

# Determination of the Reaction Rate Controlling Resistance of Goethite Iron Ore Reduction Using CO/CO<sub>2</sub> Gases From Wood Charcoal †

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**Abstract:** In the present work, an attempt is made to use non-contact charcoal in the reduction of run-off mine goethite ore at heating temperatures above 570°C. The reduction mechanism was adopted, following Levenspiel's relations for the shrinking core model at a different stage of reduction. The non-contact charcoal reduction approach is adopted to maximize the benefit of using CO/CO<sub>2</sub> gases from charcoal for reduction without the need for beneficiation and concentration. The rate-controlling steps for the reduction kinetics of average particle size 5, 10, 15, and 20 mm at 570, 700, 800, 900, and 1000°C were studied after heat treatment of the ore-wood charcoal at a total reduction time of 40 minutes using activated carbon reactor. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis are done to investigate the spectrometric phase change and metallic components of the ore sample after reduction, respectively. The average percentage metallic iron content of 56.6, 60.8, and 61.7% and degree of metallization of 91.62, 75.96, and 93.6% are achieved from the SEM/EDX analysis of the reduced ore sample at reduction temperature of 570, 800, and 1000°C, respectively. The results indicate the tendency of high carbon deposit at the wustite stage of the reduction process at the least temperature and residence time of 570°C and 10 minutes, respectively. This study demonstrates that diffusion through the ash layer is the controlling resistance of the overall reduction process.

**Keywords:** Goethite ore; Wood charcoal; Controlling resistance; Degree of metallization; Reduction kinetics

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## 1. Introduction

It is a well-established assertion that iron is rated as the fourth most abundant elements Okoro, *et al.* [1] and it is considered as the most abundant rock-forming element constituting 5% of the Earth's crust Kiptarus, *et al.* [2] that are being explored worldwide for engineering applications. To acquire iron metal in its elemental form, the impurities must be removed from its ore via a chemical reduction since it is rarely found in its free state (Alamsari, *et al.* [3]; Babich, *et al.* [4]). The need to extract it from its oxide form and covert it to its pure metallic form through direct or indirect reduction of iron-oxide have become a crucial research concern in the years [5]. Aside from the many conventional techniques for carrying out reduction reactions on sourced iron ore, the associated reduction reaction kinetics using natural reductants (coal, charcoal, etc.) are attracting intense research interest [6-7]. Arising from the challenges associated with acquisitions of coking coal in many ore mines of iron, research attempts for experimental investigative

analysis of the kinetics of direct reduction of iron ore using reducing gases from charcoal as the reducing agent has become highly quintessential. The attempts are necessary to bypass the coking coal Blast Furnace (BF) process. The use of BF is considered the popular reduction process for iron ore worldwide [8]. The blast furnace is a plant used for iron ore reduction by charging in metallurgical coke, iron ore Heikkila, *et al.* [8]; Cecca, *et al.* [9] and usual limestone for removal of impurities. The exorbitant operation cost implications of the BF further hinder the use of the BF process [10-11]. Sequel to the aforementioned, it is vital to have a basic understanding of the basic mechanism involved in the sulfur-free Direct Reduction process using charcoal as the reductant. Some chemical governing equations would be required to estimate reduction time steps of the ore, rate of reaction, reaction control time, conversion factor, swelling extent, degree of metallization, and other relevant parameters at selected time steps intervals and operating temperatures.

The kinetics of reduction of iron ore generally involves a study of the rate of iron oxide conversion to metallic iron by the removal of oxygen as the chemical reaction rate increases with temperature. Whereas in indirect reduction processes, iron is reduced in its solid-state, the maximum temperature is lower than the melting temperature and the reaction rates are slower. In the direct reduction of iron ore, the mechanisms are complex because the oxide is expected to undergo a series of stepwise changes for the process of conversions to be complete [12]. The slowest step in the process is the determinant of the overall reaction rate. This is often referred to as the rate-controlling step. Dydo, *et al.*, [13] reiterates that the path of reduction of haematite iron ore using CO/CO<sub>2</sub> at low reduction temperature can take the following schemes: Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> → Fe (below 570°) and Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> → FeO → Fe (above 570°). The mechanism of Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> reduction necessitates the transformation of oxygen sublattice combined with iron atoms dislocation. The second step of Fe<sub>3</sub>O<sub>4</sub> → Fe reduction entails the nucleation sites of the metallic Fe phase. The third step of Fe<sub>3</sub>O<sub>4</sub> → FeO reduction does not require any transformation of oxygen sublattice. It can take place at higher temperatures above 570°C. As a result of the reverse disproportionation reaction, the reduction mechanism becomes a more intricate process in a two-step sequence such as FeO → Fe<sub>3</sub>O<sub>4</sub> → Fe or even a three-step sequence such as FeO → Fe<sub>3</sub>O<sub>4</sub> → FeO → Fe reduction at a temperature higher than 570°C [14]. Although iron oxides reduction behaviours are similar for all characterized iron ores, it is strongly influenced by their particle size, crystallinity, and the conditions of temperature, time, and reaction rate control dependent reduction [15].

In Jozwiak, *et al.* [16] and Kowitzarangkul, *et al.* [17], reduction kinetics of iron ore lumps by H<sub>2</sub> and CO mixture at different chemical compositions are reported. Their study revealed that the reaction rate is linearly proportional to the reactants gases (H<sub>2</sub> and CO). Mania [18] and Mania [19] carried out an experimental analysis on reduction kinetics of different types of samples, such as pellets, fines, and powders by thermo-gravimetric analysis (TGA) methods. The influence of iron oxide density on reduction extent and reduction rate of hematite ore using the H<sub>2</sub>-CO gas mixture as the reducing agent was investigated by Levenspiel, [20]; Kumar *et al.*, [21]. The outcome garnered from the study describes how the iron ore pellets prepared at different reduction temperatures (700°C and 950°C) often contain some carbon deposition [18, 22]. Reduction kinetics of iron ore using coal and charcoal placed simultaneously in an externally heated cylindrical container positioned in a muffle furnace have been studied. Reduction temperatures ranging from 850 to 1000°C were used to study the reduction kinetics potential of coal and charcoal as reductants [19, 23]. Despite the laudable research efforts that have been made as indicated in the foregoing review, the literature neither explains how to ascertain the reaction controlling the resistance of the reduction processes nor gives a detailed description of stage-by-stage reaction kinetics of the direct reduction process of the iron ore samples. Therefore, this paper entails the kinetic study of the reduction of selected goethite iron ore lump by CO/CO<sub>2</sub> gases from wood charcoal using a locally fabricated reactor (activated carbon furnace) under isothermal conditions at a specified

reduction time. The reduction kinetics of the goethite hematite ore is also extensively investigated by visual inspection using appropriate reduction kinetic equations for solid-solid reactions. The Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses are used to determine the rate-controlling resistance of the reaction with the experimental procedure as described below.

## 2. MATERIALS AND METHODS

### 2.1 Experimental Procedure and Sample Preparation

In this present work, three sets of commercially obtained goethite iron ore lumps of several weights and sizes were used. Each set of samples was categorized into Set-I (5-9.99 mm), Set-II (10-14.99 mm), and Set-III (15-20 mm) as shown in Fig.1. The initial sizes and weights of the iron ore samples were measured individually using the digital Vernier caliper and the weighing balance.

