Model for Evaluation of Quantity of Heat Absorbed by Hydrogen Peroxide Solution relative to Solution Temperature during Leaching of Iron Oxide Ore.

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Abstract: Model for evaluating the quantity of heat absorbed by hydrogen peroxide solution relative to solution temperature (during leaching of iron oxide ore) has been derived and validated. The values of the absorbed heat as predicted by the model: $Q = e^{(0.195T)}$ was found to agree with those obtained from the experiment in showing that the leaching process is endothermic in nature, culminating in the positive values of the absorbed heat. It was found that the validity of the model stems on the expression $\ln Q = NT$ where both sides of the equation are approximately equal to 5. The maximum deviation of the model-predicted quantities of absorbed heat from the corresponding experimental values is less than 25% which is quite within the acceptable range of deviation limit of experimental results. [Researcher 2010:2(2):30-36] (ISSN: 1553-9865).

Keywords: Model, Heat absorbed, Hydrogen peroxide, Leaching, Iron oxide ore, Solution temperature.

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:

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

$$Q = K_C\,\mu \qquad (2)$$

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

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 150μm and leaching temperature of 30^{0}C. The constants of proportionality K and K_C associated with the respective derived models were evaluated to be

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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:

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

Where

T = Leaching temperature (^{0}C) in the experiment (Nwoye2006), 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 (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.

τ = 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^{0}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^{0}C), at initial pH 5.5 and average grain size of 150μm.

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^{0}C, initial solution pH 5.5 and average ore grain size; 150μm).

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$_2$O$_3$ dissolved. The model can be expressed as;

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

Where

K$_1$ and K$_2$ = dissolution constants of Fe and Fe$_2$O$_3$ respectively

γ = 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$_2$O$_3$ dissolved in the oxalic acid solution at a particular final solution pH by taking Fe or Fe$_2$O$_3$ 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 (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; 150μm and leaching temperature; 30^{0}C. The model 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)

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

%Fe$_2$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, 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

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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;

$$P = e^{(12.25/\alpha)} \qquad (7)$$

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%.

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;

$$\%Fe = e^{-2.0421(\ln T)} \qquad (8)$$

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%.

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

$$\beta = \text{Antilog}[0.2439 \text{Log}(\alpha^{4.1}(\ln t)^{1/2}/3.6)] \qquad (9)$$

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;

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

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.

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;

$$\gamma = \exp\left[K_C[(\%Fe_2O_3/\%Fe)^N]\right] \qquad (11)$$

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 calculating the quantity of heat absorbed by oxalic acid solution during leaching of iron oxide ore has been derived (Nwoye, 2009). It was observed that the validity of the model is rooted on the expression $\ln Q = \gamma^N$ where both sides of the expression are approximately equal to 7. The mode;

$$Q = e^{(\gamma\, 1.02)} \qquad (12)$$

was found to depend on the value of the final solution pH measured during the experiment. The maximum deviation of the model-predicted Q values 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 positive values of heat absorbed as obtained from experiment and model agree and show that the leaching process is endothermic in nature.

Model for predictive analysis of the quantity of heat absorbed by oxalic acid solution during leaching of iron oxide ore has been derived. It was

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observed that the validity of the model is rooted in the expression $(\ln Q)/N = \sqrt{T}$ where both sides of the relationship are correspondingly almost equal. The model;

$$Q = e^{(0.987(\sqrt{T}))} \qquad (13)$$

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 indicate and agree that the leaching process is endothermic in nature.

2. Model

The solid phase (ore) is assumed to be stationary, contains the un-leached iron remaining in the ore. Hydroxyl ions from the hydrogen peroxide solution 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;

$$\ln Q = NT \qquad \text{(approximately)} \qquad (14)$$

Introducing the exponent of both sides of equation (14) reduces it to;

$$Q = e^{NT} \qquad (15)$$

Introducing the value of N into equation (15)

$$Q = e^{(0.195T)} \qquad (16)$$

Equation (16) is the derived model.

where

    Q = Quantity of heat energy absorbed by hydrogen peroxide during the leaching process. (J)

    N = 0.195 (Resultant temperature coefficient for hydrogen peroxide solution during iron oxide ore leaching at time t) determined in the experiment (Nwoye, 2007).

    T = Solution temperature after time t of starting the leaching process (^{0}C)

    M = Mass-input of iron oxide ore (g)

Table 1. Variation of the quantity of heat absorbed by H_2O_2 with mass-input of iron oxide ore and solution temperature

M (g)	T (^{0}C)	Q (J)
22	27.5	171.60
26	27.7	182.52
30	27.9	226.20
34	27.4	212.16
38	27.2	217.36
42	27.0	218.40

3. Boundary and Initial Conditions.

Consider iron oxide ore in cylindrical flask 30cm high containing leaching solution of hydrogen peroxide. 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 (22-42)g were used for the iron oxide ore. The initial pH of the leaching solutions is 7.34 and leaching time; 30minutes. A constant leaching temperature of 25°C was used. Ore grain size; 150µm, volume of leaching solution; 0.1 litre and hydrogen peroxide concentration; 0.28 mol/Litre. These and other process conditions are as stated in the experimental techniques (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, 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 model formulated was validated by direct analysis and comparison of the Q from model data and those from experimental data (Nwoye,2007) for equality or near equality. Q values from model were obtained by substituting the values of T from the experiment (Nwoye, 2007) into the model correspondingly.

Analysis and comparison between these data reveal deviations of model data from experimental data. This is attributed to the non-consideration of the surface properties of the iron oxide ore and the physiochemical interactions between the ore and leaching solution which were found to play vital roles during the leaching process (Nwoye, 2007).

