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Model for Calculating the Quantity of Heat Absorbed by Oxalic Acid Solution Relative to the Final Solution pH during Leaching of Iron Oxide Ore

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Abstract

Model for calculating the quantity of heat absorbed by oxalic acid solution during leaching of iron oxide ore has been derived. It was observed that the validity of the model is rooted on the expression InQ = γ^N where both sides of the expression are approximately equal to 7. The model 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.

Keywords: Model, Results, Heat Absorbed, Solution pH, Oxalic Acid, Iron Oxide Ore and Leaching.

1.0 Introduction

Chemical leaching of an iron oxide ore (using chemicals containing hydrogen) involves the attack on the ore by hydrogen ions which act as reducing agents. The main function of these ions is to reduce the oxide ore to metallic or near metallic state depending on the concentration and nature of the chemical involved. During this process, some iron and other components of iron dissolve in the solution.

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°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

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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;

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

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 (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_2O_3 dissolved. The model can be expressed as;

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

where

K_1 and K_2 are the dissolution constants of Fe and Fe_2O_3 respectively.

γ is the final pH of leaching solution (after time t).

It was also found that the model (Nwoye, 2008b) 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 formula. The prevailing process conditions under which the model works include: leaching time of 30 mins., constant leaching temperature of 30°C, 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^{0}C. The model (Nwoye, 2009) can be stated as

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

where

Q is the quantity of heat absorbed in Joules by oxalic acid solution during the leaching process.

γ is the final pH of the leaching solution (at time t).

$\%Fe_2O_3$ is the 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 (2009) carried out further work on the model using the same process conditions and observed that on re-arranging the model as;

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

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;

$$\%Fe = e^{-2.0421(\ln T)} \qquad \ldots 5$$

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 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; $(lnt)^{1/2} = N(\beta^{C}/\alpha^{C})$ 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;

$$\gamma = \exp\left(K_c\left([\%Fe_2O_3 / \%Fe]^N\right)\right) \qquad ...8$$

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 is the 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 is the 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 $lnP = N/\alpha$ 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 is the solution temperature in °C at time t when the concentration of dissolved iron is evaluated.
N = 0.35 (pH coefficient for sulphuric acid solution during leaching of iron oxide ore) determined in the experiment (Nwoye, 2007).
α is the final pH of the leaching solution at the time t when the concentration of dissolved iron is evaluated.

It has been discovered (Nwoye, 2008a; Pinches, 1975) that the initial and final pH of leaching solution plays vital role in determining the extent of metal dissolution from their respective mineral ores. Other factors were said to include leaching temperature, grain size of ore, concentration of chemical used as leachant as well as oxygen content of the leaching solution.

Past report (Okeke,1987) has shown that, heat lost by a solid on being transferred to a solution equals heat gained/absorbed by the solution (if temperature is lower) on making contact with the ore, provided heat was not lost to the surroundings of the reaction vessels.

The aim of this work is to derive a model for calculating the quantity of heat absorbed by oxalic acid solution relative to the final solution pH during oxalic acid leaching of Itakpe (Nigerian) iron oxide ore.

2.0 Materials and method

Iron ore mined at Itakpe was homogenized and average grain size determined by hydrometer method as 150µm. Known weights of the iron oxide ore were respectively placed in a cylindrical flask containing oxalic acid of concentration 0.1 mol/litre of the leaching solution. The initial pH of the solution was 6.9. Leaching of each weight of the ore was carried out at a temperature of 25^{0}C for 30 minutes. During this process, hydrogen ions from the oxalic acid attacked the ore within the liquid phase in the presence of oxygen. Also heat is expected to be lost and gained during this process.

The quantity of heat lost by the iron oxide ore on getting in contact with the leaching solution is given by the equation (Okeke,1987) which is expressed as;

$$Q = M\,C\,\Delta T \qquad ...11$$

where

Q is the quantity of heat loss in Joules by the iron oxide ore.
M is the weight-input of iron oxide ore (g)
C is the specific heat capacity in J/g/K of the iron oxide ore
ΔT is the change in temperature in K within the solution.

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, gave rise to Table 2 which indicate that;

$$lnQ = \gamma^N \quad \text{(approximately)} \qquad ...12$$

$$Q = e^{(\gamma^N)} \qquad ...13$$

Introducing the value of N into equation (13)

$$Q = e^{(\gamma^{1.02})} \qquad ...14$$

where

γ is the final solution pH during the leaching process at the time (30 minutes) when Q is evaluated.
N = 1.02(pH coefficient for oxalic acid solution during leaching of iron oxide ore) determined in the experiment. (Nwoye, 2005)
Qexp is the quantity of heat energy absorbed in Joules by the oxalic acid solution during the leaching process determined in the experiment (Nwoye, 2005).

