

Model for Calculating the Concentration of Dissolved Iron Relative to the Final Solution pH and Temperature during Oxalic Acid Leaching of Iron Oxide Ore.

Chukwuka I. Nwoye¹ and Ihuoma E. Mbuka²

¹Department of Materials and Metallurgical Engineering, Nnamdi Azikiwe University P.M.B 5025 Awka, Nigeria

²Department of Materials and Metallurgical Engineering Federal University of Technology, P.M.B 1526 Owerri, Nigeria.
chikeyn@yahoo.com

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

$$\%Fe = 1.1849(/T)^3$$

was found to calculate the concentration of dissolved iron being dependent on the values of the final leaching solution pH and temperature measured during the leaching process. It was observed that the validity of the model is rooted in the expression $(\%Fe/N)^{1/3} = /T$ where both sides of the expression are approximately equal to 0.2. The maximum deviation of the model-predicted concentration of dissolved iron from the corresponding experimental values was found to be less than 18% which is quite within the acceptable range of deviation limit of experimental results. Concentrations of dissolved iron per unit rise in the solution temperature as obtained from experiment and derived model were evaluated as 0.0011 and 0.0015 %/°C respectively, indicating proximate agreement. [Journal of American Science. 2011;7(1):12-18]. (ISSN: 1545-1003).

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1. Introduction

The mixed potential model of leaching assumes that the charge transfer processes occurring at the mineral surfaces are those that control the rate of dissolution (Kanevskii et al, 1963).

Nwoye et al. (2009a) derived a model for predicting the initial solution pH at assumed final pH and leaching time during leaching of iron oxide ore in hydrogen peroxide solution. It was observed that the validity of the model is rooted in the mathematical expression; $(\text{Int})^{1/2} = N(C / C)$ where both sides of the relationship are approximately equal to 2. The model is expressed as;

$$= \text{Antilog}[0.2439\text{Log}({}^{4.1}(\text{Int})^{1/2}/3.6)] \quad (1)$$

The model shows that the initial solution pH is dependent on the values of the final solution pH and leaching time. The respective positive or negative deviation of the model-predicted final pH from its corresponding experimental value was found to be less than 8%, which is quite within the acceptable deviation limit of experimental results depicting the validity of the model.

Model for calculating the solution pH during hydrogen peroxide leaching of iron oxide ore has also been derived by Nwoye et al. (2009b). It was

observed that the validity of the model is rooted in the expression $\ln = K_C[(\%Fe_2O_3/\%Fe)^N]$ where both sides of the equation are correspondingly approximately equal to 2. The model is expressed as;

$$= \exp K_C[(\%Fe_2O_3/\%Fe)^N] \quad (2)$$

The final solution pH was found to depend on the values of the % concentrations of dissolved iron and haematite from experiment. The respective deviation of the model-predicted pH values from the corresponding experimental values was found to be less than 20% which is quite within the acceptable range of deviation limit of experimental results.

Nwoye et al. (2008) derived a model for evaluation of the concentration of dissolved iron (relative to the final solution pH and temperature) during leaching of iron oxide ore in sulphuric acid solution. It was observed that the validity of the model was rooted in expression $(\%Fe/N)^{1/3} = /T$ where both sides of the expression are approximately equal to 0.2. The model is expressed as;

$$\%Fe = 0.35(/T)^3 \quad (3)$$

Where

T = Solution temperature at the time t when the concentration of dissolved iron is

evaluated. ($^{\circ}\text{C}$)

$N = 0.35$ (pH coefficient for sulphuric acid solution during leaching of iron oxide ore) determined in the experiment (Nwoye, 2007).

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

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 by Nwoye (2009). The model is expressed as;

$$P = e^{(12.25/\gamma)} \quad (4)$$

Where

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

$N = 12.25$; (pH coefficient for phosphorus dissolution in oxalic acid solution) determined in the experiment (Nwoye, 2003).

