Model for Computational Analysis of the Solution Temperature during Leaching of Iron Oxide Ore in Oxalic Acid Solution

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Abstract: 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 has been derived. The model;

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

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 $\ln T = K_c/p$ 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. [Journal of American Science 2010;6(6):31-37]. (ISSN: 1545-1003).

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

1. Introduction

The dissolution of iron oxide is believed to take place through a photo-electro chemical reduction process, involving 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 (Taxiarchour et al, 1997a). 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 (Lee et al, 2006). 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 (Fe_2O_3) (105-140μm) follows a diffusion-controlled shrinking core model.

The presence of Fe^{2+} was found to significantly enhance the leaching of iron extraction from silica sand at a temperature even as low as 25°C (Taxiarchour et al, 1997b). 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 inert gas was found to enhance the reaction kinetics.

It has been reported (Lee et al, 1999) that the leaching of 3g/L pure haematite (98.2% purity, 105-140μm size range) using 0.048-0.48M oxalic acid at 80-100^{0}C passed through a maximum peak at pH 2.5. Dissolution of haematite was found to be slower than magnetite ($FeO.Fe_2O_3$) and other hydrated iron oxide such as goethite (α-FeOOH), lapidochrosite (γ-FeOOH) and iron hydroxide ($Fe(OH)_3$) (Lee et al, 1999).

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).

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. (2009). The model;

$$\%Fe_2O_3 = \left[\frac{N}{N_c} \left(\frac{1}{\gamma} \right) \right] \qquad (1)$$

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 $\%Fe_2O_3$ (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 (2008) 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;

$$\gamma = 0.5\left(\frac{K_1}{\%Fe} + \frac{K_2}{\%Fe_2O_3}\right) \qquad (2)$$

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, 2008) 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^oC, average ore grain size; 150μm and 0.1M oxalic acid.

Nwoye (2009) 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 (Nwoye, 2009) can be stated as

$$Q = K_N\left(\frac{\gamma}{\%Fe_2O_3}\right) \qquad (3)$$

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 (Nwoye, 2008).

Nwoye (2009) carried out further work on the model using the same process conditions and observed that on re-arranging the model as;

$$\%Fe_2O_3 = K_N\left(\frac{\gamma}{Q}\right) \qquad (4)$$

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, 2009) 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. (2009) 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;

$$\%Fe = e^{-2.0421(lnT)} \qquad (5)$$

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 $\ln(\%Fe) = N(lnT)$ 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%.

Nwoye et al. (2009) derived a model for predicting the initial solution pH at determined 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; $(lnt)^{1/2} = N(\beta^C/\alpha^C)$ where both sides of the relationship are approximately equal to 2. The model is expressed as;

$$\beta = \text{Antilog}[0.2439\text{Log}(\alpha^{4.1}(lnt)^{1/2}/3.6)] \qquad (6)$$

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 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;

$$\%Fe = 0.987(\mu/T) \qquad (7)$$

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.

Model for calculating the solution pH during hydrogen peroxide leaching of iron oxide ore has also been derived by Nwoye et al. (2009). It was observed that the validity of the model is rooted in the expression $\ln\gamma = K_C[(\%Fe_2O_3/\%Fe)^N]$ where both sides of the equation are correspondingly approximately equal to 2. The model expressed as;

$$\gamma = \exp\left[K_C[(\%Fe_2O_3/\%Fe)^{\ N}] \right] \qquad (8)$$

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.

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;

$$P = e^{(12.25/\alpha)} \qquad (9)$$

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).

α = 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 $\ln P = N/\alpha$ 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.

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 $(\%Fe/N)^{1/3} = \alpha/T$ where both sides of the expression are approximately equal to 0.2. The model is expressed as;

$$\%Fe = 0.35(\alpha/T)^3 \qquad (10)$$

Where

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

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

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 computational analysis of the solution temperature relative to the final pH of the solution during leaching of Itakpe (Nigerian) iron oxide ore using 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, 2005) carried out at SynchroWell Research Laboratory, Enugu were used for this work.

Results of the experiment as presented in report (Nwoye, 2005) and used for the model formulation are as shown in Table 1.

