

Model for the Calculation of the Concentration of Sulphur Removed during Oxidation of Iron Oxide Ore by Powdered Potassium Chlorate

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Abstract: Model for the calculation of the concentration of sulphur removed (during oxidation of iron oxide ore by powdered potassium chlorate) has been derived. The model;

$$\%S = \left(\frac{0.0717}{\text{Log}\alpha} \right)$$

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 (KClO₃) during the desulphurization process. The validity of the model is believed to be rooted in the expression $[(\alpha)^{\beta\%S}] = T/\gamma k_n$, where both sides of the expression are approximately equal to 2. 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 30% which is quite within the range of acceptable deviation limit of experimental results. [Nature and Science 2010;8(3):110-114]. (ISSN: 1545-0740).

Keywords: Model, Sulphur Removed, Iron Oxide Ore, Oxidation, Potassium Chlorate.

1. Introduction

Past report (Uwadiel,1984) revealed that Agbaja iron ore deposit is the largest known Nigerian iron ore deposit estimated at 1250 metric tonnes of ore reserve. It consists of oolitic and pisolitic structures rich in iron oxides, in a matrix that is predominantly clay. The principal constituent mineral is goethite, with minor hematite, maghemite, siderite, quartz, kaolinite pyrite and an average of 0.09%S.

Uwadiel (1990) carried out an intensive and selective oil agglomeration of Agbaja iron ore. The researcher, starting from the crude ore Fe content (45.6%), concentrated the ore by oil agglomeration technique to 90% Fe recovery and 65% Fe assay. He stated that the ore require grinding to minus 5µm to effect adequate liberation. These results were obtained at optimum pH 9. Similar studies by Uwadiel and Whewell (1988) included the effect of temperature on magnetizing reduction of Agbaja iron ore. The results of the investigation showed that the fine-grained oolitic Agbaja iron ore, which is not responsive to conventional processing techniques, can be upgraded by the magnetizing reduction method with an Fe recovery of 87.3% and Fe assay of 60% at 600°C.

Kulkarni and Somasundaran (1980), attempted to enhance concentrate Fe recovery The researchers

stated that concentrate Fe recovery decreases progressively below pH 8. In this pH region, oleate used is present as dispersion of oleic acid, and its adsorption on the surface of the iron oxides is similar to the process of hetero-coagulation involving positively charged iron oxide particles and negatively charged oleic acid droplet.

Nwoye (2008) reported that Agbaja oolitic 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 a process referred to as pyrometallurgical-oxidation method. The researcher investigated mainly the effects of treatment temperature and oxidant (KClO₃) on the upgrading process. It was established that 800°C is the optimum temperature for the upgrading step considering the range of temperature used (500-800°C). It was observed from results of the investigation that both oxidant and temperature increase (up to 12g per 50g of iron ore and maximum of 800°C respectively) during the process are vital conditions for improving on the grade of the ore concentrate.

A model for computational analysis of the concentration of iron upgraded during dry beneficiation of iron oxide ore has been derived by Nwoye et al., (2009). The model;

$$\%Fe = 2.25[(\ln(T/\mu))^{2.58}] \quad (1)$$

shows that the concentration of upgraded iron is dependent on the treatment temperature T , used when the mass of iron oxide ore μ , added is constant.

Desulphurization of Agbaja iron oxide ore concentrate by Nwoye (2008) using solid potassium trioxochlorate (V) ($KClO_3$) as oxidant and a treatment temperature range: 500 – 800°C. revealed that simultaneous increase in both the percentage of the oxidant added (up to 15g per 50g of ore) and treatment temperature (maximum 800°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°C) are high.

Nwoye (2009) investigated the mechanism and process analysis of desulphurization of Agbaja iron ore concentrate using powdered potassium trioxochlorate (v) ($KClO_3$) as oxidant. Concentrates were treated at a temperature range 500 – 800°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°C. It was 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 SO_2 . The process analysis suggests that the mechanism of the desulphurization process involves gaseous state interaction between oxygen and sulphur through molecular combination. 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°C respectively) are the ideal conditions for the best desulphurization efficiency.