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

It was observed that the validity of the model is rooted in the relationship $\ln P = N/\gamma$ where both sides of the expression are approximately equal to 4. The model depends 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%, which is quite within the acceptable deviation limit of experimental results hence establishing the validity and precision of the model.

Model for quantitative analysis of dissolved haematite (relative to the initial solution pH) during leaching of iron oxide ore in oxalic acid solution has been derived by Nwoye et al. (2009c). The model;

$$\% \text{Fe}_2\text{O}_3 = \left[\frac{N}{N_c} \left(\frac{1}{\gamma} \right) \right] \quad (5)$$

was found to calculate the concentration of dissolved haematite being dependent on the values of the initial leaching solution pH measured during the leaching process. The respective positive and negative deviation of the model-predicted values of $\% \text{Fe}_2\text{O}_3$ (dissolved) from the corresponding experimental values was found to be less than 11% which is quite within the acceptable range of deviation limit of

experimental results. The values of the assumed coefficients of dilution (N) and dissolution of haematite (N_c) in oxalic acid solution were calculated to be 197.7503 and 700.0618 respectively.

Nwoye (2008a) 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;

$$\gamma = 0.5 \left(\frac{K_1}{\% \text{Fe}} + \frac{K_2}{\% \text{Fe}_2\text{O}_3} \right) \quad (6)$$

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 (Nwoye, 2008a) 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; $150\mu\text{m}$ and 0.1M oxalic acid. Nwoye (2008b) 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; $150\mu\text{m}$ and leaching temperature; 30°C . The model (Nwoye, 2008b) can be stated as

$$Q = K_N \left(\frac{\gamma}{\% \text{Fe}_2\text{O}_3} \right) \quad (7)$$

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).

$\% \text{Fe}_2\text{O}_3$ = 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 (Nwoye, 2008c).

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

$$\% \text{Fe}_2\text{O}_3 = K_N \left(\frac{\gamma}{Q} \right) \quad (8)$$

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, 2008b) 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.

Nwoye et al. (2009d) derived a model for calculating the concentration of leached iron during leaching of iron oxide ore in sulphuric acid solution. The model is expressed as;

$$\%Fe = e^{-2.0421(\ln T)} \quad (9)$$

The model was found to predict %Fe (leached) very close to the values obtained from the experiment, being 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 $\ln(\%Fe) = N(\ln T)$ where both sides of the expression are correspondingly approximately equal. The positive or negative deviation of each of the model-predicted values of %Fe (leached) from those of the experimental values was found to be less than 37%.

Model for predictive analysis of the concentration of dissolved iron during leaching of iron oxide ore in sulphuric acid solution was derived by Nwoye et al. (2009). The model expressed as;

$$\%Fe = 0.987(\mu/T) \quad (10)$$

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 $\%Fe = N(\mu/T)$ 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.

Nwoye (2010) derived a model for computational analysis of the solution temperature (relative to the final pH of the leaching solution) during leaching of iron oxide ore in oxalic acid solution. The model;

$$T = e^{(14.9661/p)} \quad (11)$$

is dependent depends on the value of the final pH of the leaching solution which varies with leaching time. It was observed that the validity of the model is rooted on the expression $\ln T = K_v/p$ where both sides of the equation are approximately equal to 3. The maximum deviation of the model-predicted solution temperature values from those of the experimental values were found to be less than 9% hence establishing the validity and precision of the model. The correlation between mass of iron oxide ore and solution temperature as well as between final pH of leaching solution and solution temperature as obtained from experiment and derived model (0.9296 and 0.8911 as well as 0.9395 and 0.9988) respectively are quite close, indicating proximate agreement with values from actual experiment.

The aim of this work is to derive a model for calculating the concentration of dissolved iron relative to the final solution pH and temperature during leaching of Agbaja (Nigeria) 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 (Nwoye, 2006) carried out at SynchroWell Research Laboratory, Enugu were used for this work. Results of the experiment as presented in report (Nwoye, 2006) and used for the model formulation are as shown in Table 1.