#### 2.1.1 Chemical Composition of Goethite Ore Lump

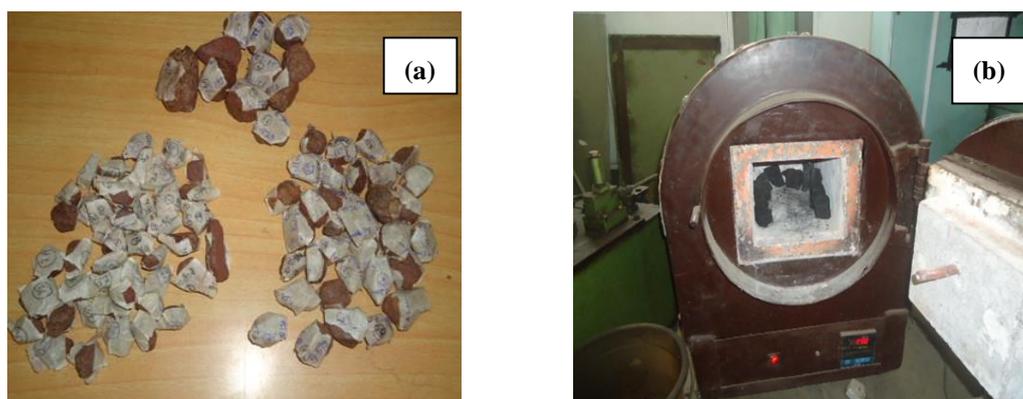
Similar to the methods of compositional examination were reported in Al-Eshaikh, *et al.* [24] and Mousa, *et al.* [25]; Li, *et al.* [26]; Wu, *et al.* [27]; Muhammad, *et al.* [28]; Sekunowo, *et al.* [29]; Babalola, *et al.* [30]; Omole, *et al.* [31]. The composition of the commercial acquired goethite hematite ore lumps was analyzed using an X-ray diffraction diffractometer with the goethite hematite ore chemical formula- Goethite Ore ( $\text{Fe}_2\text{H}_4\text{O}_5$ ,  $\text{Fe}_{1.698}\text{O}_3\text{Sn}_{0.228}$ ) and  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} \cdot x\text{H}_2\text{O}$ ,  $\text{Fe}_{1.698}\text{Sn}_{0.228}\text{O}_3$  [32]. The particle chemical compositions by weight are shown in Table 1. The sizes of particles linked with gas-solid contact surface area. The larger area is, the tendency to experience a higher reduction degree could be obtained from similar work done [33].

**Table 1:** Chemical Analysis of Goethite Ore Lump Sample [32].

Element	Hematite ( $\text{Fe}_2\text{O}_3$ )	Wustite ( $\text{FeO}$ )	$\text{SiO}_2$	$\text{TiO}_2$	$\text{MnO}$	Others
%wt	82.65	0.94	1.31	0.05	0.69	14.36

#### 2.1.2 The Reduction Reactor: Activated Carbon Furnace

The Activated Carbon Furnace as used in this present work consists of hollow chambers with a rectangular cross-section and convenient spacing which can readily contain the crucibles made of molded clay with the samples to be heat treated in the reactor. A reasonable amount of charcoal was placed in the hollow chamber where heat was generated before the reduction time of 10, 20, 30 and 40 minutes can be measured under an airtight condition at a specified temperature based on Gibbs free energy temperature profile for hematite reduction to wustite, Ogbezode, *et al.* [32]; Mousa, *et al.* [34] using digital stop-watch. The properties of charcoal mixed in with the ore were not described in this present work but the effect of carbon monoxide penetration on the different goethite iron ore sample sizes was investigated. The reduced ore samples were also characterized using SEM/EDX analysis to ascertain the degree of metallization and microstructure elemental composition of iron ore constituents [35].



**Figure 1.** (a) Goethite Iron Ore Samples Prepared at Different Size Range (b) The Reactor: Activated Carbon Furnace [32].

The reduced samples were investigated in their lump form after successful measurement of the weight and size (radius) of the sample using the digital Vernier caliper and weighing balance, respectively. The iron ore in the right proportion by weight (grams) placed into the reactor while the reactor is fired up to the right temperatures at 570, 700, 800, 900, and 1000°C for a partial reduction time step of 10, 20, 30, and 40 minutes. The heated ore lump samples were cooled under the atmospheric condition and the size (mm) and weight (grams) were retaken using the same aforementioned measuring instrument. The partially reduced heated samples with the longest reduction time of 40 minutes for 570, 800 and 1000°C, were taken to the laboratory where the X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersion X-ray (EDX) techniques were used to reveal the microstructural phases formed at these temperatures and to further study the variation in the relative composition of the phases in the three different shapes of iron ore–charcoal composite lumps before and after reduction experiment as shown from Figs. 16 to 20. The kinetics of reduction analysis of the specimen is examined for a different residence time step of the particle, the rate of reaction, conversion factor, reaction control time, degree of metallization, and swelling extent of the reduced ore is progressive determined using useful kinetic equations as described in the aforementioned. Also, the ratios of partial reduction time to complete reduction time for the fractional radius of reduction were ascertained.

## 2.2 Degree of Reduction and Swelling Extent

The reaction kinetics to be used in this present work is the shrinking core model equations as illustrated in Eqs (1) to (11). The derived kinetic model equations from existing literature Alamsari, *et al.* [3]; Levenspiel, [20]; Srinivasan, [36] have shown the relationship between the residence time, reaction control time, and conversion factor expression for various shapes of the direct reduced iron (DRI) particles for the shrinking-core model. Also, all the reduced hematite ore samples maintained their original lump shape and the degrees of reduction and swelling were calculated by using the following formulas as deduced in Prakash, [37]; Yunyun, [38].

$$\text{Degree of Reduction } (\%) = \left( \frac{W_0 - W_t}{W_\infty} \right) \times 100\% \quad (1)$$

where  $W_0$  is the initial weight of the sample,  $W_t$  is the weight of the sample at time  $t$ , and  $\infty$ ,  $W_\infty$  is the theoretical weight of oxygen present in the samples for complete reduction.

$$\text{Swelling index } (\%) = \left( \frac{V_f - V_i}{V_i} \right) \times 100\% \quad (2)$$

Where,  $V_i$  is the initial volume of the pellet/lump ore and  $V_f$  is the volume of the ore lump after reduction for a given time.

### 2.3 Kinetics and Mechanism of Reduction

According to Levenspiel's relations for the shrinking core model as developed to visualize the five steps occurring in succession for fluid-solid and solid-solid reactions is illustrated in Fig. 2. For consistency, the description of the five (5) steps involved in the reaction kinetics was adopted as follows

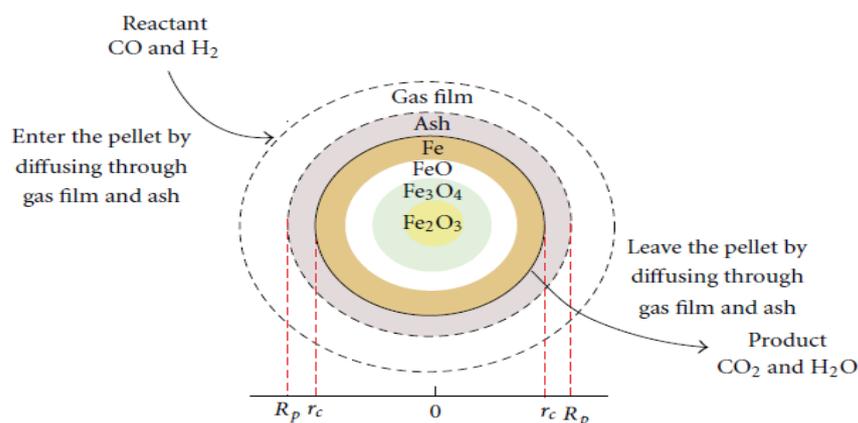
*Step 1:* Surrounding film diffusion of reactant A through solid particle surface

*Step 2:* Penetration of A through the blanket of ash to the surface of the unreacted core.

*Step 3:* Reaction of gaseous reactant A with solid at the reaction surface.

*Step 4:* Solid exterior surface by diffusion of gaseous products through ash.

*Step 5:* Diffusion of gaseous products through the gas film back into the main body of the fluid.

