Model for Calculating the Solution pH during Hydrogen Peroxide Leaching of Iron Oxide Ore

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Abstract: Model for calculating the solution pH during hydrogen peroxide leaching of iron oxide ore has been derived. It was observed that the validity of the model is rooted in equation (1) where both sides of the equation are correspondingly approximately equal to 2. The model; $\gamma = \exp(K_C(\%Fe_2O_3/\%Fe)^N)$ 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. [Nature and Science. 2009;7(3):48-54]. (ISSN: 1545-0740).

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1. Introduction

Studies [1-4] have been carried out involving the use of different acids for the leaching of iron oxide ore. Also attempts have been made to leach pyrite using strong oxidizing agent like hydrogen peroxide because of the inert nature of the pyrite.

It has been found [5] that oxalic acid (0.05-0.15M) is the best extractant for removing iron from iron compounds. The dissolution was found to increase with acid concentration within the range (0.05-0.15M) studied. In this case, both hydrogen ions and oxalate were increased. Using 0.15M oxalic acid approximately, 70% of the iron could be extracted from a slurry (20%w/v) containing 0.93% iron oxide (of goethite and haematite phases) at 100^0C within 90mins. The iron oxide concentration in the leach is equivalent to 1.86g/L Fe_2O_3.It was found [6], following studies carried out on the electrochemical dissolution of haematite (α-Fe_2O_3), maghetite, (γ-Fe_2O_3), goethite, (α-FeOOH) and lepidochrocite, (γ-FeOOH) in hydrochloric and oxalic acid using voltammetry that the hydroxyl-oxides of FeOOH can be reduced also via soluble Fe(III) species at 0.6-0.8 V (vs Ag-AgCl), where as haematite and maghetite dissolve only via direct reduction of the solid at -0.55 to -0.60V (vs AG-AgCl). These potentials were determined as peaks on voltammograms conductedwith stationary electrodes made from these iron oxides and hydroxyl-oxides. This study [6] on the electrchemical behaviour of different types of iron oxides confirms the electrochemical nature of haematite reductive dissolution. This further explains why it is easier to dissolve hydroxyl-oxides such as goethite where dissolution can take place via both reduction (solid and aqueous species) and complexation [7] whereas haematite dissolves mainly via solid reduction [8]. Oxalate can easily be reductant for such aprocess, as shown in its Eh-pH diagram [9].

It has been reported [10] that dissolution of haematite in oxalic acid is via a reductive mechanism which made Fe(III) non-existent in the solution. The overall reaction was therefore found [10] to be a redox reaction, forming two half cells: Oxidation of oxalate to form carbonic acid or carbon dioxide:

$$HC_2O_4^- = H^+2CO_2 + 2e^- \quad (1)$$

Reduction of haematite forming Fe(II) oxalate:

$$2H^+ + Fe_2O_3 + 4HC_2O_4^- + 2e^- = 2Fe(C_2O_4)_2^{2-} + 3H_2O \quad (2)$$

The dissolution reaction is therefore:

$$H^+ + Fe_2O_3 + 5\,HC_2O_4^- = 2Fe(C_2O_4)_2^{2-} + 3H_2O + 2CO_2 \quad (3)$$

The overall reaction indicates that species involved in the leaching would be hydrogen ions, oxalate and iron oxide (haematite particles).

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^{o}C [11]. 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.

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 $Fe(C_2O_4)_3^{3-}$, ferrous oxalate $Fe(C_2O_4)_2^{2-}$ acting also as an auto catalyst, and the oxalate ligand on the iron oxide surface [12]. The dissolution of iron oxides in oxalic acid was found to be very slow at temperatures within the range 25-60^{o}C, but its rate increases rapidly above 90^{o}C [13]. 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.

It has been reported [14] 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 ($Fe(OH)_3$)
[14].

It has been found [15] that increasing the concentration of HCl results in a significant reduction in the rate of pyrite dissolution. The report also states that hydrochloric acid has an inhibiting effect on the oxidation of pyrite. This was attributed to chloride ions which are known to have a high tendency for adsorption. Also the formation of chloride complexes of iron (III) was found [15] to be possible, resulting in a decreasing concentration of the free iron (III) ions. However, no work has been reported on the effect of chloride ions and HCl concentration on the dissolution of iron during leaching of iron oxide ore.

