

# Systemic Analysis of Iron Extraction from Iron Oxide Ore based on Leaching Temperature and Input Concentration of Acetic Acid

T. O. Chime<sup>1</sup> and O.D. Onukwuli<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Enugu State University of Science & Technology, Enugu, Nigeria

<sup>2</sup>Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Anambra, Nigeria

**Abstract**– This paper presents a systemic analysis of iron extraction based on the leaching temperature and input concentration of acetic acid during the leaching process. A model was derived and used as a tool for the analysis. The model is expressed as:

$$\alpha = - 3.9068 \ln\beta - 1.905 \ln\theta + 60.89,$$

The validity of the two-factorial natural logarithmic model was found to be rooted on the expression  $\alpha - 60.89 = - 3.9068 \ln\beta - 1.905 \ln\theta$  where both sides of the expression are correspondingly approximately equal. Statistical analysis of the extracted iron concentration as obtained from derived model and experiment for each value of the leaching temperature and input concentration of acetic acid considered shows standard errors of 0.4238 & 0.1386% and 0.4238 & 0.1386% respectively. Extracted iron concentrations per unit leaching temperature as obtained from derived model and experiment are 0.178 and 0.183 % /<sup>o</sup>C. Similarly, extracted iron concentrations per unit input concentration of acetic acid are 7.13 and 7.32 % / M. Deviation analysis indicates that the maximum deviation of the model-predicted iron extraction (from experimental results) is less than 1.5%, implying a confidence level above 98%.

**Keywords**– Analysis, Iron Extraction, Iron Ore, Leaching Temperature and Acetic Acid Concentration

## I. INTRODUCTION

Extraction of metal from its ore through hydrometallurgy has been widely recognized and accepted to be significantly environmental friendly. Intensive researches are unavoidably necessary to review this potentiality and also explore ways of improving on hydrometallurgical techniques that would ensure optimum results.

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  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ , ferrous oxalate  $\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}$  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<sup>o</sup>C, but its rate increases rapidly above 90<sup>o</sup>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 ( $\text{Fe}_2\text{O}_3$ ) (105-140 $\mu\text{m}$ ) 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  $\text{Fe}_2\text{O}_3$ ) at pH 1. He stated that even at 90<sup>o</sup>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%  $\text{Fe}_2\text{O}_3$ ). The iron oxide concentration in the leach is equivalent to 0.058g/L  $\text{Fe}_2\text{O}_3$ .

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  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ . At these conditions, (pH > 2.5 and an oxalate concentration higher than 0.1M) the predominant Fe(II) complex species is  $\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}$ .

Lee et al. [5] reported that the leaching of 3g/L pure haematite (98.2% purity, 105-140 $\mu\text{m}$  size range) using 0.048-0.48M oxalic acid at 80-100<sup>o</sup>C passed through a maximum peak at pH 2.5. Dissolution of haematite was found [5] to be slower than magnetite ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ) and other hydrated iron oxide such as goethite ( $\alpha\text{-FeOOH}$ ), lapidochrosite ( $\gamma\text{-FeOOH}$ ) and iron hydroxide ( $\text{Fe}(\text{OH})_3$ ).

The presence of  $\text{Fe}^{2+}$  was found to significantly enhance the leaching of iron extraction from silica sand at a temperature even as low as 25<sup>o</sup>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. Intensive researches have been conducted on the dissolution of goethite in several inorganic acids belonging to the families of the carboxylic and diphosphoric acids in the presence of reducing agents. Analysis of results generated from these extraction processes has been carried using various derived models which functioned as tools. A model for the evaluation of the concentrations of dissolved iron (relative to the final solution pH and temperature) during leaching of iron oxide ore in sulphuric acid solution has been derived [6].

$$\% \text{Fe} = 0.35(\alpha/T)^3 \quad (1)$$

The model depended on the values of the final pH and temperature of the leaching solution which varied with leaching time. The positive and negative deviations of the

model-predicting values of %Fe (dissolved) from those of the experimental values were found to be within the range of acceptable deviation limit for experimental results.

