Investigating the Optimum Operating Conditions of Some Process Parameters during Leaching of Iron Oxide Ore in Sulphuric Acid Solution

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Abstract
Studies have been carried out to determine the optimum operating conditions of some process parameters during leaching of iron oxide ore in sulphuric acid solution. Results of the investigations show that the optimum leaching temperature, grain size, and initial pH are 55^0C, 0.1mm and 6.8 respectively. The optimum initial solution temperature (just before commencement of the leaching process) required for maximum dissolution of Fe was also found to be 28^0C. Concentration of dissolved Fe was found to decrease progressively with increase in the weight-input of iron oxide ore due to continuously increased iron ore weight-input - fixed hydrogen ions concentration relationship. [Researcher. 2009;1(4):74-82]. (ISSN: 1553-9865).

Keywords: Optimum Conditions, Process Parameter, Leaching, Iron Oxide Ore, Sulphuric Acid.
1. Introduction
Studies [1,2] have shown that at a temperature as low as 25^oC, the presence of Fe^{2+} significantly enhances the leaching of iron extraction from silica sand. Air quickly oxidizes ferrous oxalate during dissolution, giving room for an induction period of a few hours unless a strong acidic environment (<pH 1) or an inert atmosphere is maintained. It has been found [3] that maintaining the high level of ferrous oxalate in the leach liquor using an inert gas enhance the reaction kinetics. It is believed that during this process, removal of phosphorus from the iron compound and subsequent dissolution of the phosphorus oxide formed were effected.

The optimum pH for dissolving iron oxide has been reported [4] to be is pH 2.5 – 3.0. The solution pH governs the distribution of various oxalate ions in the leach system. Below pH 1.5, oxalic acid exists mainly as $H_2C_2O_4$, whereas HC_2O_4 is the most predominant species at pH 2.5 – 3.0.

It has been found [5,6] that the final pH of leaching solution depend on the leaching time, initial pH for the leaching solution and the leaching temperature.

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:

$$\%Fe_2O_3 = K\,(\gamma/\mu) \qquad\qquad (1)$$
$$Q = K_C\,\mu \qquad\qquad (2)$$

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 [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 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.

Nwoye [8] 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:

$$\tau \;=\; \mathrm{Log}\!\left(\dfrac{P^{1/4}}{\dfrac{1.8}{\mathrm{Log}T}}\right) \tag{3}$$

Where

  T = Leaching temperature (^{0}C) in the experiment [9], 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 [9].

  P = Concentration of dissolved phosphorus (mg/Kg) in the experiment [9], 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 [9], 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 (45-70^0C) for its validity. It was found [9] 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. [10] 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 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 [10] include: leaching temperature of 25^0C, initial solution pH 5.5 and average ore grain size; 150μm).

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 [11] 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 [11] 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 [12] 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 [12] 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.

Nwoye et al [13] 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;

$$\%Fe \;=\; 0.35(\alpha/T)^3 \tag{4}$$

    Where

      T = Solution temperature at the time t, when the concentration of dissolved iron is
          evaluated. (^{0}C)

    0.35 = (pH coefficient for iron dissolution in sulphuric acid solution during the leaching
          process) determined in the experiment [13].

      α = 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 25^0C, initial solution pH 5.0 and average grain size; 150μm) 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.

Nwoye [14] derived a model for evaluating the final pH of the leaching solution during leaching of iron oxide ore in oxalic acid solution. The model evaluates the pH value as the sum of two parts, involving the % concentrations of Fe and Fe_2O_3 dissolved. The model can be expressed as;

$$\gamma = 0.5 \quad \frac{K_1}{\%Fe} \left(+ \frac{K_2}{\%Fe_2O_3} \quad \underline{\quad\quad} \right) \tag{5}$$

Where

K_1 and K_2 = dissolution constants of Fe and Fe_2O_3 respectively.

γ = final pH of leaching solution (after time t).

It was also found that the model [14] could predict the concentration of Fe or Fe_2O_3 dissolved in the oxalic acid solution at a particular final solution pH by taking Fe or Fe_2O_3 as the subject formular. The prevailing process conditions under which the model works include: leaching time of 30mins., constant leaching temperature of 30^oC, average ore grain size; 150µm and 0.1M oxalic acid.