Computational analysis of the experimental data (Nwoye, 2005) shown in Table 1, resulted to Table 2 which indicate that;

$$\ln T = K_c \qquad \text{(approximately)} \qquad (11)$$

$$T = e^{Kc/p} \qquad (12)$$

Introducing the value of K_c into equation (12)

$$T = e^{(14.9661/p)} \qquad (13)$$

Where

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

K_c = 14.9661; (pH coefficient for oxalic acid solution during leaching of iron oxide ore) determined in the experiment.(Nwoye, 2005)

p = Final pH of the leaching solution at the time t when the solution temperature is evaluated. Equation (13) is the derived model.

Table1: Variation of final pH of solution with
solution temperature. (Nwoye,2005)

M (g)	p	$T_{exp}(^0C)$
2	4.88	23.5
4	4.73	23.9
6	4.69	24.1
8	4.63	25.0
10	4.61	25.1
14	4.60	25.2
16	4.58	25.4

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

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. Varying weights (2-16g) of iron oxide
ore were used as outlined in Table 1. The initial pH
of leaching solution; 4.85 and leaching time of 30
minutes was used for all samples.
A constant leaching temperature of 25°C was used.
Ore grain size; 150µm, 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, 2005).
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 T 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, 2005) 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 T values from
experimental T values is given by

$$Dv = \left[\frac{Dp - DE}{DE} \right] \times 100 \qquad (14)$$

Where   Dp = Predicted data from model
            DE = Experimental data

Correction factor (Cf) is the negative of the
deviation i.e
$$Cf = -Dv \qquad (15)$$

Therefore

$$Cf = -100 \left[\frac{Dp - DE}{DE} \right] \qquad (16)$$

Introduction of the corresponding values of Cf
from equation (16) into the model gives exactly the
corresponding experimental T values. (Nwoye,
2005)

5. Results and Discussion

The derived model is equation (13).
Computational analysis of values in Table 1
resulted to Table 2.

Table 2: Variation of lnT with K_c/p

M (g)	p	lnT	K_c/p
2	4.88	3.1570	3.0668
4	4.73	3.1739	3.1641
6	4.69	3.1822	3.1911
8	4.63	3.2189	3.2324
10	4.61	3.2229	3.2464
14	4.60	3.2268	3.2535
16	4.58	3.2347	3.2677

The derived model is equation (13). An ideal
comparison of the T values as obtained from experiment
(Nwoye, 2005) 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;
$$R = \sqrt{R^2} \qquad (17)$$
using the r-squared values (coefficient of
determination) from Comparison between Figures 1-
4 show that 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 (Nwoye,
2005) and derived model; (0.9296 and 0.8911) as
well as (0.9395 and 0.9988) respectively are quite
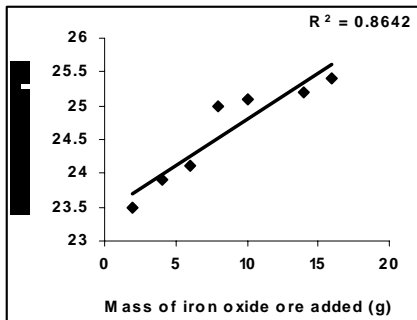close indicating proximate agreement with values
from actual experiment.

Figure 1- Effect of mass of iron oxide ore added on the solution temperature as obtained from the experiment (Nwoye, 2005)
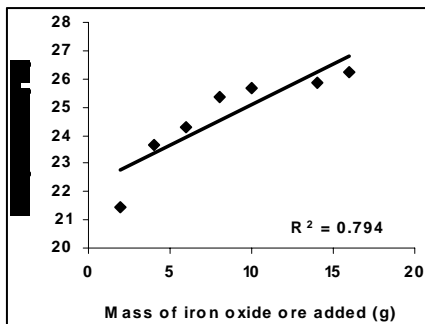

Figure 2- Effect of mass of iron oxide ore added on the solution temperature as obtained from derived model
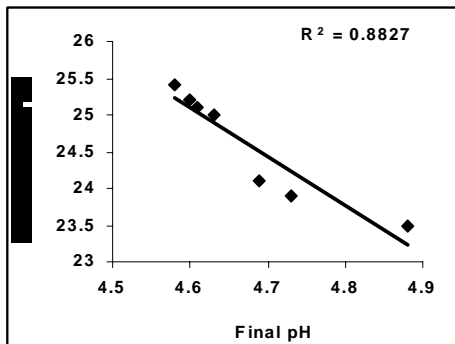

