



Model for Evaluation of Sulphur Removal Based on Its As-Beneficiated Content and Extracted Iron Concentration during Leaching

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ABSTRACT

Assessment evaluation of sulphur removal was carried out based on its as-beneficiated content and extracted iron concentration during iron ore leaching. Iron oxide ore was leached in a solution of acetic acid at a temperature of 30°C for 10 minutes. A model was derived and used as a tool for the analysis. The validity of the two-factorial model:

$$\gamma = 0.0051\alpha^2 - 0.5105\alpha + 0.07\theta^2 - 0.16\theta + 12.861$$

was rooted on the expression $\gamma + 0.16\theta - 12.861 = 0.0051\alpha^2 - 0.5105\alpha + 0.07\theta^2$ where both sides of the expression are correspondingly approximately equal. Statistical analysis of the results of removed sulphur from derived model and experiment for each value of the input concentration of acetic acid shows standard errors of 4.61×10^{-5} and 1.17×10^{-4} % respectively. The maximum deviation of the model-predicted concentration of removed sulphur iron is less than 6%, implying an operational confidence level above 94%.

Keywords: *Model, Sulphur Removal, Extracted iron concentration, Acetic Acid Solution, Iron Ore Leaching.*

1. INTRODUCTION

A lot of concern has been awakened by the failure of steel structures in hot service conditions, making the need to intensify research and development aimed at producing high quality defect free steel materials with admissible sulphur content unavoidable.

The failure of steel serving in very hot enclosure or environment has been reported (Chapman, 1972) to result from presence of a membrane of high concentration of sulphur as iron sulphide in the steel crystals. Under this condition, the material becomes embrittled and abruptly fails due to hot shortness. During heating of ingots before rolling or forging, the inter-granular sulphur-rich layers within the metal microstructure soften resulting to the destruction of the bonds between the grains and invariably results to crack formation during plastic working; a defect called hot or red shortness (Edneral, 1979).

Desulphurization of pig iron outside of or during the blast furnace operation has been widely practiced by way of filling a ladle with the pig iron and adding to it as a single charge or in a series of smaller incremental charges, soda in granulated or powder form (Kosmider and Danckert, 1973). Application of lime in various desulphurization methods has been as a mix (lime/magnesium mix) or a lone addition. The researchers observed that usage of "fluidized" lime and magnesium not only decreases explosion risks associated with usage of calcium carbide but reduces the cost of the

treatment compared to the process of using calcium carbide. This technique also has less environmental impact. The researchers also explored the potentiality of using another technique for desulphurizing pig iron which involves blow by pneumatic means lime or calcium carbide powder into the inactive pig iron in the ladle by means of an immersion lance. This complements a discontinuous method; where the pig iron to be desulphurized must first be collected in the ladle in order to desulphurize the total ladle content. Such large quantities of pig iron can be desulphurized in most metallurgical plants, however, this method is obviously relatively expensive.

Kosmider and Danckert (1973) observed that the degree of desulphurization is dependent: (1) upon the quantity of the desulphurizer (kg per ton of pig iron) (2) upon the initial sulphur content (3) upon the desired final content of sulphur in the pig iron (4) upon the grain size of the desulphurizer, (5) upon the holding time of the pig iron in the reactor and (6) upon the immersion depth of the blowing lance.

The mechanism and process analysis of desulphurizing Agbaja iron ore concentrate using powdered potassium trioxochlorate (v) (KClO₃) as oxidant has been carried out (Nwoye, 2009). Results of the study show in clear terms that the oxygen required for the desulphurization process was produced from the decomposition of KClO₃ within a temperature range 375-502°C. The researcher observed that this temperature range is the Gas Evolution Temperature Range (GETR) for sulphur present in Agbaja iron ore.

Sulphur vapour and oxygen gas produced at this temperature range were believed to have reacted to form and liberate SO₂. The process analysis suggests that the mechanism of the desulphurization process involves gaseous state interaction between oxygen and sulphur through molecular combination. The results on the extent of desulphurization reveal that simultaneous increase in both the percentage of the oxidant added and treatment temperature used (up to 15g KClO₃ per 50g of ore and maximum of 800°C respectively) are the ideal conditions for the best desulphurization efficiency.

The present work involves assessment evaluation of sulphur removal based on as-beneficiated sulphur content and concentration of extracted iron during leaching of Agbaja (Nigeria) iron ore.

