

Open System Leaching of Iron Ore in Oxalic Acid Solution and Predictability of Final Solution pH based on Initial Solution pH and Leaching Time

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Abstract: This paper presents an open system leaching of iron ore in oxalic acid solution and predictability of final solution pH based on initial solution pH and leaching time. The leaching process and final solution pH prediction was carried out within a range of process parameters such as 5.88 – 6.13, 4.65- 5.16 and 180mins. For initial solution pH, final solution pH and constant leaching time respectively. Results of the investigation reveal that the trend of variation in both the initial and final solution pH is sinusoidal at constant leaching time. Also initial solution pH varies with the final solution pH correspondingly in a sinusoidal manner. It was generally observed that the final solution pH was correspondingly lower than the initial pH in line with the derived model prediction. This was attributed to the fact that sulphur from the iron ore most likely dissolved during the leaching process and decreased the solution pH due to increased acidity of the solution. The empirical model; $\theta = \text{Antilog} [0.2857 \text{Log} (1.0022\epsilon^{3.5}/(\ln \delta)^{1/2})]$ predicts the final solution pH with maximum deviation < 7.5% (from actual results). This translated into over 92% operational confidence levels for the derived model and 0.92 dependency coefficient of final solution pH on the initial solution pH at constant leaching time. The validity of the model was rooted on the core model expression $0.00002\epsilon + (\ln \delta)^{1/2} = 1.0022(\epsilon/ \theta)^{3.5}$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the final solution pH relative to values of the actual results is 0.066%.

Key words: Open system - Iron ore leaching - Prediction - Final solution pH - Oxalic acid

INTRODUCTION

The importance of metal oxide dissolution can be drawn from cleaning iron oxide from iron metal surface and removing of iron from mineral concentrate. Removal of corrosion products from industrial equipment and heat exchangers (e.g. cooling coils in water-cooled nuclear reactors), acid leaching of iron ores as well as removal of the associated oxides, hydroxides and hydrated oxides of ferric iron (hematite, goethite and lepidocrocite etc.) from industrial minerals are all regarded as Industrial processes related to dissolution of iron oxides.

Studies [1, 2] have shown that the iron content of industrial minerals can be reduced by physical, physicochemical and chemical processing. Amongst

these processes, chemical processing is most ideal because it is very efficient during removal of the contaminated iron oxide in industrial minerals. The results of the studies indicate that even though chemical methods which has to do leaching of the minerals using organic and inorganic acids such as hydrochloric and sulphuric acids is preferred (to other processes) due to higher leaching rates observed, many researchers [3-5] have evaluated the use of oxalic acid for leaching of iron oxide ores due its cheapness and availability since it is a by-product from other industrial processes.

Dissolution Mechanisms: Many researchers [2, 6, 7] have reviewed the basic principles of iron oxide dissolution. The report of the investigation revealed that the driving force for iron oxide dissolution is under

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saturation with respect to the iron ore. Therefore under saturation is necessary for iron oxide dissolution, whereas super saturation is necessary for precipitation. It was observed that extraction of iron from its ores requires under saturated solutions in order to be efficient whereas dissolution of anodic films often requires presence of saturated solution. The researchers also submitted that in most natural systems, (soils and waters) the aqueous phase is fairly close to saturation with respect to iron oxides, resulting in slow dissolution. The researches show that redox process in the presence of chelating ligands can be used to accelerate the dissolution process.

Researchers [1, 2] have revealed that the properties of the overall system and those of the oxide are the factors affecting the rate of dissolution of iron oxides. Properties of the overall system are temperature, composition of the solution phase (e.g. pH, redox potential, concentration of acids, reductants and complexing agents) whereas properties of the oxides are stoichiometry, crystal structure, crystal habit and presence of defects or guest ions. It was observed [2] that during the study of the dissolution mechanism of iron oxides, only the concentration of the solution and tendency of the ions in solution to form surface complexes are considered important.