These deviations necessitated the introduction of correction factor to bring the model Q values to exactly that of experimental Q values.

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

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$$Dv = \left[\frac{Mv - Ev}{Ev}\right] \times 100 \qquad (17)$$

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   (18)

Therefore

$$Cf = -100 \left[\frac{Mv - Ev}{Ev}\right] \qquad (19)$$

Introduction of the corresponding values of Cf from equation (19) into the model gives exactly the corresponding experimental %Fe value (Nwoye, 2007).

5. Results and Discussion

The derived model is equation (16) Computational analysis of the experimental data (Nwoye, 2007) shown in Table 1, gave rise to Table 2

Table 2: Variation of NT with lnQ

NT	lnQ
5.3625	5.1452
5.4015	5.2069
5.4405	5.4214
5.3430	5.3573
5.3040	5.3816
5.2650	5.3863

5.1 Effect of mass-input of iron oxide ore on the quantity of heat absorbed by hydrogen peroxide solution

Critical analysis of Figure 1 shows that both values of the quantities of heat absorbed by hydrogen peroxide solution as obtained from the experiment (Nwoye, 2007) (Line ExD) and the derived model (Line MoD) in relation to the mass-input of iron oxide ore are generally quite close, hence depicting proximate agreement and validity of the model.
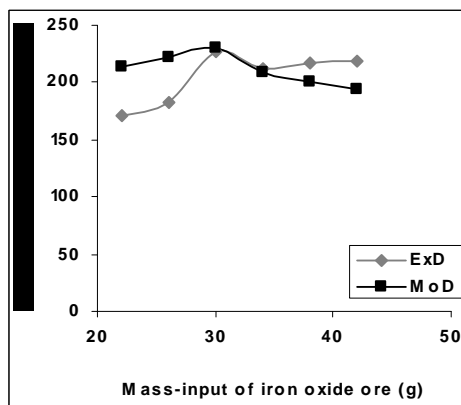

Figure 1- Comparison of the quantities of heat absorbed by hydrogen peroxide relative to the mass-input of iron oxide ore as obtained from experiment

5. 2 Variation of final solution temperature with the quantity of heat absorbed by hydrogen peroxide solution

Figure 2 shows that it is only between a temperature range: 27 - 27.4^{0}C, that the quantities of heat absorbed by hydrogen peroxide solution (relative to the final solution temperature) as obtained from the experiment (Nwoye, 2007) (Line ExD) and the derived model (Line MoD) depict proximate agreement. This implies that the model can only operate validly with respect to the final leaching solution temperature within this temperature range.
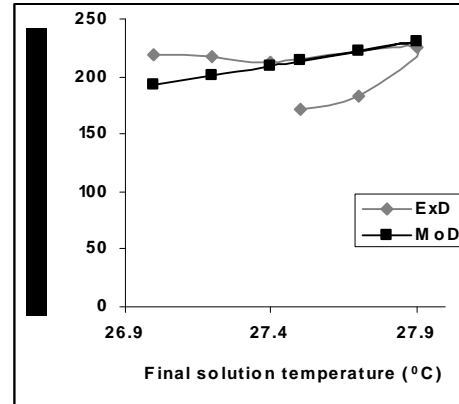

Figure 2-Comparison of the quantities of heat absorbed by hydrogen peroxide relative to the final solution temperature as obtained from experiment (Nwoye, 2007) and derived model.

(Nwoye, 2007) and derived model.

Figures 1 and 2 show that the quantities of absorbed heat as predicted by the model and obtained from the experiment are all positive hence agreeing that the leaching of the iron oxide ore using H_2O_2 solution is an endothermic process,

It was found that the validity of the model is rooted on the expressions lnQ = NT where both sides of each expression are correspondingly approximately almost equal to 5. Table 1 also agree with equation (1), following the values of ln Q and NT evaluated from Table 1 as a result of the corresponding computational analysis.

5.3 *Variation of the model-predicted quantity of heat absorbed by hydrogen peroxide with the associated deviation and correction factor*

Q_M (J)	Dv (%)	Cf (%)

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213.26	+24.28	-24.28
221.74	+21.50	-21.50
230.56	+1.93	-1.93
209.14	-1.42	+1.42
201.14	-7.46	+7.46
193.45	-11.42	+11.42

Where Q_M = Model-predicted quantity of absorbed heat (J)

A comparison of the values of quantities of heat (absorbed) from the experiment and those from the model shows maximum deviation less than 25% which is quite within the acceptable range of deviation of experimental results. (Table 3). Table 3 indicate that the highest and least deviations; +24.28 and -1.42% in relation to both the mass-input of iron oxide ore and final leaching solution temperature correspond to the model-predicted absorbed heat 213.26 and 209.14 J as against experimental values: 171.6 and 212.16 J respectively. Table 1 shows that these quantities of heat absorbed also correspond to final solution temperatures 27.5 and 27.4^{0}C and mass-inputs of iron oxide ore : 22 and 34g respectively.

5. Conclusion

The model evaluates the quantity of heat absorbed by hydrogen peroxide solution during leaching of Itakpe iron oxide ore. The validity of the model was found to be rooted on the expression ln Q = NT where both sides of the expression are approximately equal to 5. It was observed from Q values predicted by the model and those obtained from the experiment that the leaching of the iron oxide ore using H_2O_2 solution is an endothermic process, hence the positive values of Q from both model and experiment indicating heat absorbed.

The maximum deviation of the model-predicted quantities of absorbed heat from the corresponding experimental values is less than 25% 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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