2. 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 250µm. The raw Agbaja iron ore was then sent for chemical analysis using x-ray fluorescence diffraction spectrometer and atomic absorption spectrophotometer

Scrubbing process

Scrubbing was carried to remove argillaceous material 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 silicate and 25drops of oleic acid were sprinkled and distributed uniformly throughout the ore. 20liters 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 24 hours. Some quantities were sent for chemical analysis.

Chemical leaching process

The dried scrubbed iron ore was further pulverized and seized to obtain a particle size of 10microns 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 10microns of scrubbed iron ore, 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°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°C for 24hours. The experiment was repeated for different concentrations and temperature of 40,50 and 60°C. The samples were analyzed using atomic absorption spectrophotometer and x-ray fluorescence diffraction spectrometer.

Model Formulation

Computational analysis of experimental data in Table 1, resulted to Table 3 which indicates that;

$$\gamma + K\theta - S \approx N\alpha^2 - S_e\alpha + N_e\theta^2 \tag{1}$$

Introducing the values of K, S, N, S_e and N_e into equation (1)

$$\gamma + 0.16\theta - 12.861 = 0.0051\alpha^2 - 0.5105\alpha + 0.07\theta^2 \tag{2}$$

$$\gamma = 0.0051\alpha^2 - 0.5105\alpha + 0.07\theta^2 - 0.16\theta + 12.861 \tag{3}$$

Where

(γ) = Concentration of removed sulphur (%)

(α) = Concentration of Fe extracted (%)

(θ) = Initial sulphur concentration in iron ore (before leaching)(%)

K = 0.16, S = 12.861, N = 0.0051, S_e = 0.5105, N_e = 0.07

K, S, N, S_e and N_e are equalizing constant (determined using C-NIKBRAN (Nwoye, 2008))

Table 1: Variation of removed Sulphur Concentration with extracted Fe Concentration

(γ) (%)	(α) (%)	(θ) (%)
0.0701	50.23	0.08
0.0703	50.21	0.08
0.0704	50.04	0.08
0.0706	49.94	0.08
0.0708	49.93	0.08

Boundary and Initial Condition

Consider iron ore (in a reactor) placed with in acetic acid solution (oxidant). The reactor atmosphere is not contaminated i.e (free of unwanted gases and dusts). Initially, atmospheric levels of oxygen are assumed (due to air in the furnace). **Mass of iron oxide ore: (50g)**, leaching time considered: 30 mins., range of extracted Fe concentration: 49.93-50.23 %, constant treatment temperature: 30°C, constant ore grain size; 10µm, were also used.

The boundary conditions are: reactor oxygen atmosphere since the reactor was air-tight closed at the bottom and top 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.

3. RESULTS AND DISCUSSIONS

The result of the chemical analysis carried out on the beneficiated iron ore concentrate is presented in Table 1. The table shows that the percentage of total iron (Fe_T) in the as-beneficiated ore is 52.67%.

Table 2: Result of chemical analysis of iron ore used

Element/Compound	Fe _T	S	SiO ₂	Al ₂ O ₃
Unit (%)	52.67	0.08	8.983	6.986

Model Validation

The validity of the model is strongly rooted in equation (2) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 3 also agrees with equation (2) following the values of $\gamma + 0.16\theta - 12.861$ and $0.0051\alpha^2 - 0.5105\alpha + 0.07\theta^2$ evaluated from the experimental results in Table 1.

Table 3: Variation of $\gamma + 0.16\theta - 12.861$ with $0.0051\alpha^2 - 0.5105\alpha + 0.07\theta^2$

$\gamma + 0.16\theta - 12.861$	$0.0051\alpha^2 - 0.5105\alpha + 0.07\theta^2$
-12.7781	-12.7744
-12.7779	-12.7745
-12.7778	-12.7746
-12.7776	-12.7746
-12.7774	-12.7746

Furthermore, the derived model was validated by comparing removed sulphur concentrations 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.