It has been shown [1] that dissolution of iron oxides is highly influenced by pH conditions. The release of iron particularly at low pH has been observed to be due to the high affinity of protons with O^{2-} structure. It is the release of the cation, rather than the anion which is likely to be rate-limiting. The pH also indirectly influences the electrochemical surface potential and by implication the redox processes. This is because surface potential is determined largely by surface charge, which in turn, depends upon pH.

The rate of disproportion increases with decreasing pH and rising temperature, which also favour oxide reduction. To achieve a reasonable rate of dissolution, one has to determine the optimum pH, which varies from one system to another. A pH of 3.0 is used in kaolin bleaching [8], whereas in soil analysis the system is usually buffered with citrate and bicarbonate at ca. pH 7 [9].

Dissolution Kinetics: Research [10] has revealed that the rate of dissolution reactions is controlled by two mechanisms; transport-controlled (i.e. diffusion) or surface-controlled. In the transport-controlled mechanism, the concentration of dissolved species (c) immediately adjacent to the surface corresponds to the equilibrium solubility (c_e) of the solid phase, increases with the square root of time, t , i.e.

$$c = c_e + 2k_d t^{1/2} \quad (1)$$

k_d being the rate constant.

An example of transport controlled dissolution of iron oxides is the very rapid dissolution of hematite by the tris (picolinato)-V(II) species. Scientists [11, 12] have revealed that surface controlled mechanism during iron oxides dissolution is so fast that diffusion is regarded as the rate determining step. Observation has shown [13] that the slow diffusion of acid through the pores created by initial removal of haematite from the ore matrix bulk controls the acid leaching of iron oxides from bauxite.

In so many systems, chemical reactions at the solid/liquid interface more often than not is rate-determining step provided the activation energy is greater than 25kJ/mol, whereas diffusion-controlled reactions have lower activation energies. Where surface control is rate-determining, the instantaneous rate must be proportional to the surface area of the solid, i.e.

$$rate = dc/dt = k_A A \quad (2)$$

where k_A ($M s^{-1} m^{-2}$) is the kinetic rate constant and A is the surface area. At any time, t , the rate will be a function of the surface area left and a first order type of equation may be followed, i.e.

$$(1 - \alpha) = e^{-kt} \quad (3)$$

where α is the proportion dissolved at time t and k is the rate constant ($time^{-1}$). This equation is based on the assumption that the binding strengths of the ions in the solid are all the same.

An empirical model [14] has been developed for the prediction of the final solution pH and quantity of iron dissolved during leaching of iron oxide ore in oxalic acid solution. Another model [15] predicts the quantity of phosphorus removed during leaching of iron oxide in oxalic acid solution. Both researches [14,15] indicate that the final solution pH play a pivotal role in these predictions.

The researcher [14] submitted that Fe_2O_3 has greater tendency to dissolve in oxalic acid solution compared with Fe.

The aim of this work is to derive a model for predictive analysis of the final solution pH based on pre-determined initial solution pH and leaching time during oxalic acid leaching of Itakpe (Nigeria) iron oxide ore.

MATERIALS AND METHODS

Materials Preparation: 10g of dry iron oxide ore (haematite) of average grain size 150 μm was placed in a beaker containing 0.1mol/litre of oxalic acid. The initial solution pH of the leachant was measured as 5.88. The leaching process was allowed to go on for 180 mins., at a temperature of 25°C, after which the final solution pH was measured and quantities of dissolved Fe and Fe₂O₃ evaluated after filtration. This experiment was repeated using the same process parameters, but initial solution pH values adjusted to 5.71, 5.72, 5.7, 6.0, 6.32, 5.74 and 5.13 after which corresponding final solution pHs and quantities of dissolved Fe and Fe₂O₃ were evaluated respectively. The process was carried out in each case with five (5) samples and average values taken.

