

Model for Predicting the Initial Solution pH at Assumed Final pH and Leaching Time during Leaching of Iron Oxide Ore in Hydrogen Peroxide Solution

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Abstract

Model for predicting the final solution pH at determined initial pH and leaching time during leaching of iron oxide ore in hydrogen peroxide solution has been derived. 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; $\beta = \text{Antilog}[0.2439\text{Log}(\alpha^{4.1}(\ln t)^{1/2}/3.6)]$ 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. [New York Science Journal.2009;2(3):43-48].(ISSN:1554-0200).

Keywords: Model, Initial Solution pH, Final pH, Hydrogen Peroxide, Iron Oxide Ore, Leaching.

1. Introduction

Nwoye [1] derived a model for the computational analysis of the solution temperature during leaching of iron oxide ore in hydrochloric acid solution. The model is expressed as

$$T = e^{(8.9055/\gamma)} \quad (1)$$

where

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

N= 8.9055(pH coefficient for hydrochloric acid solution during leaching of iron oxide ore) determined in the experiment [1].

γ = Final pH of the leaching solution at the time t when the solution temperature is evaluated.

The model is dependent on the value of the final pH of the leaching solution which was found to also depend on the concentration of iron dissolved in the acid. The prevailed process conditions on which the validity of the model depended on include: initial pH 2.5, leaching time; 30 minutes, leaching temperature; 25⁰C, average ore grain size; 150 μ m and hydrochloric acid concentration at 0.1 mol/litre.

It has been reported [2] that phosphorus could be removed from Itakpe iron oxide ore through a leaching process using sulphuric acid solution. Chemical analysis carried out on the iron ore indicates that the percentage of phosphorus in the ore is about 1.18%, which from all indication is quite high and could cause embrittlement and other adverse effects on the service life of engineering materials made from such iron ore. This was the basis for the dephosphorization process carried out [2]. Phosphorus was removed (at a temperature of 25⁰C, average ore grain size; 150 μ m and initial leaching solution pH range 0.47-0.53) and then dissolved in the acid solution in the form of phosphorus oxide.

Nwoye et al [3] derived a model for predicting the concentration of dissolved iron during leaching of iron oxide ore in sulphuric acid solution. The model is stated as;

$$\%Fe = 0.35(\alpha/T)^3 \quad (2)$$

Where

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

0.35= (pH coefficient for iron dissolution in sulphuric acid solution during the leaching process) determined in the experiment [3].

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

The model (formulated at conditions; leaching temperature of 25⁰C, initial solution pH 5.0 and average grain size; 150 μ m) is dependent of the final pH and temperature of the leaching solution. The model shows that the concentration of iron dissolved during the leaching process is directly proportional to the third power of the ratio of final leaching and temperature.

Lee et al. [4] reported that the leaching of 3g/L pure haematite (98.2% purity, 105-140 μ m size range) using 0.048-0.48M oxalic acid at 80-100⁰C passed through a maximum peak at pH 2.5. Dissolution of haematite was found [4] to be

slower than magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) and other hydrated iron oxide such as goethite ($\alpha\text{-FeOOH}$), lapidochrosite (γFeOOH) and iron hydroxide ($\text{Fe}(\text{OH})_3$).

The dissolution of iron oxide is believed to take place via a photo-electro chemical reduction process, involving a complicated mechanism of charge transfer between the predominant oxalate species, namely ferric oxalate $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$, ferrous oxalate $\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}$ acting also as an auto catalyst, and the oxalate ligand on the iron oxide surface [5].

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 [6]. 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) (105-140 μm) follows a diffusion-controlled shrinking core model [6].

Taxiarchour et al [7] reported that it took close to 40h to dissolve 80% of pure haematite slurry (97% purity, 0.022% w/v or 0.21% g/L Fe_2O_3) at pH 1. He stated that even at 90°C, it required close to 10h to achieve 95% dissolution of iron of the slurry at pH 1. They also dissolved iron using 0.1-0.5M oxalic acid (pH1-5) to dissolve iron from a 20% w/v slurry (83% of particle size in the range 0.18-0.35mm, containing 0.029% Fe_2O_3). The iron oxide concentration in the leach is equivalent to 0.058g/L Fe_2O_3 .

The speciation of Fe(III) oxalate and Fe(II) oxalate has been found [8] to be governed by pH and total oxalate concentration. For a having pH > 2.5 and an oxalate concentration higher than 0.1M, the most predominant Fe(III) complex ion existing is $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$. At these conditions, (pH > 2.5 and an oxalate concentration higher than 0.1M) the predominant Fe(II) complex species is $\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}$.

Nwoye [9] derived a model for quantitative analysis of dissolved iron in oxalic acid solution in relation to the final pH of the solution during leaching of iron oxide ore;

$$\gamma = 0.5 \left(\frac{K_1[\% \text{Fe}_2\text{O}_3] + K_2[\% \text{Fe}]}{[\% \text{Fe}][\% \text{Fe}_2\text{O}_3]} \right) \quad (3)$$

where

K_1 and K_2 = Dissolution constants of Fe and Fe_2O_3 respectively.