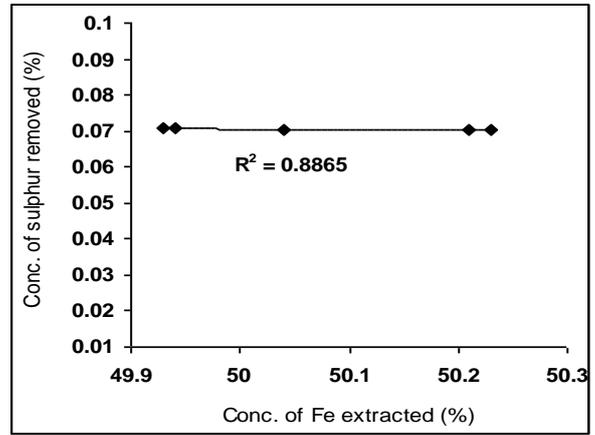


Fig. 1: Coefficient of determination between removed sulphur concentration and extracted iron concentration of as obtained from experimental results.

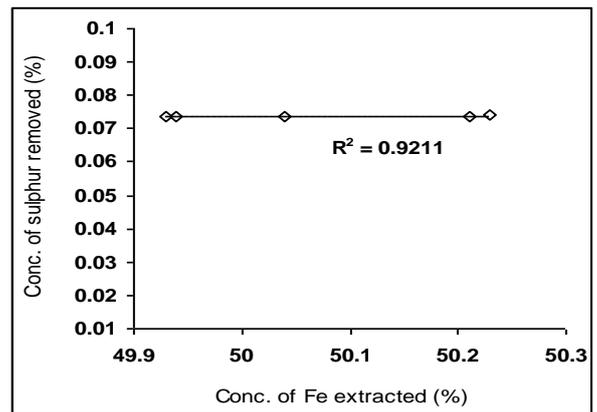


Fig. 2: Coefficient of determination between removed sulphur concentration and extracted iron concentration as obtained from model-predicted results

Statistical Analysis

Standard errors (STEYX)

The standard errors (STEYX) in predicting the removed sulphur concentration (using results from derived model and experiment) for each value of the extracted iron concentration are 4.61×10^{-5} and 1.17×10^{-4} % respectively. The standard error was evaluated using Microsoft Excel version 2003.

Correlation

$$R = \sqrt{R^2} \tag{7}$$

The correlations between removed sulphur concentration and extracted iron concentration as obtained from derived model and experiment was calculated using equation (7) considering the coefficient of determination R² from Figs. 1 and 2. The evaluated correlations are 0.9597 and 0.9415 respectively. The proximity in these correlations indicates significant reliability and hence validity of the model.

Graphical Analysis

Comparative graphical analysis of Fig. 3 shows very close alignment of the curves from model-predicted removed

sulphur 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 removed sulphur concentration.

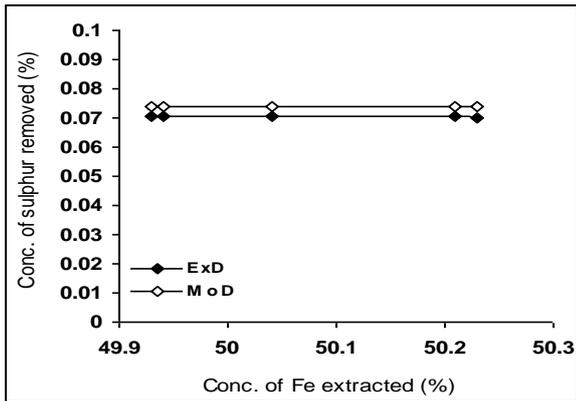


Fig. 3: Comparison of the removed sulphur concentrations (relative to the extracted iron concentration)

Deviation (Dn) (%) of model-predicted values from the experimental S values is given by

$$Dn = \gamma_m \left(\frac{\gamma_{exp} \times 100}{\gamma_{exp}} \right) \quad (8)$$

Where

γ_m = Model-predicted concentration of sulphur removed (%)

γ_{exp} = Concentration of sulphur removed as obtained from experiment (%)

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

$$Cr = -Dn \quad (9)$$

Therefore

$$Cr = -100 \left(\frac{\gamma_{exp}}{\gamma_{exp}} \right) \quad (10)$$

Introduction of the corresponding values of Cf from equation (10) into the model gives exactly the corresponding experimental values.

