

## Quadratic Model for Predicting the Concentration of Dissolved Iron Relative to the Initial and Final Solution pH during Oxalic Acid Leaching of Iron Oxide Ore

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**Abstract:** Model for predicting the concentration of dissolved iron (relative to the initial and final solution pH) during leaching of iron oxide ore in oxalic acid solution has been derived. The model;

$$\gamma^2 - \beta\gamma - \left( \frac{0.001N}{\%Fe} \right) = 0$$

was found to calculate the concentration of dissolved iron being dependent on the values of the initial and final leaching solution pH measured during the leaching process. It was found that the validity of the model is rooted on the expressions  $D = 1000\%Fe$  where both sides of each expression are correspondingly approximately almost equal. The maximum deviation of the model-predicted values of %Fe (dissolved) from the corresponding experimental values was found to be less than 28% which is quite within the acceptable range of deviation limit of experimental results. The value of the assumed coefficient of the dilution (N) was calculated to be 197.527. [Nature and Science 2010;8(3):104-109]. (ISSN: 1545-0740).

### 1. Introduction

Studies (Taxiarchour et al., 1997a and 1997b) 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. Ferrous oxalate is quickly oxidized by air 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 (Lee et al., 2006) 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.

Panias et al. (1996) reported that the optimum pH for dissolving iron oxide 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. 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 (Nwoye, 2008a). These models are:

$$\%Fe_2O_3 = K (\gamma/\mu) \quad (1)$$

$$Q = K_C \mu \quad (2)$$

Where

$\%Fe_2O_3$  = Concentration of dissolved haematite in oxalic acid solution.

$\gamma$  = Final pH of the leaching solution at time t at which  $\%Fe_2O_3$  was obtained.

$\mu$  = 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

Nwoye (2008a) 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 (Nwoye, 2008a) 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 150 $\mu$ m and leaching temperature of 30 $^{\circ}$ C. 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 (2008b) 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:

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

Where

T = Leaching temperature ( $^{\circ}$ C) in the experiment (Nwoye,2006), taken as specified leaching temperature ( $^{\circ}$ 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 (Nwoye, 2006).

P= Concentration of dissolved phosphorus (mg/Kg) in the experiment (Nwoye, 2006) taken as pre-quantified concentration of phosphorus expected to dissolve after a leaching time t (mg/Kg) in the model.

$\tau$  = Leaching time (sec.) in the experiment (Nwoye, 2006) 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 $^{\circ}$ C) for its validity. It was found (Nwoye, 2006) that the time for dissolution of any given concentration of phosphorus decreases with increase in the leaching temperature (up to 70 $^{\circ}$ C), at initial pH 5.5 and average grain size of 150 $\mu$ m.

Nwoye et al. (2008) 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 (Nwoye et al. 2008) include: leaching temperature of 25 $^{\circ}$ C, initial solution pH 5.5 and average ore grain size; 150 $\mu$ m).

Nwoye (2008c) 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<sub>2</sub>O<sub>3</sub>

dissolved. The model can be expressed as;

$$\gamma = 0.5 \left( \frac{K_1}{\%Fe} + \frac{K_2}{\%Fe_2O_3} \right) \quad (4)$$

Where

$K_1$  and  $K_2$  = dissolution constants of Fe and Fe<sub>2</sub>O<sub>3</sub> respectively

$\gamma$  = final pH of leaching solution (after time t).

It was also found that the model (Nwoye, 2008c) could predict the concentration of Fe or Fe<sub>2</sub>O<sub>3</sub> dissolved in the oxalic acid solution at a particular final solution pH by taking Fe or Fe<sub>2</sub>O<sub>3</sub> as the subject formular. The prevailing process conditions under which the model works include: leaching time of 30mins., constant leaching temperature of 30 $^{\circ}$ C, average ore grain size; 150 $\mu$ m and 0.1M oxalic acid.

Nwoye (2008d) 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; 150 $\mu$ m and leaching temperature; 30 $^{\circ}$ C. The model [14] can be stated as

$$Q = K_N \left( \frac{\gamma}{\%Fe_2O_3} \right) \quad (5)$$

Where

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

$\gamma$  = Final pH of the leaching solution (at time t).

%Fe<sub>2</sub>O<sub>3</sub> = 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 (Nwoye, 2008d).

Nwoye (2008d) carried out further work on the model using the same process conditions and observed that on re-arranging the model as;

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

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 (Nwoye, 2008d) 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 (Nwoye, 2009). 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%.