Nwoye [15] has reported that the heat absorbed by oxalic acid solution during leaching of iron oxide ore can be predicted using the model he derived which works under the process condition; initial pH 6.9, average ore grain size; 150µm and leaching temperature; 30^0C. The model [15] can be stated as

$$Q = K_N \quad \gamma \tag{6}$$

$$\%Fe_2O_3 \left(\underline{\quad\quad} \right)$$

Where

Q = Quantity of heat absorbed by oxalic acid solution during the leaching process. (J)

γ = Final pH of the leaching solution (at time t).

$\%Fe_2O_3$= Concentration of haematite dissolved in oxalic acid solution during the leaching process.

K_N = 4.57(Haematite dissolution constant in oxalic acid solution) determined in the experiment [15].

Nwoye [15] carried out further work on the model using the same process conditions and observed that on re-arranging the model as;

$$\%Fe_2O_3 = K_N \quad \frac{\gamma}{Q} \left(\underline{\quad\quad} \right) \tag{7}$$

the concentrations of haematite predicted deviated very insignificantly from the corresponding experimental values. In this case, the value of Q was calculated by considering the specific heat capacity of oxalic acid. Values of heat absorbed by the oxalic acid solution during the leaching of iron oxide ore as predicted by the model [15] agree with the experimental values that the leaching process is endothermic. This is because all the predicted values of the heat absorbed by the oxalic acid solution were positive. The model shows that the quantity of heat absorbed by oxalic acid solution during the leaching process is directly proportional to the final pH of the solution and inversely proportional to the concentration of haematite dissolved.

Model for 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 has been derived [16]. 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; $P = e^{(12.25/\alpha)}$ is dependent 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%.

Temperature measured at the reaction sites gives an idea of whether the reaction is speeding up or stopping especially when it is measured consistently.

It has been reported [17] that the temperature of a reaction system plays the major role in controlling the rate of the reaction.

Past report [18] has shown that measurement of the temperature of a reaction system consistently shows whether the reaction involved is endothermic or exothermic.

Nwoye [19] derived a model for the computational analysis of the solution temperature during leaching of iron oxide ore in hydrochloric acid solution. The model is expressed as:

$$T = e^{(8.9055/\gamma)} \hspace{3cm} (8)$$

where

   T= Solution temperature during leaching of iron oxide ore using hydrochloric acid.(^{0}C)

   N= 8.9055(pH coefficient for hydrochloric acid solution during leaching of iron
     oxide ore) determined in the experiment [19].

  γ = Final pH of the leaching solution at the time t when the solution temperature is evaluated.

  The model is dependent on the value of the final pH of the leaching solution which was found to also depend on the concentration of iron dissolved in the acid. The prevailed process conditions on which the validity of the model depended on include: initial pH 2.5, leaching time; 30 minutes, leaching temperature; 25°C, average ore grain size; 150µm and hydrochloric acid concentration at 0.1mol/litre.

  The aim of this work is to investigate the optimum operating conditions of some process parameters during leaching of Agbaja (Nigerian) iron oxide ore in sulphuric acid solution.

2. Materials and Methods

Iron oxide ore collected from different spots at the Agbaja (Nigeria) iron ore deposit was homogenized and then sieved into 0.06, 0.08, 0.1, 0.3, 0.4mm.1000ml of sulphuric acid solution was prepared using 10ml of 0.1M sulphuric acid. The leaching solution was divided into ten and each part placed in a different conical flask for each sample investigated. Investigations on the effects of variation of grain size, mass of iron oxide ore, initial pH and leaching temperature on the dissolution of iron were carried out using 2, 6-24, 5 and 4g of iron oxide ore respectively. The initial solution pH and temperatures (just before the commencement of the leaching process) were recorded where necessary. Sodium hydroxide was used to regulate the initial solution pH. Leaching time of 30 minutes was used for all samples. Ten different samples were used for investigation in the case of each variable and average values taken.

3. Results and Discussion

Table 1 shows that the ore contains some elements; sulphur and phosphorus which can be oxidized to form gases capable of dissolved in water to produce acids.

