The 1st International Electronic Conference on Metallurgy and Metals

Topic:

- Determination of the Reaction Rate Controlling Resistance of Goethite Iron Ore Reduction Using CO/CO_2 Gases From Wood Charcoal

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HIGHLIGHTS

- INTRODUCTION
- LITERATURE REVIEW
- METHODOLOGY
- RESULT AND DISCUSSION
- CONCLUSION
- RECOMMENDATIONS

1. INTRODUCTION

Iron is believed to be the fourth most abundant element in the earth crust. It comprises more than 90% of all used metals tonnage produced worldwide.

Iron is extracted from its ore as it is almost never found in its free element state. To obtain iron in its elemental form, the impurities must be removed by chemical reduction.

OBJECTIVE

1.1 Direct Reduction of Iron Ore

Direct reduced iron (DRI) is the product of reduction iron ores (lumps, pellets or fines) in solid state by gas or coal reducing agents (Dongchen 2016). The reaction temperature range is 700^0C to 1000^0C.

- **Reduction by Carbon (direct reduction)**

For solid carbon in a DR process, the following three reduction reactions can be written:

$$3Fe_2O_3 + C \rightarrow 2Fe_3O_4 + CO$$
$$Fe_3O_4 + C \rightarrow 3FeO + CO$$
$$FeO + C \rightarrow Fe + CO$$

1.2. Indirect Reduction of Iron Ore

- **Reduction by CO (indirect reduction):**

Above 570^0C, iron oxide is reduced by CO in three stages:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
$$FeO + CO \rightarrow Fe + CO_2$$

Below 570^0C, Fe_2O_3 is directly reduced to Fe bypassing the wustite (FeO) stage. Also existing literatures have shown that under 570^oC, rate of chemical reaction are not fast enough to cause significant errors except devolatilization.

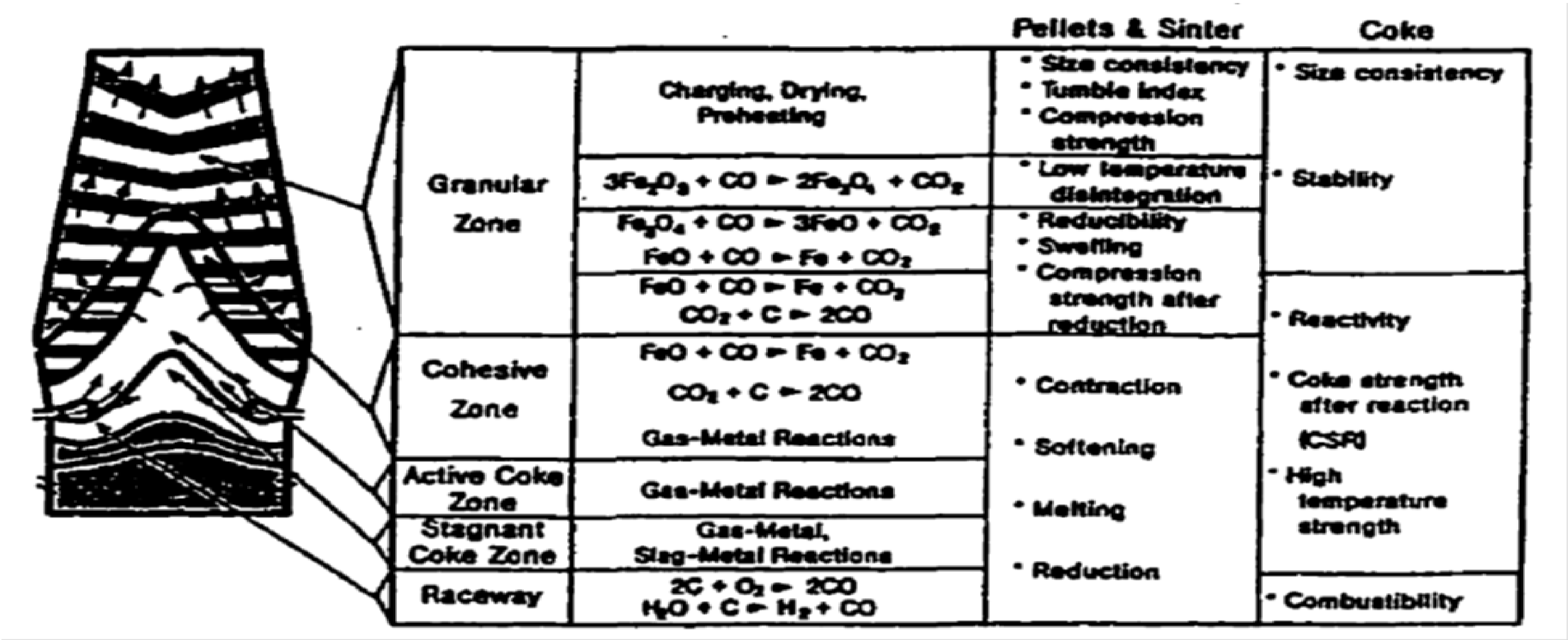
Reduction by Hydrogen (indirect reduction):

Reduction by Hydrogen occurs in three stages as follows:

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$$
$$Fe_3O_4 + H_2 \rightarrow 3\ FeO + H_2O$$
$$FeO + H_2 \rightarrow Fe + H_2O$$

