Model for Predictive Analysis of the Concentration of Sulphur Removed by Molecular- Oxygen-Induced Desulphurization of Iron Oxide Ore

Chukwuka Ikechukwu Nwoye *[1], Charles Nnabuihe Anyakwo [1], Uchenna Chigozie Nwoye [2], Stanley Inyama [3], Reginald Ejimofor [1], Chinedu Chris Nwakwuo [4]

[1]Department of Materials and Metallurgical Engineering, Federal University of Technology, Owerri, Nigeria.
[2]Data Processing, Modelling and Simulation Unit, Weatherford Nig. Ltd. Port-Harcourt Nigeria.
[3]Department of Industrial Mathematics, Federal University of Technology, Owerri, Nigeria.
[4]Department of Material Science, Oxford University, United Kingdom.
chikeyn@yahoo.com

Abstract: Model for predictive analysis of the concentration of sulphur removed by molecular-oxygen-induced desulphurization of iron oxide ore (powdered potassium chlorate being the oxidant) has been derived. The model; %S = 0.0415/Logγ was found to predict the concentration of sulphur removed, very close to the corresponding %S values obtained from the actual experimental process. It was found that the model is dependent on the values of the weight input of the oxidant ($KClO_3$) during the desulphurization process. The validity of the model is believed to be rooted in the expression $k_n[(\gamma)^{\mu\%S}] = T/\alpha$ where both sides of the expression are correspondingly almost equal. The positive or negative deviation of each of the model-predicted values of %S from those of the corresponding experimental values was found to be less than 33% which is quite within the range of acceptable deviation limit of experimental results. [Nature and Science. 2009;7(3):36-40]. (ISSN: 1545-0740).

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1. Introduction

Agbaja iron ore has been found to consist principally of goethite, with minor hematite, maghemite, siderite, quartz, kaolinite pyrite and an average of 0.09%S [1]. It was also found to have oolitic and pisolitic structures rich in iron oxides, in a matrix that is predominantly clay. It has been reported [2] that sulphur transfer from metal to slag or slag to gas during desulphurization involves oxygen transfer in the opposite direction. They found [2] that the mechanism of such desulphurization involves oxidation of sulphur resident in the metal or slag by oxygen from the slag through ionic exchange between the oxygen and sulphur, since the whole system is made up of liquid/molten condition during this process. They maintained that oxygen in the slag comes from CaO, which is one of the products of decomposition of $CaCO_3$ being deposited into the slag as a slag forming agent.

Studies [3] carried out on gas-slag system during iron making, indicates that at oxygen partial pressure below about 10^{-5} atm., sulphur dissolves in the melt as sulphide ions; at oxygen partial pressure higher than 10^{-3} atm., sulphur enters the melt as sulphate ions. In both cases, it was reported [3] that both the sulphide and sulphate ions leave the furnace through the slag. It was therefore concluded [3] that the mechanism of such desulphurization process is oxidation of sulphur by oxygen from the slag through ionic exchange between the two participating elements.

Turkdogan and Darken [4] found that at a temperature well below about 1600^0C, the pyrosulphate reaction also occurs. They found that this reaction was an enhancement to the desulphurization process actually taking place in the furnace. Also oxygen for this process was found [4] to come from the slag, engaging sulphur in ionic exchange; being the mechanism of such process.

It was discovered that one of the most important factors influencing the desulphurization process during iron making is the state of oxidation of the bath [5].

Nwoye [6] found that Agbaja iron ore which has not been responsive to so many upgrading processes, has been upgraded to 73.4% Fe assay (starting from as-received concentrate assaying 56.2%Fe) by pyrometallurgical-oxidation method. Main parameters investigated were the effects of treatment temperature and oxidant ($KClO_3$) on the upgrading process. It was established [6] that 800^0C is the optimum temperature for the upgrading step considering the range of temperature used (500-800^0C). It was also observed from results of the investigation that both oxidant and temperature increase (up to 12g per

50g of iron ore and maximum of 800^{0}C respectively) during the process are vital conditions for improving on the grade of the ore concentrate.