Calculations of the concentrations of leached iron during leaching of iron oxide ore in sulphuric acid solution has been achieved through application of a model [7]. The model is expressed as:

$$\%Fe = e^{-2.0421(\ln T)} \quad (2)$$

The predicted concentrations of leached Fe were observed to be very close to the values obtained from the experiment. The model shows that the concentrations of leached Fe were 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.

A model was successfully derived for predictive analysis of the concentrations of dissolved iron during leaching of iron oxide ore in sulphuric acid solution [8]. The model expressed as:

$$\%Fe = 0.987(\mu/T) \quad (3)$$

It was able to predict the concentrations of dissolved Fe with a high degree of precision. It was observed that the model was dependent on the values of the leaching temperature and weight of iron oxide ore added. The validity of the model was found to be rooted in the expression  $\%Fe = N(\mu/T)$  where both sides of the relationship are correspondingly approximately equal. The maximum deviation of the model-predicted concentration of dissolved Fe from those of the experimental values was found to be less than 19% which is quite within the acceptable range of deviation limit for experimental results, hence depicting the usefulness of the model as a tool for predictive analysis of the dissolved iron during the process.

The aim of this work is to take a systemic analysis of iron extraction from iron oxide ore based on leaching temperature and input concentration of acetic acid.

## II. MATERIALS AND METHODS

Agbaja (Nigeria) iron ore was mined and collected from the deposit, beneficiated and the resultant concentrate used for this research work. The iron ore was crushed for the purpose of liberation size. Tyler standard was employed to produce particle size of 250 $\mu$ m. The raw iron Agbaja iron ore was then sent for chemical analysis using X-ray fluorescence diffraction spectrometer and atomic absorption spectrophotometer.

### Scrubbing process

Scrubbing was carried out to remove argillaceous materials from the raw iron ore. The iron ore was poured into a head pan and water was poured to a reasonable level. The ore was washed and the water decanted. This was repeated for five times until clear water was observed. At this point 5g of sodium silicate and 25drops of oleic acid were sprinkled and distributed uniformly throughout the ore. 20litres of distilled water was also introduced into the pan and the content mixed

thoroughly. After mixing, the argillaceous materials were removed leaving behind the iron ore. The residue was washed thoroughly and was sun dried for 24hours. Some quantities were sent for chemical analysis.

### Chemical leaching process

The dried scrubbed iron ore was further pulverized and sieved to obtain a particle size of 10 $\mu$ m. Analar grade of acetic acid solutions of different moles of 0.25M, 0.5M, 0.75M, 1.00M and 1.25M were prepared. 50grams of constant particle size of 10 $\mu$ m of scrubbed iron ore was poured into the crucible (reactor). 25ml of 0.25M of acetic acid was poured into the crucible containing the iron ore. The mixture was thoroughly mixed to ensure homogeneity. The content was allowed to leach for 10, 20, 30, 40, 50 and 60minutes at 30 $^{\circ}$ C. At the end of each period the solution was cooled and filtered. The residue was collected, washed to neutrality with distilled water, air dried and oven dried at 150 $^{\circ}$ C for 24hours. The experiment was repeated for different concentrations and temperature of 40,50 and 60 $^{\circ}$ C. The samples were analyzed using atomic absorption spectrophotometer and X-ray fluorescence diffraction spectrometer.

### Model Formulation

Experimental data obtained from the highlighted research work were used for the model derivation. Computational analysis of these data shown in Table 1, gave rise to Table 3 which indicate that;

$$\alpha - K = -S \ln \beta - N \ln \theta \quad (4)$$

Introducing the values of K, S and N into equation (4).

$$\alpha - 60.89 = -3.9068 \ln \beta - 1.905 \ln \theta \quad (5)$$

$$\alpha = -3.9068 \ln \beta - 1.905 \ln \theta + 60.89 \quad (6)$$

Where,

( $\alpha$ ) = Conc. of extracted iron (%)

( $\theta$ ) = Input concentration of acetic acid (M)

( $\beta$ ) = Leaching temperature ( $^{\circ}$ C)

$$K = 60.89, S = 3.9068, N = 1.905$$

K, S and N are equalizing constant (determined using C-NIKBRAN [9].