2. LITERATURE REVIEW

2.1 The Blast Furnace Process



		Pellets & Sinter	Coke
Granular Zone	Charging, Drying, Preheating	• Size consistency • Tumble index • Compression strength	• Size consistency • Stability
	$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$	• Low temperature disintegration	
	$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$ $FeO + CO \rightarrow Fe + CO_2$	• Reducibility • Swelling • Compression strength after reduction	
	$FeO + CO \rightarrow Fe + CO_2$ $CO_2 + C \rightarrow 2CO$		• Reactivity • Coke strength after reaction (CSR) • High temperature strength
Cohesive Zone	$FeO + CO \rightarrow Fe + CO_2$ $CO_2 + C \rightarrow 2CO$ Gas-Metal Reactions	• Contraction • Softening • Melting • Reduction	
Active Coke Zone	Gas-Metal Reactions		
Stagnant Coke Zone	Gas-Metal, Slag-Metal Reactions		
Raceway	$2C + O_2 \rightarrow 2CO$ $H_2O + C \rightarrow H_2 + CO$		• Combustibility

Fig: 1: Reaction zones and inner state of a blast furnace (Stanley, 1997)

I. High Cost of maintenance

II. High operation temperature

III. Cause environmental Pollution

IV. Kinetics of Ore reduction in the furnace are not considered.

3.0 METHODOLOGY

Flow of Operation

Acquisition of Iron ore lump and Wood Charcoal

Physical | **Chemical**

Experimentation using Tubular Reactor

Activated Carbon Furnace | **Weight and size**

Product Analysis

Reduction Kinetics | **Microstructural (SEM/EDX)**

The Activated Carbon Reactor (ACR)

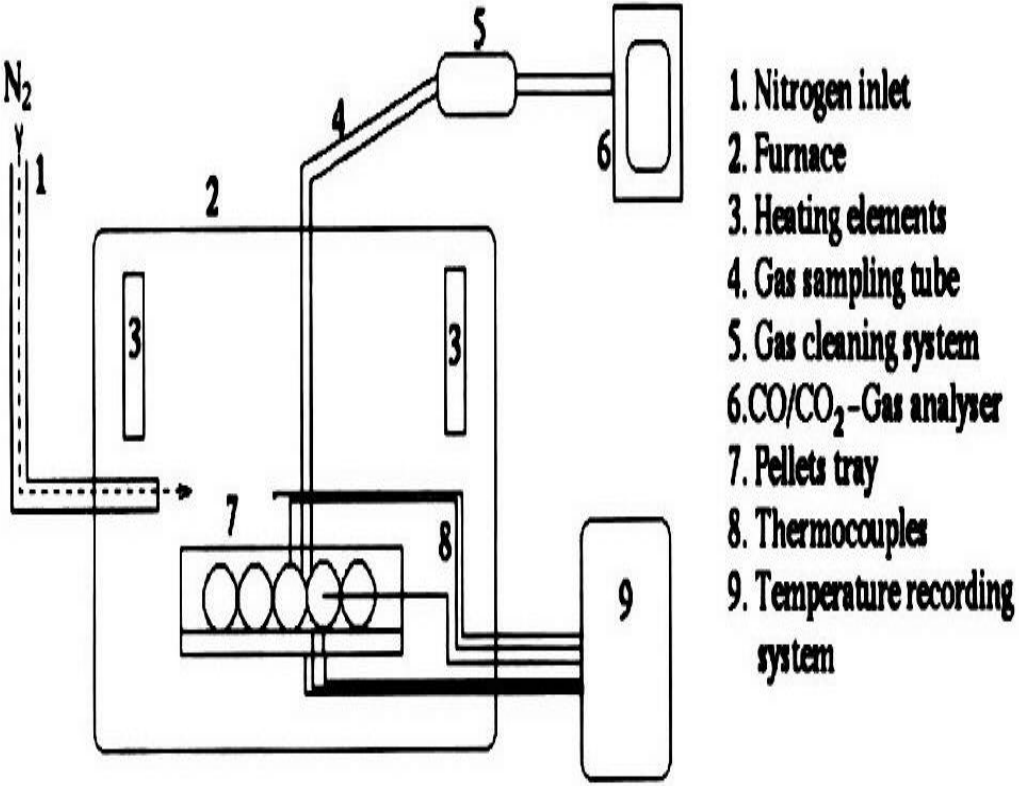


Fig. 3.1: Schematics of Experimental Set-up

3.0 METHODOLOGY (Cont'd)

Fig. 3.2: (a) Samples of size ranges (b) Vernier Calipers

Fig. 3.3:(a) Sample Measurement stage (b) Electric weighing balance

4.1 The Shrinking Core Model

The stages involved in the kinetics are stated as follows:

Step 1: **Diffusion of gaseous reactant through the film surrounding the particle to the surface of the solid.**

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

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

Step 4: **Diffusion of gaseous products through the ash back to the exterior surface of the solid.**