Table 1. Results of chemical analysis of the as-received Agbaja iron oxide ore

Element/compound	Fe	S	P	SiO$_2$	Al$_2$O$_3$
(%)	45.6	0.10	0.76	11.91	3.82

Effect of leaching temperature on the dissolution of iron in sulphuric acid solution

Investigation carried out over a leaching temperature range 40-85^{0}C shows (Fig.1) that the optimum temperature for maximum dissolution of Fe during the leaching process is 55^{0}C. It was also observed that the maximum iron dissolution concentration associated with this temperature is 0.0734%. It was also observed that above this temperature, precipitates of Fe(OH)$_3$ were formed in the leaching solution, hence the decrease in the dissolution of Fe.
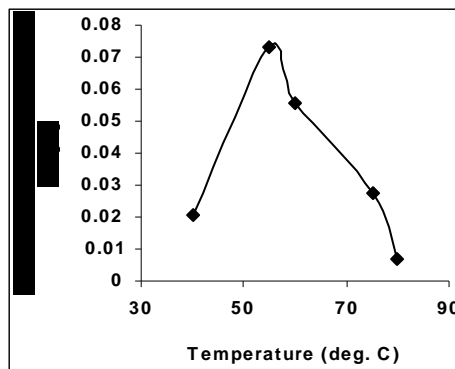

Fig.1-Effect of variation in leaching temperature on the concentration of dissolved iron

Effect of grain size on the dissolution of iron in sulphuric acid solution

The effect of grain size on the dissolution of iron was investigated over a range of grain size 0.06-0.4mm. It was found (as in Fig.2) that the optimum grain size for maximum dissolution of Fe during the leaching process is 0.1mm (100μm). This implies that the dissolution of Fe increased with increased grain size up till a size of 0.1mm after which decrease in Fe dissolution was recorded with larger grains. Fig. 2 shows that the maximum dissolution of Fe associated with the optimum grain size (0.1mm) is 0.1222%.
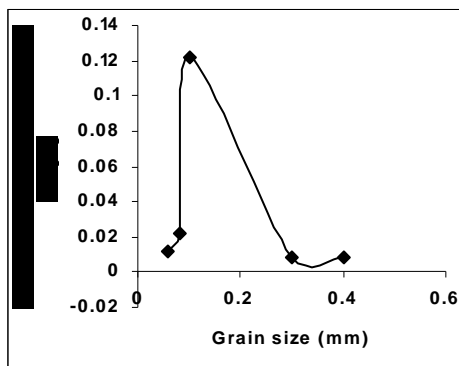
Fig.2-Effect of variation in grain size of iron oxide ore on the concentration of dissolved iron

Effect of initial solution pH on the dissolution of iron in sulphuric acid solution

The effect of initial solution pH on the dissolution of iron was ascertained using a range of pH values 6.63-6.82. Comparison of Figs. 3 and 4 show that increase in the initial solution pH (just before commencement of the leaching process) increases the initial solution temperature (just before commencement of the leaching process) and then increases concentration of Fe dissolved in the sulphuric acid solution during the leaching process up to an optimum value; 6.8.
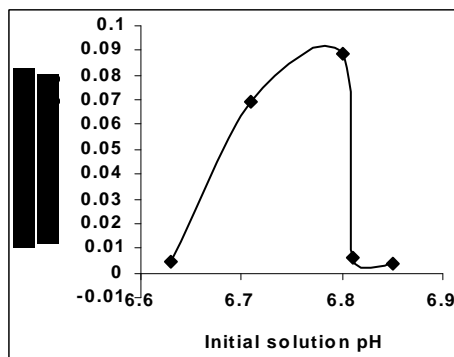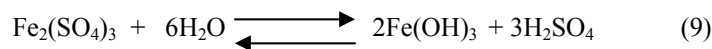

Fig.3-Effect of variation in initial solution pH on the concentration of dissolved iron

It was found that above this optimum pH value, the concentration of dissolved Fe dropped. This is due to the fact that above pH6.8, ferric sulphate becomes hydrolyzed to precipitate $Fe(OH)_3$ in the sulphuric acid solution in agreement with past experiment by Pinches [5]. This process of hydrolysis is expressed as;

$$Fe_2(SO_4)_3 \; + \; 6H_2O \; \rightleftharpoons \; 2Fe(OH)_3 \; + 3H_2SO_4 \qquad (9)$$