Table 1: Variation of extracted iron concentration with leaching temperature and input concentration of acetic acid from experiment

Fe (%)	Leaching temp ( $^{\circ}$ C)	(M)
49.92	30	0.25
48.27	40	0.5
46.47	50	0.75
44.43	60	1.0

### Boundary and Initial Conditions

Consider iron ore (in a reactor) placed within hydrogen peroxide solution (oxidant). The reactor atmosphere is not contaminated i.e., (free of unwanted gases and dusts). Initially, atmospheric levels of oxygen are assumed just

before the decomposition of acetic acid (due to air in the reactor). **Mass of iron oxide ore: (50 g)**, leaching time considered: 40 mins., range of input concentration of acetic acid: 0.25-1.0 M, range of leaching temperature: 30-60°C and ore grain size; 10µm, were also used.

The boundary conditions are: reactor oxygen atmosphere at the top and bottom of the ore particles interacting with the gas phase. At the bottom of the particles, a zero gradient for the gas scalar are assumed and also for the gas phase at the top of the particles. The reduced iron is stationary. The sides of the particles are taken to be symmetries.

**III. RESULTS AND DISCUSSIONS**

**Model Validation**

The validity of the model is strongly rooted in equation (5) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 3 also agrees with equation (5) following the values of  $\alpha$  - 60.89 and  $-3.9068 \ln\beta - 1.905 \ln\theta$  evaluated from the experimental results in Table 1.

Table 3: Variation of  $\alpha$  - 60.89 with  $-3.9068 \ln\beta - 1.905 \ln\theta$

$\alpha$ - 60.89	$-3.9068 \ln\beta - 1.905 \ln\theta$
-10.97	-10.65
-12.62	-13.10
-14.62	-14.74
-16.46	-16.00

Furthermore, the derived model was validated by comparing the extracted iron concentration predicted by the model and that obtained from the experiment. This was done using various evaluative techniques such as computational, statistical, graphical and deviational analysis.

**Computational Analysis**

Computational analysis of the experimental and model-predicted extracted iron concentration was carried out to ascertain the degree of validity of the derived model. This was done by comparing extracted iron per unit leaching time as well as extracted iron per unit concentration of removed phosphorus evaluated from model-predicted results with those from actual experimental results.

Extracted iron concentration per unit leaching temperature  $\alpha_T$  (%/°C) was calculated from the equation;

$$\alpha_T = \alpha / T \tag{7}$$

Therefore, a plot of the extracted iron concentration against leaching temperature as in Fig. 1 using experimental results in Table 2, gives a slope, S at points (30, 49.92) and (60, 44.43) following their substitution into the mathematical expression;

$$\alpha_T = \alpha / T \tag{8}$$

Equation (8) is detailed as:

$$\alpha_T = \alpha_2 - \alpha_1 / T_2 - T_1 \tag{9}$$

Where,

$\Delta \alpha$  = Change in extracted iron concentrations of  $\alpha_2, \alpha_1$  at two leaching temperature values  $T_2, T_1$ . Considering the points (30, 49.92) and (60, 44.43) for  $(T_1, \alpha_1)$  and  $(T_2, \alpha_2)$  respectively, and substituting them into equation (9), gives the slope as  $-0.183 \%/^\circ\text{C}$  which is the extracted iron concentration per unit leaching temperature during the actual leaching process.