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

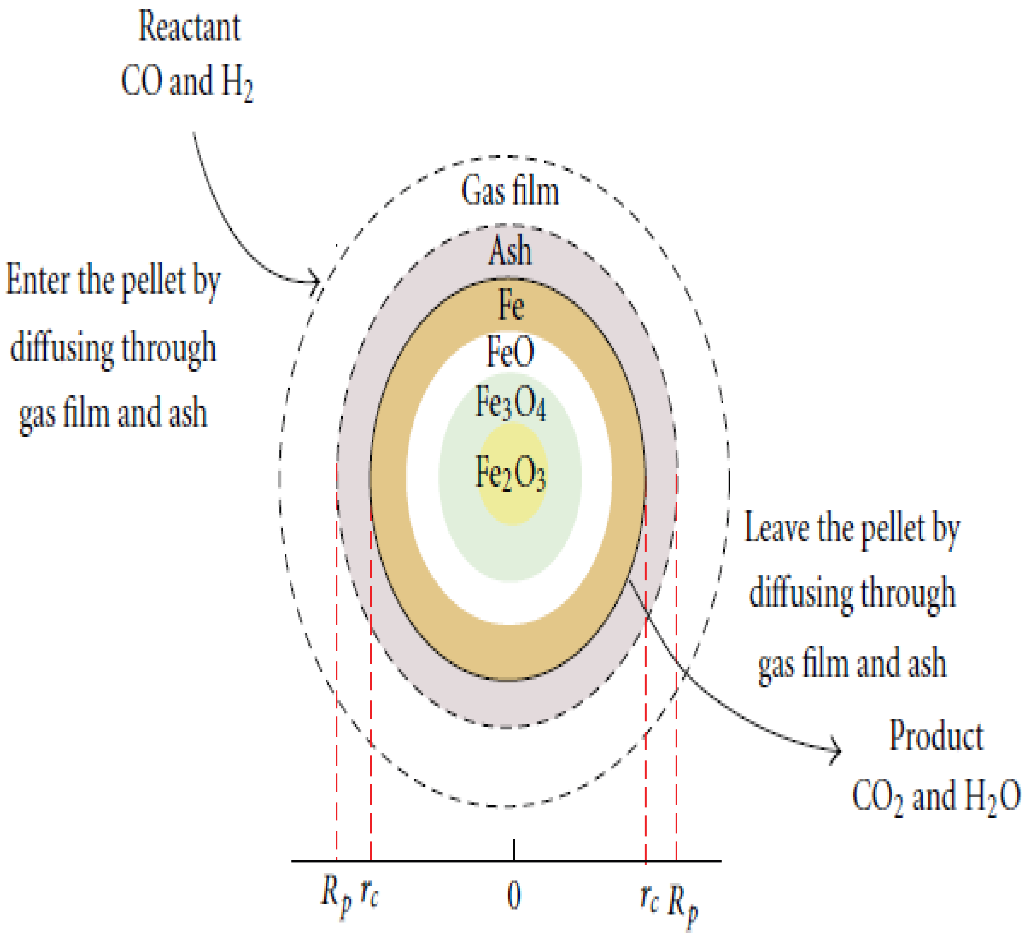


Fig. 4.1: The shrinking core model showing contact surface area of reaction Alamsari, *et al*. (2011)

4.2 Chemical Composition of goethite [α-FeO(OH)] Ore

The composition of the commercial pure goethite hematite ore samples were analyzed using X-ray diffraction (XRD) measurement with chemical empirical formula- $Fe_2H_4O_5$, $Fe_{1.698}O_3Sn_{0.228}$ and chemical formula- $Fe_2O_3 \cdot H_2O \cdot xH_2O$, $Fe_{1.698}Sn_{0.228}O_3$.

Table 4-1: Chemical analysis of commercial pure sample

Element	**Hematite (Fe_2O_3)**	**Wustite (FeO)**	**SiO_2**	**TiO_2**	**MnO**
%wt	82.65	0.94	1.31	0.05	0.69

$$\%O_2 = \left(\frac{82.65\,x\,\frac{(16x3)}{(16x3)+(56x2)} + 0.94\,x\,\left(\frac{16}{(16+56)}\right) + 1.31\left(\frac{16x2}{28+(16x2)}\right)}{(82.65+0.94+1.31)} \right) x\,100\%$$

$$\%O_2 = 30.2\%\ or\ 0.302$$

4.3 Derived Reaction Kinetics Models

The following are the representation of the three major reaction kinetic stages as regards the ore particle for possibilities for reaction rate controlling resistances according to Levenspiel relation.

Diffusion Through Gas Film Control

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

Diffusion Through Ash Layer Control

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

Chemical Reaction Control

- $\frac{t}{\tau} = 1 - {}^{r_c}/_{R}$

4.4 Kinetic Model Equations (Cont’d)

Reduction time, t: is the specified time required for the ore sample (lump/pellet) to be exposed to the reducing gas in the furnace at specified furnace temperature.

Reaction Control Time, Ţ: This is the total time required by iron ore sample to experience total conversion to metallic iron at specified furnace temperature.

Conversion factor, $^{t}/_{\tau}$: This the ratio between reaction residence time and reaction control time. It is used to determine the rate controlling stage of the reduction process (i.e. gas film, ash layer and chemical control stage)

$$Swelling\ index\ (\%) = \left(\frac{V_f - V_i}{V_i}\right) x\ 100\%$$

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

$$Degree\ of\ Reduction = \left(\frac{W_o - W_t}{W_\infty}\right) x100\% = \left(\frac{W_o - W_t}{\%O_2\, W_o}\right) x100\%$$

$\%O_2$ is the percentage weight of the total oxygen content in the hematite lump sample where W_0 is the initial weight of sample, W_t is the weight of sample at time t, and ∞,

5.0 RESULT AND DISCUSSION

5.1 Crack Propagation and Structural Changes during Reduction

Fig. 5.1: Crack formation and iron grain disintegration of fired hematite ore samples of different sizes as reduced for 40mins (a) $700^{o}C$ (b) $800^{o}C$ (c) $1000^{o}C$

Fig. 5.2: Effect of structural changes on reduction behavior at different temperatures in charcoal at reduction time of 40mins. (a) $570^{o}C$ (b) $700^{o}C$ (c) $900^{o}C$