Computational analysis of the experimental data (Nwoye, 2006) shown in Table 1, resulted to Table 2 which indicate that;

$$\left(\frac{\%Fe}{N}\right)^{1/3} = \left(\frac{1}{T}\right) \quad (\text{approximately}) \quad (12)$$

$$\%Fe = N \left(\frac{1}{T}\right)^3 \quad (13)$$

Introducing the value of N into equation (13)

$$\%Fe = 1.1849 \left(\frac{1}{T}\right)^3 \quad (14)$$

Where

T= Solution temperature during leaching of iron oxide ore using oxalic acid ($^{\circ}\text{C}$)

N= 1.1849 (pH coefficient for iron dissolution in oxalic acid solution during leaching of iron oxide ore) determined in the experiment (Nwoye,2006).

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

Equation (14) is the derived model.

Table 1: Variation of dissolved iron with final solution pH and temperature. (Nwoye,2006)

()	T ($^{\circ}\text{C}$)	%Fe
4.33	25.10	0.0074
4.43	25.30	0.0063
4.48	25.50	0.0055
4.64	25.70	0.0074
4.84	26.10	0.0085

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 attach bacteria. Initially, atmospheric levels of oxygen are assumed. Range of mass of iron oxide ore was used: (6-20g). The initial pH of leaching solution; 4.5 and leaching time of 30 minutes was used for all samples. A constant leaching temperature of 25°C was used. Ore grain size; $150\mu\text{m}$, volume of leaching solution; 0.1litre and oxalic acid concentration; 0.1mol/litre were used. These and other process conditions are as stated in the experimental technique (Nwoye, 2006).

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 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 (Nwoye, 2006) 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. (Table 3)

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

$$Dv = \left(\frac{Dp - DE}{DE} \right) \times 100 \quad (15)$$

Where Dp = Predicted data from model
DE = Experimental data

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

$$Cf = -Dv \quad (16)$$

Therefore

$$Cf = -100 \left(\frac{Dp - DE}{DE} \right) \quad (17)$$

Introduction of the corresponding values of Cf from equation (17) into the model gives exactly the corresponding experimental %Fe values (Nwoye, 2006).

5. Results and Discussion

The derived model is equation (14).

Computational analysis of values in Table 1 resulted to Table 2.

Table 2: Variation of $(\%Fe/N)^{1/3}$ with $/T$

$(\%Fe/N)^{1/3}$	$/T$
0.1842	0.1725
0.1745	0.1751
0.1668	0.1757
0.1842	0.1805
0.1929	0.1854

An ideal comparison of the %Fe values as obtained from experiment (Nwoye, 2006) and as predicted by the model for the purpose of testing the validity of the model is achieved by considering the R^2 values (coefficient of determination). The values of the correlation coefficient, R calculated from the equation;

$$R = R^2 \quad (18)$$

using the r-squared values (coefficient of determination) from Figures 1-4. Comparison between these figures shows a better correlation between final solution temperature and dissolved iron as well as

between final solution pH and dissolved iron for derived model (0.9748 and 0.9946) compared to that obtained from experiment (Nwoye, 2006) (0.8590 and 0.8574).

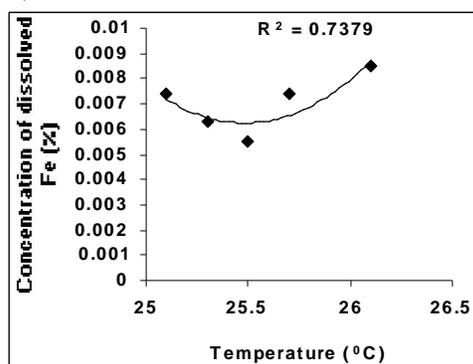


Figure 1- Effect of solution temperature on the concentration of dissolved iron (as obtained from experiment (Nwoye, 2006))

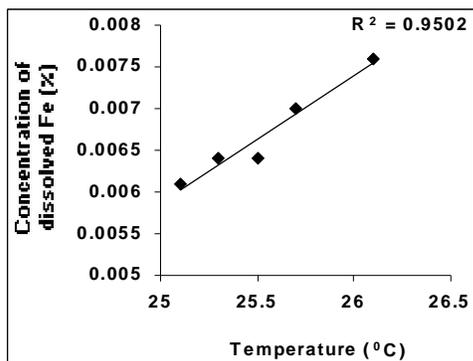


Figure 2- Effect of solution temperature on the concentration of dissolved iron (as predicted by derived model).