Desulphurization of Agbaja iron oxide ore concentrate using solid potassium trioxochlorate (V) ($KCI0_3$) as oxidant has been carried out [7]. The concentrate was treated at a temperature range 500 – 800^{0}C. The results of the investigation revealed that simultaneous increase in both the percentage of the oxidant added (up to 15g per 50g of ore) and treatment temperature (maximum 800^{0}C) used give the ideal conditions for increased desulphurization efficiency. This translates into high desulphurization efficiency when both oxidant concentration (up to 15g per 50g of ore) and treatment temperature (maximum 800^{0}C) are high.

The mechanism and process analysis of desulphurization of Agbaja iron ore concentrate using powdered potassium trioxochlorate (v) ($KCIO_3$) as oxidant has been reported [8]. Concentrates were treated at a temperature range 500 – 800^{0}C. Results of the process analysis indicate that oxygen required for the desulphurization process was produced following decomposition of $KClO_3$ within a temperature range 375-502^{o}C. It was observed [8] 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 SO_2. The process analysis suggests that the mechanism of the desulphurization process involves gaseous state interaction between oxygen and sulphur through molecular combination [8].The results for 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 [8].

The aim of this work is to derive a model for predictive analysis of the concentration of sulphur removed by molecular-oxygen-induced desulphurization of Agbaja (Nigeria) iron oxide ore. In the actual experimental work [9] preceding the present, powdered potassium chlorate was used as oxidant.

2. Model

The solid phase (ore) is assumed to be stationary, contains some unreduced iron remaining in the ore. It was found [9] that oxygen gas from the decomposition of $KClO_3$ attacked the ore in a gas-solid reaction, hence removing (through oxidation) the sulphur present in the ore in the form of SO_2 .Equations (1) and (2) show this.

$$2KClO_{3\,(s)} \longrightarrow 2KCl_{(s)} + 3O_{2\,(g)} \qquad (1)$$

$$S_{(s)} \xrightarrow{\text{Heat}} S_{(g)} + O_{2\,(g)} \longrightarrow SO_{2\,(g)} \qquad (2)$$

2.1 Model Formulation

Experimental data obtained from research work [9] carried out at SynchroWell Research Laboratory, Enugu were used for this work. Results of the experiment as presented in report [9] and used for the model formulation are as shown in Table 1.

Computational analysis of the experimental data shown in Table 1, gave rise to Table 2 which indicate that;

$$k_n[(\gamma)^{\mu\%S}] = T/\alpha \quad \text{(approximately)} \qquad (3)$$

Taking logarithm of both sides

$$\text{Log}\,(k_n[(\gamma)^{\mu\%S}]) = \text{Log}\,(T/\alpha) \qquad (4)$$

$$\text{Log}k_n + \text{Log}[(\gamma)^{\mu\%S}] = \text{Log}T - \text{Log}\,\alpha \qquad (5)$$

$$\text{Log}k_n + \mu\%S\text{Log}\gamma = \text{Log}T - \text{Log}\,\alpha \qquad (6)$$

$$\mu\%S\text{Log}\gamma = \text{Log}T - \text{Log}\,\alpha - \text{Log}k_n \qquad (7)$$

$$\%S = \frac{\text{Log}T - \text{Log}\,\alpha - \text{Log}k_n}{\mu\,\text{Log}\gamma} \qquad (8)$$

Introducing the values of μ, T, k_n and α into equation (8) (since they are constants) and evaluating further, reduces it to;

$$\%S = \frac{0.0415}{\text{Log}\gamma} \qquad (9)$$

$$\%S = \frac{D_e}{\text{Log}\gamma} \qquad (10)$$

Where

%S = Concentration of sulphur removed during the pyrometallurgical-oxidation process.

k_n= 9.75 (Decomposition coefficient of $KClO_3$ at the treatment temperature (600^{0}C)) determined

in the experiment [9].
(μ) = 2.1739 (Oxidation coefficient of $KClO_3$ relative to the treatment temperature (600^0C)) determined in the experiment [9]
(α) = Weight of iron oxide ore added (g)
T = Treatment temperature used for the process (^0C)
(γ) = Weight of $KClO_3$ added (g)
D_e = 0.0415 (Assumed Desulphurization Enhancement Factor)

Table 1: Variation of concentration of sulphur removed with weight input of $KClO_3$.[9]