Nwoye [16] derived a model for computational analysis of the concentration of dissolved haematite and heat absorbed by oxalic acid solution during leaching of iron oxide ore.
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. The model [16] indicated that values of Q obtained from both the experiment and model 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 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 derived model were evaluated to be 0.0683 and 66.88 respectively.

Nwoye [17] 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:

$$T = e^{(8.9055/\gamma)} \qquad (4)$$

where

T= Solution temperature during leaching of iron oxide ore using hydrochloric acid.(^{0}C)
N= 8.9055(pH coefficient for hydrochloric acid solution during leaching of iron oxide ore) determined in the experiment [17].
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; 25^{o}C, average ore grain size; 150µm and hydrochloric acid concentration at 0.1mol/litre.

The mixed potential model of leaching assumes that the charge transfer processes occurring at the mineral surface are those that control the rate of dissolution [18].

The dissolution of iron ore has been investigated in the presence of oxygen at elevated temperatures and pressures [19-23]. The result of the works indicates that presence of oxygen enhances dissolution of iron. The use of hydrogen peroxide as the oxidizing agent for hydrometallurgical processes has been increasingly studied. McKibben [19] studied the kinetics of aqueous oxidation of pyrite by hydrogen peroxide at pH 1-4 and 293-313K.

Model for computational analysis of heat absorbed by hydrogen peroxide solution (relative to the weight of iron oxide ore added) has been derived [24]. 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:

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

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[24].
W = Weight of iron oxide ore used (g)

Model for the calculation of the concentration of dissolved haematite during hydrogen peroxide leaching of iron oxide ore has been derived [25]. The model; $\%Fe_2O_3/\%Fe = (\mu)^{1/6}$ was found to depend on both the % concentration of dissolved iron and weight input of iron oxide ore from experiment. The validity of the model was found to be rooted on the expression $\%Fe_2O_3 \approx \%Fe\sqrt{(\mu)}^{1/3}$ where both sides of the relationship are correspondingly almost equal. The deviation of the model-predicted concentration of dissolved haematite from the corresponding experimental values is less than 30% which is quite within the acceptable range of deviation limit of experimental results. The model indicates that the dissolved % ratio of extreme oxidation stage of iron to that of its extreme reduction stage is approximately equal to one-sixth (1/6th) power of the weight input of iron oxide ore during the leaching process.

It has been discovered [26,27] that the initial pH of a leaching solution plays vital role in determining the extent 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.

The aim of this work is to derive a model for calculating the solution pH (concentrations of dissolved Fe and Fe_2O_3 being known) during leaching of Itakpe (Nigerian) iron oxide ore in hydrogen peroxide 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 hydrogen peroxide attack the ore within the liquid phase in the presence of oxygen.

2.1 Model Formulation

Experimental data obtained from research work [28] carried out at SynchroWell Research Laboratory, Enugu were used for this work. Results of the experiment as presented in report [28] and used for the model formulation are as shown in Table 1. Computational analysis of the experimental data [28] shown in Table 1, gave rise to Table 2 which indicate that;

$$\mathrm{In}\gamma = K_C\left(\frac{\%Fe_2O_3}{\%Fe}\right)^N \text{ (approximately)} \qquad (6)$$

Introducing the values of the constants K_C and N into equation (6)

$$\mathrm{In}\gamma = 1.2111\left(\frac{\%Fe_2O_3}{\%Fe}\right)^{1.33} \qquad (7)$$

$$\gamma = \exp\left(1.2111\left(\frac{\%Fe_2O_3}{\%Fe}\right)^{1.33}\right) \qquad (8)$$

Where $\%Fe_2O_3$ = Concentration of dissolved haematite in hydrogen peroxide solution during leaching (%) %Fe = Concentration of dissolved iron in hydrogen peroxide solution during leaching (%)
N = 1.33 (Iron oxidation-reduction endpoint ratio) determined in the experiment [28].
(γ) = pH of the leaching solution after time t (30 minutes)
K_C = 1.2111(Fe_2O_3-Fe leachibility coefficient) determined in the experiment [28].
Equation (8) is the derived model .

