

Model for Predicting the Concentration of Phosphorus Removed as Impurity during Hydro-Processing of Iron Oxide Ore Designated for Production of Orthopedics Devices

C. I. Nwoye^{1*}, I. E. Mbuka¹, M. Obi² and K. Okeke³

¹Department of Materials and Metallurgical Engineering Federal University of Technology, Owerri, Imo State.

²Department of Industrial Mathematics, Federal University of Technology, Owerri, Imo State Nigeria.

³Department of Dental Technology, Federal University of Technology, Owerri, Imo State Nigeria.

chikeyn@yahoo.com

Abstract: A model for predicting the concentration of phosphorus removed as impurity during leaching of iron oxide ore in sulphuric acid solution has been derived. The model; $P = 10^{4.86\gamma}$ was found to depend on the value of the final pH of the leaching solution which varies with leaching time. It was observed that the validity of the model is rooted in the expression $\text{Log}P = N\gamma$ where both sides of the relationship are approximately equal to 2.3. The maximum deviation of the model-predicted phosphorus concentration (removed) from the corresponding value obtained from the experiment was found to be less than 8% which is quite within the acceptable deviation limit of experimental results.

[C. I. Nwoye, I. E. Mbuka, M. Obi and K. Okeke. Model for Predicting the Concentration of Phosphorus Removed as Impurity during Hydro-Processing of Iron Oxide Ore Designated for Production of Orthopedics Devices. Life Science Journal 2010;7(4):26-30]. (ISSN: 1097-8135).

Keywords: Model, Phosphorus Removal, Sulphuric Acid, Iron Oxide Ore, Leaching.

Steel has been found [1] to be chiefly made up of over 95% Fe and carbon less than 1%. Increasing addition of Cr into the Fe and C matrix and structure re-designs the steel to stainless steel. Addition of nickel to the stainless steel microstructure causes the austenite structure to be maintained at room temperature hence producing austenitic stainless steel [2]. It has been found [2] that 316 stainless steel finds application in early hip implants due to its good strength, ability to work harden and pitting corrosion resistance. The mechanical properties of stainless steel includes: ultimate tensile strength; 190-690Mpa and elongation; 12-40% [2]. Stainless steel usage in biomedical engineering is restricted to temporary device such as screws, plates, fittings and wires for orthopaedics due to potential long term release of Ni^{2+} , Cr^{3+} , and Cr^{6+} into the body [2].

Presence of phosphorus in iron designated for production of engineering materials has been found to enhance embrittlement when these materials are put into use. Furthermore, application of iron with high phosphorus content for production of orthopedic devices endangers the health of the patient involved since phosphorus is very poisonous. This formed the basis for several attempts already made to reduce the concentration of phosphorus inherent in iron oxide ores designated for production of engineering materials.

Several works [3-8] have been carried out to remove phosphorus from steel during steel making. All these works carried out, pointed out low treatment

1.0 Introduction

temperature and high oxygen activity as the only essential and unavoidable process conditions which can enhance the rate of dephosphorization. High activity of CaO; a product of decomposition of CaCO_3 and a slag forming material is required for enhancement of the dephosphorization process with the phosphorus forming part of the slag. This process involves pyrometallurgy and is capital intensive.

It has been reported [9] that the removal of phosphorus from iron can be achieved only by oxidation during steel making, under a basic slag.

Nwoye [10] derived a model for predicting the time for dissolution of pre-quantified concentration of phosphorus during leaching of iron oxide ore in oxalic acid solution as:

$$\text{Log}T = \frac{\tau \left(\frac{\text{Log} P^{1/4}}{1.8} \right)}{\quad} \quad (1)$$

Where

T= Leaching temperature ($^{\circ}\text{C}$) in the experiment [11], taken as specified leaching temperature ($^{\circ}\text{C}$) aiding the expected dissolution of phosphorus .

N= 1.8 (Dissolution coefficient of phosphorus in oxalic acid solution during leaching of iron oxide ore) determined in the experiment [11].

P = Concentration of dissolved phosphorus (mg/Kg) in the experiment [11], taken as pre-quantified concentration of phosphorus expected to dissolve after a leaching time t (mg/Kg) in the model.

τ = Leaching time (sec.) in the experiment [11], taken as time for dissolution of the pre-quantified concentration of phosphorus (hrs) in the model.

The model was found to depend on a range of specified leaching temperatures (45-70°C) for its validity. It was found [11] that the time for dissolution of any given concentration of phosphorus decreases with increase in the leaching temperature (up to 70°C), at initial pH 5.5 and average grain size of 150 μ m.