γ = pH of leaching solution after time t (mins.).

The values of the dissolution constants compared with those of % Fe and % Fe_2O_3 from the experiment [9] indicate clearly that the constants K_1 and K_2 are numerical equivalence of the chemical resistance to the dissolution of Fe and Fe_2O_3 (respectively) in oxalic acid solution. It was found that $K_1 \approx 2K_2$ indicating twice chemical resistance to the dissolution Fe compare to that of Fe_2O_3 . This expression agreed with the higher percentage of Fe_2O_3 dissolved compared to that of the corresponding Fe. The model also predicted the final pH of the leaching solution when the concentrations of Fe and Fe_2O_3 dissolved (at a temperature of 30°C and average ore grain size; 150 μm) are known.

Model has been derived [10] for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution. The model is expressed as;

$$P = \left(\frac{150.5}{\mu\alpha} \right) \quad (4)$$

Where

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

(μ) = Weight input of iron oxide ore (g)

(α) = Final pH of the leaching solution at the time t when P is evaluated

150.5 = (pH coefficient for phosphorus dissolution in oxalic acid solution during the process) determined in the experiment [10].

The model [10] predicted the concentration of phosphorus removed, with high degree of precision being dependent on the final pH of the leaching solution and weight input of the iron oxide ore. It also shows that the concentration of phosphorus removed (at a temperature of 25°C, average ore grain size; 150 μm and initial leaching solution pH 5.5) is inversely proportional to the product of the final pH of the leaching solution and the weight input of the iron oxide ore.

Model for computational analysis of heat absorbed by hydrogen peroxide solution (relative to the weight of iron oxide ore added) has been derived [11]. The values of the heat absorbed Q as predicted by the model were found to agree with those obtained from the experiment that the leaching process is endothermic in nature hence the positive values of Q and the absorbed heat. The deviations of the predicted Q values from the experimental values were found to be within the acceptable range. The model was found to be dependent on the weight of iron oxide ore added to solution in the course of leaching.

The model is stated as:

$$Q = e^{1.04(\sqrt{W})} \quad (5)$$

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

$N = 1.04$ (Weight-input coefficient) determined in the experiment[11].
 W = Weight of iron oxide ore used (g)

It has been found [12, 13] that the final pH of the leaching solution depend on the leaching time, initial pH for the leaching solution and the leaching temperature.

The aim of this work is to derive a model for predicting the initial solution pH at assumed final pH and leaching time during hydrogen peroxide leaching of Itakpe (Nigeria) iron oxide ore. This derivation is embarked on in furtherance of the previous work [14].

2. Model

The ore is assumed to be stationary in the reaction vessel during the leaching process and contains the unleached iron as part of reaction remnants. The ore is attacked by hydrogen ions from hydrogen peroxide within the liquid phase, and in the presence of oxygen.

2.1 Model Formulation

Results from experimental work [14] carried out at SynchroWell Research Laboratory, Enugu were used for the model derivation. These results are as presented in Table 1.

Computational analysis of these experimental results [14] shown in Table 1, resulted to Table 2 which indicate that;

$$(\text{Int})^{1/2} = N \left(\frac{\beta^C}{\alpha^C} \right) \quad (\text{approximately}) \quad (6)$$

$$(\text{Int})^{1/2} = N \left(\frac{\beta}{\alpha} \right)^C \quad (7)$$

Introducing the values of N and C into equation (6):

$$(\text{Int})^{1/2} = 3.6 \left(\frac{\beta}{\alpha} \right)^{4.1} \quad (8)$$

However in evaluating the initial solution pH β , equation (8) becomes

$$\beta^{4.1} = \left(\frac{\alpha^{4.1} (\text{Int})^{1/2}}{3.6} \right) \quad (9)$$

Taking logarithm of both sides of equation (9)

$$\text{Log}\beta^{4.1} = \text{Log} \left(\frac{\alpha^{4.1} (\text{Int})^{1/2}}{3.6} \right) \quad (10)$$

$$4.1\text{Log}\beta = \text{Log} \left(\frac{\alpha^{4.1} (\text{Int})^{1/2}}{3.6} \right) \quad (11)$$

$$\text{Log}\beta = 0.2439\text{Log} \left(\frac{\alpha^{4.1} (\text{Int})^{1/2}}{3.6} \right) \quad (12)$$

$$\beta = \text{Antilog} \left(0.2439\text{Log} \left(\frac{\alpha^{4.1} (\text{Int})^{1/2}}{3.6} \right) \right) \quad (13)$$

Where

$C = 4.1$ (pH index for oxalic acid solution within the leaching time) determined in the experiment [14].

t = Leaching time (minutes)

β = Initial pH of the hydrogen peroxide leaching solution just before the leaching process started.

α = Final pH of the hydrogen peroxide leaching solution at time t.
 N = 3.6 (Dissolution coefficient of iron in hydrogen peroxide solution at time, t) determined in the experiment [14].
 Equation (13) is the derived model.