Equation (14) is the derived model**.**

Table 1: Variation of Quantity of Heat Absorbed by Oxalic Acid Solution with Final Solution pH and Weight Input of Iron Oxide Ore.

Qexp (J)	(γ)	μ (g)
1228.92	6.90	22
1258.18	6.90	26
1254.00	6.92	30
1195.48	6.91	34
1254.00	6.91	38
1224.74	6.91	42

where μ is the mass of iron oxide ore used for the leaching process

(Source: Nwoye, 2005)

Table 2: Variation of InQ with γ^N

*ln*Q	γ^N
7.1139	7.1718
7.1374	7.1718
7.1341	7.1930
7.0863	7.1824
7.1341	7.1824
7.1105	7.1824

3.0 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. Varying weights (22-42g) of iron oxide ore were used as outlined in Table 1. The initial pH of leaching solution; 6.9 and leaching time; 30 minutes were used. A constant leaching temperature of 25°C was used. Ore grain size; 150µm, volume of leaching solution; 0.1 litre and oxalic acid concentration; 0.1mol/litre were used. It was assumed that no heat was lost to the surroundings of the reaction vessels. Also heat lost by the ore on being transferred to the leaching solution was assumed to be equal to heat gained/absorbed by the acid.

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.

4.0 Model Validation

The formulated model was validated by direct analysis and comparison of Q values predicted by model and the corresponding experimental Q values for equality or near equality.

Analysis and comparison between these Q values reveal deviations of model-predicted Q 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, 2005) were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted Q values to those obtained from the experiment (Table 3).

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

$$Dv = \left(\frac{QM - Q\exp}{Q\exp}\right)\times 100 \qquad \ldots 15$$

where

Dp is the predicted Q values from model

DE is the experimental Q values

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

$$Cf = -Dv \qquad \ldots 16$$

Therefore

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

Introduction of the corresponding values of Cf from equation (17) into the model gives exactly the corresponding experimental Q values (Nwoye, 2005).

5.0 Results and Discussion

The derived model is equation (14). Figure 1 shows that both values of the quantity of heat absorbed by the oxalic acid solution from the experiment (Nwoye, 2005) shown in line Qexp and the derived model (line QM) in relation to the weight-input of iron oxide ore are generally quite close hence depicting the reliability and validity of the model.

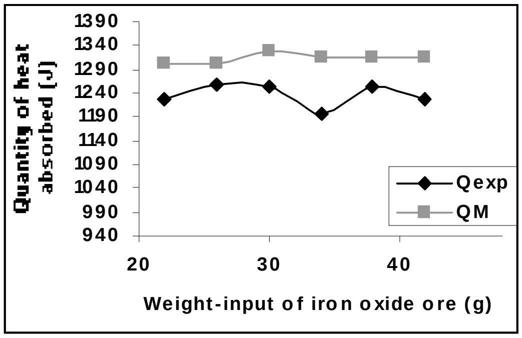

Figure 1: Comparison of the quantities of heat absorbed by the oxalic acid solution in relation to the weight-input of iron oxide ore as obtained from experiment (Nwoye,2005) and derived model.

Table 3: Variation of deviation and correction factor with model-predicted quantity of heat absorbed by oxalic acid solution.

Q_M	Dv (%)	Cf (%)
1302.19	+05.96	-05.96
1302.19	+03.50	- 03.5
1330.09	+06.07	-06.07
1316.06	+10.09	-10.09
1316.06	+04.95	-04.95
1316.06	+07.46	-07.46

(where Q_M is the Q values predicted by model)

A comparison of the values of Q from the experiment and those from the model shows low positive and negative deviation hence depicting the reliability and validity of the model. This is shown in Table 3. The respective positive and negative deviations of the model-predicted Q values from the corresponding experimental Q values is less than 11%which is quite within the acceptable range of deviation limit of experimental results. Table 2 also agrees with equation (12) following the values of *ln*Q and γ^N evaluated from Table 1The validity of the model is believed to be rooted on equation (12) where both sides of the equation are approximately equal to 7. The positive values of heat absorbed as obtained from experiment and model agree and show that the leaching process is endothermic in nature.

6.0 Conclusion

The model calculates the quantity of heat absorbed by oxalic acid solution during leaching of Itakpe iron oxide ore. The model was found to depend on the value of the final pH of the leaching solution measured during the experiment. The validity of the model is believed to be rooted on the expression $lnQ = \gamma^N$ where both sides of the expression are approximately equal to 7. The deviation of the model-predicted Q values from the corresponding experimental Q values is 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.

Further works should incorporate more process parameters into the model with the aim of reducing the deviations of the model-predicted Q values from those of the experiment.

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