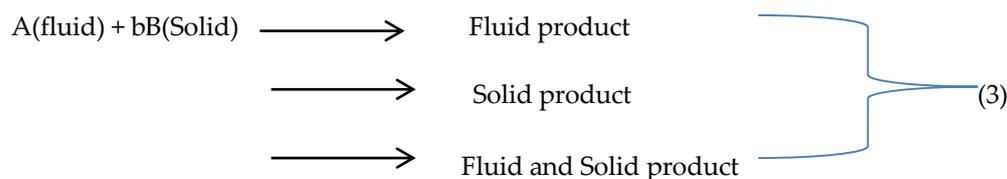


**Figure 2.** The Shrinking Core Model Showing Contact Surface Area of Reduction Reaction [3, 20].

In some situations, some of these steps do not exist. For example, if no gaseous products are formed, steps 4 and 5 do not contribute directly to the resistance of the reaction. Also, the resistances of the different steps usually vary greatly from one to another. In such cases, there is a need to consider that step with the highest resistance to be rate-controlling resistance. In this treatment, conversion equations were formulated for spherical particles in which steps 1, 2, and 3, in turn, are rate-controlling stages. The analysis is then extended to non-spherical particles and to situations where the combined effect of these three resistances was required to be considered. Developing the conversion equation for spherical particles in which steps 1, 2, and 3 are the rate-controlling steps. Further analysis was then extended to non-spherical particles in a situation where the combined effect of the three resistances is required to be considered.

#### 2.3.1 Diffusion through Gas Film Controls

Attention is focused on the unchanging exterior surface of a particle from the stoichiometry Eq. 1, 2, and 3 as shown in Eq. 3 and 4.



The Stoichiometry of equation:  $-dN_B = -bdN_A$

$$-\frac{1}{s_{ex}} \frac{dN_A}{dt} = -\frac{1}{4\pi R^2} \frac{dN_B}{dt} = -\frac{b}{4\pi R^2} \frac{dN_B}{dt} = bK_g(C_{Ag} - C_{As}) = bK_g C_{Ag} = \text{Constant} \quad (4)$$

Taking the limit of integral from  $R$  to  $r_c$  and  $0$  to time  $\tau$ , where  $\tau$  is the time for complete conversion of the particle, then  $r_c = 0$ . Therefore, the radius of unreacted core in terms of fractional time or conversion factor for the complete conversion is given as:

$$\frac{t}{\tau} = \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right] = X_B \quad (5)$$

### 2.3.2 Diffusion through Ash Layer Controls

Here, the resistance to diffusion through the ash layer is assumed to control the rate of reaction. The relationship between the time and radius of the ore with constant heat flux is described in Eq. 6 and 7.

$$-\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{AS} = 4\pi r_c^2 Q_{AC} = \text{Constant} \quad (6)$$

Integrating across the layer from  $R$  to  $r_c$  and taking the limits  $C_{AC} = 0$  and  $C_{AC} = C_{Ag}$  where other variables remain constant. Thus, taking further integration between  $R = r_c$  to  $r_c$  and from  $0$  to any particular time 't' at the complete conversion of particle  $r_c = 0$ , the required fractional time/ conversion factor is expressed as:

$$\frac{t}{\tau} = \left[ 1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3 \right] \quad (7)$$

Recall equation 5 and substitute it into Eq. 7, we have.

$$\frac{t}{\tau} = \left[ 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \right] \quad (8)$$

### 2.3.3 Chemical Reaction Controls

Consider the chemical reaction itself as the rate resistance control based on the unreacted core unit surface for the stoichiometry. This yields Eqn. 9.

$$-\frac{1}{s_{ex}} \frac{dN_A}{dt} = -\frac{b}{4\pi r_c^2} \frac{dN_A}{dt} = bK'' C_{Ag} = \text{Constant} \quad (9)$$

Integrate and make  $t$  the subject of the relation, and let  $\tau$  be the required time for complete conversion  $r_c = 0$ .

Therefore, the decrease in radius or Increase in fractional conversion in terms of  $\tau$  is given as:

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} \quad (10)$$

Recall equation 5 and substitute into Eq. 10 to obtain the relationship for time conversion as follows

$$\frac{t}{\tau} = [1 - (1 - X_B)^{1/3}] \quad (11)$$

Eqns. 5,8 and 11 are the analogy to the general symbols that refer to the diffusion through gas film diffusion through ash layer  $c$ , chemical reaction controls are the relation used to determine the rate-controlling process to ascertain the possible reduction resistance between the ore particles and the CO/CO<sub>2</sub> gases the rate-controlling resistance. Where  $r_c$  = radius of the unreacted core,  $t$  = initial residence time,  $\tau$  = final residence time  $R$  = radius of the particle,  $\frac{t}{\tau}$  = time fraction,  $X_B$  = conversion rate

Thus, the derived kinetic reduction equations as expressed above are used to analyze the relationship between the time and radius of reduced iron ore to ascertain the rate-controlling steps at each stage of the reduction processes as culled from Levenspiel, [20] and Srinivasan, [36].

#### 2.4 Method of Data Analysis of Reduced Hematite product.

The method of data collection and analysis as used in this research work was derived by taking visual inspection of the reduced ore lump which entails the measuring of the initial, final weight, and particle sizes. Other reduction parameters such as volume change which was measured manually, swelling index, and percentage of the degree of reduction in the process are achieved using Microsoft Excel version 2010 manually inputted for easy plotting of graphs and variation of other relevant parameters as related to the objectives of this work.

The microstructures and chemical compositions of samples were investigated by using Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray (EDX) spectroscopy. Combustion tests were applied for the analysis of carbon contents in the number of ore lumps reduced by H<sub>2</sub>-CO mixtures from the charcoal at specified preheated temperature. X-ray powder diffraction was used for the identification of different phases in samples for their empirical content by chemical composition.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of Reduction Time on Conversion Factor

The reaction rate conversion factor which is defined as the ratio between the reaction residence time and reaction control time is used to determine the rate-controlling stage (i.e. gas film, ash layer, and chemical control stage) of the reduction process of iron oxide to metalized iron as shown in Figs. 3 to 6. This depicts that the rate of conversion increases with reaction residence time for all sizes of iron oxide undergoing a reduction reaction in the furnace. This is due to an increase in gaseous diffusion into the hematite ore sample as it stays longer in the reactor over a while irrespective of the size of the iron oxide and furnace temperature.

Consequently, the effect of the conversion factor on the reaction residence time has shown that the rate of conversion of hematite to magnetite to wustite to iron is fastest at the gas film stage and the slowest at the ash layer control. This implies that the rate of formation of reducing gas films around the iron ore inside the reactor is fastest compared to the rate of carbon deposition on the outer surface of the ore irrespective of the sizes of lump ore and the preset temperature of the furnace. Thus, the rate of formation and infiltration of reducing gas (CO/CO<sub>2</sub> and H<sub>2</sub>) around the lump surface may occur much faster than the formation of ash layer and chemical reaction stage as shown in Figs. 3 to 6.

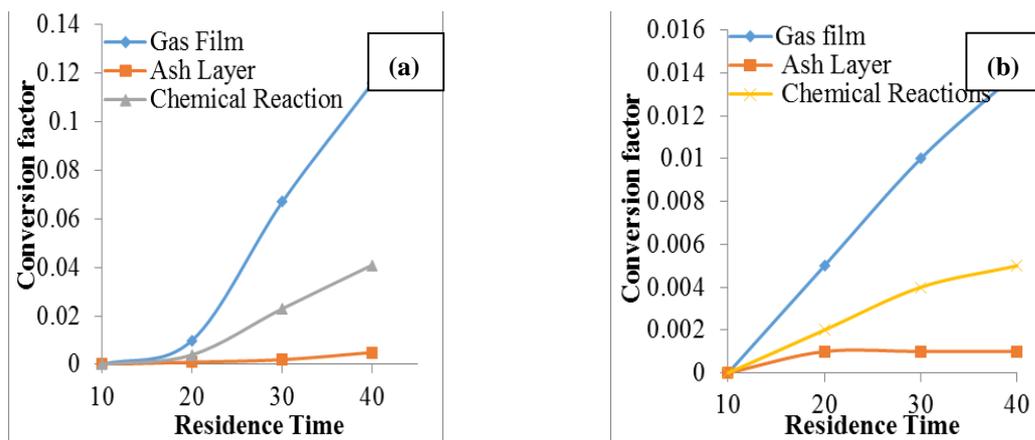


Figure 3: Determination of rate control stages based on the conversion factor for iron-ore samples of different size ranges at 570°C (a) 10-14.99 mm (b) 15-20 mm