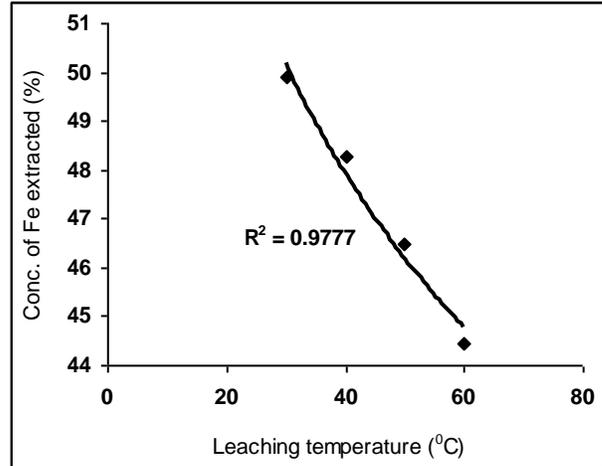


Fig. 1: Coefficient of determination between extracted iron concentration and leaching temperature as obtained from experiment

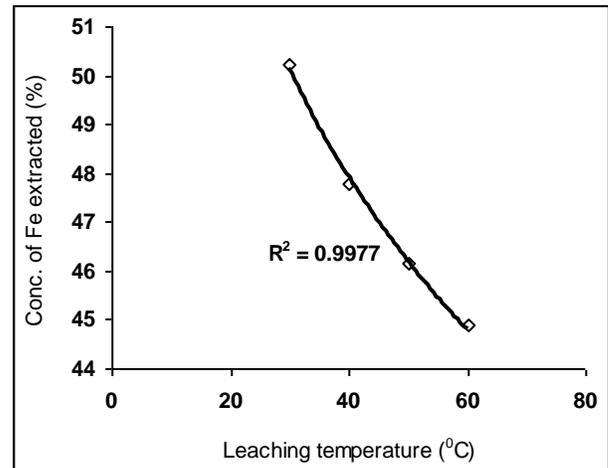


Fig. 2: Coefficient of determination between extracted iron concentration and leaching temperature as obtained from derived

A plot of the concentration of extracted iron against leaching temperature (as in Fig. 2) using derived model-predicted results gives a slope:  $-0.178\%/^\circ\text{C}$  on substituting the points (30, 50.2431) and (60, 44.8942) for  $(T_1, \alpha_1)$  and  $(T_2, \alpha_2)$  respectively into equation (9). This is the model-predicted extracted iron concentration per unit leaching temperature.

Extracted iron concentration per unit input concentration of acetic acid  $\alpha_C$  was calculated from the equation;

$$\alpha_C = \alpha / C \tag{10}$$

Therefore, a plot of the extracted iron concentration against leaching temperature as in Fig. 3 using experimental results in Table

2, gives a slope, S at points (30, 49.92) and (60, 44.43) following their substitution into the mathematical expression;

$$\alpha_C = \alpha / C \tag{11}$$

Equation (11) is detailed as:

$$\alpha_C = \alpha_2 - \alpha_1 / C_2 - C_1 \tag{12}$$

Where,  $\Delta \alpha$  = Change in extracted iron concentrations of  $\alpha_2, \alpha_1$  at two values of the input concentrations of acetic acid  $C_2, C_1$ . Considering the points (0.25, 49.92) and (1.0, 44.43) for  $(C_1, \alpha_1)$  and  $(C_2, \alpha_2)$  respectively, and substituting them into equation (12), gives the slope as  $- 7.32 \% / M$  which is the extracted iron concentration per unit input concentration of acetic acid during the actual leaching process.

A plot of the concentration of extracted iron against input concentration of acetic acid (as in Fig. 4) using derived model-predicted results gives a slope:  $- 7.13 \% / M$  on substituting the points (0.25, 50.2431) and (1.0, 44.8942) for  $(C_1, \alpha_1)$  and  $(C_2, \alpha_2)$  respectively into eq. (12). This is the model-predicted extracted iron concentration per unit input concentration of acetic acid.