Nwoye et al. [12] also formulated a model for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution. The model is expressed as;

$$P = 150.5/\mu\alpha \quad (2)$$

It was found to predict the removed phosphorus concentration, with utmost dependence on the final pH of the leaching solution and weight input of the iron oxide ore. The model indicates that the concentration of phosphorus removed is inversely proportional to the product of the weight input of the iron oxide ore and the final pH of the leaching solution. Process conditions considered during the formulation of the model [12] include: leaching temperature of 25°C, initial solution pH 5.5 and average ore grain size; 150 μ m).

Nwoye [13] derived a model for the 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. It was observed that the validity of the model is rooted in the relationship $\ln P = N/\alpha$ where both sides of the expression are approximately equal to 4. The model expressed as;

$$P = e^{(12.25/\alpha)} \quad (3)$$

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%.

Nwoye [14] also derived a model for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution. The model is expressed as;

$$P = [(1.8(T)^5)]^4 \quad (4)$$

was found to be dependent on leaching temperature ranging from 45-70°C and specified leaching time of 0.1381hr (497secs.) recorded during experiment, for

its validity. It was found that the validity of the model is rooted in the expression $(P^{1/4})/N = (T)^\tau$ where both sides of the expression are correspondingly almost equal. The maximum deviation of the model-predicted values of P from the corresponding experimental values was found to be less than 29% which is quite within the range of acceptable deviation limit of experimental results.

Model for predictive analysis of the concentration of phosphorus removed (relative to the initial and final pH of the leaching solution) during leaching of iron oxide ore in sulphuric acid solution has been derived by Nwoye and Ndulu [15]. It was observed that the validity of the model is rooted in the mathematical expression; $(P/N)^{1/3} = (e^{\tau/\alpha})$ where both sides of the relationship are almost equal. The model;

$$P = 4.25(e^{\tau/\alpha})^3 \quad (5)$$

shows that the concentration of phosphorus removed is dependent on the values of the initial and final pH of the leaching solution.

Biological processes for phosphorus removal have also been evaluated based on the use of several types of fungi, some being oxalic acid producing. Anyakwo and Obot [16] recently presented their results of a study on the use of *Aspergillus niger* and their cultural filtrates for removing phosphorus from Agbaja (Nigeria) iron oxide ore. The results of this work [16] show that phosphorus removal efficiencies at the end of the 49 days of the leaching process are 81, 63 and 68% for 5, 100 and 250 mesh grain sizes respectively.

An attempt has been made in the past [17] to leach Itakpe iron oxide ore using oxalic acid solution in order to determine the maximum concentration of phosphorus that is removable. Results of chemical analysis of the ore indicate that the percentage of phosphorus in the ore is about 1.18%, which from all indication is quite high and likely to affect adversely the mechanical properties of the steel involved; hence the need for dephosphorization. It was reported [17] that phosphorus can be removed from this iron oxide ore through a process associated with hydrometallurgy. Phosphorus was removed at a temperature of 25°C and initial solution pH 2.5, leading to the dissolution of the phosphorus oxide formed. This involved using acid leaching process to remove phosphorus from the iron oxide ore in readiness for steel making process.

The aim of this work is to derive a model for predicting the concentration of phosphorus removed (as impurity) relative to the final pH of the solution during leaching (hydrometallurgical processing) of Itakpe (Nigerian) iron oxide ore using sulphuric acid solution. This derivation is embarked on in furtherance of the previous work. [17]

The solid phase (ore) is assumed to be stationary, contains the un-leached iron remaining in the ore.

2. Model

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 [17] carried out at SynchroWell Research Laboratory, Enugu were used for this work.

Results of the experiment as presented in report [17] and used for the model formulation are as shown in Table 1.

Computational analysis of the experimental data [17] shown in Table 1, resulted to Table 2 which indicate that;

$$\text{LogP} = N\gamma \quad (\text{approximately}) \quad (6)$$

$$P = 10^{N\gamma} \quad (7)$$

Introducing the value of N into equation (7)

$$P = 10^{4.86\gamma} \quad (8)$$

where

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

N= 4.86; (pH coefficient for phosphorus dissolution in sulphuric acid solution) determined in the experiment. [17]

γ = Final pH of the leaching solution at the time t when the concentration of phosphorus removed is evaluated.

Equation (8) is the derived model.