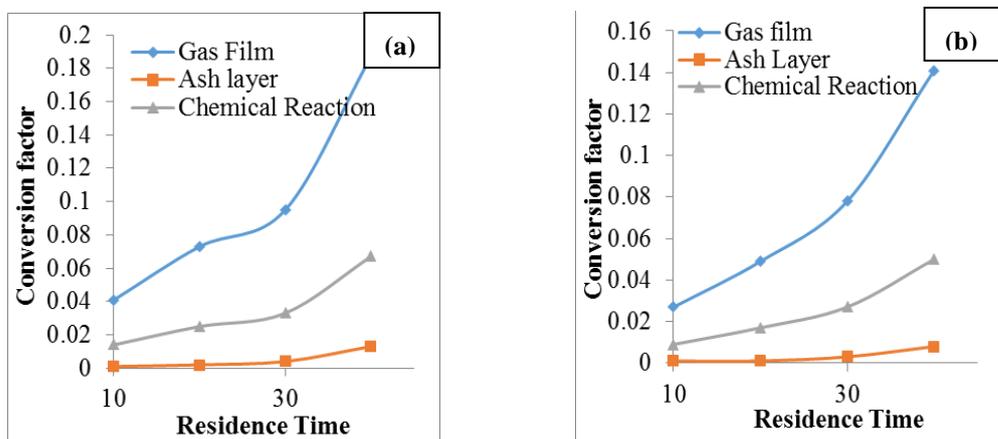


Figure 4. Determination of rate control stages based on the conversion factor for iron-ore samples of different size ranges at 700°C (a) 10-14.99 mm (b) 15-20 mm

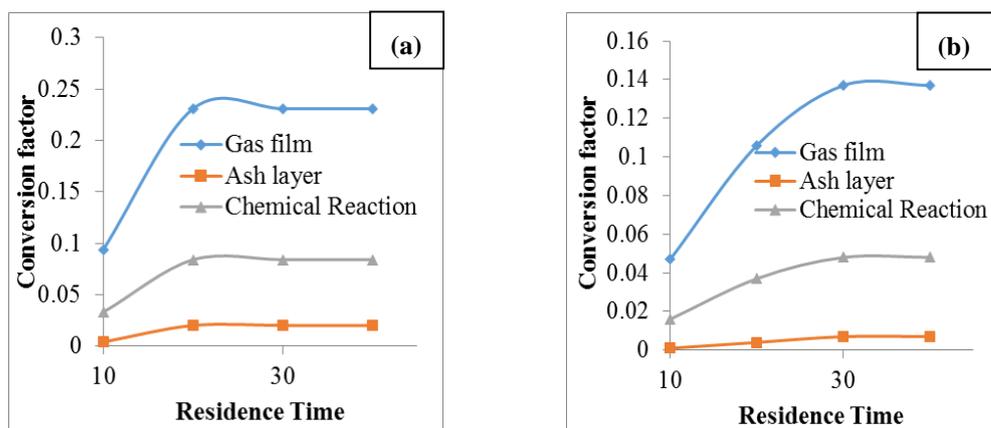
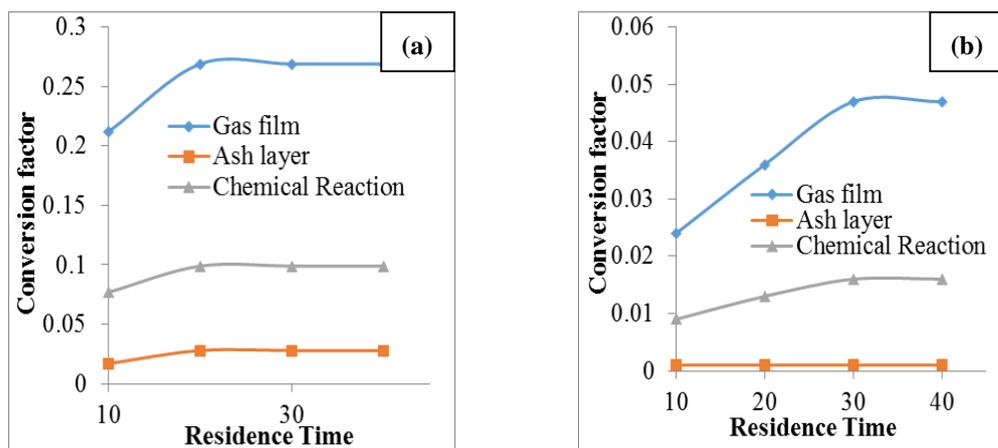


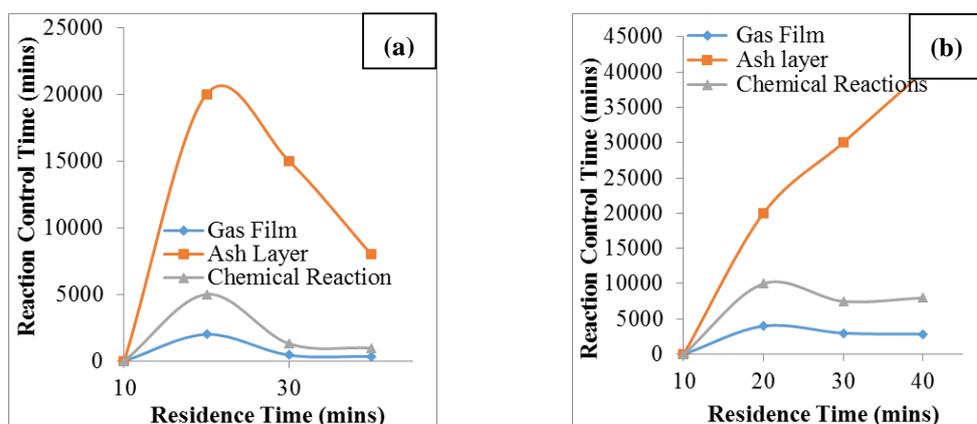
Figure 5. Determination of rate control stages based on the conversion factor for iron-ore samples of different size ranges at 800°C (a) 10-14.99 mm (b) 15-20 mm



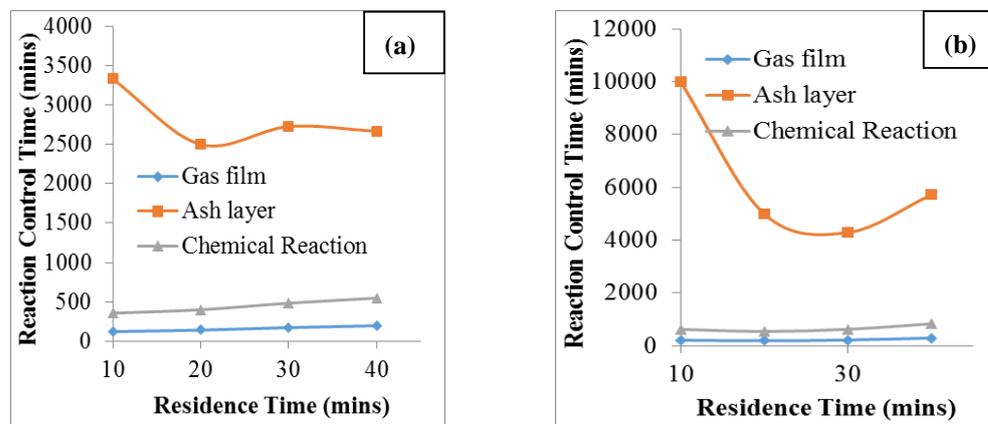
**Figure 6.** Determination of rate control stages based on the conversion factor for iron-ore samples of different size ranges at 900°C (a) 10-14.99 mm (b) 15-20 mm