A comparison of this set of values for extracted iron concentration (per unit leaching temperature and input concentration of acetic acid)

also shows proximate agreement and a high degree of validity of the derived model. It is important to state that the negative signs preceding the evaluated values of the extracted iron concentrations per unit leaching temperature ( $- 0.178$  and  $- 0.183 \% / ^\circ C$ ) as well as the extracted iron concentrations per unit input concentration of acetic acid ( $- 7.13$  and  $- 7.32 \% / M$ ) indicates that the slopes are negative. Therefore, the magnitudes of the extracted iron concentration per unit leaching temperature and input concentration of acetic acid as obtained from derived model and experiment are  $0.178$  &  $0.183 \% / ^\circ C$  as well as  $7.13$  &  $7.32 \% / M$  respectively.

**Statistical Analysis**

*Standard Error (STEYX)*: Statistical analysis of the extracted iron concentration as obtained from derived model and experiment for each value of the leaching temperature and input concentration of acetic acid considered shows standard errors of  $0.4238$  &  $0.1386\%$  and  $0.4238$  &  $0.1386\%$  respectively. The standard error was evaluated using Microsoft Excel version 2003.

Also the correlations between extracted iron concentration and leaching temperature as well as extracted iron concentration and input concentration of acetic acid as obtained from experiment and derived model considering the coefficient of determination  $R^2$  from Fig. 1 to Fig. 4 was calculated using the equation:

$$R = \sqrt{R^2} \tag{13}$$

The evaluations show correlations  $0.9888$  &  $0.9988$  and  $0.9699$  &  $0.9988$  respectively. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from actual experiment.

**Graphical Analysis**

Comparative graphical analysis of Fig. 5 shows very close alignment of the curves from model-predicted extracted iron concentration (MoD) and that of the experiment (ExD). The degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted extracted iron concentration.

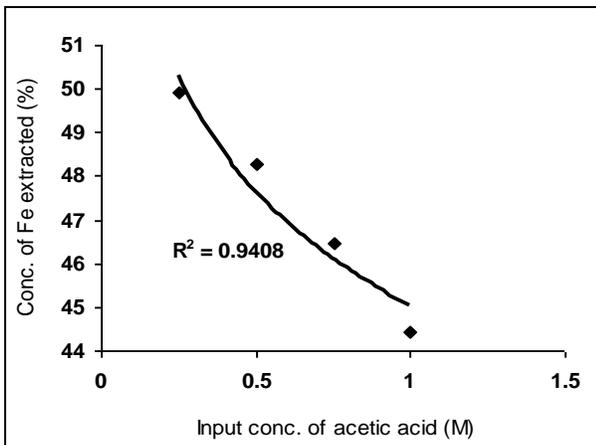


Fig. 3: Coefficient of determination between extracted iron concentration and input conc. of acetic acid as obtained from experiment

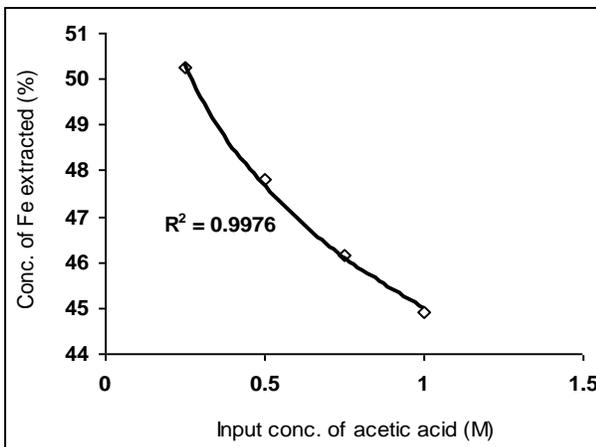


Fig. 4: Coefficient of determination between extracted iron concentration and input conc. of acetic acid as obtained from derived