Figure 3- Effect of final pH of solution on the solution temperature as obtained from the experiment (Nwoye, 2005)
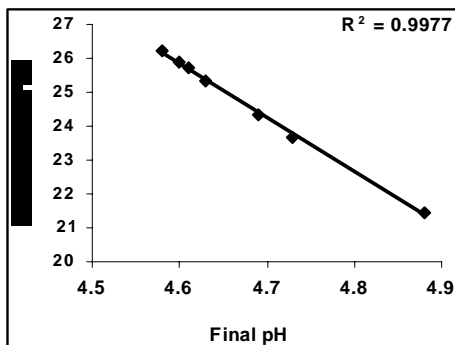

Figure 4- Effect of final pH on the solution temperature as obtained from derived model

Figures 5 and 6 show very close alignment of the curves from model-predicted values of T (MoD) and that from the corresponding experimental values (ExD). The degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted values T.
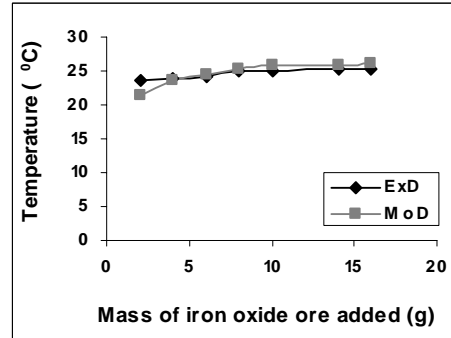

Figure 5- Comparison of solution temperatures resulting from the addition of iron oxide ore as obtained from experiment (Nwoye, 2005) and derived model
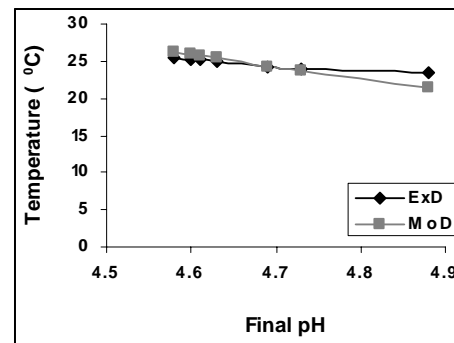

Figure 6- Comparison of solution temperatures relative to the final pH as obtained from experiment (Nwoye, 2005) and derived model

Table 3 shows that the maximum deviation of the model-predicted values of T from the corresponding experimental values (Nwoye, 2005) is less than 9% which is quite very insignificant and 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 (11) where both sides of the equation are approximately equal to 3. Table 2 also agrees with equation (11) following the values of lnT and K_c/p evaluated from Table 1 as a result of computational and statistical analysis.

The least and highest magnitude of deviation of the model-predicted T (from the corresponding experimental values) are + 0.01% and - 8.64% which correspond to solution temperature 25.34 and 21.47 respectively. Table 3 indicates that a correction factor of - 0.01% and + 8.64% make up for the least and highest deviation of + 0.01% and – 8.64% resulting from final pH of 4.63 and 4.88 due to addition of 8 and 2g of iron oxide ore

respectively. 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.

Table:3 Variation of model-predicted solution temperature with the associated deviation and correction factors

T_M (^{0}C)	Dv (%)	Cf (%)
21.47	-8.64	+8.64
23.67	-0.96	+0.96
24.31	+0.87	-0.87
25.34	+0.01	-0.01
25.70	+0.02	-0.02
25.88	+0.03	-0.03
26.25	+0.03	-0.03

T_M = T values predicted by model.

6. Conclusion
The model computes the solution temperature relative to the final solution temperature during leaching of Itakpe iron oxide ore. The validity of the model is believed to be rooted on the expression $lnT = K_c$ where both sides of the expression are approximately equal to 3. The maximum deviation of the model-predicted values of T from the corresponding experimental values is less than 9% which is quite very insignificant and 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 data from that of the experimental.

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