Table1: Variation of initial pH with final pH of the leaching solution at constant leaching time.[14]

| (β) | (α) | t |
|-------------|--------------|--------|
| 7.57 | 8.67 | 180.00 |
| 7.83 | 8.80 | 180.00 |
| 7.40 | 8.87 | 180.00 |
| 7.86 | 8.99 | 180.00 |
| 8.10 | 8.95 | 180.00 |
| 9.25 | 10.19 | 180.00 |
| 9.26 | 10.20 | 180.00 |

Table 2: Variation of β^c and α^c with N (β^c/α^c)

| β^c | α^c | ($\ln t$) ^{1/2} | N (β^c/α^c) |
|-----------|------------|----------------------------|--------------------------|
| 4020.62 | 7012.59 | 2.2788 | 2.0640 |
| 4617.67 | 7453.82 | 2.2788 | 2.2302 |
| 3663.11 | 7699.93 | 2.2788 | 1.7126 |
| 4690.64 | 8136.07 | 2.2788 | 2.0755 |
| 5306.26 | 7988.67 | 2.2788 | 2.3912 |
| 9144.95 | 13599.22 | 2.2788 | 2.4209 |
| 9185.55 | 13654.03 | 2.2788 | 2.4218 |

3. Boundary and Initial Condition

Iron oxide ore was placed in cylindrical flask 30cm high containing leaching solution of hydrogen peroxide. The leaching solution is non flowing (stationary). Before the start of the leaching process, the flask was assumed to be initially free of attached bacteria and other micro organism. Initially, the effect of oxygen on the process was assumed to be atmospheric. In all cases, weight of iron oxide ore used was 10g. The initial pH range of leaching solutions used; 7.40-9.26 and leaching time of 3 hrs (180 minutes) were used for all samples. A constant leaching temperature of 25°C was used. Hydrogen peroxide concentration at 0.28mol/litre and average ore grain size; 150 μ m were also used. Details of the experimental technique are as presented in the report [14].

The leaching process boundary conditions include: atmospheric levels of oxygen (considering that the cylinder was open at the top) at both the top and bottom of the ore particles in the gas and liquid phases respectively. A zero gradient was assumed for the liquid scalar at the bottom of the particles and for the gas phase at the top of the particles. The sides of the particles were assumed to be symmetries.

4. Model Validation

The formulated model was validated by calculating the deviation of the model-predicted initial pH from the corresponding experimental pH values.

The deviation recorded 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 play vital roles during the leaching process [14] were not considered during the model formulation. It is expected that introduction of correction factor to the predicted initial pH, gives exactly the experimental initial pH values.

Deviation (Dv) (%) of model-predicted initial pH values from those of the experiment is given by

$$Dv = \frac{Pp - Ep}{Ep} \times 100 \quad (14)$$

$$\left(\frac{Pp - Ep}{Ep} \right)$$

Where Pp = Predicted initial pH values

Ep = Experimental initial pH values

Since correction factor (Cr) is the negative of the deviation,

$$Cr = - Dv \quad (15)$$

Substituting equation (14) into equation (15) for Dv,

$$Cr = -100 \left(\frac{Pp - Ep}{Ep} \right) \quad (16)$$

It was observed that addition of the corresponding values of Cr from equation (16) to the model-predicted initial pH gave exactly the corresponding experimental initial pH values [14].

5. Results and Discussion

The derived model is equation (13). Insignificant positive and negative deviations were found to have resulted on comparing values of the initial pH from the experimental data and those from the model, hence depicting the reliability and validity of the model. This can be deduced from Table 3. The positive and negative deviations of the model-predicted initial pH values from those of the experiment were found to be less than 8% which is quite within the acceptable deviation limit of experimental results. The validity of the model is believed to be rooted on equation (6) where both sides of the equation are approximately equal to 2. Table 2 also agrees with equation (6) following the values of $(\ln t)^{1/2}$ and $N (\beta^C/\alpha^C)$ evaluated after statistical and computational analysis carried out on experimental results in Table 1.

Table 3: Comparison between initial pH as predicted by model and as obtained from experiment [14].

| β_{exp} | α_M | Dv (%) | Cr (%) |
|---------------|------------|--------|--------|
| 7.57 | 7.75 | +2.44 | -2.44 |
| 7.83 | 7.87 | +0.51 | -0.51 |
| 7.40 | 7.93 | +7.16 | -7.16 |
| 7.86 | 8.04 | +2.30 | -2.30 |
| 8.10 | 8.01 | -1.11 | +1.11 |
| 9.25 | 9.11 | -1.51 | +1.51 |
| 9.26 | 9.12 | -1.51 | +1.51 |

Where β_{exp} = Initial pH from experiment [14]
 β_M = Initial pH predicted by model.

6. Conclusion

The model predicts the initial solution pH of the leaching solution of hydrogen peroxide during the leaching of Itakpe (Nigeria) iron oxide ore. This prediction could be done during the leaching process providing the expectant final pH of the solution and leaching time are known. The validity of the model is believed to be rooted on equation (6) where both sides of the equation are approximately equal to 2. The respective deviation of the model-predicted initial solution pH value from that of the corresponding experimental value is less than 8% which is quite within the acceptable deviation limit of experimental results.

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