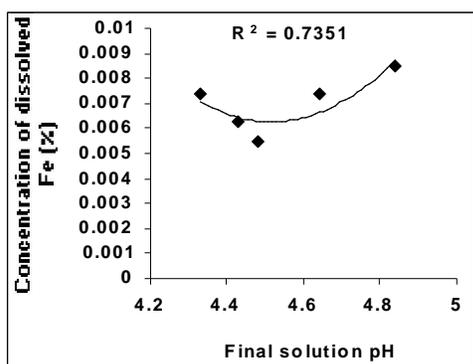


Figure 3- Effect of final solution pH on the concentration of dissolved iron (as obtained from experiment (Nwoye, 2006))

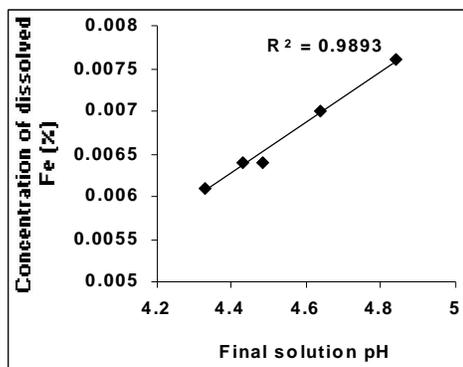


Figure 4- Effect of final solution pH on the concentration of dissolved iron (as predicted by derived model).

Figures 5 and 6 show very close alignment of the curves from model-predicted values (line MoD) and that from the corresponding experimental values (line ExD). The degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted values of dissolved iron. The model predicts (from Figures 2 and 4) that the final solution pH plays a better role (than final solution temperature) towards enhancing the concentration of dissolved iron. However, experimental results (Nwoye, 2006) as shown in Figures 1 and 3 indicate that final solution temperature plays a better role.

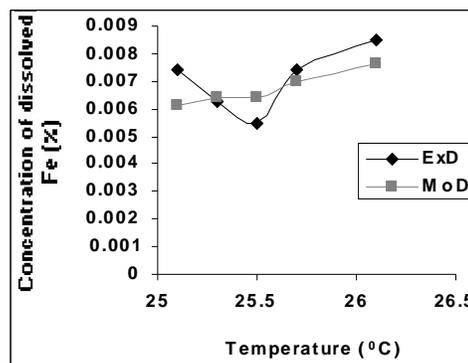


Figure 5- Comparison of the concentrations of dissolved iron relative to the final solution temperature as obtained from experiment (Nwoye, 2006) and derived model

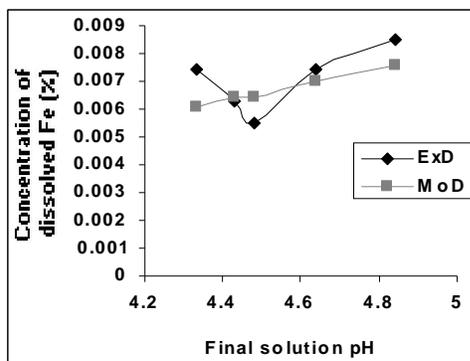


Figure 6- Comparison of the concentrations of dissolved iron relative to the final solution pH as obtained from experiment (Nwoye, 2006) and derived model

The concentration of dissolved iron per unit rise in the solution temperature during the leaching process was determined following comparison of the concentration of dissolved iron per unit rise in the solution temperature obtained by calculations involving experimental results as well as derived model.