5.2 Effects of Temperature and Time

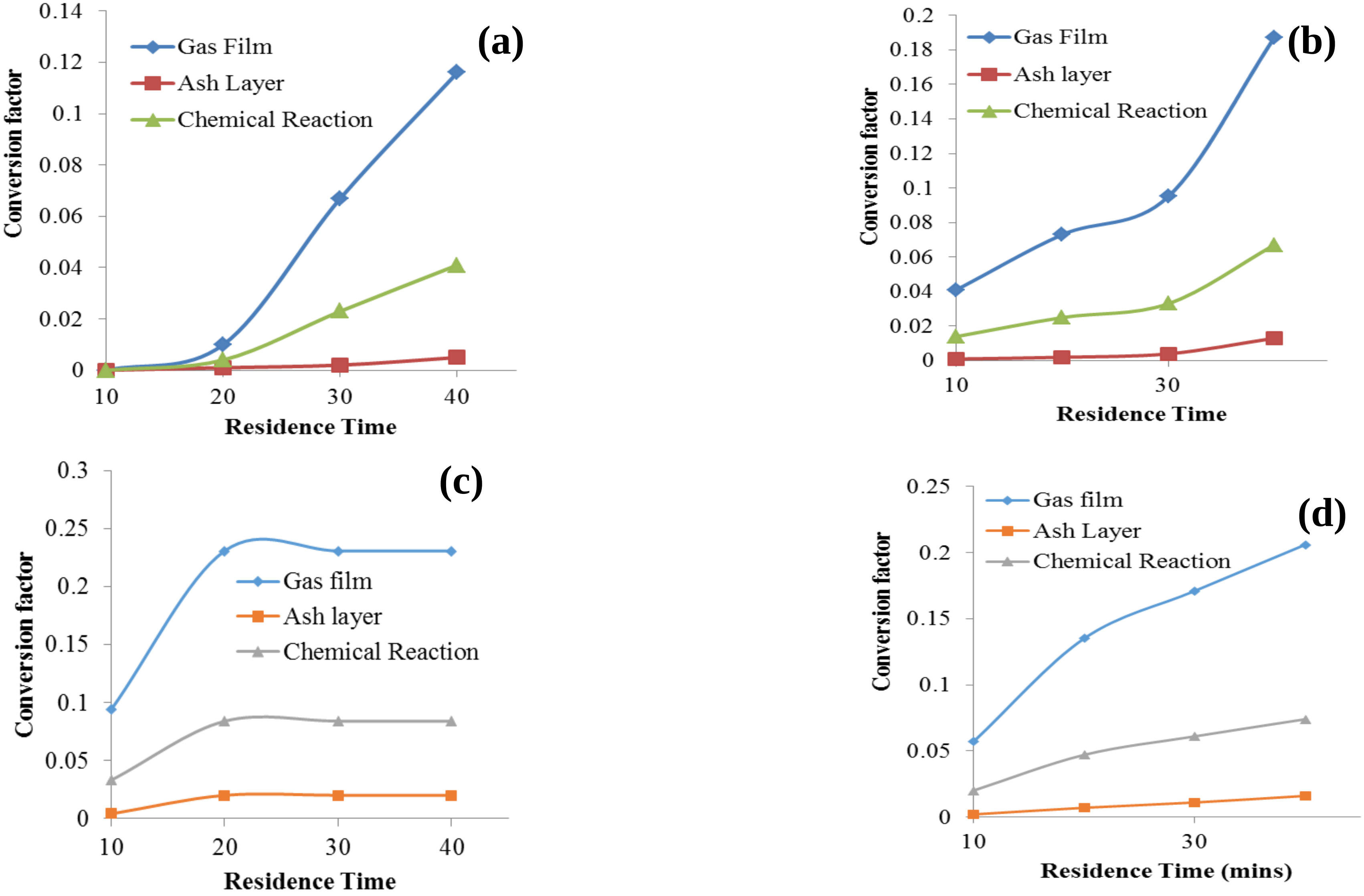


Fig. 5.3: Determination of rate control stages based on conversion factor at for Ore sample size range 10-14.99mm **(a)** 570ºC **(b)** 700ºC **(c)**800ºC **(d)** 1000ºC