Investigations made by Bardenheuer and Geller (1934) indicated that the sulphur transfer from metal to slag or slag to gas during desulphurization involves oxygen transfer in the opposite direction. They posited 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 $CaCO_3$ deposited into the slag as a slag forming agent.

Studies (St Pierre and Chipman, 1956) on gas-

slag system during iron making shows 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, they stated that both the sulphide and sulphate ions leave the furnace through the slag. They therefore concluded 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 (1961) established that at a temperature well below about 1600°C, 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 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 (Pehlke et al. 1975).

A model has been derived (Nwoye et al., 2009) for the predictive analysis of the concentration of sulphur removed as result of the molecular-oxygen-induced desulphurization of iron oxide ore (potassium chlorate being the oxidant). The model;

$$\%S = \left(\frac{0.0415}{\text{Log } \gamma} \right) \quad (2)$$

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 γ , ($KClO_3$) during the desulphurization process. The validity of the model is believed to be rooted in the expression $k_n[(\gamma)^{\mu\%S}] = T/a$ 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.

Nwoye et al (2009) derived a model for computational analysis of the concentration of sulphur removed during oxidation of iron oxide ore by powdered potassium chlorate. The model;

$$\%S = \left(\frac{0.0357}{\text{Log } \alpha} \right) \quad (3)$$

indicates that the predicted %S is dependent on the weight-input of $KClO_3$, α , added during the

desulphurization process. The maximum deviation of the model-predicted values of %S from those of the corresponding experimental values was found to be less than 37%

Model for predicting the concentration of sulphur removed during gaseous desulphurization of iron oxide ore has been derived by Nwoye et al. (2009). The model;

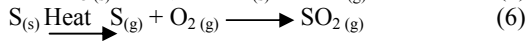
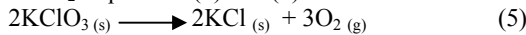
$$\%S = \left(\frac{0.0745}{\text{Log}T} \right) \quad (4)$$

shows that the predicted %S is dependent on the treatment temperature T, used during the desulphurization process.

The aim of this work is to derive a model for predicting the concentration of sulphur removed during temperature enhanced oxidation of Agbaja (Nigerian) iron oxide ore

2. Model

The solid phase (ore) is assumed to be stationary, contains some unreduced iron remaining in the ore. It was found (Nwoye, 2008) that oxygen gas from the decomposition of KClO₃ attacked the ore in a gas-solid reaction, hence removing (through oxidation) the sulphur present in the ore in the form of SO₂. Equations (5) and (6) show this.



2.1 Model Formulation

Experimental data obtained from research work (Nwoye,2007) carried out at SynchroWell Research Laboratory, Enugu were used for this work. Results of the experiment as presented in report (Nwoye, 2007) 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;

$$[(\alpha)^{\beta\%S}] = T/\gamma \quad (\text{approximately}) \quad (7)$$

$$k_n[(\alpha)^{\beta\%S}] = T/\gamma \quad (8)$$

Taking logarithm of both sides

$$\text{Log} (k_n[(\alpha)^{\beta\%S}]) = \text{Log} (T/\gamma) \quad (9)$$

$$\text{Log}k_n + \text{Log}[(\alpha)^{\beta\%S}] = \text{Log}T - \text{Log} \gamma \quad (10)$$

$$\text{Log}k_n + \beta\%S\text{Log} \alpha = \text{Log}T - \text{Log} \gamma \quad (11)$$

$$\beta\%S\text{Log} \alpha = \text{Log}T - \text{Log} \gamma - \text{Log}k_n \quad (12)$$

$$\%S = \frac{\text{Log}T - \text{Log} \gamma - \text{Log}k_n}{\beta \text{Log} \alpha} \quad (13)$$

Introducing the values of β, T, k_n and γ into equation (13) (since they are constants) and evaluating further, reduces it to;

$$\%S = \frac{0.0717}{\text{Log} \alpha} \quad (14)$$

$$\%S = \frac{D_e}{\text{Log} \alpha} \quad (15)$$

Where

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

k_n= 9.75 (Decomposition coefficient of KClO₃ at the treatment temperature (800⁰C)) determined in the experiment (Nwoye,2007).