Determination of the concentration of dissolved iron per unit rise in the solution temperature

Concentration of dissolved iron during leaching in oxalic acid solution per unit rise in the solution temperature I_T ($\%/\text{C}$) is calculated from the equation;

$$I_T = I/T \quad (19)$$

Therefore, a plot of concentration of dissolved iron against solution temperature (as in Figure 1) gives a slope, S at points (0.0074, 25.1) and (0.0085, 26.1) following their substitution into the mathematical expression;

$$S = I/T \quad (20)$$

Eqn. (20) is detailed as

$$S = I_2 - I_1 / T_2 - T_1 \quad (21)$$

Where

I = Change in the concentrations of iron dissolved I_2, I_1 at solution temperature values T_2, T_1 . Considering the points (0.0074, 25.1) and (0.0085, 26.1) for (I_1, T_1) and (I_2, T_2) respectively, and substituting them into eqn. (21), gives the slope as 0.0011 $\%/\text{C}$ which is the concentration of dissolved iron per unit rise in the solution temperature during the actual experimental (Nwoye, 2006) leaching process. Also similar plot (as in Figure 2) of model-predicted results gives a slope. Considering points (0.0061, 25.1) and (0.0076, 26.1) for (I_1, T_1) and (I_2, T_2) respectively and substituting them into eqn. (21)

gives the value of slope, S as 0.0015 $\%/\text{C}$. This is the model-predicted concentration of dissolved iron per unit rise in the solution temperature. A comparison of these two values of dissolved iron concentrations per unit rise in the final solution temperature shows proximate agreement.

Table 3 shows that the maximum deviation of the model-predicted values of %Fe from the corresponding experimental values (Nwoye, 2006) is less than 18% which is quite within the acceptable range of deviation limit of experimental results hence depicting the reliability and validity of the model. The validity of the model is believed to be rooted on equation (12) where both sides of the equation are approximately equal to 0.2. Table 2 also agrees with equation (12) following the values of $(\%Fe/N)^{1/3}$ and $1/T$ evaluated from Table 1 as a result of computational and statistical analysis.

Table:3 Variation of model-predicted concentration of dissolved iron with the associated deviation and correction factors

%Fe	Dv(%)	Cv (%)
0.0061	-17.57	+17.57
0.0064	+1.59	-1.59
0.0064	+16.36	-16.36
0.0070	-5.41	+5.41
0.0076	-10.59	+10.59

The least and highest magnitude of deviation of the model-predicted %Fe (from the corresponding experimental values) are + 1.59% and -17.57% which correspond to solution temperatures 25.3 and 25.1 $^{\circ}\text{C}$ respectively. Table 3 indicates that a correction factor of -1.59 % and + 17.57% make up for the least and highest deviation of +1.59% and -17.57% resulting from final solution pH of 4.43 and 4.33. It is pertinent to state that the actual deviations are just the modulus of the values. The role of the sign attached to the values is just to show when the deviation is surplus or deficit.

6. Conclusion

The model computes the concentration of dissolved iron relative to the final solution pH and temperature during leaching of Agbaja iron oxide ore. The validity of the model is believed to be rooted in the expression $(\%Fe/N)^{1/3} = 1/T$ than 18% where both sides of the expression are approximately equal to 0.2. The maximum deviation of the model-predicted values of %Fe from the corresponding experimental values is less than 18% which is quite within the acceptable range of deviation limit of

experimental results. The concentrations of dissolved iron per unit rise in the solution temperature as obtained from experiment and derived model were evaluated as 0.0011 and 0.0015 %/^oC respectively, indicating proximate agreement.

Further works should incorporate more process parameters into the model with the aim of reducing the deviations of the model data from that of the experimental.

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Correspondence to:

Dr. Chukwuka Ikechukwu Nwoye
Department of Materials and Metallurgical
Engineering, Nnamdi Azikiwe University P.M.B
5025 Awka, Anambra State, Nigeria.
Cellular phone: 0806 800 6092
Email: chikeyn@yahoo.com

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