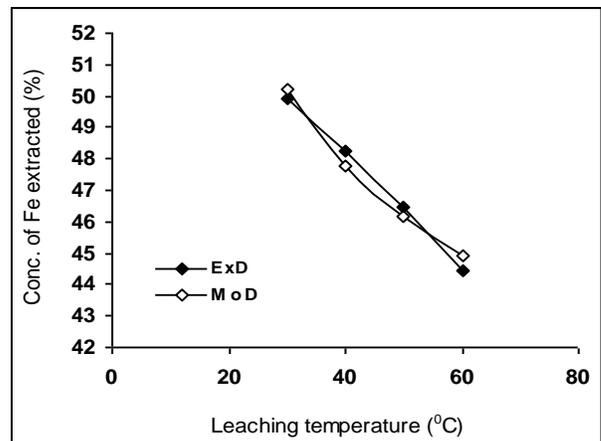


Fig. 5: Comparison of the extracted iron concentration (relative to leaching temperature) as obtained from experiment and derived model

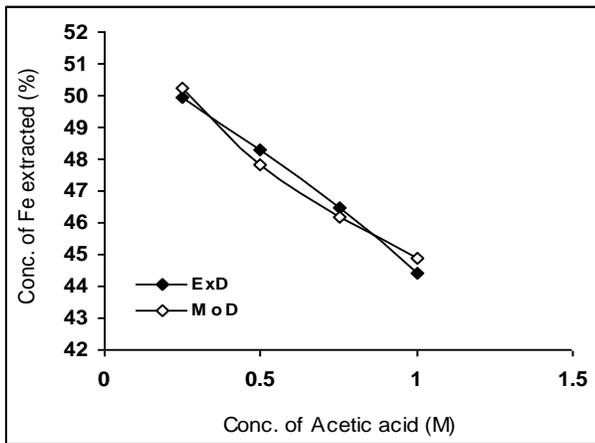


Fig. 6: Comparison of the extracted iron concentration (relative to input conc. of acetic acid) as obtained from experiment and derived model

**Deviation Analysis**

Analysis of extracted iron concentrations from the experiment and derived model revealed deviations on the part of the model-predicted values relative to values obtained from the experiment. This is attributed to the fact that the surface properties of the iron ore and the physiochemical interactions between the ore and the acid which were found to have played vital roles during the process were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted extracted iron concentration to those of the corresponding experimental values.

Deviation (Dn) of model-predicted extracted iron concentration from that of the experiment is given by:

$$Dn = \left( \frac{Pv - Ev}{Ev} \right) \times 100 \quad (14)$$

Where,

Pv = Extracted iron concentration as predicted by derived model

Ev = Extracted iron concentration as obtained from experiment

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

$$Cr = -Dn \quad (15)$$

Therefore,

$$Cr = - \left( \frac{Pv - Ev}{Ev} \right) \times 100 \quad (16)$$

Introduction of the corresponding values of Cr from equation (16) into the derived model gives exactly the extracted iron concentration as obtained from experiment.

Fig. 7 and Fig. 8 show that the maximum deviation of the model-predicted extracted iron concentration from the corresponding experimental values is less than 1.5% and quite within the acceptable deviation limit of experimental results. The figure shows that the least and highest magnitudes of deviation of the model-predicted extracted iron concentration (from the corresponding experimental values) are + 0.65 and

+ 1.04 % which corresponds to extracted iron concentrations: 50.2431 and 44.43 %, leaching temperatures: 30 and 60 °C as well as input concentration of acetic acid: 0.25 and 1M respectively.

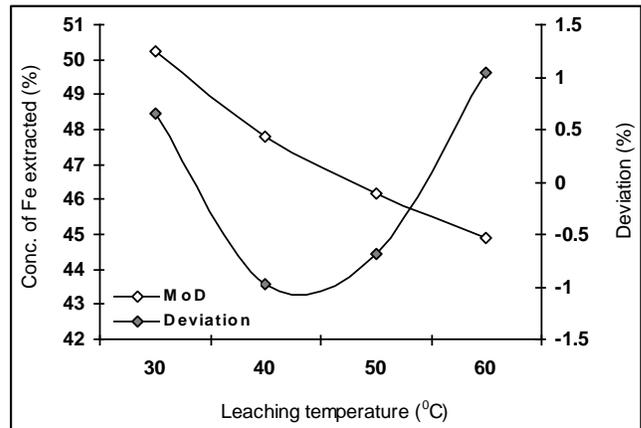


Fig. 7: Variation of model-predicted extracted iron concentration with associated deviation from experimental results (relative to leaching temperature)

