

INVESTIGATION OF THE OPTIMUM DISSOLUTION TEMPERATURES OF PHOSPHORUS IN SULPHURIC, NITRIC AND OXALIC ACID SOLUTIONS DURING LEACHING OF IRON OXIDE ORE

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Abstract

Studies were carried out to determine the optimum dissolution temperatures of phosphorus in oxalic, nitric and sulphuric acid solutions during leaching of iron oxide ore. Phosphorus dissolution rates and dissolution per unit rise in temperature were determined and compared to ascertain the preferred acid in terms of effective dephosphorization of iron oxide ore using leaching process. The results of the investigation show that the optimum dissolution temperatures of phosphorus in these acids were found to be 45, 55 and 70°C respectively. Phosphorus dissolutions per unit rise in temperature in these acid solutions during the increasing and decreasing stage of dissolution were 9.4 and -3.07 mg/kg/°C 2.88 and -4.7 mg/kg/°C and also 2.16 and -7.95 mg/kg/°C respectively. Phosphorus dissolution rates in these acid solutions during the increasing and decreasing stage of dissolution were also determined as 0.67 and -0.13 mg/kg/s, 0.14 and -0.19 mg/kg/s and also 0.1 and 0.44 mg/kg/s for oxalic, nitric and sulphuric acid solutions respectively. This confers to oxalic acid a better dissolution power on phosphorus over nitric and sulphuric acid, followed by nitric acid.

Keywords: Dissolution Temperature, Phosphorus, Sulphuric, Nitric, Oxalic Acid, Iron Oxide Ore, Leaching.

Nomenclature	
K	Constant of proportionality associated with haematite dissolution
K_c	Constant of proportionality associated with heat absorption
N	Dissolution coefficient of phosphorus in oxalic acid solution
P	Concentration of dissolved phosphorus, mg/kg
P_T	Phosphorus dissolution per degree rise in temperature, mg/kg/°C
Q	Quantity of heat absorbed, J
S	Slope
T	Temperature, °C
t	Time elapsed during dissolution of phosphorus in oxalic, nitric and sulphuric acid solutions, hrs
<i>Greek Symbols</i>	
α	Final pH of leaching solution (in the presence of dissolved phosphorus)
γ	Final pH of leaching solution (in the presence of dissolved iron)
μ	Weight of iron oxide ore added into the leaching Solution, g
τ	Time elapsed during dissolution of pre-quantified concentration of phosphorus in oxalic acid, hrs

1. INTRODUCTION

Studies have shown that the presence of Fe^{2+} significantly enhances the leaching of iron extraction from silica sand at a temperature even as low as 25°C [1, 2]. Ferrous oxalate, however, is oxidized quickly by air during the dissolution and in general an induction period of a few hours was observed 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 [3]. It is believed that during this process, removal of phosphorus from the iron compound and subsequent dissolution of the phosphorus oxide formed were effected.

It has been found that the optimum pH for dissolving iron oxide is pH 2.5–3.0 [4]. The solution pH governs the distribution of various oxalate ions in the leach system. Below pH 1.5, oxalic acid exists mainly as $\text{H}_2\text{C}_2\text{O}_4$, whereas HC_2O_4 is the most predominant species at pH 2.5–3.0. Final pH of leaching solution has been found to depend on the leaching time, initial pH for the leaching solution and the leaching temperature [5,6].

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 [7]. These models are:

$$\% \text{Fe}_2\text{O}_3 = K (\gamma/\mu) \quad (1)$$

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

Nwoye [7] 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 [7] 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 150 μm and leaching temperature of 30°C. The constants of proportionality K and K_C associated with the respective derived models were evaluated to be 0.0683 and 66.88 respectively.

A model has been derived [8] for predictive analysis of the concentration of phosphorus removed during leaching of iron oxide ore in sulphuric acid solution. The model;

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

shows that the concentration of phosphorus removed is dependent on the values of the initial and final pH of the leaching solution. 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. 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 29%, which is quite within the acceptable deviation limit of experimental results hence establishing the validity and precision of the model in its application for predicting quantitatively the concentration of phosphorus removed during the leaching process.

Nwoye [9] 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. The model was found to depend on a range of specified leaching temperatures (45-70°C) for its validity. It was found [10] that the time for dissolution of any given concentration of phosphorus decreases with the increase in the leaching temperature (up to 70°C), at initial pH 5.5 and average grain size of 150 μm .

Nwoye et al. [11] 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

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

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 [11] include: leaching temperature of 25°C, initial solution pH 5.5 and average ore grain size of 150 µm.