### 3.2 Effect of Reduction Time on Reaction Control Time

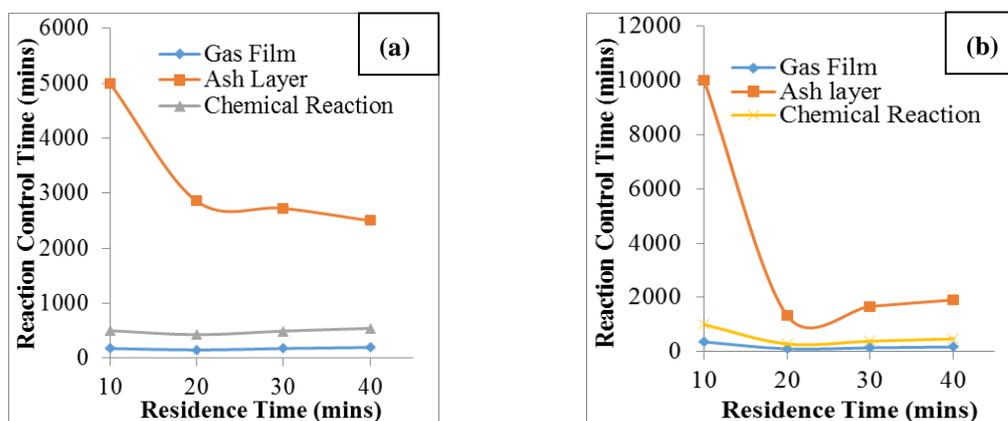
The reduction time is the specified time required for the ore lump samples to be exposed to the reduction of gases in the furnace at specified firing temperatures. It is also known as the reaction residence time. Equations 5, 7, and 10 are used to calculate the reaction control time to determine the time required for the complete conversion of hematite to metallic iron. This is also used to know the rate-determining stage of reaction (i.e. Gas film, Ash layer, and Chemical Reaction Controls) as shown in Figs. 7 to 9 considering the iron ore sample of size ranges 10-14.99 mm and 15-20 mm as depicted in Figs. 7 to 9 at firing temperatures of 570, 800, and 1000°C. The graphical illustrations (Figs. 7 to 9) have shown that total reaction control time increases with reduction time at the firing temperatures except at 800 and 1000°. A steep slope curve was observed at 570°C. This indicates the easy bypass of the wustite stage during the reduction of ore samples at a firing temperature below 570°C with little or less carbide formation of carbon deposition at the said temperature. This may likely be more rampant when iron ore lump of intermediate diameter sizes (10-15 mm) was used.



**Figure 7.** Determination rate control stages based on reaction control time for iron-ore samples of different size ranges at 570°C (a) 10-14.99 mm (b) 15-20 mm



**Figure 8.** Determination of rate control stages based on reaction control time for iron-ore samples of different size ranges at 800°C (a) 10-14.99 mm (b) 15-20 mm



**Figure 9.** Determination of rate control stages based on reaction control time for iron-ore samples of different size ranges at 1000°C (a) 10-14.99 mm (b) 15-20 mm.

### 3.3 Effect of Firing Temperature on Degree of Reduction and Swelling Extent

The reduction of iron oxide or any ferruginous raw material with a reducing material involves stepwise reactions, as oxygen atoms mostly undergo severe-adjustment, which increases the volume by more than 25 percent. Furthermore, the study of the kinetics of reduction based on phase-boundary reaction control as expressed in the equations of the shrinking core model described earlier in terms of the sample fraction already reacted  $X_B$  has revealed that the rate-controlling stage of the process in respect to the required firing temperature where a greater degree of reduction can be attained with the minimal swelling extent of the ore lump sample. The change in volume fraction and reacted ore fraction can also be envisaged under isothermal/non-isothermal conditions regardless of the reduction time. Therefore, the result in Figs. 9 to 15 depicts the relationship between conversion time factor, degree of reduction, and swelling extent in various phase boundary conditions for commercially acquired iron ore lump sample on reduction with charcoal for 40 minutes under an isothermal condition as used in present work.

#### 3.3.1 The Gas Film Control

When the resistance of the gas film controls the reactions, the concentration profile for the gas-phase reactant is as shown in Fig. 1. The mass transfer of the boundary-layer gas film

becomes negligible in the reaction of solids with a gas stream flowing above critical gas velocities. Different kinetic models can be used for the various reduction mechanisms whose graphical illustration is based on the effect of rate conversion factor on the degree of reduction of the iron ore samples at specified firing temperatures as shown in Fig. 10.

The result is obtained in Figs. 10 and 11 have revealed that, for smallest sized iron ore lump samples (5-9.99 mm), the rate conversion factor under gas film condition increases with the degree of reduction and the swelling extent at any firing temperature. Thus, other firing temperatures have proved to maintain their stabilized conditions regardless of increment in their degree of reduction and swelling extent while the case seems different at 700°C and 570°C, respectively. For more samples of medium-sized (10-14.99 mm), as shown in Fig. 10, the required firing temperature for a sustainable increase in the degree of reduction is observed at 700° while subjecting the ore lump sample to temperatures above 800°C could generate an abnormal swelling index of 30% or more. Also, the highest degree of reduction of more than 40 percent is observed at 570°C as shown in Fig. 11, and with an increase in swelling extent at 1000°C. This indicates at the wustite stage, the ash layer formation is conveniently bypassed for larger ore samples (15-20 mm) than the smaller sized samples due to the large contact surface area of the ore sample. This in-turn aids the diffusivity of the reductant gas (CO-H<sub>2</sub>) mixture into the system for more effective penetration of such gasses into the ore lump samples at low firing temperature.

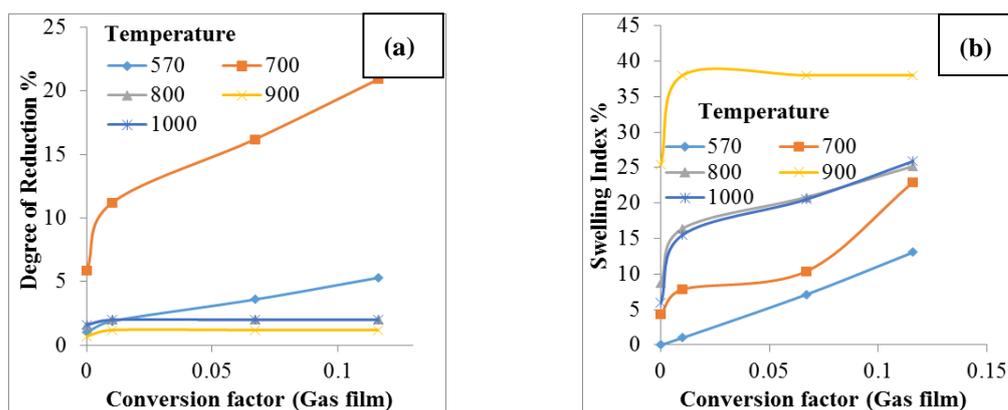


Figure 10. Effect of particle firing temperature and gas film rate control stage of reduced iron ore lump size range 10-14.99 mm (a) degree of reduction (b) the swelling extent