Table 1: Variation of the concentrations of dissolved haematite and iron with pH of leaching solution.[28]

$\%Fe_2O_3$	%Fe	(γ)
0.0017	0.0012	6.78
0.0020	0.0014	6.82
0.0501	0.0350	6.89
0.0013	0.0009	7.40
0.0042	0.0029	7.57
0.0022	0.0016	7.83
0.0079	0.0054	9.25
0.0081	0.0053	9.26

Table 2: Variation of $K_C(\%Fe_2O_3/\%\ Fe)^{1.33}$ with Inγ

$K_C(\%Fe_2O_3/\%\ Fe)^{1.33}$	Inγ
1.9247	1.9140
1.9464	1.9199
1.9513	1.9301
1.9749	2.0015
1.9821	2.0242
1.8498	2.0580
2.0089	2.2246
2.1290	2.2257

3. Boundary and Initial Condition

Consider iron 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. Weight of iron oxide ore used; (10g). The initial pH of leaching solution; 6.5 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 hydrogen peroxide concentration; 0.28mol/litre were also used.. These and other process conditions are as stated in the experimental technique [28].

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 comparism of γ values predicted by model and those obtained from the experiment for equality or near equality.

Analysis and comparison between these γ values reveal deviations of model-predicted values of γ 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 [28] were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted γ values to those obtained from the experiment.

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

$$Dv = \frac{Dp - DE}{DE} \times 100 \qquad (9)$$

Where Dp = Predicted γ values from model
DE = Experimental γ values

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

$$Cf = -Dv \qquad (10)$$

Therefore

$$Cf = -100\left(\frac{Dp - DE}{DE}\right) \qquad (11)$$

Introduction of the values of Cf from equation (11) into the model gives exactly the corresponding experimental γ values. [28]

5. Results and Discussion

The derived model is equation (8). A comparison of the values of γ from the experiment and those from the model shows minimum positive and negative deviation hence depicting the reliability and validity of the model. This is shown in Table 3. The respective positive and negative deviation of the model-predicted γ values from the corresponding experimental γ values is less than 20% which is quite within the acceptable range of deviation limit of experimental results. Table 2 also agrees with equation (6) following the values of $K_C[(\%Fe_2O_3/\%Fe)^{1.33}]$ and Inγ evaluated from Table 1. The validity of the model is believed to be rooted on equation (6) where both sides of the equation are correspondingly approximately equal to 2.

Table 3: Comparison between γ as predicted by model and as obtained from experiment [28].

γ_{exp}	γ_M	Dv (%)	Cf (%)
6.78	6.85	+1.03	-1.03
6.82	7.00	+2.64	-2.64
6.89	7.04	+2.18	-2.18
7.40	7.21	-2.57	+2.57
7.57	7.26	-4.10	+4.10
7.83	6.36	-18.77	+18.77
9.25	7.45	-19.46	+19.46
9.26	8.41	-9.18	+9.18

Where γ_{exp} = γ values from experiment [28]
γ_M = γ values predicted by model

6. Conclusion

The model calculates the pH of the leaching solution relative to known concentrations of dissolved iron and haematite during hydrogen peroxide leaching of Itakpe iron oxide ore. The validity of the model is rooted on equation (6) where both sides of the equation are correspondingly approximately equal to 2. The deviation of the model-predicted γ values from the corresponding experimental γ values is less than 20% 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 γ values from those of the experiment.

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References

[1] Panias, D., Taxiarchou, M., Paspaliaris, I., Kontopoulos, A. (1996) Mechanism of Dissolution of Iron Oxides in Aqueous Oxalic Acid. Hydrometallurgy 42, 257-265.

[2] Taxiarchour, M., Panias, D., Doumi, I., Paspaliaris, I., Kontopoulos, A. (1997a) Removal of Iron from Silica Sand by Leaching with Oxalic Acid, Hydrometallurgy, 46, 215-227.

[3] Taxiarchou, M., Parnias, D., Douni. I., Paspaliaris, I., Kontopoulous, A. (1997a) Dissolution of Haematite in Acidic Oxalate Solutions. Hydrometallurgy, 44, 1997, 287-299.

[4] Lee, S. O., Tran, T., Park, Y.Y., Kim, S. J., Kim, M.J. (2006a) Study on the Kinetics of Iron Leaching by Oxalic Acid. Int. J. Miner process, 80, 144-152.

[5] Ambikadevi, V. R., Lalithambika, M., (2000) Effects of Organic Acids on Ferric Iron Removal from Iron-Stained Kaolinite. Appl. Clay Sci. 16, 133-145.

