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Model for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution

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Abstract

Model for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution has been derived. The model; $P = [(1.8(T)^{\tau})]^4$ was found to be dependent on leaching temperature ranging from 45-70^{0}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 positive and negative 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. Phosphorus removal per unit rise in the leaching temperature as obtained from experiment and derived model were evaluated as 1.3 and 0.93 mg/Kg/^{0}C respectively.

Keywords: Model; dephosphorization; temperature and time; oxalic acid; iron oxide ore; leaching

1. Introduction

Iron oxide dissolution 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. (Taxiarchour et al, 1997a). 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 (Lee et al, 2006). 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 (Lee et al, 2006). Taxiarchour et al. (1997b) discovered that presence of Fe^{2+} significantly enhance the leaching of iron extraction from silica sand at a temperature even as low as 25^{o}C. 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 to enhance the reaction kinetics.

Models for computational analysis of the concentration of dissolved haematite and heat absorbed by oxalic acid solution during leaching of iron oxide ore have been derived (Nwoye,2008). These models are:

$$\%Fe_2O_3 = K(\gamma/\mu) \quad (1)$$

$$Q = K_C \mu \quad (2)$$

Where
$\%Fe_2O_3$ = Concentration of dissolved haematite in oxalic acid solution.
γ = Final pH of the leaching solution at time t at which $\%Fe_2O_3$ was obtained.
μ = Weight of iron oxide added into the oxalic acid leaching solution (g).
K = Constant of proportionality associated with haematite dissolution.
K_C = Constant of proportionality associated with heat absorption.
Q = Quantity of heat absorbed by oxalic acid solution during the leaching process (J).

Nwoye (2008) found that optimization of the weight input of iron oxide ore could be achieved using the model; ($\%Fe_2O_3 = K(\gamma/\mu)$) by comparing the concentrations of dissolved haematite at different

weights input of the iron oxide ore, with the view to identifying the optimum weight input of iron oxide ore that gives the maximum dissolution of Fe_2O_3. 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.

It was also found (Nwoye,2008) that values of Q obtained from both the experiment and model ($Q = K_C \mu$) 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 (as calculated from the model; $Q = K_C \mu$) 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 30^0C. The constants of proportionality K and K_C associated with the respective derived models were evaluated to be 0.0683 and 66.88 respectively.

Several works (Zea, 1945; Turkdogan and Pearson, 1953; Kootz *et al.*, 1961; Decker, 1962; Dukelov, 1962; Kootz *et al.*, 1965) have been carried out to remove phosphorus from steel during steel making. All these works carried out, pointed out low treatment 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 (Zea,1945) that the removal of phosphorus from iron can be achieved only by oxidation during steel making, under a basic slag.

Nwoye (2008) 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:

$$\tau = \left(\frac{\mathrm{Log}\left(\frac{P^{1/4}}{1.8} \right)}{\mathrm{Log}T} \right) \quad (3)$$

Where

T = Leaching temperature (^{0}C) in the experiment (Nwoye,2006), taken as specified leaching temperature (^{0}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(Nwoye,2006) .

P = Concentration of dissolved phosphorus (mg/Kg) in the experiment (Nwoye,2006), taken as pre-quantified concentration of phosphorus expected to dissolve after a leaching time t (mg/Kg) in the model.

t = Leaching time (sec.) in the experiment (Nwoye,2006), 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^{0}C) for its validity. It was found (Nwoye,2006) that the time for dissolution of any given concentration of phosphorus decreases with increase in the leaching temperature (up to 70^0C), at initial pH 5.5 and average grain size of 150μm.

Nwoye et al. (2008) also formulated a model for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution. 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 expressed as;

$$P = 150.5/\mu\alpha \quad (4)$$

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 (Nwoye et al., 2008) include: leaching temperature of 25^0C, initial solution pH 5.5 and average ore grain size; 150μm).

Nwoye (2009) 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;

$$P = e^{(12.25/\alpha)} \quad (5)$$

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 Ndlu (2009). It was observed that the validity of the model is rooted in the mathematical expression; $(P/N)^{1/3} = (e^{\gamma/\alpha})$ where both sides of the relationship are almost equal. The model;

$$P = 4.25(e^{\gamma/\alpha})^3 \quad (6)$$

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

Nwoye et al., (2010) derived a model for quantitative analysis of the concentration of phosphorus removed (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 expression $\ln P = (\gamma + N\ln\gamma)$ where both sides of the expression are correspondingly approximately equal. The model;

$$P = e^{(\gamma + 0.57 \ln\gamma)} \quad (7)$$

depends on the value of the final pH of the leaching solution which varies with leaching time. The maximum deviation of the model-predicted concentration of removed phosphorus from the corresponding concentration obtained from the experiment was less than 22%. The concentrations of phosphorus removed per unit mass of iron oxide ore added as obtained from experiment and derived model are 3.8329 and 4.0614 mg/kg/g respectively which are in proximate agreement.