Model Formulation:

Table 1: Variation of initial pH ε with final pH ϑ of the leaching solution at constant leaching time λ

(ε)	(ϑ)	(λ)
5.88	4.65	180.00
5.71	4.40	180.00
5.72	4.42	180.00
5.70	4.48	180.00
6.00	4.66	180.00
6.32	5.38	180.00
5.74	4.68	180.00
6.13	5.16	180.00

Computational analysis of the actual results shown in Table 1, gave rise to Table 2 which indicate that;

$$h\epsilon + (\ln\lambda)^{1/2} \approx N(\epsilon^C / \vartheta^C) \tag{4}$$

$$h\epsilon + (\ln\lambda)^{1/2} = N(\epsilon / \vartheta^C) \tag{5}$$

Introducing the values of h, N and C into equation (5) reduces it to;

$$0.00002\epsilon + (\ln\lambda)^{1/2} = 1.0022(\epsilon / \vartheta)^{3.5} \tag{6}$$

Evaluating the final pH equation (6) becomes

$$\vartheta^{3.5} = \left(\frac{1.0022\epsilon^{3.5}}{(\ln\lambda)^{1/2} + 0.00002\epsilon} \right) \tag{7}$$

Taking logarithm of both sides of equation (7)

$$\text{Log } \vartheta^{3.5} = \left(\frac{\text{Log}1.0022\epsilon^{3.5}}{(\ln\lambda)^{1/2} + 0.00002\epsilon} \right) \tag{8}$$

$$3.5\text{Log } \vartheta = \text{Log} \left(\frac{1.0022\epsilon^{3.5}}{(\ln\lambda)^{1/2} + 0.00002\epsilon} \right) \tag{9}$$

$$\text{Log } \vartheta = 0.2857\text{Log} \left(\frac{1.0022\epsilon^{3.5}}{(\ln\lambda)^{1/2} + 0.00002\epsilon} \right) \tag{10}$$

$$\vartheta = \text{Antilog} \left(h\text{Log} \left(\frac{1.0022\epsilon^{3.5}}{(\ln\lambda)^{1/2} + 0.00002\epsilon} \right) \right) \tag{11}$$

where

(ε) = Initial solution pH

(ϑ) = Final solution pH

(λ) = Leaching time (mins)

N = 1.0022, h = 0.00002, C = 3.5; equalizing constants (determined using C-NIKBRAN [16]) and K = 0.2857; empirical constant

Boundary and Initial Conditions: Iron oxide ore was placed in cylindrical flask 30cm high containing leaching solution of oxalic acid acid. 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 ; 5.70-6.32 and leaching time of 3 hrs (180 minutes) were used for all samples. A constant leaching temperature of 25°C was used. Oxalic acid concentration at 0.1mol/litre and average ore grain size; 150μm were also used. Details of the experimental technique are as presented in the report.

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.

RESULTS AND DISCUSSION

Table 2: Variation of $0.00002\epsilon + (\ln\delta)^{1/2}$ with $N (\epsilon^C/9^C)$

$0.00002\epsilon + (\ln\delta)^{1/2}$	$N (\epsilon^C/9^C)$
2.2788	2.2787
2.2788	2.4951
2.2788	2.4709
2.2788	2.3283
2.2788	2.4274
2.2788	1.7609
2.2788	2.0478
2.2788	1.8314

Model Validity: The validity of the model is strongly rooted on the core model equation (6) where both sides of the equation are correspondingly almost equal. Table 2 also agrees with equation (6) following the values of $0.00002\epsilon + (\ln\delta)^{1/2}$ and $1.0022 (\epsilon/9)^{3.5}$ evaluated from the actual results in Table 1. Comparative analysis of results of the experiment in Figs. 1-4 shows that the trend of variation in both the initial and final solution pH is sinusoidal at constant leaching time. Also initial solution pH varies with the final solution pH correspondingly in a sinusoidal manner. It was generally observed that the final solution pH was correspondingly lower than the initial pH in line with the derived model prediction.

