Evaluation of Sulphur Removal Based on Its As-Beneficiated Content and Leaching Temperature during Iron Ore Processing in Acetic Acid Solution

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Abstract

This paper presents an assessment evaluation of sulphur removal based on as-beneficiated sulphur content and leaching temperature during iron ore processing in acetic acid solution. The acid solution and ore contained in the reaction vessel were allowed to react at a temperature range: $30\text{-}60^0$C for 40 minutes. The two-factorial derived model was used as a tool for the evaluation. The validity of the model expressed as:

$$\gamma = -6 \times 10^{-6} \beta^2 + 0.0006 \beta - 0.1\theta^2 + 0.0078\theta + 0.0568$$

was rooted on the expression $\gamma - 0.0078\theta - 0.0568 = -6 \times 10^{-6} \beta^2 + 0.0006 \beta - 0.1\theta^2$ 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 leaching temperature shows standard errors of 8.5×10^{-4} and 8.1×10^{-4} % respectively. Removed sulphur per unit rise in the leaching temperature as obtained from derived model-predicted and experimental results are 1.2×10^{-4} and 1.7×10^{-4} %/ ^{0}C. The maximum deviation of the model-predicted concentration of removed sulphur (from experimental result) is less than 4% which is quite within the admissible limit of deviation from experimental results.

Keywords: Evaluation, Sulphur Removal, Acetic Acid Solution, Iron Ore Leaching

Introduction

Steel structures fail abruptly in hot service conditions, resulting in oil spillages and loss of other fluids which has been stored in tanks for specific purposes. Economically, such phenomenom translates into loss of millions of naira. This has arousing and awakened a lot of concern and the need to intensify research and development aimed at producing high quality defect free steel materials with admissible sulphur content.

Failure of steel serving in very hot enclosure or environment results from presence of a membrane of high concentration of sulphur as iron sulphide in the steel crystals (Chapman,1972). Basically, under this condition, the material becomes embrittled and abruptly fails due to hot shortness. Edneral (1979) reported that on 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.

Kosmider and Danckert (1973) discovered that desulphurization of pig iron could be carried out outside of or during the blast furnace operation 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. Furthermore, 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.

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

Nwoye (2009) carried out studies on the mechanism and process analysis of desulphurizing Agbaja iron ore concentrate using powdered potassium trioxochlorate (v) ($KClO_3$) as oxidant. Results of the study indicate in clear terms that the oxygen required for the desulphurization process was produced from the decomposition of $KClO_3$ within a temperature range 375-502°C. Further investigations show that this temperature range is the Gas Evolution Temperature Range (GETR) for sulphur present in Agbaja iron ore. Also, at this temperature range, sulphur vapour from the iron ore and oxygen gas produced were strongly believed to have reacted to form and liberate SO_2. It was discovered from the reaction process analysis 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 $KClO_3$ per 50g of ore and maximum of 800^{0}C respectively) are the ideal conditions for the best desulphurization efficiency.

Nwoye et al (2009 & 2010) derived models for predicting the removed sulphur concentration based on reaction temperature. These models were formulated using results generated from solid state oxidations of iron oxide ore by powdered potassium chlorate ($KClO_3$). These models indicate that the removed sulphur concentration is inversely proportional to the logarithm of the reaction temperature. Nwoye et al. (2010) carried out the oxidation reaction at temperature range: 600-800^{0}C while Nwoye et al. (2009) considered a temperature range of 500-700^{0}C. In both reactions, the oxidizing specie is oxygen produced during the decomposition of $KClO_3$.

The present work is to derive a model for evaluation of sulphur removal based on as-beneficiated sulphur content and leaching temperature during leaching of Agbaja (Nigeria) iron ore in acetic acid solution.