5.3 Effect of Reduction Time on Reaction Control Time

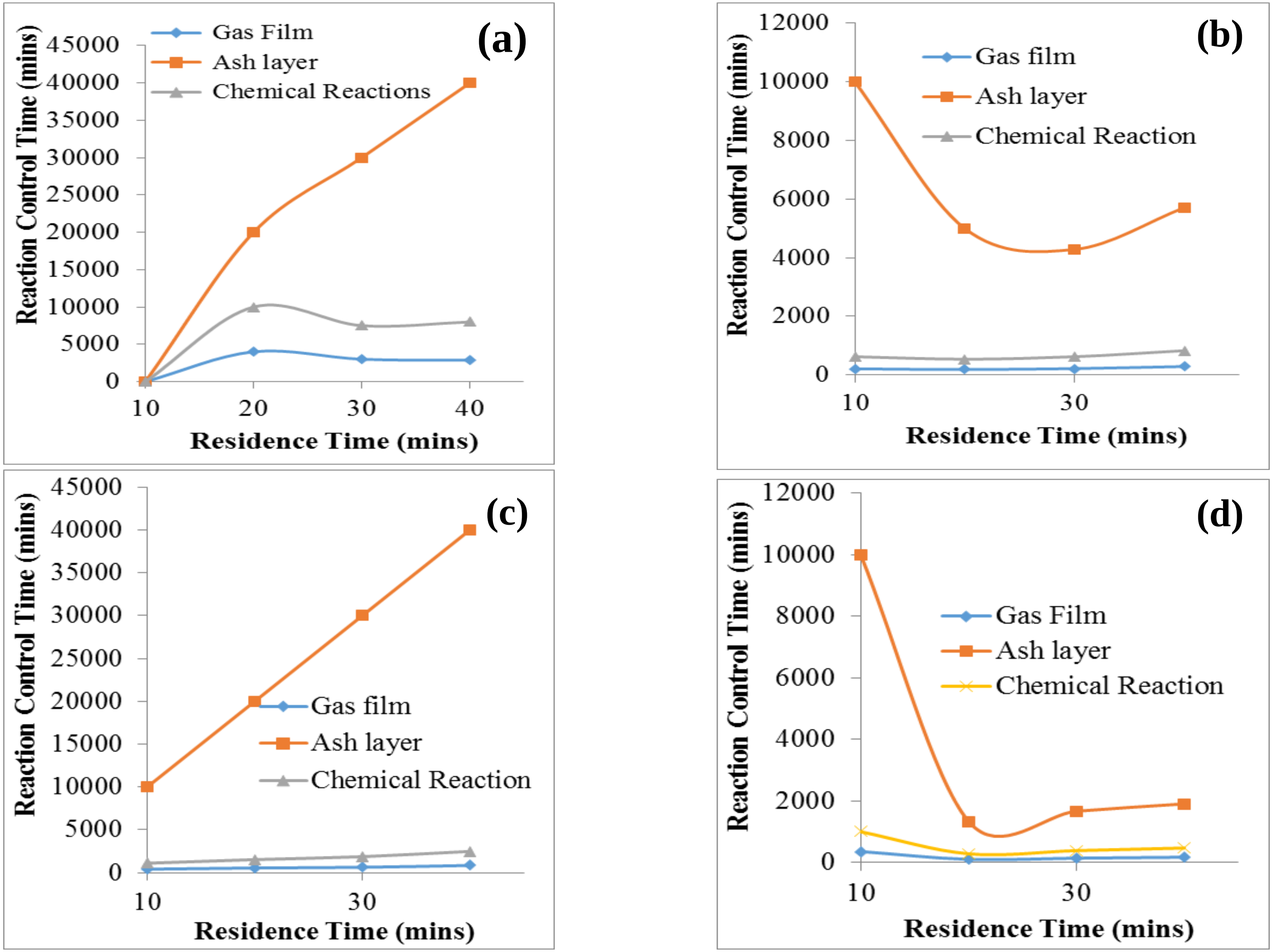


Fig. 5.4: Determination rate control stages based on reaction control time for Ore samples of size ranges at 15-20mm **(a)** 570^{o}C **(b)** 800^{o}C **(c)** 900^{o}C **(d)** 1000^{o}C

5.4 Effect of Particle Reduction time on Degree of Reduction

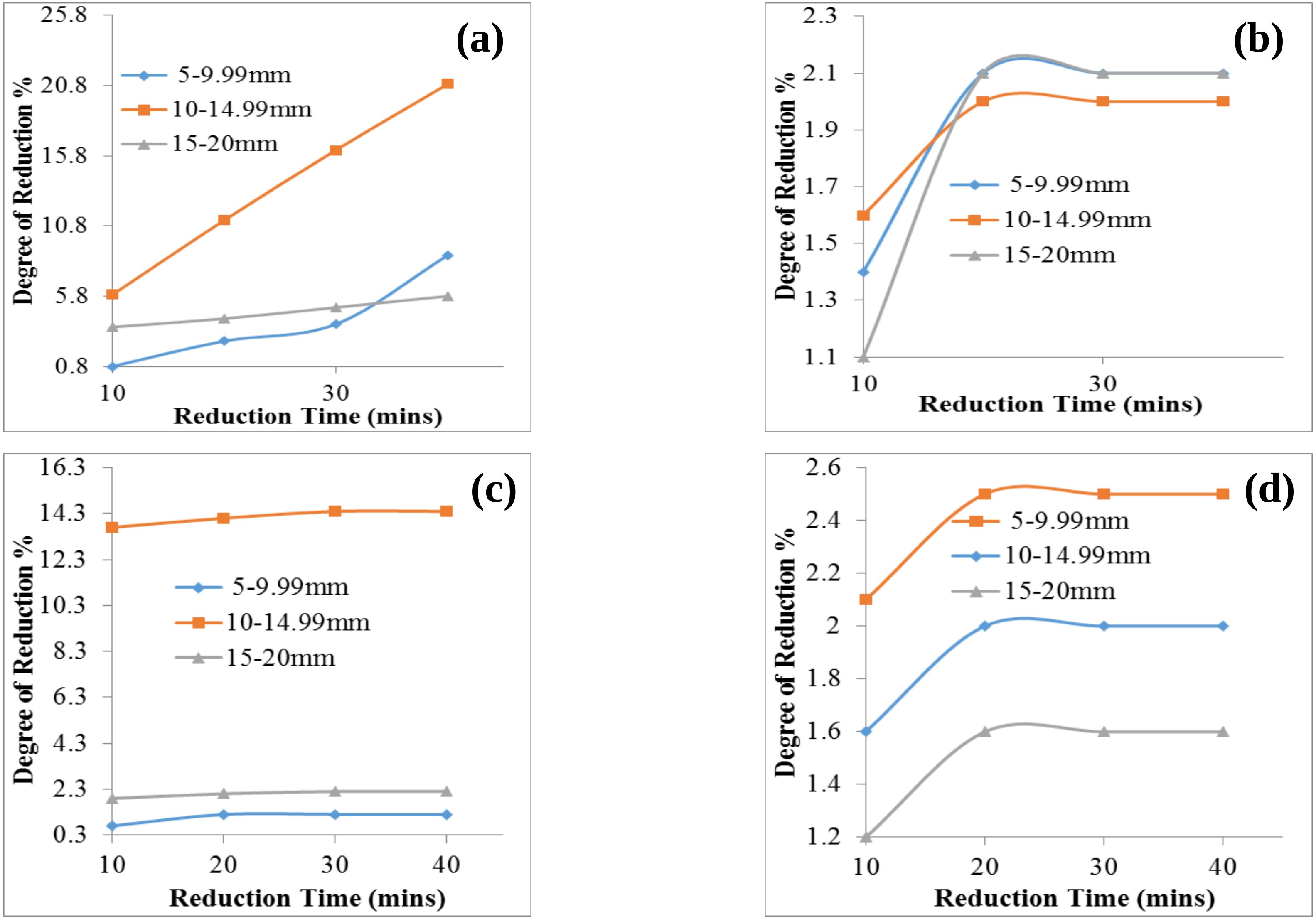


Fig. 5.5: Effects of reduction time and Iron lump sizes on the degree of reduction of fired hematite lumps reduced in commercially derived wood charcoal (a) 700°C (b) 800°C (c) 900°C (d) 1000°C