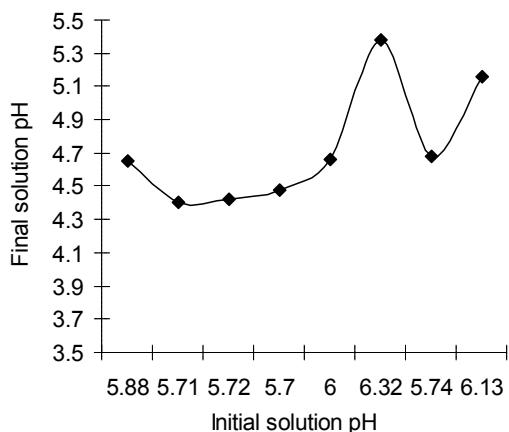


Fig.1: Coefficient of determination between final solution pH and initial solution pH as obtained from actual results

This was attributed to the fact that sulphur from the iron ore most likely dissolved during the leaching process and decreased the solution pH due to increased acidity of the solution. The derived model was also validated by comparing the final solution pH predicted by the model and that obtained from the experiment. This was done using various analytical techniques which includes statistical, graphical and deviational analyses.

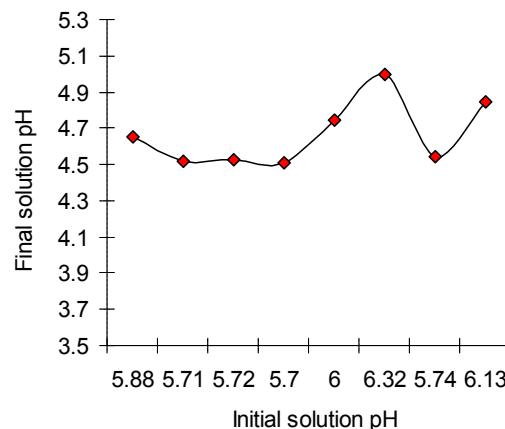


Fig. 2: Coefficient of determination between final solution pH and initial solution pH as obtained from predicted results

Statistical Analysis

Standard Error (STEYX): The standard error incurred in predicting the model-based final solution pH relative to values of the actual results is 0.066%. The standard error was evaluated using Microsoft Excel version 2003.

Graphical Analysis: The validity of the derived model was further verified by plotting (using Microsoft Excel (version 2003)) values of the predicted final solution pH besides those of the actual results. The essence of the plots was to evaluate the trend of results. Comparative analysis of Figs. 3-5 indicate very close alignment and dimensions of curves and shapes respectively which depicted significantly similar trend of data point's distribution for the actual and derived model-predicted final solution pH. Actual and model-predicted results were in very proximate agreement.

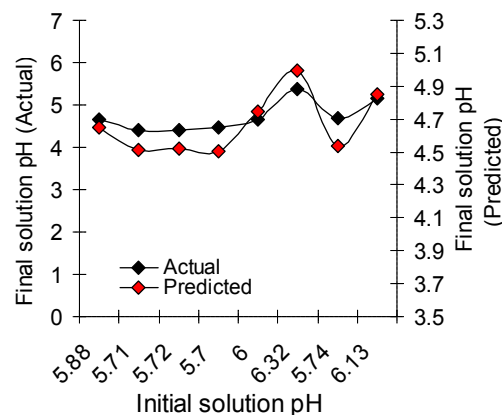


Fig. 3: Variation of final solution pH with initial solution pH as obtained from actual and model-predicted results

Deviational Analysis: Analysis of the final solution pH obtained from the actual and model-predicted results shows deviation on the part of model-predicted results. This was attributed to the fact that the effect of the surface properties of the iron oxide ore which played vital roles during the ore leaching in oxalic acid solution were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted final solution pH to those of the corresponding actual values.

The deviation Dv , of model-predicted final solution pH from the corresponding actual result was given by

$$Dv = \left(\frac{\vartheta_P - \vartheta_E}{\vartheta_E} \right) \times 100 \quad (12)$$

where

ϑ_E and ϑ_P are final solution pHs evaluated from actual and model-predicted respectively.

The empirical model; $\theta = \text{Antilog} [0.2857 \text{Log} (1.0022e^{3.5/(\ln \delta)^{1/2}})]$ predicts the final solution pH with maximum deviation < 7.5% (from actual results). This translated into over 92% operational confidence levels for the derived model and 0.92 dependency coefficient of final solution pH on the initial solution pH at constant leaching time. Fig. 4 shows that the least and highest deviations of model-predicted results (from actual results) are -0.01 and -7.1 %.