MATERIALS AND METHODS
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

decanted. This was repeated for five times until clear water was observed. At this point 5g of sodium silicate and 25 drops of oleic acid were sprinkled and distributed uniformly throughout the ore. 20 litres 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 sieved 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 10 microns 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 30ºC. 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 150ºC for 24 hours. The experiment was repeated for different concentrations and temperatures of 40, 50 and 60ºC. 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;

$$\gamma - K\theta - S \approx -N\beta^2 + S_e\beta - N_e\theta^2 \qquad (1)$$

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

$$\gamma - 0.0078\theta - 0.0568 = -6 \times 10^{-6}\beta^2 + 0.0006\beta - 0.1\theta^2 \qquad (2)$$

$$\gamma = -6 \times 10^{-6}\beta^2 + 0.0006\beta - 0.1\theta^2 + 0.0078\theta + 0.0568 \qquad (3)$$

Where

(γ) = Concentration of removed sulphur (%)
(β) = Leaching temperature (^{0}C)
(θ) = As- beneficiated sulphur concentration (%)
K = 0.0078, S = 0.0568, N = 6×10^{-6}, S_e = 0.0006, N_e = 0.1

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 leaching temperature

(γ) (%)	(β) (^{0}C)	(θ) (%)
0.0704	30	0.08
0.0729	40	0.08
0.0738	50	0.08
0.0741	60	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 reactor). Mass of iron oxide ore: (50g), leaching time considered: 40 mins., range of leaching temperature considered: 30- 60°C, constant ore grain size; 10µm, were also used.

The boundary conditions are: reactor oxygen atmosphere since the furnace 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.

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%. Equation (3) is the derived model.

Table 2: Result of chemical analysis of iron ore used

Element/Compound	Fe_T	S	SiO_2	Al_2O_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 $\gamma - 0.0078\theta - 0.0568$ and $-6 \times 10^{-6} \beta^2 + 0.0006 \beta - 0.10\theta^2$ evaluated from the experimental results in Table 1.

Table 3: Variation of $\gamma - 0.0078\theta - 0.0568$ with $-6 \times 10^{-6} \beta^2 + 0.0006 \beta - 0.10\theta^2$

$\gamma - 0.0078\theta - 0.0568$	$-6 \times 10^{-6} \beta^2 + 0.0006 \beta - 0.10\theta^2$
0.0130	0.0120
0.0155	0.0138
0.0164	0.0144
0.0167	0.0138

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.

Computational Analysis

Computational analysis of the experimental and model-predicted removed sulphur concentration was carried out to ascertain the degree of validity of the derived model. This was done by comparing removed sulphur concentration per unit rise in leaching temperature evaluated from model-predicted results with those from actual experimental results

Removed sulphur concentration per unit rise in leaching temperature γ_T (%/ ^{0}C) was calculated from the equation;

$$\gamma_T = \gamma / T \tag{4}$$

Therefore, a plot of the removed sulphur concentration against leaching temperature as in Fig. 1 using experimental results in Table 3, gives a slope, S at points (30, 0.0704) and (50, 0.0738) following their substitution into the mathematical expression;

$$\gamma_T = \Delta\gamma / \Delta T \tag{5}$$

Equation (5) is detailed as

$$\gamma_T = \gamma_2 - \gamma_1 \,/\, T_2 - T_1 \tag{6}$$

Where

$\Delta\gamma$ = Change in removed sulphur concentrations of γ_2, γ_1 at two values of leaching temperatures T_2, T_1. Considering the points (30, 0.0704) and (50, 0.0738) for (T_1, γ_1) and (T_2, γ_2) respectively, and substituting them into equation (6), gives the slope as 1.7×10^{-4} %/ ^{0}C which is the removed sulphur concentration per unit rise in leaching temperature during the actual leaching process.
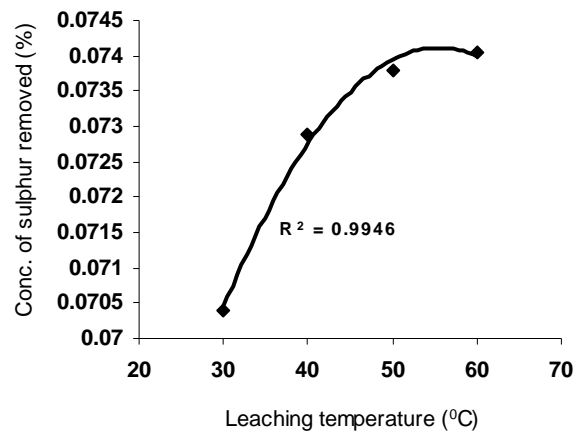