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 (2008) 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 (Anyakwo and Obot,2008) 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 (Nwoye,2003) 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 indications is quite high and likely to affect adversely the mechanical properties of the steel involved; hence the need for dephosphorization. It was reported (Nwoye,2003) that phosphorus can be removed from iron oxide ore through a process associated with hydrometallurgy. Phosphorus was removed at a temperature of 25^0C 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.

Final pH of leaching solution has been found to depend on the leaching time, initial pH for the leaching solution and the leaching temperature (Pinches, 1975; Nwoye, 2008).

The aim of this work was to derive a model for predicting the concentration of phosphorus removed at specified leaching temperature and time during oxalic acid leaching of Itakpe (Nigeria) iron oxide ore.

2. Experimentation and method

Iron ore mined at Itakpe was homogenized and average grain size determined by hydrometer method as 150μm.2g of Ore was placed in a cylindrical flask containing oxalic acid of concentration 0.1 mol/litre of the leaching solution. The initial pH of the solution was 5.5. Leaching was carried out at a temperature range 40-70^0C for 497 seconds (Nwoye, 2006).

2.1. Model

The solid phase (ore) is assumed to be stationary, contains the un-leached iron remaining in the ore. Hydrogen ions from the oxalic acid attack the ore within the liquid phase in the presence of oxygen.

2.2. Model formulation

Model formulation was achieved using experimental data derived in previous work (Nwoye, 2006) as shown in Table 1. Results of the experiment as presented in report (Nwoye, 2006) and used for the model formulation are as shown in Table 1.

Computational analysis of the experimental data (Nwoye,2006) shown in Table 1, gave rise to Table 2 which indicate that;

$$(T)^{\tau} = \frac{P^{1/4}}{N} \text{ (approximately)} \quad (8)$$

$$N(T)^{\tau} = P^{1/4} \quad (9)$$

$$P = [(N(T)^{\tau})]^4 \quad (10)$$

Introducing the values of N into equation (10)

$$P = [(1.8(T)^{\tau})]^4 \quad (11)$$

Where

T= Leaching temperature (^{0}C)

N= 1.8 (Dissolution coefficient of phosphorus in oxalic acid solution during leaching of iron oxide ore) determined in the experiment (Nwoye,2006)

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

τ = Leaching time (hr) Equation (11) is the derived model

Table 1
Variation of leaching temperature with concentration of phosphorus removed

T(^{0}C)	(τ) (sec)	P (mg/Kg)
45	497	120.50
50	497	112.00
55	497	97.25
60	497	93.87
65	497	91.96
70	497	88.00

Source: (Nwoye,2006)

Table 2
Variation of $(T)^{\tau}$ with $(P^{1/4})/N$

$(T)^{\tau}$	(τ) (hrs)	$(P^{1/4})/N$ (mg/Kg)
1.6916	0.1381	1.8407
1.7164	0.1381	1.8073
1.7392	0.1381	1.7446
1.7602	0.1381	1.7293
1.7798	0.1381	1.7204
1.7981	0.1381	1.7016

3. Boundary and initial condition

Iron ore in cylindrical flask 30cm high containing leaching solution of oxalic acid was considered. The leaching solution is stationary i.e (non-flowing). The flask was assumed to be initially free of attached bacteria. Initially, atmospheric levels of oxygen were assumed. Weight of iron oxide ore used; 2g, initial pH of leaching solution; 5.5, leaching time; 497sec., and Leaching temperature range; 45-70^{o}C were used. Ore grain size; 150µm, volume of leaching solution; 0.1litre and oxalic acid concentration; 0.1mol/litre were also used. These and other process conditions are as stated in the experimental technique (Nwoye, 2006).

The boundary conditions were: 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 were assumed and also for the gas phase at the top of the particles. The leaching solution was stationary. The sides of the particles were taken to be symmetries.

4. Model validation

The formulated model was validated by direct analysis and comparison of P values predicted from model and those from the experiment for equality or near equality.

Analysis and comparison between these P values revealed deviations of model-predicted P values from the experimental values. This was 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 (Nwoye,2006) were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted P values to that of the experimental values.

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

$$Dv = \left(\frac{Dp - DE}{DE}\right) x\,100 \qquad (12)$$

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

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

$$Cf = -Dv \qquad (13)$$

Therefore

$$Cf = -100\left(\frac{Dp - DE}{DE}\right) \qquad (14)$$

Introduction of the corresponding values of Cf from equation (14) into the model gives exactly the corresponding experimental P values. (Nwoye, 2006).