Nwoye [12] 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

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

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 [13] 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

$$P = [1.8 (T)^\tau]^{1.4} \quad (6)$$

was found to be dependent on leaching temperature ranging from 45-70°C and specified leaching time of 0.1381 hr (497 s) 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.

An attempt has been made in the past [14] 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 [14] that phosphorus can be removed from 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 determine the optimum dissolution temperatures of phosphorus as well as phosphorus dissolution rates and dissolution per unit rise in temperature in oxalic, nitric and sulphuric acid solutions during leaching of Itakpe (Nigeria) iron oxide ore.

2. Materials and Method

A specified quantity (2g) of iron oxide ore of grain size 150 μm was measured out and put in 0.1 litre of oxalic, nitric and sulphuric acid solutions respectively and the resulting pH for each solution noted. The concentrations of all the acids in their respective solutions were kept uniform at 0.1 mole/litre. A set of three flasks, each containing respective acid solution and the ore were placed in an oven and heated to a temperature of 40°C and the concentrations of phosphorus dissolved in each case determined through chemical analysis of the filtrate obtained using atomic absorption spectrometer. This procedure was repeated for temperatures; 45, 50, 55, 60 up to 85°C. The procedure was carried out five times for each of the temperatures used and at different leaching times. The average of the results generated during the experiment was taken in each case.

3. Results and Discussion

Results of the chemical analysis carried out on the iron oxide ore to determine the chemical composition of some of its constituents (as shown in Table 1) indicate that the ore contains 0.16% of phosphorus which is in oxide form. This is quite high and capable of affecting adversely the mechanical properties of steel made from the iron ore, hence the need for the phosphorus removal process.

Table 1. Result of Chemical Analysis of Iron Oxide Ore (as Mined) (%).

Fe	SiO ₂	S	P ₂ O ₅	MgO
65.7	9.78	0.09	0.16	1.71

3.1. Variation of leaching temperature with dissolution of phosphorus in oxalic, nitric and sulphuric acid solutions

Figures 1, 2 and 3 show that the dissolution of phosphorus increases with the increase in the leaching temperature up to a maximum of 120.5, 152.25 and 147.25 mg/kg for oxalic, nitric and sulphuric acid solutions respectively. It was observed that the dissolution of phosphorus in these acid solutions decreased just after these maximum values were reached. These figures also show that the leaching temperatures at which these maximum dissolution values were attained are 45, 55 and 70°C for oxalic, nitric and sulphuric acid solutions respectively. This clearly shows that the optimum dissolution temperatures for phosphorus in oxalic, nitric and sulphuric acid solutions are 45, 55 and 70°C respectively. This implies that higher concentration of phosphorus can dissolve in oxalic acid solution at lower temperature (45°C) compared with nitric and sulphuric acids at higher temperatures; 55 and 70°C respectively. The minimum phosphorus dissolutions in these respective acid solutions were found to be 73.5, 105.25 and 28 mg/kg at 40, 65 and 85°C respectively.

3.2. Determination of phosphorus dissolution per unit rise in leaching temperature for oxalic, nitric and sulphuric acid solutions

Phosphorus dissolution in oxalic, nitric and sulphuric acid solution per degree rise in leaching temperature P_T (mg/kg/°C) is calculated from the equation;

$$P_T = P/T \quad (7)$$

Therefore, a plot of concentration of phosphorus dissolved (in oxalic acid solution) against leaching temperature T during the increasing stage of the dissolution process (as shown in Fig. 1) gives a slope, S , at points (120.5, 45) and (73.5, 40) following their substitution into the mathematical expression;

$$S = \Delta P / \Delta T \quad (8)$$

Equation (8) is detailed as

$$S = (P_2 - P_1) / (T_2 - T_1) \quad (9)$$

where

ΔT is the change in the concentrations of phosphorus dissolved P_2 and P_1 at two leaching temperature values T_2 , and T_1 . Considering the points (120.5, 45) and (73.5, 40) for (P_2, T_2) and (P_1, T_1) respectively, and substituting them into Eq. (9), gives the slope as 9.4 mg/kg/°C which is the concentration of phosphorus dissolved per unit rise in temperature during the increasing stage of the dissolution process.