Figs. 3 and 4 show that the maximum initial solution temperature and dissolution of Fe associated with the optimum initial pH are 28^0C and 0.0889% respectively.
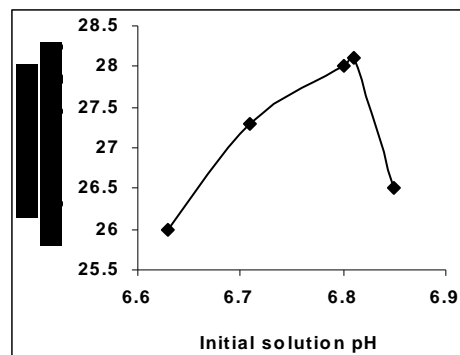
Fig.4-Effect of variation in initial solution pH on the initial solution temperature

Fig.4 shows that the initial solution temperature increases with increase in the initial solution pH up to 6.8. Above this optimum pH value, the initial solution temperature dropped with further increase in the initial solution pH. It is suspected that the increment in the initial solution temperature (as the initial solution pH increases) resulted from the interaction of H^+ and OH^- to produce more water in the leaching solution i.e

$$H^+ + OH^- \longrightarrow H_2O \qquad \text{(exothermic)} \qquad (10)$$

Furthermore, this reaction is believed to be exothermic in nature, hence the temperature increment. Above the optimum pH, implying addition of more OH^-, the reaction in equation (10) is suspected to become endothermic as a result of absorption of the heat of reaction between H^+ and OH^- by water already formed, hence the drop in the temperature.
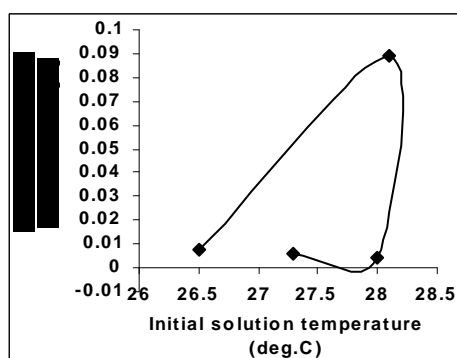

Fig.5. Effect of variation in initial solution temperature on the concentration of dissolved iron

Comparison of Figs. 4 and 5 show that at an initial solution pH6.8, the associated initial solution temperature 28^0C which is optimum gives the maximum dissolution of Fe because at the initial stage of the leaching process, increment in the solution temperature translates into an increase in the activation energy required for the commencement of the leaching process. This invariably enhanced Fe dissolution by reducing the chemical resistance to the dissolution process. However, decrease in the initial solution temperature occasioned by further increase in the initial solution pH reduced the activation energy required to ensure progressive dissolution of Fe and this resulted to a decrease in the concentration of Fe dissolved. This is in accordance with studies by King et al. [21].

Effect of variation in weight-input of iron oxide ore on the dissolution of iron in sulphuric acid solution
  Fig. 6 shows that increase in the weight-input of iron oxide ore decreases the concentration of Fe dissolved. This is because the concentration of the aggressive ions which control the leaching process (H^+) is fixed for all weights-input of iron oxide ore. These hydrogen ions attack the ore thereby enhancing the leaching and dissolution of Fe. Increasing the iron oxide ore increases the quantity of ore to be attacked per H^+. This makes the H^+ unable to react with the whole quantity of ore within the stipulated time; enhancing leaching and dissolution of Fe, instead it reacts with just a part of the larger ore quantity. This results to lower leaching and dissolution of Fe for each increment in weight-input of the ore.
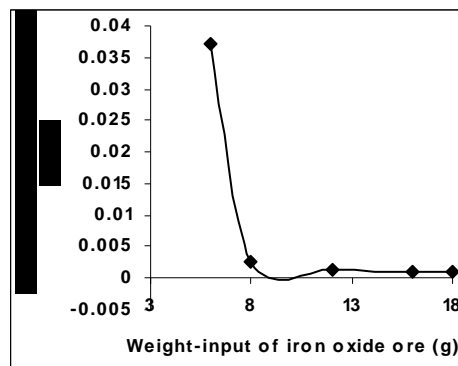
Fig.6-Effect of variation in weight-input of iron oxide ore on the concentration of dissolved iron