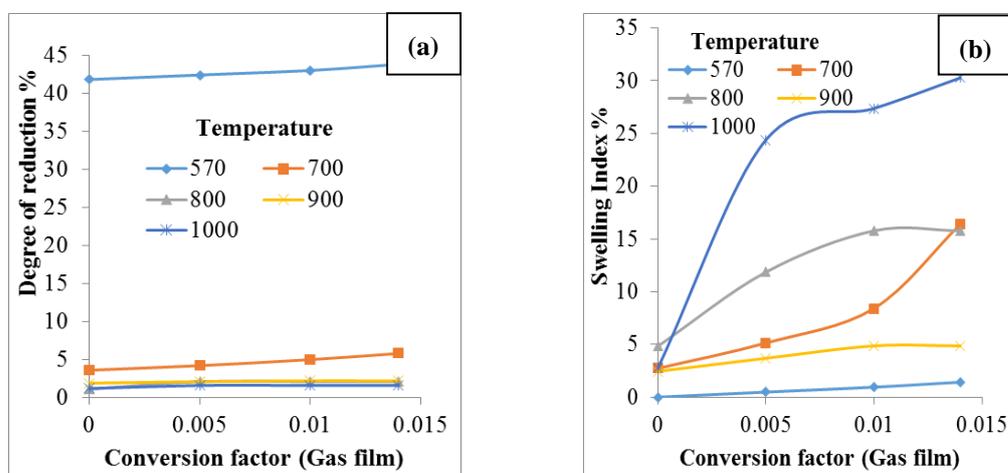
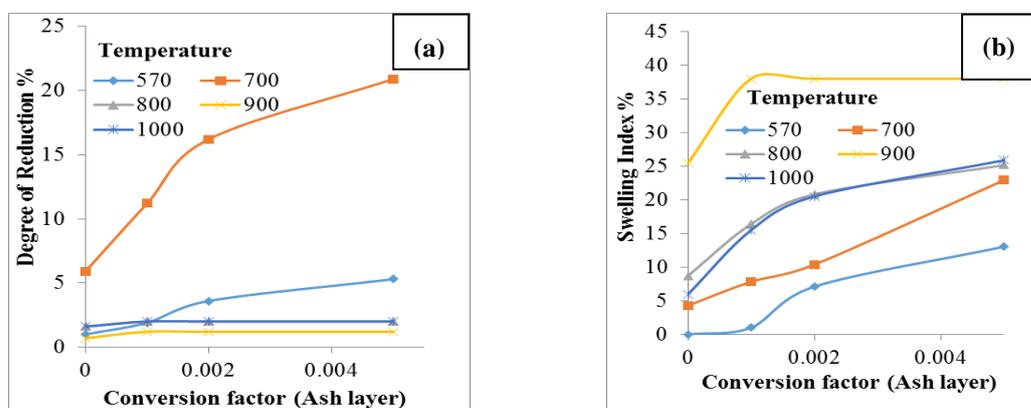


Figure 11: Effect of particle firing temperature and gas film rate control stage of reduced iron ore lump size range 15-20 mm (a) degree of reduction (b) the swelling extent

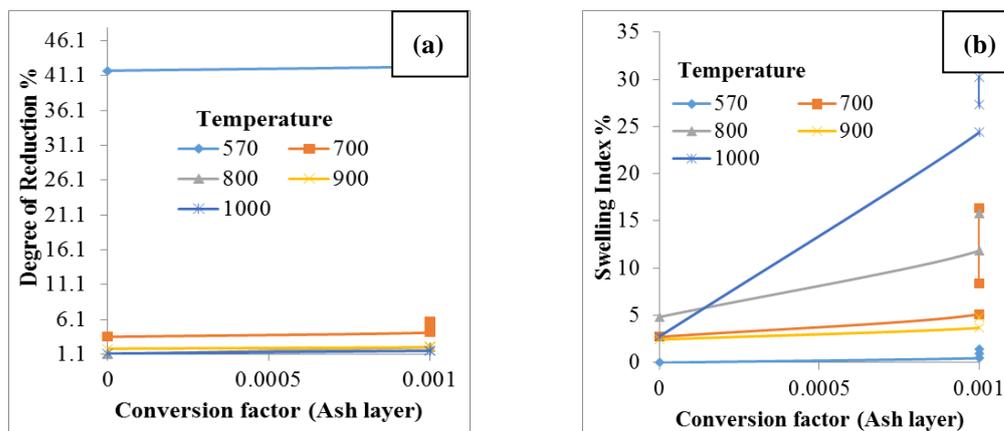
### 3.3.2 The Ash Layer Control

The effect of ash layer control on the rate of reduction of iron oxide is based on the phase boundary change of the hematite sample using CO/CO<sub>2</sub> and H<sub>2</sub> gases as the reductants. These have shown an appreciable increase in the degree of reduction and swelling extent of their samples [32, 37]. It is also worthy of note that the results illustrated in Figs. 13 and 14 indicate an apparent increase in the degree of reduction with a rate conversion factor. This implies that the rates of reaction increase linearly with the hydrogen contents of the gaseous mixtures. Thus, the presence of large CO/CO<sub>2</sub> contents in the charcoal, since the reaction was conducted under an airtight condition, may cause an apparent decrease in rates of reaction as all reduction experiments with CO and H<sub>2</sub>-CO mixtures are always accompanied by carbon deposition which usually results into ash layer formation on the reduced iron ore samples which results into low reducing gas penetration, thereby generating a little degree of reduction, high swelling extent, and incomplete reduction.

Figs. 13 also affirmed that the large size (15-20 mm) samples do possess the highest degree of reduction at the lowest firing temperature of 570° with its highest swelling index at 1000°C. This may be due to the large reducing gas-contact surface area of the ore sample. This also has established a relationship between the degree of reduction and ore sample size as the most sustainable firing temperature to derive progressive increase in the degree of reduction with minimal swelling extent (less than 20%) may likely be achieved at this stage. Figs. 12 and 13 also show the progressive tendency for an increase in the degree of reduction at 700°C while reduction remain stabilized at other firing temperatures and abnormal swelling extent of 50% and above at 1000°C for the smaller size (5-9.99 mm) ore samples and greater than 20% at 700°C with a swelling index of 35% or more for the medium size (10-14.99 mm) ore samples as obtained experimentally. This indicates the tendency for an increase in large carbon depositions on reduced samples for the small size range (5-9.99 mm) iron ore lumps.



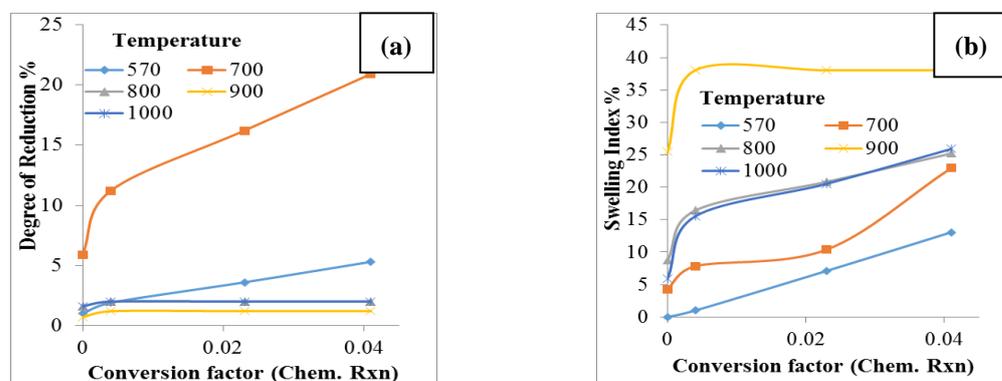
**Figure 12.** Effect of particle firing temperature and ash layer rate control stage of reduced iron ore lump size range 10-14.99 mm (a) degree of reduction (b) the swelling extent



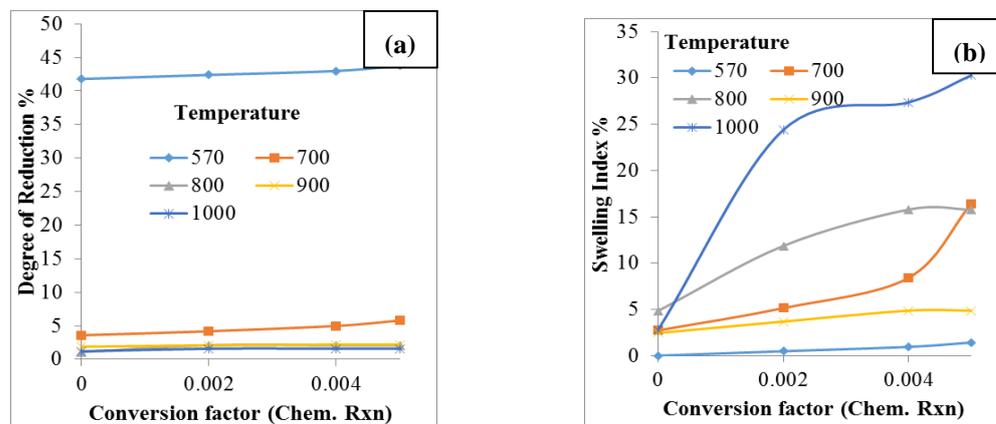
**Figure 13.** Effect of particle firing temperature and ash layer rate control stage of reduced iron ore lump size range 15-20 mm (a) degree of reduction (b) the swelling extent.

