

## Model for Calculating the Concentration of Leached Iron Relative to the Final Solution Temperature during Sulphuric Acid Leaching of Iron Oxide Ore

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**Abstract:** Model for calculating the concentration of leached iron during leaching of iron oxide ore in sulphuric acid solution has been derived. The model  $\%Fe = e^{-2.0421(\ln T)}$  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% which is quite within the range of acceptable deviation limit for experimental results, hence indicating the usefulness of the model as a predictive tool. [New York Science Journal. 2009;2(3):49-54]. (ISSN: 1554-0200).

**Keywords:** Model, Calculation, Leached Iron, Sulphuric Acid, Iron Oxide Ore, Solution Temperature

### 1. Introduction

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 [1]. 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 [2]. 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 [2]. Taxiarchour et al [3] 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 [4] 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  $Fe(C_2O_4)_3^{3-}$ . At these conditions, ( $pH > 2.5$  and an oxalate concentration higher than 0.1M) the predominant Fe(II) complex species is  $Fe(C_2O_4)_2^{2-}$ .

Lee et al. [5] reported 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 [5] to be slower than magnetite ( $FeO \cdot Fe_2O_3$ ) and other hydrated iron oxide such as goethite ( $\alpha$ - $FeOOH$ ), lapidochrosite ( $\gamma$ - $FeOOH$ ) and iron hydroxide ( $Fe(OH)_3$ ).

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 [3]. 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 an inert gas, was found [3] to enhance the reaction kinetics.

Ambikadevi and Lalithambika [6] evaluated the effectiveness of several organic acids (such as acetic, formic, citric, ascorbic acids etc.) used for dissolving iron from iron compounds. Oxalic acid was found to be the most promising because of its acid strength, good complexing characteristics and high reducing power, compared to other organic acids. Using oxalic acid, the dissolved iron can be precipitated from the

leach solution as ferrous oxalate, which can be re-processed to form pure haematite by calcinations [7]. Many researchers have studied the use of oxalic acid to dissolve iron oxide on a laboratory scale [8-14]. Lee et al [15] used 0.19-0.48M oxalic acid to dissolve hydrated iron oxide. Iron dissolution was found [15] to reach 90% for a 20% slurry within 60mins. using 0.19M oxalic for the finer fraction (< 150µm) containing 0.56% Fe<sub>2</sub>O<sub>3</sub>. The coarser fraction (>150µm) containing 1.06% Fe<sub>2</sub>O<sub>3</sub> achieved a lower iron removal, reaching a steady state of only 78% after 1 h of leaching. Although the pH was not measured or controlled, it was expected that the liquor pH is < pH1 at the oxalic acid concentration range studied (0.19-0.48M). Taxiarchou et al.[7] found that the maximum iron dissolution of only 40% is within 3h at temperatures in the range 90-100°C. At 0.5M oxalate and all temperatures (25, 60 and 80°C) the dissolution of iron was faster at a lower pH in the range pH 1-5 studied. Biological processes for iron dissolution have been evaluated by several researchers based on the use of several micro organisms that were easily sourced and isolated. Mandal and Banerjee [16] recently presented their findings on the study of the use of *Aspergillus niger* and their cultural filtrates for dissolving iron present in iron compounds.

Nwoye [17] 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;

$$\gamma = 0.5 \left( \frac{K_1[\%Fe_2O_3] + K_2[\%Fe]}{[\%Fe][\%Fe_2O_3]} \right) \quad (1)$$

where

$K_1$  and  $K_2$  = Dissolution constants of Fe and Fe<sub>2</sub>O<sub>3</sub> respectively.

$\gamma$  = pH of leaching solution after time t (mins.).

The values of the dissolution constants compared with those of % Fe and % Fe<sub>2</sub>O<sub>3</sub> from the experiment [17] indicate clearly that the constants  $K_1$  and  $K_2$  are numerical equivalence of the chemical resistance to the dissolution of Fe and Fe<sub>2</sub>O<sub>3</sub> (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<sub>2</sub>O<sub>3</sub>. This expression agreed with the higher percentage of Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> dissolved (at a temperature of 30°C and average ore grain size; 150µm) are known.

Model has been derived [18] for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution. The model is expressed as;

$$P = \left( \frac{150.5}{\mu\alpha} \right) \quad (2)$$

Where

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

( $\mu$ ) = Weight input of iron oxide ore (g)

( $\alpha$ ) = 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 [18].

The model [18] 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; 150µm 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.

It has been found [19, 20] that the final pH of the leaching solution depend on the leaching time, initial pH for the leaching solution and the leaching temperature.

It has been reported [21] 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 [21]. Phosphorus was removed (at a temperature of 25°C, average ore grain size; 150µm 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 [22] 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;

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

Where

T = Solution temperature at the time t, when the concentration of dissolved iron is evaluated. ( $^{\circ}C$ )

0.35= (pH coefficient for iron dissolution in sulphuric acid solution during the leaching process) determined in the experiment [22].