(β) = 3.0 (Oxidation coefficient of KClO₃ relative to the treatment temperature (800⁰C)) determined in the experiment (Nwoye,2007)

(γ) = Weight of iron oxide ore added (g)

T = Treatment temperature used for the process (⁰C)

(α) = Weight of KClO₃ added (g)

D_e = 0.0717 (Assumed Desulphurization Enhancement Factor)

Table 1: Variation of concentration of sulphur removed with weight input of KClO₃ (Nwoye,2007)

(α)	M	%S
8	50	0.069
9	50	0.072
10	50	0.080
12	50	0.083
15	50	0.087

Table 2: Variation of T/γk_n with [(α)^{β%S}]

T/γk _n	[(α) ^{β%S}]
1.6410	1.5379
1.6410	1.6074
1.6410	1.7378
1.6410	1.8566
1.6410	2.0275

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 KClO₃ (due to air in the furnace).Weight, M of iron oxide ore used; (50g), and treatment time; 360secs.

were used. Treatment temperature; 800°C, ore grain size; 150µm, and range of weight of KClO₃ (oxidant) used; 8-15g were also used. These and other process conditions are as stated in the experimental technique (Nwoye, 2007).

The boundary conditions are: furnace oxygen atmosphere due to decomposition of KClO₃ (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 (Nwoye, 2007) 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).

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

$$Dv = \left(\frac{Sp - Se}{Se} \right) \times 100 \quad (16)$$

Where

Sp = Predicted %S values from model

Se = Experimental %S values

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

$$Cf = -Dv \quad (17)$$

Therefore

$$Cf = - \left(\frac{Sp - Se}{Se} \right) \times 100 \quad (18)$$

Introduction of the corresponding values of Cf from equation (18) into the model gives exactly the corresponding experimental %S values (Nwoye, 2007).

5. Results and Discussion

The derived model is equation (14) or (15). A comparison of the values of %S from the experiment and those from the model shows

maximum deviations less than 30% 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 (7) where both sides of the equation are correspondingly almost equal.

Table 2 also agrees with equation (7) following the values $T/\gamma k_n$ and $[(\alpha)^{\beta\%S}]$ evaluated from Table 1 as a result of corresponding computational

%S _e	%S _M	Dv (%)	Cf (%)
0.069	0.0794	+15.07	-15.07
0.072	0.0751	+4.31	-4.31
0.080	0.0717	-10.38	+10.38
0.083	0.0664	-20.00	+20.00
0.087	0.0610	-29.89	+29.89

analysis. The value 0.0717 has a direct relationship with the value of %S as shown in equation (14). 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_f

Table 3: Comparison between %S removed as predicted by model and as obtained from experiment (Nwoye, 2007).

Where

%S_e = %S values from experiment (Nwoye, 2007)

%S_p = %S values predicted by model

6. Conclusion

The model calculates the concentration of sulphur removed during desulphurization of the iron oxide ore (using powdered potassium chlorate as oxidant). The validity of the model is rooted in The model calculates the concentration of sulphur removed during desulphurization of the iron oxide ore (using powdered potassium chlorate as oxidant). The validity of the model is rooted in the expression $[(\alpha)^{\beta\%S}] = T/\gamma$ where both sides of the equation are approximately equal to 2. The maximum deviation of the model-predicted %S values from those of the experiment is less than 30% 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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