Fig. 1: Coefficient of determination between removed sulphur concentration and leaching temperature as obtained from experimental results

Similarly, a plot of the removed sulphur concentration against leaching temperature (as in Fig. 2) using derived model-predicted results gives a slope: 1.2×10^{-4} %/ ^{0}C on substituting the points (30, 0.0694) and (50, 0.0718) for (T_1, γ_1) and (T_2, γ_2) respectively into equation (6). This is the model-predicted removed sulphur concentration per unit rise in the leaching temperature.
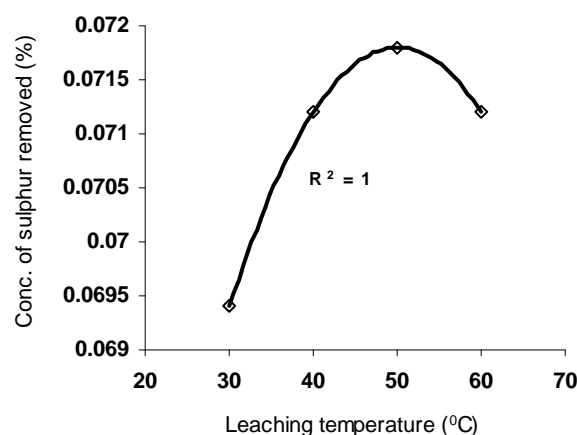

Fig. 2: Coefficient of determination between removed sulphur concentration and leaching temperature as obtained from model-predicted results

A comparison of this set of values for removed sulphur concentration (per unit rise in leaching temperature) also shows proximate agreement and a high degree of validity of the derived model.

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 leaching temperature are 8.5×10^{-4} and 8.1×10^{-4} % respectively. The standard error was evaluated using Microsoft Excel version 2003.

Correlation

$$R = \sqrt{R^2} \qquad\qquad (7)$$

The correlations between removed sulphur concentration and leaching temperature as obtained from derived model and experiment was calculated using equation (7) considering the coefficient of determination R^2 from Figs. 1 and 2. The evaluated correlations are 1.0000 and 0.9973 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.
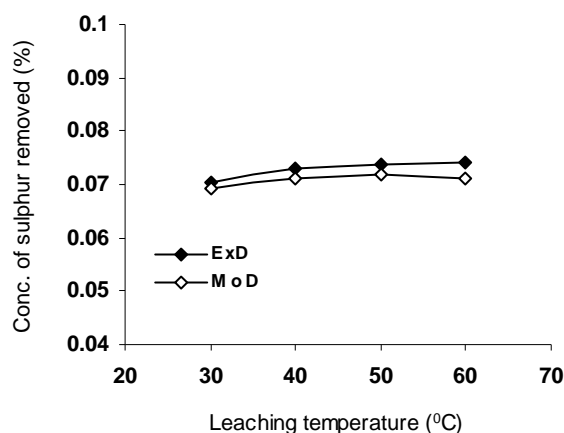

Fig. 3: Comparison of the removed sulphur concentrations (relative to the leaching temperature).

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.