$\alpha$  = 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  $25^{\circ}C$ , initial solution pH 5.0 and average grain size;  $150\mu m$ ) 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.

The aim of this work is to derive a model for calculating the concentration of leached iron relative to the final solution temperature during leaching of Agbaja (Nigeria) iron oxide ore in sulphuric acid 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 sulphuric acid attack the ore within the liquid phase in the presence of oxygen.

### 2.1 Model Formulation

Experimental data obtained from research work [23] carried out at SynchroWell Research Laboratory, Enugu were used for this work.

Results of the experiment as presented in report [23] and used for the model formulation are as shown in Table 1.

Computational analysis of the experimental data [23] shown in Table 1, gave rise to Table 2 which indicate that;

$$\ln(\%Fe) = N(\ln T) \quad (\text{approximately}) \quad (4)$$

$$\%Fe = e^{N(\ln T)} \quad (5)$$

Introducing the value of N into equation (5)

$$\%Fe = e^{-2.0421(\ln T)} \quad (6)$$

where

$\%Fe$  = Concentration of leached iron during the leaching process.

T= Leaching solution temperature at the time t when the concentration of leached iron is evaluated. ( $^{\circ}C$ )

N= -2.0421(Temperature coefficient for iron dissolution in sulphuric acid solution during leaching of iron oxide ore) determined in the experiment [23].

Equation (6) is the derived model.

**Table1: Variation of weight input of iron oxide ore with final leaching solution temperature and leached iron. [23]**

M	T ( $^{\circ}C$ )	$\%Fe (10^{-3})$
8	26.01	1.7820
12	26.00	1.4000
14	25.90	1.6000
16	25.80	1.3000
18	25.76	1.0000
20	26.20	2.0000

**Table 2: Variation of In(%Fe) with N(InT)**

In( %Fe)	N(InT)
-6.3300	-6.6541
-6.5713	-6.6534
-6.4378	-6.6455
-6.6454	-6.6376
-6.9078	-6.6344
-6.2146	-6.6690

### 3. Boundary and Initial Condition

Consider iron ore in cylindrical flask 30cm high containing leaching solution of sulphuric 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. Weight of iron oxide ore used; (8-20g), initial pH of leaching solution; 5.0 and leaching time; 30 minutes were used. Leaching temperature used; 25°C. Ore grain size; 150µm, volume of leaching solution; 0.1 litre and sulphuric acid concentration; 0.1mol/litre was used. These and other process conditions are as stated in the experimental technique [23]. 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 comparison of %Fe values from model data and those from the experimental data for equality or near equality.

Analysis and comparison between these data reveal deviations of model data from experimental data. 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 [23] were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model data to that of the experimental values. (See Table 3)

Deviation (Dv) (%) of model %Fe values from experimental %Fe values is given by

$$Dv = \left( \frac{Dp - DE}{DE} \right) \times 100 \quad (7)$$

Where Dp = Predicted %Fe values from model

DE = Experimental %Fe values

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

$$Cf = -Dv \quad (8)$$

Therefore

$$Cf = \left( \frac{Dp - DE}{DE} \right) \times 100 \quad (9)$$

Introduction of the corresponding values of Cf from equation (9) into the model gives exactly the corresponding experimental %Fe values [23].

**Table 3: Comparison between %Fe dissolved as predicted by model and as obtained from experiment [23].**

%Fe <sub>exp</sub> (10 <sup>-3</sup> )	%Fe <sub>M</sub> (10 <sup>-3</sup> )	Dv (%)	Cf (%)
1.7820	1.2887	-27.68	+27.68
1.4000	1.2897	-7.88	+7.88
1.6000	1.3000	-18.75	+18.75
1.3000	1.3102	+0.78	-0.78
1.0000	1.3143	+31.43	-31.43
2.0000	1.2697	-36.52	+36.52

Where

%Fe<sub>exp</sub> = %Fe values from experiment [23]

%Fe<sub>M</sub> = %Fe values predicted by model

### 5. Results and Discussion

The derived model is equation (6). A comparison of the values of %Fe from the experimental data and those from the model shows positive and negative deviations less than 37% which is quite within the range of acceptable deviation limit of experimental results, hence depicting the reliability and validity of the model. This is shown in Table 3. The validity of the model is believed to be rooted on equation (4) where both sides of the equation are correspondingly approximately equal. Table 2 also agrees with equation (4) following the values of  $\ln[\%Fe]$  and  $N(\ln T)$  evaluated from Table 1 as a result of corresponding computational analysis.

### 6. Conclusion

The model calculates the concentration of leached iron relative to the final leaching solution temperature during leaching of Agbaja iron oxide ore in sulphuric acid solution. The validity of the model is believed to be rooted on equation (4) where both sides of the equation are correspondingly approximately equal. The deviation of the model-predicted %Fe values from those of the experiment is less than 37% which is quite within the range of acceptable deviation limit of experimental results. The model is therefore useful as a predictive tool.

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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