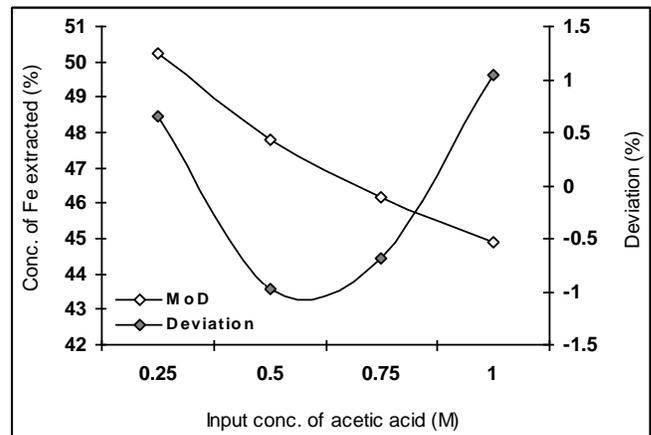


Fig. 8: Variation of model-predicted extracted iron concentration with associated deviation from experimental results (relative to input conc. of acetic acid)

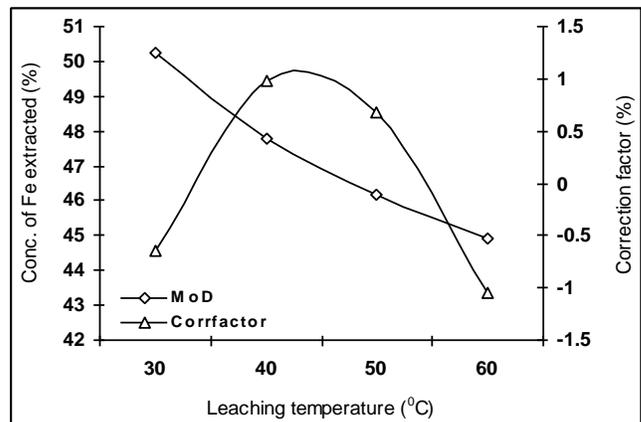


Fig. 9: Variation of model-predicted extracted iron concentration with associated deviation from experimental results (relative to leaching temperature)

Comparative analysis of Fig. 7 – Fig. 10 indicates that the orientation of the curve in Fig. 9 and Fig. 10 is opposite that of the deviation of model-predicted extracted iron concentration (Fig. 7 and Fig. 8). This is because correction factor is the negative of the deviation as shown in equations (15) and (16).

It is believed that the correction factor takes care of the effects of surface properties of the iron ore and the physiochemical interactions between the ore and the oxidant which have played vital roles during the process, but were not considered during the model formulation. Figs. 9 and 10 indicate that the least and highest magnitudes of correction factor to the model-predicted extracted iron concentration (from the corresponding experimental values) are - 0.65 and - 1.04 % which corresponds to extracted iron concentrations: 50.2431 and 44.43 %, leaching temperatures: 30 and 60 °C as well as input concentration of acetic acid: 0.25 and 1M respectively.

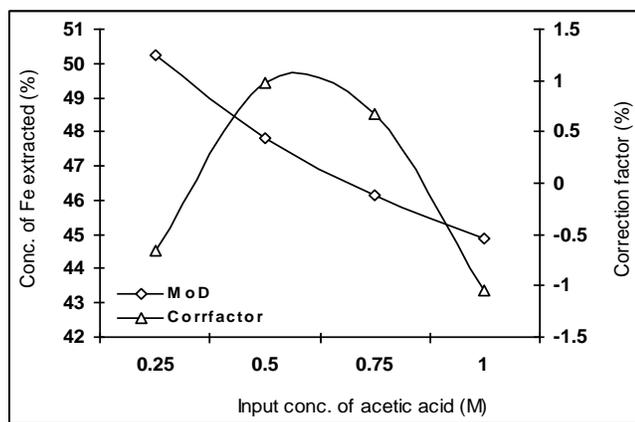


Fig. 10: Variation of model-predicted extracted iron concentration with associated deviation from experimental results (relative to input concentration of acetic acid)

It is important to state that the deviation of model predicted results from that of the experiment is just the magnitude of the value. The associated sign preceding the value signifies that the deviation is a deficit (negative sign) or surplus (positive sign).