[6] Cepria, G., Uson, A., Perez-Arantgui, J., Castillo, J. R. (2003) Identification of Fe(III) Oxide and Hydroxyl-Oxides by Voltammetry of Immobilized Microparticles. Anal. Chim. Acta. 477, 157-168.

[7] Stumm.,W., Furrer, G. (1987) The Dissolution of Oxides and Aluminum Silicates : Examples of Surface-Coordination-Controlled-Kinetics. In Stumm, W. (ed.), Aquatic Surface Chemistry. J Wiley and Sons, New York, pp. 97-219.

[8]Banwart, S., Davies, S., Stumm, W., (1989) The Role of Oxalate in Accelerating the Reductive Dissolution of Haematite (α-Fe_2O_3) by Ascorbate. Colloids Surf. 39, 303-309.

[9] Pourbaix, M., (1958) Atlas of Electrochemical Equilibria in Aqueous Solution. Pergamon Press.

[10]Lee, S. O., Tran, T., Park, Y.Y., Kim, S.J., Kim, M.J. (2006b) Study on the Kinetics of Iron Leaching by Oxalic Acid. Int. J. Miner process, 80, 144-152.

[11]Taxiarchou, M., Parnias, D., Douni, I., Paspaliaris, I., and Kontopoulous, A., (1997b) Dissolution of Haematite in Acidic Oxalate Solutions. Hydrometallurgy, 287-299.

[12] Taxiarchour, M., Panias, D., Doumi, I., Paspaliaris, I., Kontopoulos, A., (1997b) Removal of Iron from Silica Sand by Leaching with Oxalic Acid, Hydrometallurgy, 46, 215-227.

[13] Lee, S.O., Tran, T., Park.,Y.Y., Kim, S.J., and Kim, M. J., (2006) Study on the Kinetics of Iron Leaching by Oxalic Acid. Int. J. Miner process, 80, 144-152.

[14] Lee, S.O., Oh, J. K., Shin, B.S., (1999) Dissolution of Iron Rust Materials using Oxalic Acid. J. Min. Metall. Inst. Jpn. 115, 815-819.

[15] Dimitrijevic, M., Antonijevic, M. M., Dimitrijevic, V. (1999) Investigation of the Kinetics of Pyrite Oxidation by Hydrogen Peroxide in Hydrochloric Acid Solutions. Min. Eng. 12 (12), 165-174.

[16] Nwoye, C. I. (2008) Model for Computational Analysis of Dissolved Haematite and Heat Absorbed by Oxalic Acid Solution during Leaching of Iron Oxide Ore, J. Eng.& App. Sc., 4, 22-25.

[17] Nwoye, C. I., (2006) SynchroWell Research Work Report, DFM Unit, No. 2021196, 28-43.

[18]Kanevskii, E.A., and FilippovA.P., (1963) Influence of the Ionic Composition of Solutions of Fe(iii) on the Solution of Uranium Dioxide. Soviet Radiochemistry (Eng. Trans. Of Radiokhimiya), 5.

[19] McKibben, M.A., (1984) Ph.D Thesis, Pennsylvania State University.

[20] Bailey, L. K., Peter, E., (1976) Can. Metall. Q., 15, 333-344.

[21] Gerlach, J., Hahne, H., Pawlek, F., (1966) Erzmetall, 19, 66-74.

[22] McKay, D. R., Halpern, J., (1958) Trans Metall. Soc. AIME, 6, 301-309.
[23] Vracar, R. Z. (1987) Prikl.Khim. 60, 1458-465.
[24] Nwoye, C. I. (2009) Model for Computational Analysis of Quantity of Heat Absorbed by Hydrogen Peroxide Solution relative to Weight-Input of Iron Oxide Ore during Leaching. J. Eng.& App. Sc., I 5(2), 40-52.
[25] Nwoye, C. I., Model for the Calculation of the Concentration of Dissolved Haematite during Hydrogen Peroxide Leaching of Iron Oxide Ore . JMMCE (in press)
[26] Nwoye, C. I., Ph.D Thesis, Metallurgical and Materials Engineering Department, Federal University of Technology, Owerri. 2008, 178.
[27] Pinches, A., (1975) Bacterial Leaching of an Arsenic Bearing Sulphide Concentrate .The Institute of Mining and Metallurgy England, 34.
[28]Nwoye, C. I., (2005) SynchroWell Research Work Report, DFM Unit, No 2401171, 2005, 15-25.