### 3.3.3 The Chemical Reaction Control

In the case where direct chemical reaction controls the rate of reduction of the iron oxide sample, it was noticed that the inlet reducing gas (CO/H<sub>2</sub>) do have a little or no restriction on the ash layer region around the iron ore which implies that the use of a catalyst such as quicklime may not be necessary as the in-gas penetration suffers minimum or less restriction due to the absence of carbide formation in the process (i.e. no carbon deposition). Figs. 13 and 14 have shown a progressive increase in the degree of reduction as chemical reaction control the rate of reaction of the reduction process as the sustainable temperature which guarantees progressive reduction was noticed at 570 and 700 °C. This attests to the fact previously mentioned that the wustite stage where the ash layer possesses its highest concentration is easily bypassed at low firing temperature with less carbide formation on the reduced iron ore sample. The size range of the iron oxide also determines its tendency for a faster degree of reduction as iron ore sizes of more than 15 mm can easily be metalized to iron when heat-treated at 700 °C or less. Thus, introducing a firing temperature above 700 °C can generate an abnormal swelling index above 50% where chemical reaction controls the rate of reaction regardless of the size of iron ore samples (5-9.99 mm). This is due to the presence of carbon deposition and ash layer formation which may slow down the reaction rate and degree of reduction of the process. Although, the swelling extent of the sample decreases with the ore sample size and increases with the firing temperature.



**Figure 14.** Effect of particle firing temperature and chemical reaction control stage of reduced iron ore lump size range 10-14.99 mm (a) degree of reduction (b) the swelling extent

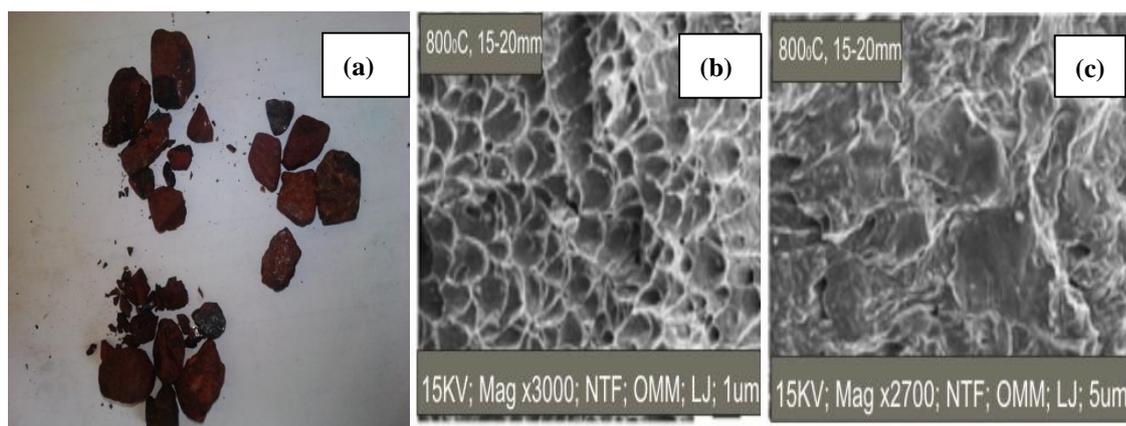


**Figure 15.** Effect of particle firing temperature and chemical reaction control stage of reduced iron ore lump size range 15-20 mm (a) degree of reduction (b) the swelling extent

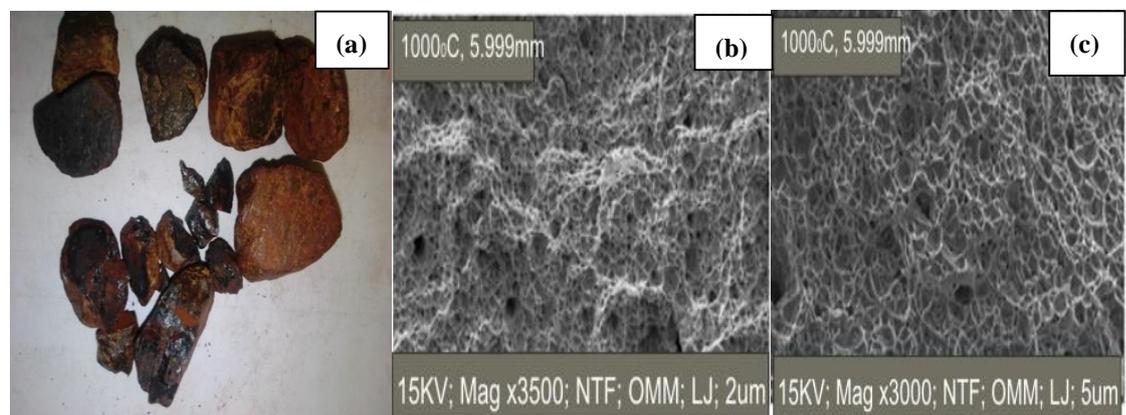
### 3.4 Correlation between Degree of Reduction and Swelling Index

The relationship between the Swelling Index (%) and Degree of Reduction (%) to the reduction of time is shown in Figs. 16 to 20. From the figures, it can be seen that abnormal swelling extent (25-30%) was observed at around 15-45% reduction at firing temperature 800, 900, and 1000°C which led to the disintegration of the rescued ore sample after a short reduction time of 40 minutes. The iron particles are shown in Figs. 16 and 17 for the  $\text{FeO} \rightarrow \text{Fe}$  reduction step at 800 and 900°C respectively. However, the swelling was highest in the reduced iron ore lump as observed at 900 and 1000°C, respectively but this is quite contrary to similar reports obtained from existing literature. Thus, the reduction process is expected to be done at high temperatures with high carbon deposition on the ore sample which may likely lead to crack formation in the samples as shown in Figs. 16(a) and 17(a). The SEM/EDX analysis of this present work was done to practically identify the microstructural segregation in the components of the hematite ore lump sample as well as the presence of silicon in the different shapes and sizes of the reduced iron ore lump. The SEM/EDX analysis of the reduced iron ore presents the spectrum form of the lump-shaped ore-silicon composites as reduced at 570, 800, and 1000°C as shown in Figs. 18 to 20.

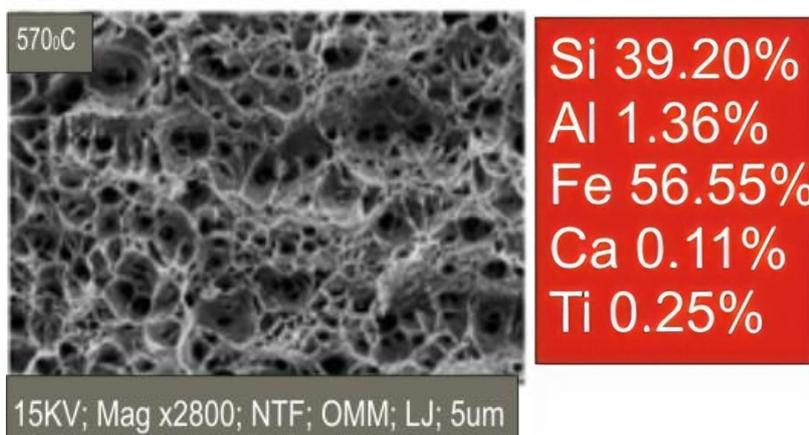
It is worthy of note that the microstructural spectrum of virtually all the tested samples shows a high percentage of silicon (39.20%, 29.59%, and 33.90%) respectively. This connotes the presence of a slag region on the reduced ore surface where the reduced iron oxide is mixed with the silicate. It is also observed that the silicon present in the spectrum analyzed in the fired ore-charcoal mixture at 570 and 800°C is as high as 39.2% and 29.56%, respectively. This also implies some significantly unreduced oxide especially at 800°C due to the presence of a slag zone regardless of the size range of the reduced ore sample as some micro-spots in the ore-charcoal lump-shaped composite can also be identified. Such a spot only contains metallic irons due to its devoid of slags after reduction time steps of 10, 20, 30, and 40 minutes which is shown in Fig. 20.