5.5 Effect of Residence Time on Particle Swelling Extent

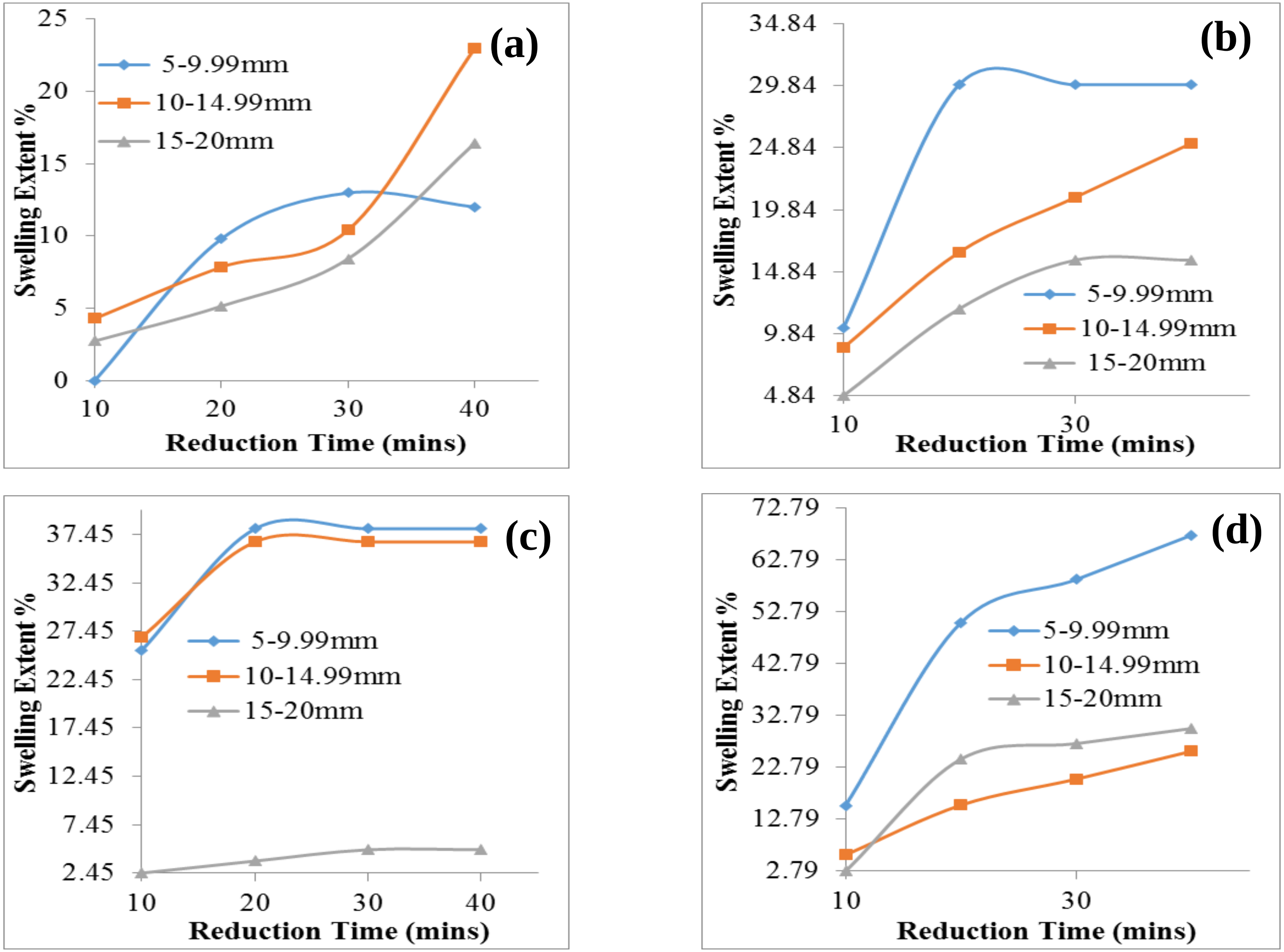
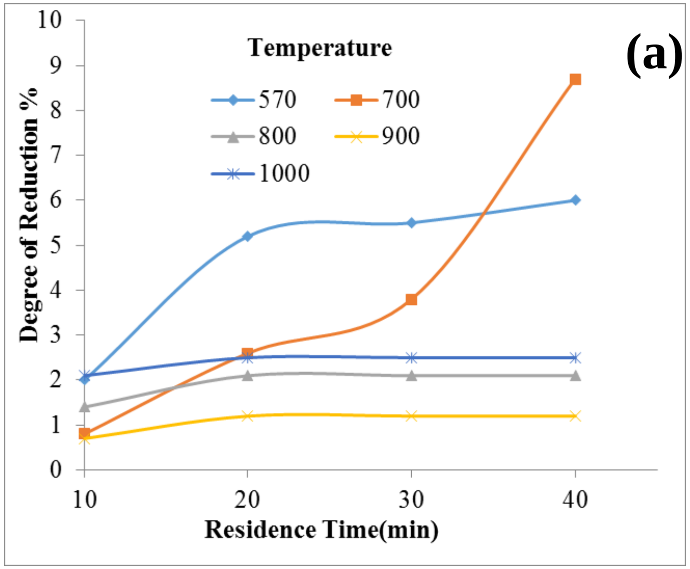
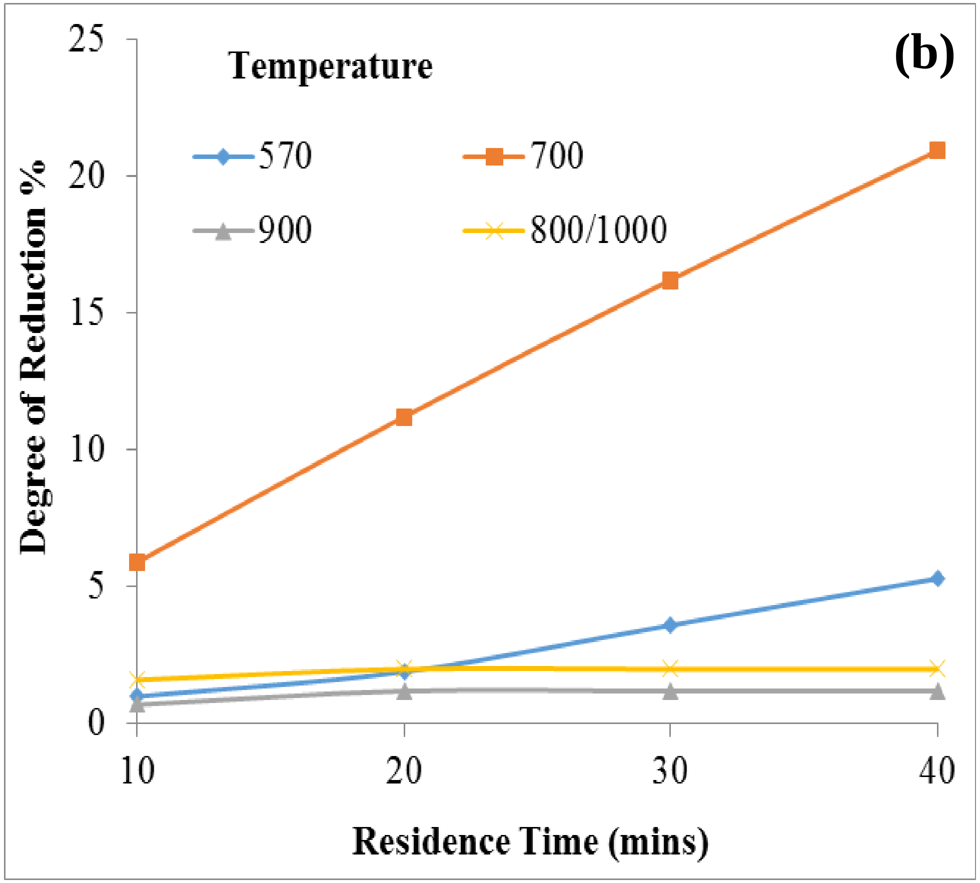