Deviation (Dn) (%) of model-predicted γ_m values from the experimental γ_{exp} values is given by

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

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

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

Therefore

$$Cr = -100 \left[\frac{\gamma_m - \gamma_{exp}}{\gamma_{exp}} \right] \qquad (10)$$

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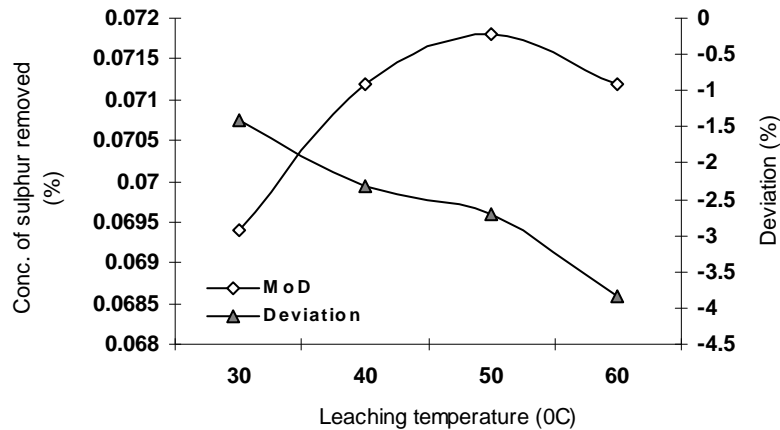

Fig. 4: Variation of leaching temperature with the deviation of model-predicted removed sulphur concentration (from experimental values)

Fig. 4 shows that the maximum deviation of the model-predicted removed sulphur concentration from the corresponding experimental value is less than 4%. The figure shows that the least and highest magnitudes of deviation of the model-predicted removed sulphur concentration (from the corresponding experimental values) are -1.42 and - 3.85 % which corresponds to removed sulphur concentrations: 0.0694 and 0.0712 % and leaching temperatures: 30 and 60 ^{0}C 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).
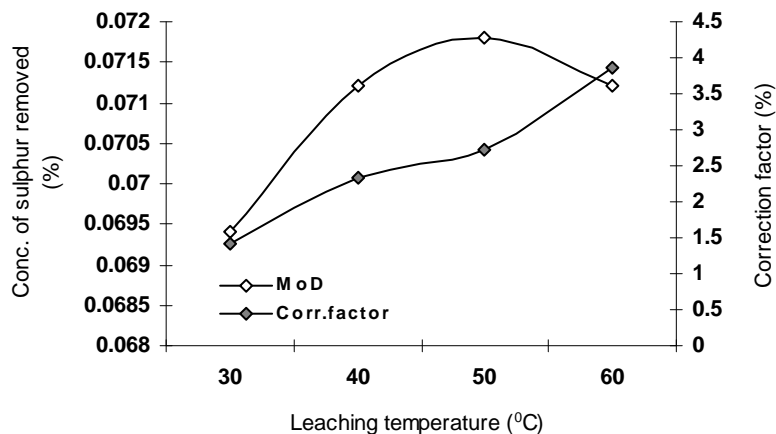

Fig. 5: Variation of model-predicted concentration of removed sulphur with its associated correction factor.

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 + 1.42 and + 3.85%. These correction factors correspond to removed sulphur concentrations: 0.0694 and 0.0712 % and leaching temperatures: 30 and 60 ^{0}C 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).

Conclusion

Sulphur removal during iron ore processing in acetic acid solution, was evaluated based on as-beneficiated sulphur content and the leaching temperature. The validity of the derived two-factorial model used for the evaluation was rooted on the expression $\gamma - 0.0078\theta - 0.0568 = -6 \times 10^{-6} \beta^2 + 0.0006 \beta - 0.1\theta^2$ 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 leaching temperature shows standard errors of 8.5×10^{-4} and 8.1×10^{-4} % respectively. Removed sulphur per unit rise in the leaching temperature as obtained from derived model-predicted and experimental results are 1.2×10^{-4} and 1.7×10^{-4} %/ ^{0}C The maximum deviation of the model-predicted concentration of removed sulphur (from experimental result) is less than 4% which is quite within the admissible limit of deviation from experimental results.

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