5. Results and discussion

The derived model is equation (11). A comparison of the values of P from the experiment and those from the model as in Figs. 1-3 shows low positive and negative deviations hence depicting the reality, reliability and validity of the model. The respective positive and negative deviation of the model-predicted P values from the corresponding experimental values is less than 29% which is within the acceptable range of deviation limit of experimental results. The validity of the model is believed to be rooted in the expression $(T)^{\tau} = (P^{1/4})$ since both sides of the expression are correspondingly almost equal. Table 2 also agrees with equation (8) following the values of $(T)^{\tau}$ and $(P^{1/4})/N$ evaluated from Table 1 as a result of the corresponding computational analysis. Phosphorus removed per unit rise in the leaching temperature during the leaching process was determined following comparison of the concentration of phosphorus removed per unit rise in the leaching temperature obtained by calculations involving experimental results as well as derived model.

5.1. Determination of the concentration of phosphorus removed per unit rise in the leaching temperature

Concentration of phosphorus removed during leaching in oxalic acid solution per unit rise in the leaching temperature P_T (mg/kg/^{0}C) is calculated from the equation;

$$P_T = P/T \qquad (15)$$

Therefore, a plot of concentration of phosphorus removed against leaching temperature (as in Fig.1) gives a slope, S at points (109.73, 70) and (85.97, 45) following their substitution into the mathematical expression;

$$S = \Delta P/\Delta T \qquad (16)$$

Eqn. (16) is detailed as

$$S = P_2 - P_1 / T_2 - T_1 \qquad (17)$$

Where
ΔP = Change in the concentrations of phosphorus removed P_2, P_1 at leaching temperature values T_2, T_1. Considering the

points (109.73, 70) and (85.97, 45) for (P_2, T_2) and (P_1, T_1) respectively, and substituting them into eqn. (17), gives the slope as 0.93 mg/kg/^{0}C which is the concentration of phosphorus removed per unit rise in the leaching temperature as predicted by derived model.

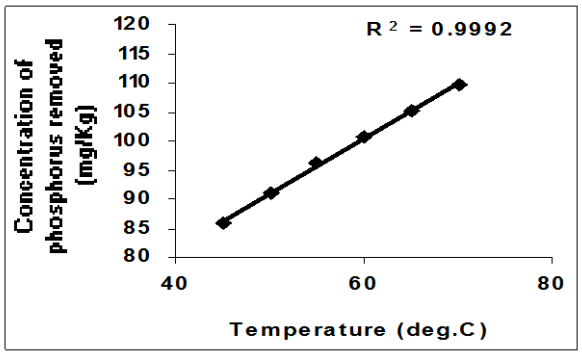


Fig.1.Variation of the concentration of phosphorus removed with treatment temperature (as predicted by derived model).

Also similar plot (as in Fig. 2) experimental results (Nwoye, 2006) gives a slope. Considering points (88.0, 70) and (120.5, 45) for (P_2, T_2) and (P_1, T_1) respectively and substituting them into eqn. (17) gives the value of slope, S as - 1.3 mg/kg/^{0}C. This is the concentration of phosphorus removed per unit rise in the leaching temperature during the actual leaching process. A comparison of these two values of removed phosphorus concentrations per unit rise in the leaching temperature used shows proximate agreement.

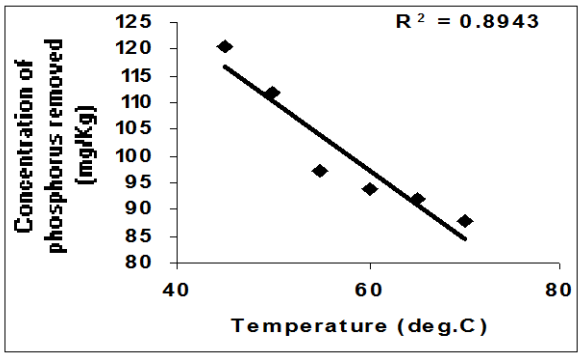


Fig. 2. Variation of the concentration of phosphorus removed with treatment temperature (as obtained from experiment (Nwoye, 2006)).

This indicates a very high degree of validity for the model. It is important to state that the negative sign preceding 1.3mg/Kg^{0}C merely shows an inverse relationship between the concentration of removed phosphorus and leaching temperature (as obtained from experimental results) which culminated in a negative slope; opposite to the case involving model-predicted results. However, the real value of the concentration of phosphorus removed per unit rise in the leaching temperature as obtained from the experiment (Nwoye,2006) is just the magnitude which is 1.3 mg/Kg/^{0}C. The difference in the sign preceding the values of the concentrations of phosphorus removed per unit rise in the leaching temperature as obtained from experiment and derived model resulted from non-consideration of the surface properties of the ore and the physiochemical interaction between the ore and the leaching solution (which affected experimental results) during the model formulation.