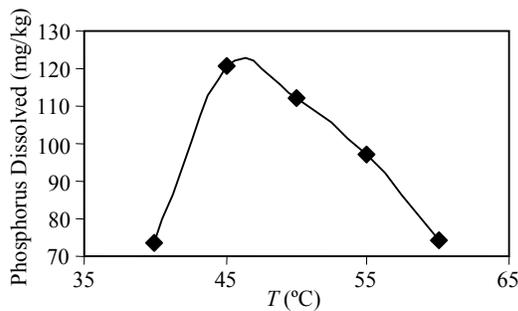


Fig. 1. Effect of Leaching Temperature on the Dissolution of Phosphorus in Oxalic Acid Solution.

Similarly, during the decreasing stage of the dissolution process, the slope obtained considering the points (74.5,60) and (120.5,45) for (P_2, T_2) and (P_1, T_1) respectively equals -3.07 mg/kg/°C. This number is the concentration of phosphorus dissolved per degree rise in temperature during the decreasing stage of the dissolution process.

Results of phosphorus dissolution in nitric acid solution (as shown in Fig. 2) gives slopes of 2.88 and -4.7 mg/kg/°C on substituting into Eq. (9) points (152.25, 55) and (109, 40) for the increasing stage of the dissolution process and (105.25,65) and (152.25,55); decreasing stage, for (P_2, T_2) and (P_1, T_1) respectively.

These slopes represent the phosphorus dissolution per degree rise in temperature during the increasing and decreasing stage of the dissolution process respectively.

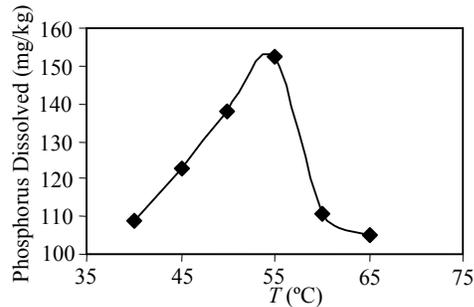


Fig. 2. Effect of Leaching Temperature on the Dissolution of Phosphorus in Nitric Acid Solution.

Similarly, considering the points (147.25, 70) and (82.5, 40) for the increasing stage of the dissolution process (in sulphuric acid solution), also (28, 85) and (147.25, 70); decreasing stage, (as shown in Fig. 3) for (P_2, T_2) and (P_1, T_1) respectively and substituting them into Eq. (9), gives the slopes S as 2.16 and $-7.95 \text{ mg/kg}^\circ\text{C}$ respectively.

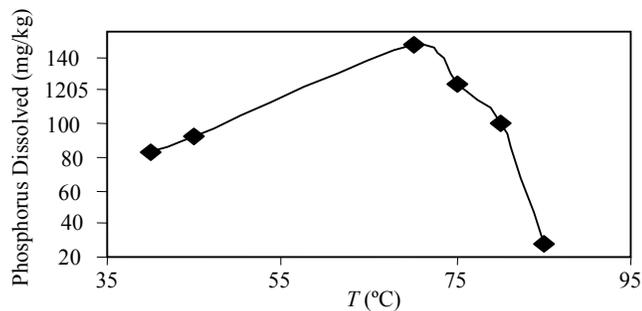


Fig. 3. Effect of Leaching Temperature on the Dissolution of Phosphorus in Sulphuric Acid Solution.

These numbers are the concentrations of phosphorus dissolved in sulphuric acid per degree rise in temperature during the increasing and decreasing stages of the dissolution process respectively. The negative sign preceding the concentrations of dissolved phosphorus only indicates that the dissolution occurred during the decreasing stage of the process hence a negative slope.

3.3. Variation of leaching time with dissolution of phosphorus in oxalic, nitric and sulphuric acid solutions

It was also found that phosphorus dissolution in oxalic, nitric and sulphuric acid solution increases with the increase in the leaching time up to a maximum of 120.5, 152.25 and 147.25 mg/kg for oxalic, nitric and sulphuric acid solutions respectively as

shown in Figs. 4, 5 and 6. It was also observed that phosphorus dissolution decreases (just after these maximum values were reached) with further increase in the leaching time. Figures 4, 5 and 6 show that maximum phosphorus dissolution in oxalic, nitric and sulphuric acid solutions were attained after 267, 497 and 840 seconds respectively of starting the leaching process.