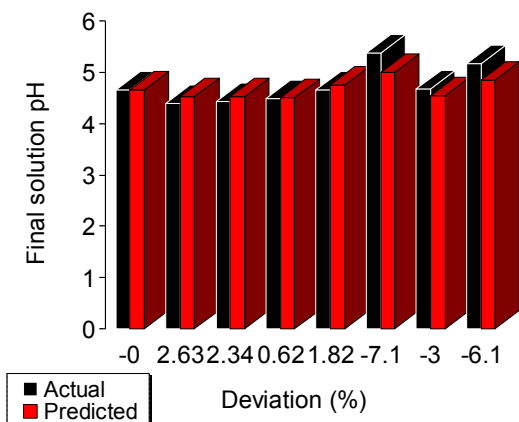


Fig. 4: Deviation of model-predicted results from actual values

These deviations correspond to model-predicted final solution pHs: 4.6496 and 4.9980 and initial solution pHs: 5.88 and 6.32 respectively.

Correction factor, Cf to the model-predicted results was given by;

$$Cf = - \left(\frac{\vartheta_P - \vartheta_E}{\vartheta_E} \right) \times 100 \quad (13)$$

Critical analysis of Fig. 4 and Fig. 5 show that the evaluated correction factors are negative of the deviation as shown in equations (12) and (13).

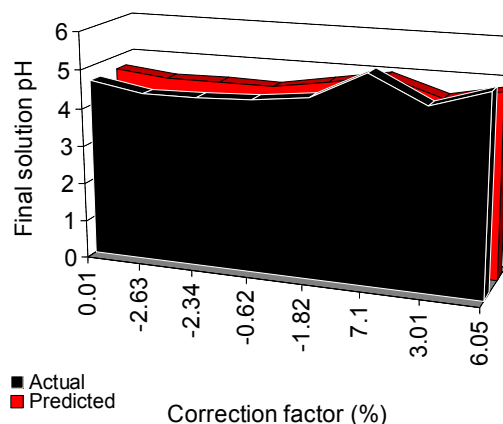


Fig. 5: Correction factor to model-predicted results

The correction factor took care of the negligence of operational contributions of the effect of surface properties of the iron oxide ore which actually affected the corrosion process. Introduction of the corresponding values of Cf from equation (13) into the model gives exactly the corresponding actual final solution pH. Fig. 5 indicates that the maximum correction factor to the model-predicted final solution pH was less than 7.5%. The table shows that the least and highest correction factors to the model-predicted results (from actual results) are 0.01 and 7.1 %. These correction factors also correspond to model-predicted final solution pHs: 4.6496 and 4.9980 and initial solution pHs: 5.88 and 6.32 respectively.

The deviation of model predicted results from that of the actual is just the magnitude of the value. The associated sign preceding the value signifies deviation deficit (negative sign) or surplus (positive sign).

CONCLUSION

Following open system leaching of iron ore in oxalic acid solution and predictability of the final solution pH based on initial solution pH and leaching time, the trend of variation in both the initial and final solution pH was sinusoidal at constant leaching time. Also the initial solution pH varied with the final solution pH correspondingly in a sinusoidal manner. The final solution pH was correspondingly lower than

the initial pH in line with the derived model prediction. This was attributed to the fact that sulphur from the iron ore most likely dissolved during the leaching process and decreased the solution pH due to increased acidity of the solution. The empirical model; $\theta = \text{Antilog} [0.2857 \text{ Log} (1.0022\varepsilon^{3.5} / (\ln \delta)^{1/2})]$ clearly predicted the final solution pH with maximum deviation < 7.5% (from actual results). This translated into over 92% operational confidence levels for the derived model and 0.92 dependency coefficient of final solution pH on the initial solution pH at constant leaching time. The validity of the model was rooted on the core model expression $0.00002\varepsilon + (\ln \delta)^{1/2} = 1.0022(\varepsilon / \theta)^{3.5}$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the final solution pH relative to values of the actual results is 0.066%.

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