An ideal comparison of the concentrations of phosphorus removed from as obtained from experiment and as predicted by the model for the purpose of testing the validity of the model is achieved by considering the R^2 values (coefficient of determination). The values of the correlation coefficient, R calculated from the equation;

$$R = \sqrt{R^2} \quad (18)$$

using the r-squared values (coefficient of determination) from Figs.1 and 2 show a better correlation (0.9996) with model-predicted concentration of removed phosphorus than that obtained from experiment (0.9457). This suggests that the model predicts more accurate, reliable and ideal concentration of removed phosphorus than the actual experiment despite its deviation from experimental values. Based on the foregoing, the model is believed to be very valid as a predicted tool.

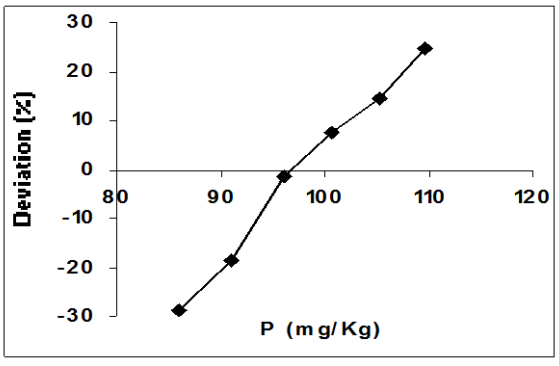


Fig. 3. Plot of model-predicted concentration of removed phosphorus against its deviation from experimental values (Nwoye, 2006).

The positive and negative deviations of the model-predicted concentration of removed phosphorus from actual experiment show linear relationship (as in Fig. 3) with the concentration of P removed. This implies that deviation increases with increase in the concentration of phosphorus removed. Correction factor for the model-predicted concentration P (shown in Fig. 4) however shows an inverse relationship with P.

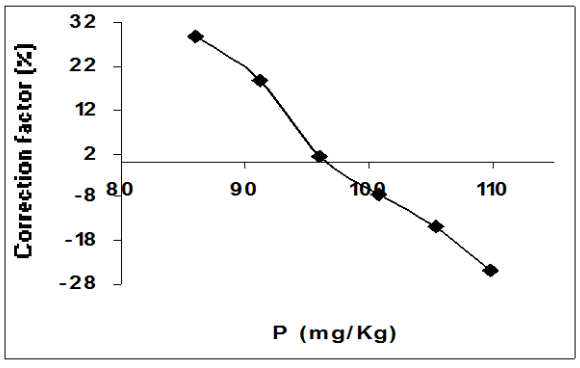


Fig. 4. Plot of model-predicted concentration of removed phosphorus against its correction factor.

This is because correction factor is the negative of the deviation as shown in eqns. (13) and (14). It is believed that the correction factor takes care of the effects of the surface properties of the ore and the physiochemical interaction between the ore and the leaching solution which (affected experimental results) were not considered during the model formulation.

Fig.5 shows that the relationship between deviation of model-predicted concentration of P and the leaching temperature is linear. Comparison of Figs. 1, 3 and 5 indicates that this relationship is due to the linear relationship existing between leaching temperature and the concentration of P removed. Also Figs. 3 and 5 show linear relationship between the respective parameters; T, P and deviation.

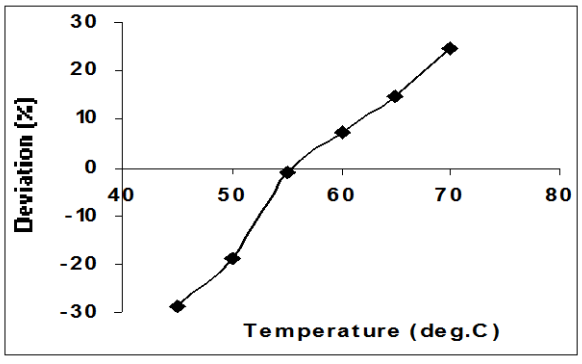


Fig. 5. Plot of deviation of model-predicted concentration of removed phosphorus against leaching temperature.

Based on the foregoing, the presentation in Fig.5 indicates that a leaching temperature of 45 and 70^0C gives the least and highest deviation (respectively) of model-predicted P value from the corresponding experimental value.

6. Conclusion

The model predicted the concentration of phosphorus removed at specified leaching temperature and time during leaching of Itakpe iron oxide ore in oxalic acid solution. 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 deviation of the model-predicted P values from those of the experiment was less than 29% which is quite within the acceptable range of deviation limit of experimental results. Phosphorus removal per unit rise in the leaching temperature as obtained from experiment and derived model were evaluated as 1.3 and 0.93 mg/Kg/^{0}C respectively.

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

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