Fig.7 shows that the initial solution temperature decreases with increase in the weight-input of iron oxide ore. This is as a result of the absorption of heat present in the leaching solution which resulted from the process in equation (10) following the relationship in Fig. 4. It is strongly believed that as the iron oxide ore is increasingly being added to the leaching solution, the heat present in the solution would continuously be mopped-up, hence decreasing the initial solution temperature.
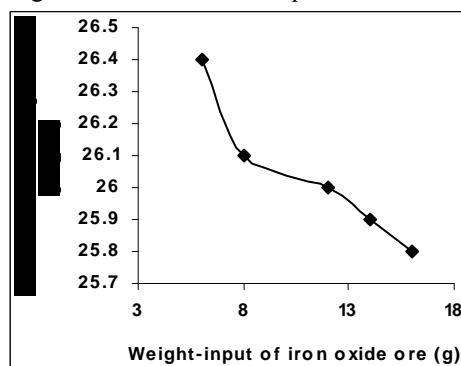

Fig.7-Effect of variation in weight-input of iron oxide ore on the initial solution temperature

It has been found (Fig.8) that increase in the weight of iron oxide ore added to the leaching solution (just before the leaching process) decreases the initial solution pH. It is strongly believed that presence of sulphur and phosphorus in the ore was responsible for the drop in the pH. It is also believed that increased quantities of sulphur and phosphorus dissolved in the leaching solution for each increment in the weight of iron oxide ore added, hence the progressive drop in the pH with increase in weight-input of iron oxide ore.
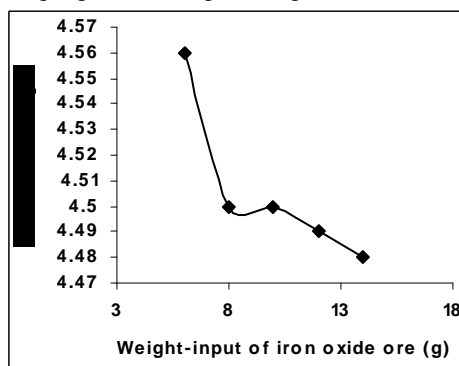

Fig.8-Effect of variation in weight-input of iron oxide ore on the initial solution pH

It was found that increase in the initial solution temperature resulted to increased dissolution of Fe in the leaching solution (Fig.9). This increment in the initial solution temperature is believed to have translated into an increase in the activation energy required for the commencement of the leaching process in

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agreement with previous report [21]. This invariably enhanced Fe dissolution by reducing the chemical resistance to the dissolution process. Fig.9 shows that maximum initial solution temperature resulted to maximum Fe dissolved concentration. This is also in accordance with studies [21] by King et al.
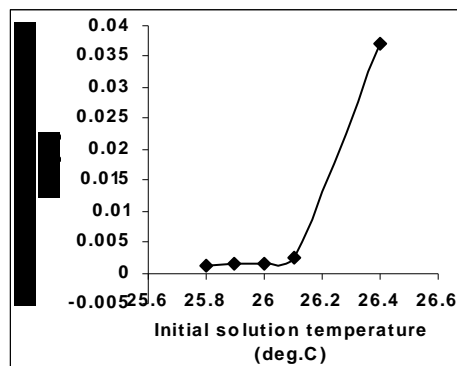

Fig.9-Effect of variation in initial solution temperature on the concentration of dissolved iron

Conclusion
Following results of investigations carried out to determine the optimum operating conditions of some process parameters during leaching of iron oxide ore in sulphuric acid solution, it is concluded that the optimum leaching temperature, grain size, and initial pH are 55^0C, 0.1mm and 6.8 respectively. The optimum initial solution temperature required for maximum dissolution of Fe was also found to be 28^0C. Concentration of dissolved Fe was found to decrease progressively with increase in the weight-input of iron oxide ore. Concentration of dissolved Fe was found to decrease progressively with increase in the weight-input of iron oxide ore due to continuously increased iron ore weight-input - fixed hydrogen ions concentration relationship.

Acknowledgement

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