(γ)	(α)	%S
8	50	0.0346
9	50	0.0360
10	50	0.0400
11	50	0.0470
12	50	0.0500
		Table 1: Variation of concentration of dissolved iron with weight input of iron oxide ore and final solution pH. (Nwoye;2006)

Table 2: Variation of T/α with $k_n[(\gamma)^{\mu\%S}]$

T/α	$k_n[(\gamma)^{\mu\%S}]$
12	11.4003
12	11.5804
12	11.9125
12	11.9973
12	11.9982

3. Boundary and Initial Condition

Consider iron ore (in a furnace) mixed with potassium chlorate (oxidant). The furnace atmosphere is not contaminated i.e (free of unwanted gases and dusts). Initially, atmospheric levels of oxygen are assumed just before the decomposition of $KClO_3$ (due to air in the furnace).Weight of iron oxide ore used; (50g), and treatment time; 360secs. were used. Treatment temperature; 600°C, ore grain size; 150μm, and weight of $KClO_3$ (oxidant); (8-12g) were also used. These and other process conditions are as stated in the experimental technique [9].

The boundary conditions are: furnace oxygen atmosphere due to decomposition of $KClO_3$ (since the furnace was air-tight closed) 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.

4. Model Validation

The formulated model was validated by direct analysis and comparison of %S values predicted by the model and those obtained from the experiment for equality or near equality.

Analysis and comparison between these %S values reveal deviations of model-predicted %S values from those of the experiment. This is attributed to the fact that the surface properties of the ore and the physiochemical interactions between the ore and the oxidant (under the influence of the treatment temperature) which were found to have played vital roles during the oxidation process [9] were not considered during the model formulation. This necessitated the introduction of correction factor; to bring the model-predicted %S values to those of the experimental %S values.

Table 3: Comparison between %S removed as predicted by model and as obtained from experiment [9].

$\%S_{exp}$	$\%S_M$	Dv (%)	Cf (%)
0.0346	0.0460	+32.95	-32.95
0.0360	0.0435	+20.83	-20.83
0.0400	0.0415	+3.75	-3.75
0.0470	0.0399	-15.11	+15.11
0.0500	0.0385	-23.00	+23.00
		-26.67	-26.67

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

$$Dv = \frac{Sp - Se}{Se} \times 100 \qquad (11)$$

Where Sp = Predicted %S values from model
Se = Experimental %S values

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

$$Cf = -Dv \qquad (12)$$

Therefore

$$Cf = -\left(\frac{Sp - Se}{Se} \times 100\right) \qquad (13)$$

Introduction of the corresponding values of Cf from equation (13) into the model gives exactly the corresponding experimental %S values [9].

5. Results and Discussion

The derived model is equation (9). A comparison of the values of %S from the experiment and those from the model shows positive and negative deviations less than 33% which is quite within the acceptable deviation limit of experimental results hence depicting the reliability and validity of the model. This is shown in Table 3. The validity of the model is believed to be rooted in equation (3) where both sides of the equation are correspondingly almost equal. Table 2 also agrees with equation (3) following the values of $k_n[(\gamma)^{\mu\%S}]$ and T/α evaluated from Table 1 as a result of corresponding computational analysis. The value 0.0415 has a direct relationship with the value of %S as shown in equation (9). This indicates that the constant contributes directly (as a multiplying factor) to the predicted concentration of sulphur removed from the ore. Based on the foregoing, the constant is denoted as Desulphurization Enhancement Factor D_e.

Where $\%S_{exp}$ = %S values from experiment [9].
$\%S_M$ = %S values predicted by model

6. Conclusion

The model predicts the concentration of sulphur removed by molecular-oxygen-induced desulphurization of the iron oxide ore. The validity of the model is rooted in equation (3) where both sides of the equation are correspondingly almost equal. The deviation of the model-predicted %S values from those of the experiment is less than 33% which is quite within the acceptable deviation limit of experimental results.

Further works should incorporate more process parameters into the model with the aim of reducing the deviations of the model-predicted %S values from those of the experiment

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Corresponding author:
Chukwuka Ikechukwu Nwoye
Department of Materials and Metallurgical Engineering, Federal University of Technology, Owerri,
Nigeria. chikeyn@yahoo.com

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