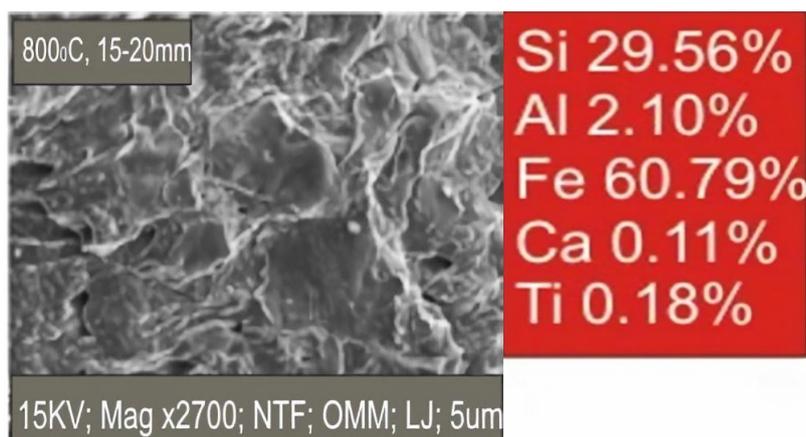
**Figure16.** Reduction and SEM micrographs of Set III hematite lump sample 15-20 mm at Reduction time 40mins for 800°C: (a) Cracks and Disintegration (b) External Surface Structure (c) Internal Surface Structure



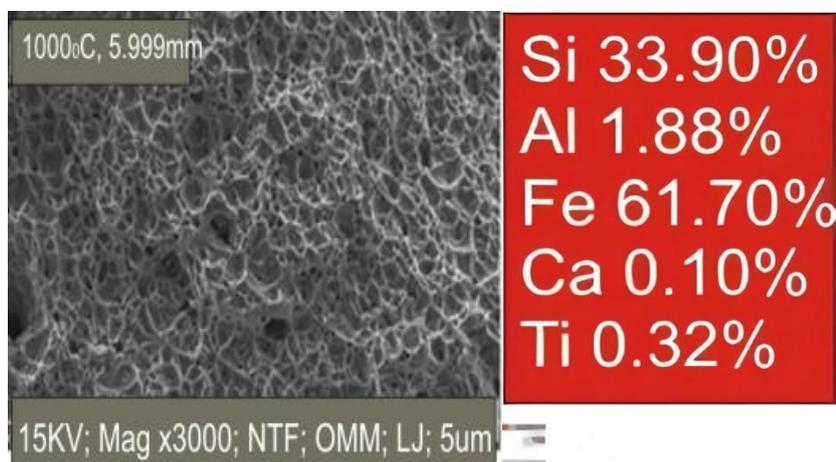
**Figure 17.** Reduction and SEM micrographs of Set I for hematite lump sample 5-9.99 mm at Reduction time 40 minutes for 1000°C: (a) Cracks and disintegration (b) External Surface Structure (c) Internal Surface Structure



**Figure 18.** SEM/EDX Micrograph and Spectrum view at 570°C with size range 5-9.99 mm



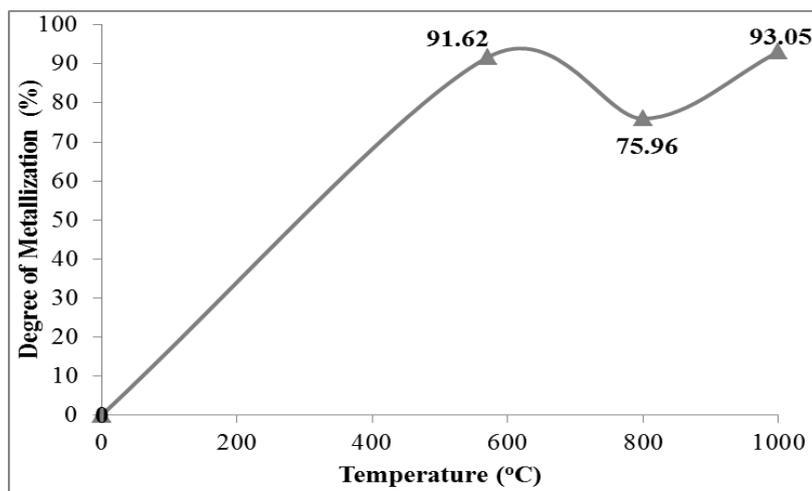
**Figure 19.** SEM/EDX Micrograph and Spectrum view at 800°C with size range 15-20 mm



**Figure 20.** SEM/EDX Micrograph and Spectrum view at 1000°C with size range 5-9.99 mm

### 3.5 Effect of Rate Controlling Resistance on Reduced Samples

The respective percentages of iron in the metallic composition as derived from Scanning Electron Microscopy (SEM) and Energy Dispersion X-ray (EDX) Spectrometry are illustrated in Figs. 17 to 20. It can be deduced from the figures that the reaction control stages or step-by-step mechanism of the reduction process can fully be ascertained based on these two factors which include: increase in weight due to carbon deposition and incomplete/partial reduction of the samples. It can be deduced from Fig. 21 that the higher infiltration of CO/CO<sub>2</sub> gases into the hematite lump sample produces large amounts of oxide which are entrapped in the iron crystal layers are a direct possibility for incomplete reduction of the iron oxide when heat-treated in the reactor. The sharp drop in the degree of metallization of the reduced ore samples is better observed at intermediate temperature (i.e. 700, 800, 900°C) of the reduction process. This indicates the tendency of high carbon deposit at the said wustite stage of the reduction process coupled with the possibility of high oxygen-silicon content as contained in the remains of the heat-treated reduced iron ore samples at the least temperature and residence time at 570°C and 10 minutes, respectively.



**Figure 21.** Degree of metallization as a function of Reduction Gas Firing Temperature at Residence time of 40 minutes.

#### 4.0 Conclusion

In this study, non-contact direct reduction using wood charcoal fines was carried out at heating temperatures above 570°C. Levenspiel's relations for the shrinking core model were used for describing the reduction kinetics and mechanism. The reaction kinetics involves diffusion through gas film controls; diffusion through ash layer controls; and the chemical reaction itself as the rate resistance control based on the unreacted core unit surface. The rate-controlling steps for the reduction kinetics of average particle size 5-20 mm at 570-1000°C were studied after heat treatment of the ore-wood charcoal in an activated carbon reactor at a total reduction time of 40 minutes. The conclusions include:

1. The adapted kinetic model provides good analysis for describing the degree of ore reduction, the swelling extent of the reduced iron ore by rate contact, and resident time of reaction.
2. This work was able to show the ash layer as the controlling resistance for the reduction of goethite iron ore with the possibility of high carbon depositions or carbide formation alongside the reduced iron ore. The foregoing indicates an incomplete reduction of the direct reduced iron ore. The most convenient firing temperature to sustain the controlling resistance of the ash layer formation for this work is 700°C. There is a uniform increase in the degree of reduction in the reduced samples with a steady swelling index most firing likely to be obtained at the temperature of 700°C.
3. The degree of metallization was found to be enhanced as CO/CO<sub>2</sub> composition, reduction firing temperature, and reduction time, increase. However, a reduction firing temperature of more than 1000°C is prone to the formation of undesirable sticky iron (whiskers).
4. The study revealed that an increase in firing temperature, as well as reducing time, increases the degree of reduction and swelling extent of the reduction process.
5. It was established that an increase in the fixed carbon content of reduction gases, increases the degree of reduction and swelling extent as the final degree of metallization of more than 90 percent was achieved in the overall reduction process at 570 and 1000°C compared to the least value of metallization degree value of 75.6 percent as obtained at 800°C, respectively.

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## Conflict of Interest

The authors declared they have no conflict of interest relevant to this article

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