluated from Table 1 as a result of corresponding computational analysis.

Table3: Comparison between %Fe dissolved as predicted by model and as obtained from experiment [29]

$\%Fe_{exp}$	$\%Fe_{M}$	Dv (%)	Cf (%)
0.0734	0.0718	-2.18	+2.18
0.0725	0.0693	-4.41	+4.41
0.0556	0.0658	+18.35	-18.35
0.0554	0.0607	+9.57	-9.57
0.0552	0.0580	+5.07	-5.07
0.0551	0.0564	+2.36	-2.36

Where

$\%Fe_{exp}$ = %Fe values from experiment [29]

$\%Fe_{M}$ = %Fe values predicted by model

6. Conclusion

The model predicts quantitatively the concentration of dissolved iron (relative to the weight input of ore and leaching temperature used) during leaching of Agbaja iron oxide ore. The validity of the model is believed to be rooted on equation (1) where both sides of the equation are correspondingly approximately. The deviation of the model-predicted %Fe values from those of the experiment is less than 19% which is quite within the acceptable 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-predicted %Fe values from those of the experiment.

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