3.4. Determination of phosphorus dissolution rates in oxalic, nitric and sulphuric acid solutions

Phosphorus dissolution rates in oxalic, nitric and sulphuric acid solutions P_r (mg/kg/s) is calculated from the equation;

$$P_r = P/t \quad (10)$$

A plot of concentration of phosphorus dissolved (in oxalic acid solution) against leaching time, t , during the increasing stage of the dissolution process (Fig. 4) gives a slope, S , at points (120.5, 267) and (73.5, 197) following their substitution into the mathematical expression;

$$S = \Delta P / \Delta t \quad (11)$$

Equation (11) is detailed as

$$S = (P_2 - P_1) / (t_2 - t_1) \quad (12)$$

ΔP is the change in the concentrations of phosphorus dissolved P_2 and P_1 at two leaching time values t_2 , and t_1 . Considering the points (120.5, 267) and (73.5, 197) for (P_2, t_2) and (P_1, t_1) respectively, and substituting them into Eq. (12), gives the slope as 0.67 mg/kg/s which is the phosphorus dissolution rate during the increasing stage of the dissolution process.

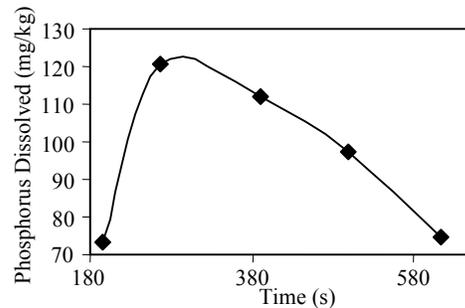


Fig. 4. Variation of Concentration of Dissolved Phosphorus (in Oxalic Acid) with Leaching Time.

Similarly, during the decreasing stage of the dissolution process, the slope obtained considering the points (74.5, 613) and (120.5, 267) for (P_2, t_2) and (P_1, t_1) respectively equals -0.13 mg/kg/s. This number, -0.13 mg/kg/s, is the phosphorus dissolution rate during the decreasing stage of the dissolution process.

Results of phosphorus dissolution in nitric acid solution (shown in Fig. 5) gives slopes of 0.14 and -0.19 mg/kg/s on substituting into Eq. (12) points (152.25, 497) and (109, 197) for the increasing stage of the dissolution process and (105.25,743) and (152.25,497) for the decreasing stage. These slopes represent the phosphorus dissolution rate during the increasing and decreasing stages of the dissolution process respectively.

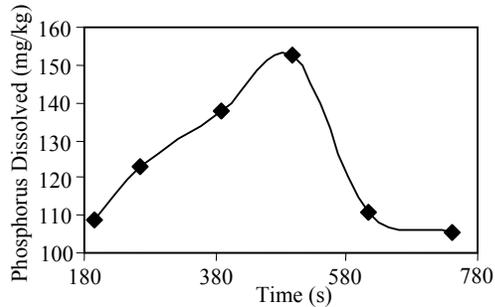


Fig. 5. Variation of Concentration of Phosphorus Dissolved (in Nitric Acid) with Leaching Time.

Similarly, considering the points (147.25, 840) and (82.5, 197) for the increasing stage of the dissolution process (in sulphuric acid solution), also (28, 1108) and (147.25,840);decreasing stage, (as in Fig. 6) for (P_2, t_2) and (P_1, t_1) respectively and substituting them into Eq. (12), gives the slopes, S , as 0.1 and -0.44 mg/kg/s respectively. These are the phosphorus dissolution rates solution during the increasing and decreasing stages of the dissolution process respectively. The negative sign preceding the concentrations of dissolved phosphorus also only indicates that the dissolution occurred during the decreasing stage of the process thereby resulting to a negative slope.

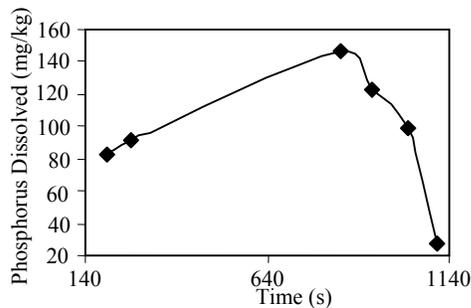


Fig. 6. Variation of Concentration of Phosphorus Dissolved (in Sulphuric Acid) with Leaching Time.

Based on the foregoing, it is clear that oxalic acid gives the highest phosphorus dissolution rate and dissolution per unit rise in temperature both during the increasing and decreasing stages of the dissolution process compared with nitric and sulphuric acids.

4. Conclusions

Based on the results of this study, oxalic acid gives the highest phosphorus dissolution rate and dissolution per unit rise in the leaching temperature both during the increasing and decreasing stages of the dissolution process compared with nitric and sulphuric acid. The optimum dissolution temperatures of phosphorus in these acids are 45, 55 and 70°C for oxalic, nitric and sulphuric acids respectively.

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