Fig. 5.6: Effects of reduction time and hematite lumps on the swelling index of reduced ore samples in wood charcoal for 40mins **(a)** 700^{o}C **(b)** 800^{o}C **(c)** 900^{o}C **(d)** 1000^{o}C.

5.6 Effect of Firing Temperature on Degree of Reduction and Swelling Extent





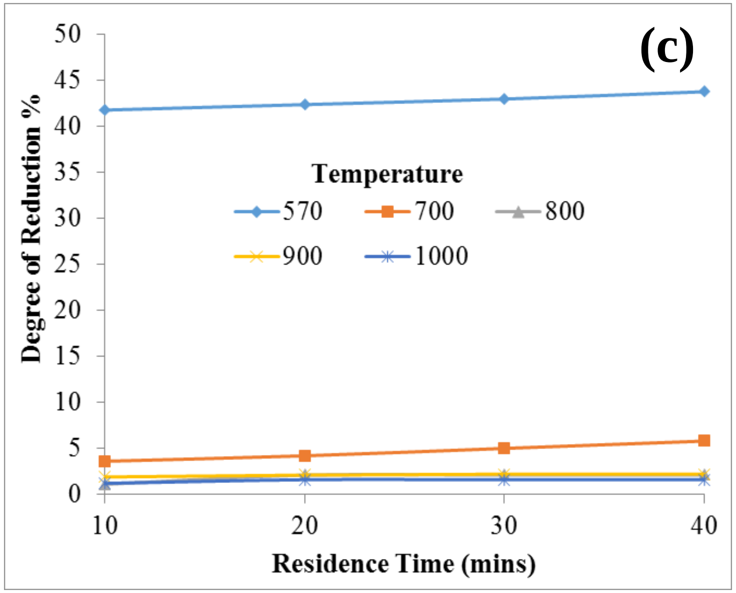
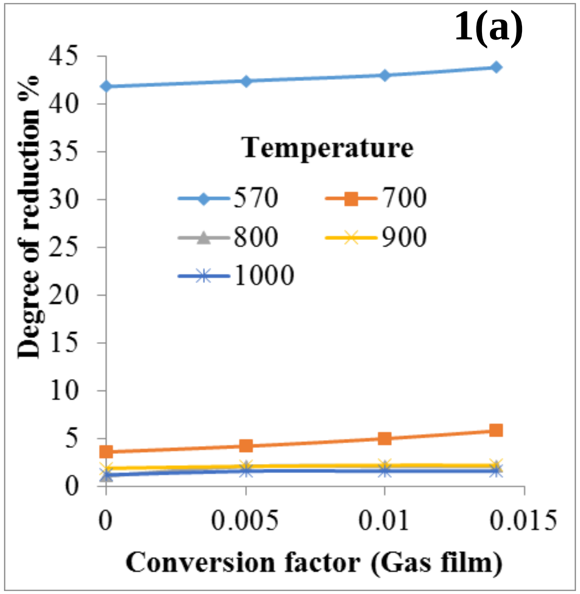
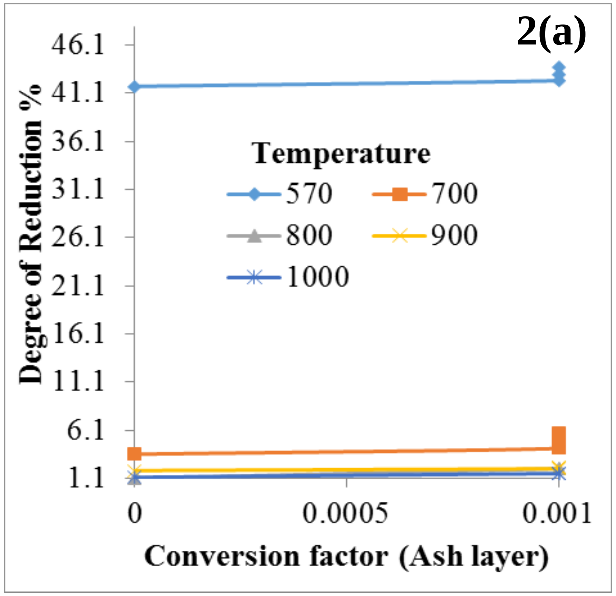
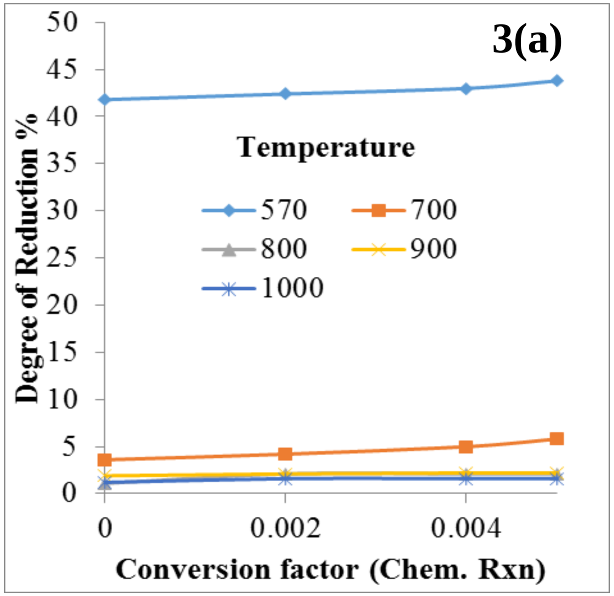