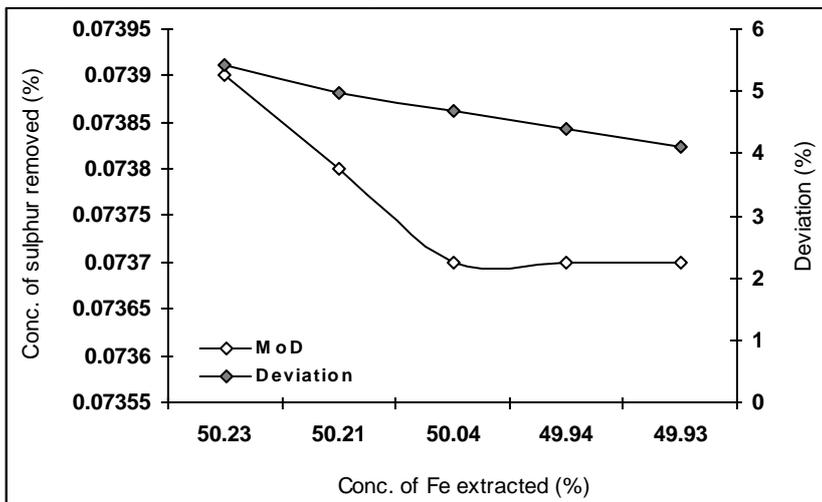


Fig. 4: Variation of input concentration of acetic acid with the deviation of model-predicted removed sulphur concentration (from experimental values)

Fig. 4 shows that the maximum deviation of the model-predicted removed sulphur concentration from the corresponding experimental value is less than 6%. The figure shows that the least and highest magnitudes of deviation of the model-predicted removed sulphur concentration (from the corresponding experimental values) are 4.1 and 5.42 % which corresponds to removed sulphur concentrations: 0.0737 and

Deviational Analysis

Critical analysis of removed sulphur concentration 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 acetic acid solution 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 removed sulphur concentration to those of the corresponding experimental values.

0.0739 % and extracted iron concentration: 49.93 and 50.23 respectively.

Comparative analysis of Figs. 4 and 5 indicates that the orientation of the curve in Figs. 5 is opposite that of the deviation of model-predicted removed sulphur concentration

(Fig.4). This is because correction factor is the negative of the

deviation as shown in equations (9) and (10).

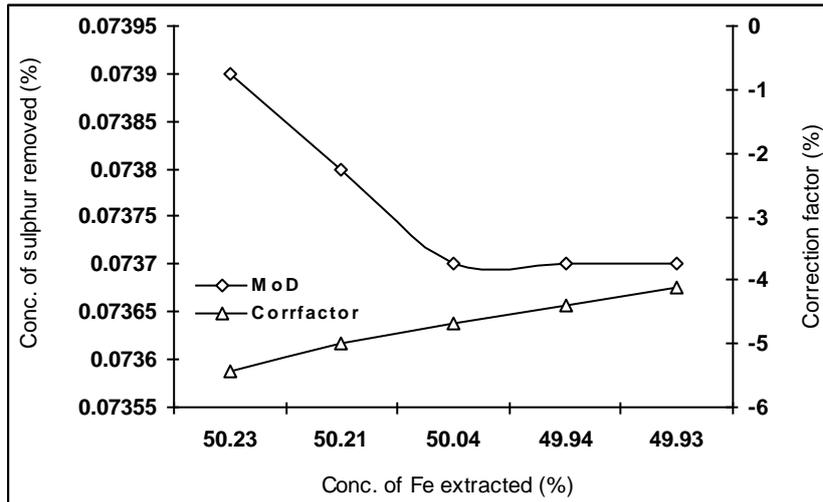


Fig. 5: Variation of model-predicted removed sulphur concentration with its associated correction factor

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 acetic acid solution which have played vital roles during the process, but were not considered during the model formulation. Fig. 5 indicates that the least and highest magnitudes of correction factor to the model-predicted removed sulphur concentration are 4.1 and 5.42 % which corresponds to removed sulphur concentrations: 0.0737 and 0.0739 % and extracted iron concentration: 49.93 and 50.23% respectively.

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).

4. CONCLUSION

Assessment evaluation of sulphur removal was carried out based on its as-beneficiated content and extracted iron concentration during iron ore leaching. The validity of the two-factorial model derived and used as a tool for the analysis was rooted on the expression $\gamma + 0.16\theta - 12.861 = 0.0051\alpha^2 - 0.5105\alpha + 0.07\theta^2$ where both sides of the expression are correspondingly approximately equal. Statistical analysis of the results of removed sulphur from

derived model and experiment for each value of the input concentration of acetic acid shows standard errors of 4.61×10^{-5} and 1.17×10^{-4} % respectively. The maximum deviation of the model-predicted concentration of removed sulphur iron is less than 6%, implying an operational confidence level above 94%.

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