The aim of this work is to derive a quadratic model for predicting the concentration of dissolved iron relative to the initial and final solution pH during oxalic acid leaching of iron oxide ore.

## 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 (Nwoye, 2007) carried out at SynchroWell Research Laboratory, Enugu were used for this work.

Results of the experiment as presented in report (Nwoye, 2007) and used for the model formulation are as shown in Table 1.

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

$$\gamma \propto \left( \frac{1}{D} \right) \quad (7)$$

$$D = 1000\%Fe \quad (8)$$

Introducing a constant of proportionality into equation (7)

$$\gamma = \left( \frac{N}{D} \right) \quad (9)$$

Substituting equation (7) into equation (8) gives

$$\gamma = \left( \frac{N}{1000\%Fe} \right) \quad (10)$$

Where

$$\gamma = \text{Initial pH of the leaching solution at time } t = 0$$

N=Constant of proportionality assumed as the coefficient of dilution for oxalic acid solution

D= Dilution factor

%Fe = Concentration of dissolved iron in oxalic acid during leaching.

To introduce the effect of the final pH (on the leaching process) the differential pH (between initial and final pH) is considered.

ie ;

$$D_{pH} = \text{Initial pH } (\gamma) - \text{Final pH } (\beta) \quad (11)$$

Based on the foregoing,

$$D_{pH} = \gamma - \beta \quad (12)$$

From Table 1,  $\gamma > \beta$ ; therefore  $\gamma - \beta$  is positive. It is assumed that very little iron dissolved within the little time elapse just before the initial pH was taken timer set as well as just after the final pH was taken prior to chemical analysis of the filtrate containing the dissolved iron. Therefore to confine the dissolution of the iron to the time elapse at which the initial and final pH were taken, the value of %Fe in equation (10) was multiplied by the differential pH (correction factor) to get the real value of %Fe.

Based on the foregoing,

$$\gamma = \left( \frac{N}{1000\%Fe (\gamma - \beta)} \right) \quad (13)$$

To evaluate the percentage concentration of dissolved iron, equation (13) becomes;

$$\%Fe = \left( \frac{N}{1000\gamma(\gamma - \beta)} \right) \quad (14)$$

Forming a quadratic expression from equation (14)

$$\gamma^2 - \beta\gamma = \left( \frac{N}{1000\%Fe} \right) \quad (15)$$

$$\gamma^2 - \beta\gamma = \left( \frac{0.001N}{\%Fe} \right) \quad (16)$$

$$\gamma^2 - \beta\gamma - \left( \frac{0.001N}{\%Fe} \right) = 0 \quad (17)$$

Equation (17) could be re-written as

$$\gamma^2 - \beta\gamma - \theta = 0 \quad (18)$$

Where

$$\theta = \left( \frac{0.001N}{\%Fe} \right)$$

is a constant and dimensionless.

Equation (17) or (18) is the derived quadratic model. The concentration of dissolved iron could be calculated directly (for prediction) using equation (17) and indirectly using equation (18). The values of N were calculated from equation (10) and Table 1 for each of the samples (A-F) and average value taken since all samples were subjected to the same experimental process conditions (except initial solution pH). This was done by substituting the values of  $\gamma$  and %Fe obtained (after a leaching time of 180mins.) for samples A-F into equation (10).

Table 1: Variation of concentration of dissolved iron with initial and final solution pH. (Nwoye, 2007)

Sample Code	%Fe	D	$\gamma$	$\beta$
A	0.031	31.166	5.88	4.65
B	0.032	31.633	5.71	4.40
C	0.034	34.012	6.00	4.66
D	0.029	28.500	6.32	5.38
E	0.039	38.591	5.74	4.68
F	0.035	35.168	6.13	5.16

### 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. Constant weight 10g of iron oxide ore was used. The range of initial pH of leaching solution used; 5.71-6.32 and leaching time; 180 minutes were used. A constant leaching temperature of 25°C was used. Average ore grain size; 150 $\mu$ m, and oxalic acid concentration; 0.1mol/litre was used. These and other process conditions are as stated in the experimental technique (Nwoye, 2007).

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 comparison of %Fe values predicted by model and the corresponding experimental %Fe values for equality or near equality.

Analysis and comparison between these %Fe values reveal deviations of model-predicted %Fe 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 (Nwoye, 2007) were not considered during the model formulation. This necessitated the introduction of correction factor to bring the model-predicted %Fe values to those obtained from the experiment (Table 3).