#### IV. CONCLUSIONS

A systemic analysis of iron extraction was carried out based on the leaching temperature and input concentration of acetic acid during the leaching process. A model was derived and used as a tool for the analysis. Statistical analysis of the extracted iron concentration as obtained from derived model and experiment for each value of the leaching temperature and input concentration of acetic acid considered shows standard errors of 0.4238 & 0.1386% and 0.4238 & 0.1386% respectively. Extracted iron concentrations per unit leaching temperature as obtained from derived model and experiment are 0.178 and 0.183 % / °C. Similarly, extracted iron concentrations per unit input concentration of acetic acid are 7.13 and 7.32 % / M. Deviation analysis indicates that the maximum deviation of the model-predicted iron extraction

(from experimental results) is less than 1.5%, implying a confidence level above 98%.

#### REFERENCES

- [1]. Taxiarchour, M., Parnias, D., Doumi, I., Paspaliaris, I., Kontopoulos, A., (1997a) Removal of Iron from Silica Sand by Leaching with Oxalic Acid, *Hydrometallurgy*, 46, 215-227.
- [2]. Lee, S.O, Tran, T., Park Y.Y., Kim S.J., and Kim, M. J. (2006) Study on the Kinetics of Iron Leaching by Oxalic Acid. *Int. J .Miner Process*, 80, 144-152.
- [3]. Taxiarchou, M., Parnias, D., Doumi, I., Paspaliaris, I., and Kontopoulos, A. (1997a) Dissolution of Haematite in Acidic Oxalate Solutions. *Hydrometallurgy*, 44, 287-299.
- [4]. Parnias, D., Taxiarchou, M., Paspaliaris, I., Kontopoulos, A. (1996) Mechanism of Dissolution of Iron Oxides in Aqueous Oxalic Acid. *Hydrometallurgy*, 42, 257-265.
- [5]. Lee, S. O., Oh, J. K., Shin, B. S. (1999) Dissolution of Iron Rust Materials using Oxalic Acid. *J. Min. Metall. Inst. Jpn.* 115, 815-819. Alafara, A. Baba, D., Adekola, F. A., Folashade, A. O. (2005). Quantitative Leaching of a Nigerian Iron Ore in Hydrochloric Acid, *J. Appl. Sci. Environ. Mgt.* 9(3):15 - 20
- [6]. Nwoye, C. I., Amara, G. N., and Onyemaobi, O. O. (2008). Model for Evaluating Dissolved Iron during Leaching of Iron Oxide Ore in Sulphuric Acid Solution, *Inter. J. Nat. Appl. Sc.*, 4(2): 209-211.
- [7]. Nwoye, C. I., Obasi, G. C., Mark, U., Inyama, S., Nwakwuo, C. C. (2009). Model for Calculating the Concentration of Leached Iron Relative to the Final Solution Temperature during Sulphuric Acid Leaching of Iron Oxide Ore. *New York Science Journal*, 2(3):49-54.
- [8]. Nwoye, C. I., Ofoegbu, S. U., Obi, M. C., Nwakwuo, C. C. (2009). Model for Predictive Analysis of the Concentration of Dissolved Iron Relative to the Weight Input of Iron Oxide Ore and Leaching Temperature during Sulphuric Acid Leaching. *Nature and Science Journal*. 7(3):41-47.
- [9]. Nwoye, C. I. (2008). C-NIKBRAN: Data Analytical Memory