3. Boundary and Initial Condition

Consider iron oxide 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. Varying weights (4-14g) of iron oxide ore were used as outlined in Table 1. The initial pH of leaching solution; 0.52 and leaching time of 30minutes were used for all samples. A constant leaching temperature of 25°C was used. Ore grain size; 150 μ m, volume of leaching solution; 0.1 litre and sulphuric acid concentration; 0.1mol/litre were used. These and other process conditions are as stated in the experimental technique [17].

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.

Table1: Variation of final solution pH with concentration of phosphorus removed. [17]

M (g)	γ	P (mg/Kg)
4	0.48	214.00
6	0.47	203.00
8	0.48	199.75
10	0.48	232.25
12	0.47	198.00
14	0.47	183.00

Where M = Mass of iron oxide ore used for the leaching process (g).

Table 2: Variation of LogP with $N\gamma$

M (g)	LogP	$N\gamma$
4	2.3304	2.3328
6	2.3075	2.2842
8	2.3005	2.3328
10	2.3660	2.3328
12	2.2967	2.2842
14	2.2625	2.2842

4. Model Validation

The formulated model was validated by direct analysis and comparison of the model-predicted P values and those from the experiment [17] for equality or near equality. Analysis and comparison between these P values reveal deviation of model-predicted P values from the corresponding experimental P 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 play vital roles during the leaching process [17] were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted P values to that of those of the experiment.

Deviation (Dv) (%) of model- predicted P values from experimental P values is given by

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

Where Dp = Model-predicted P values
DE = Experimental P values

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

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

Therefore

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

Introduction of the corresponding values of Cf from equation (11) into the model gives exactly the corresponding experimental P values. [17]

5. Results and Discussion

The derived model is equation (8). A comparison of the values of P from the experiment and those from the model (Table 3) shows very insignificant positive and negative deviations, hence depicting the reliability and validity of the model. The maximum deviation of the model-predicted P values from those of the experiment is 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 2.3. Table 2 also agrees with equation (6) following the values of LogP and Ny obtained after statistical and computational analysis were carried out on the experimental results in Table 1. A comparison of these two concentrations of removed phosphorus (Tables 1 and 3) from the iron oxide ore shows proximate agreement. The close alignment of the curves; ExD and MoD in Figure 1 also shows proximate agreement between experimental [17] and model-predicted values of removed phosphorus. This indicates a very high degree of validity for the model as a reliable tool for predicting the concentration of phosphorus removed as impurity during hydrometallurgical processing of iron oxide ore designated for production of orthopedic devices.

Table 3: Variation of the model-predicted concentration of removed phosphorus with the associated deviation and correction factor.

P _M (mg/Kg)	Dv (%)	Cf (%)
215.18	+0.55	-0.55
192.40	-5.22	+5.22
215.18	+7.72	-7.72
215.18	-7.35	+7.35
192.40	-2.83	+2.83
192.40	+5.14	-5.14

P_M = P values predicted by model.

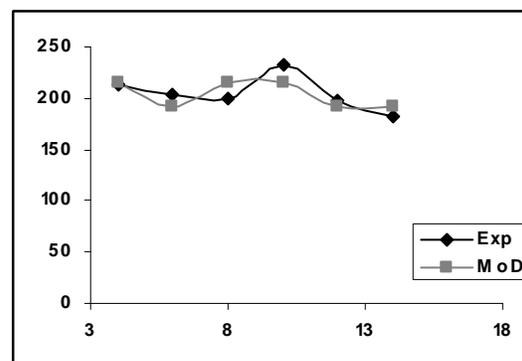


Figure 1. Comparison of the concentrations of phosphorus removed as obtained from experiment (line ExD) [17] and derived model (line MoD).

6. Conclusion

The model predicts the concentration of phosphorus removed (relative to the final solution pH) as impurity during hydrometallurgical processing of iron oxide ore designated for production of orthopedic devices. The validity of the model is believed to be rooted on the expression $\text{LogP} = N\gamma$ where both sides of the expression are approximately equal to 2.3. It was observed that the maximum deviation of the model-predicted P values from those of the experiment is less than 8% which is quite insignificant and within the acceptable deviation limit of experimental results.

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

Acknowledgement

The author thanks Dr. Ekeme Udoh, a modelling expert at Linkwell Modelling Centre Calabar for his technical inputs. The management of SynchroWell Nig. Ltd. Enugu is also appreciated for permitting and providing the experimental data used in this work.

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8/1/2010