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

$$Dv = \left( \frac{Mv - Ev}{Ev} \right) \times 100 \quad (19)$$

Where Mv = Predicted %Fe values from model

Ev = %Fe values obtained from experimental data

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

$$Cf = -Dv \quad (20)$$

Therefore

$$Cf = -100 \left( \frac{Mv - Ev}{Ev} \right) \quad (21)$$

Introduction of the corresponding values of Cf from equation (21) into the model gives exactly the corresponding experimental %Fe value (Nwoye, 2007).

### 5. Results and Discussion

The derived model is equation (17) or (18). Computational analysis of the experimental data (Nwoye, 2007) shown in Table 1, gave rise to Table 2

Sample Code	N
A	183.26
B	180.62
C	204.07
D	180.12
E	221.51
F	215.58

Table 2: Values of assumed

coefficient of dilution for oxalic acid solution

*Effect of initial and final pH of leaching solution on the concentration of dissolved iron*

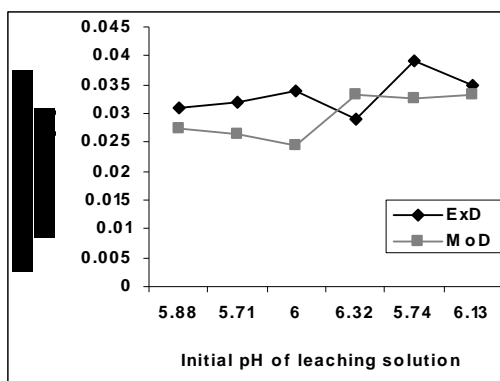


Figure 1-Comparison of the concentrations of Fe dissolved in relation to initial solution pH as obtained from experiment (Nwoye, 2007) and derived model.

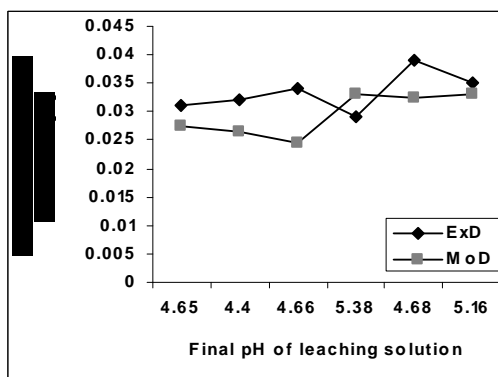


Figure 2-Comparison of the concentrations of Fe dissolved in relation to final solution pH as obtained from experiment (Nwoye, 2007) and derived model.

Comparison of Figures 1 and 2 show that both values of dissolved iron concentration obtained from the experiment (Nwoye, 2007) (Line ExD) and the derived model (Line MoD) in relation to both the initial ore and final solution pH are generally quite close, hence depicting proximate agreement and validity of the model.

It was found that the validity of the model is rooted on the expressions  $D = 1000\%Fe$  where both sides of each expression are correspondingly approximately almost equal. Table 1 also agree with equation (8), following the value  $1000\%Fe$  evaluated from Table

$\%Fe_M$	Dv (%)	Cf (%)
0.0273	-11.94	+11.94
0.0264	-17.50	+17.50
0.0246	-27.65	+27.65
0.0332	+14.48	-14.48
0.0325	-16.67	+16.67
0.0332	-5.14	+5.14

1 as a result of the corresponding computational analysis. The value of the assumed coefficient of dilution (N) for oxalic acid solution was evaluated to be 197.527.

*Variation of deviation and associated correction factor with the concentration of dissolved iron*

A comparison of the values of %Fe from the experiment and those from the model shows maximum deviation less than 28% which is quite within the acceptable range of deviation of experimental results. (Table 3)

Table 3 Variation of model-predicted concentrations of dissolved iron with associated deviations and correction factors.

$$\%Fe_M = \%Fe \text{ predicted by model.}$$

Table 3 indicate that the highest and least deviations; -27.65 and -5.14% in relation to both the initial and final leaching solution pH corresponds to the model-predicted Fe dissolved concentrations 0.0246 and 0.0332% respectively. Table 1 shows that these percent deviations also correspond to initial and final solution pH: 6.0 & 6.13 and 4.66 & 5.16 respectively.

**6. Conclusion**

The model predicts the concentration of dissolved iron relative to the initial and final solution pH during oxalic acid leaching of Itakpe (Nigeria) iron oxide ore. The respective deviations of the model-predicted %Fe values from the corresponding experimental %Fe values were less than 28% 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-predicted %Fe values from those of the experiment.

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