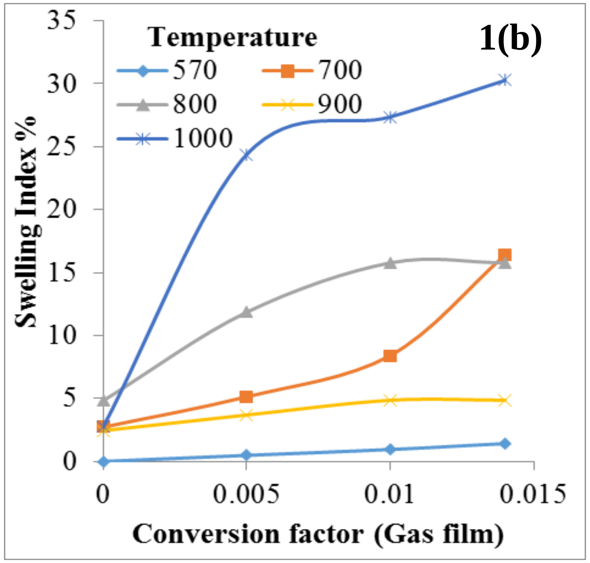
Fig. 5.7: Effect of reduction firing temperatures, residence time on the degree of reduction of iron ore sample for size range **(a)** 5-9.99mm **(b)**10-14.99mm **(c)** 15-20mm

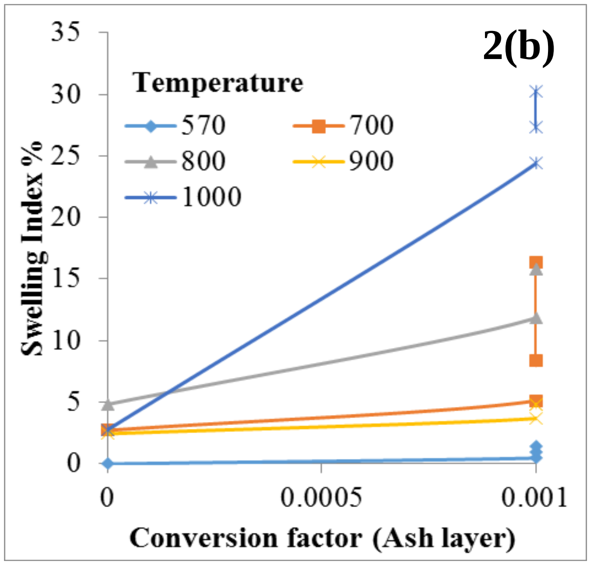
5.7 Effect of Reaction rate control on D. R. and S.I. on Ore Sizes(15-20mm)

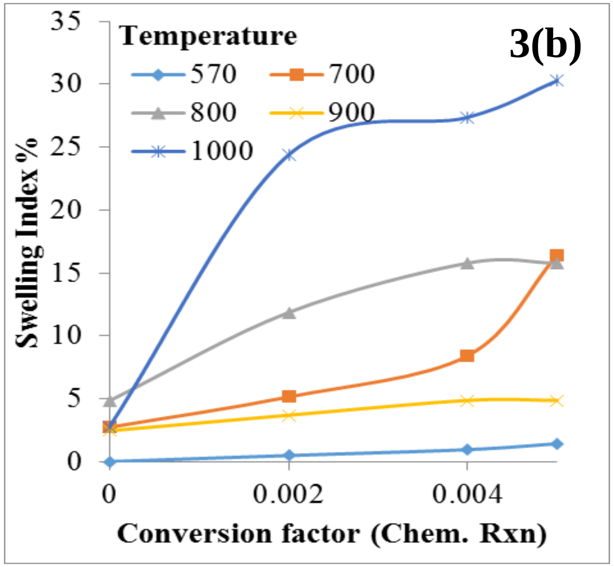












5.8 Analysis of Reduced Hematite Lump Sample by SEM/EDX

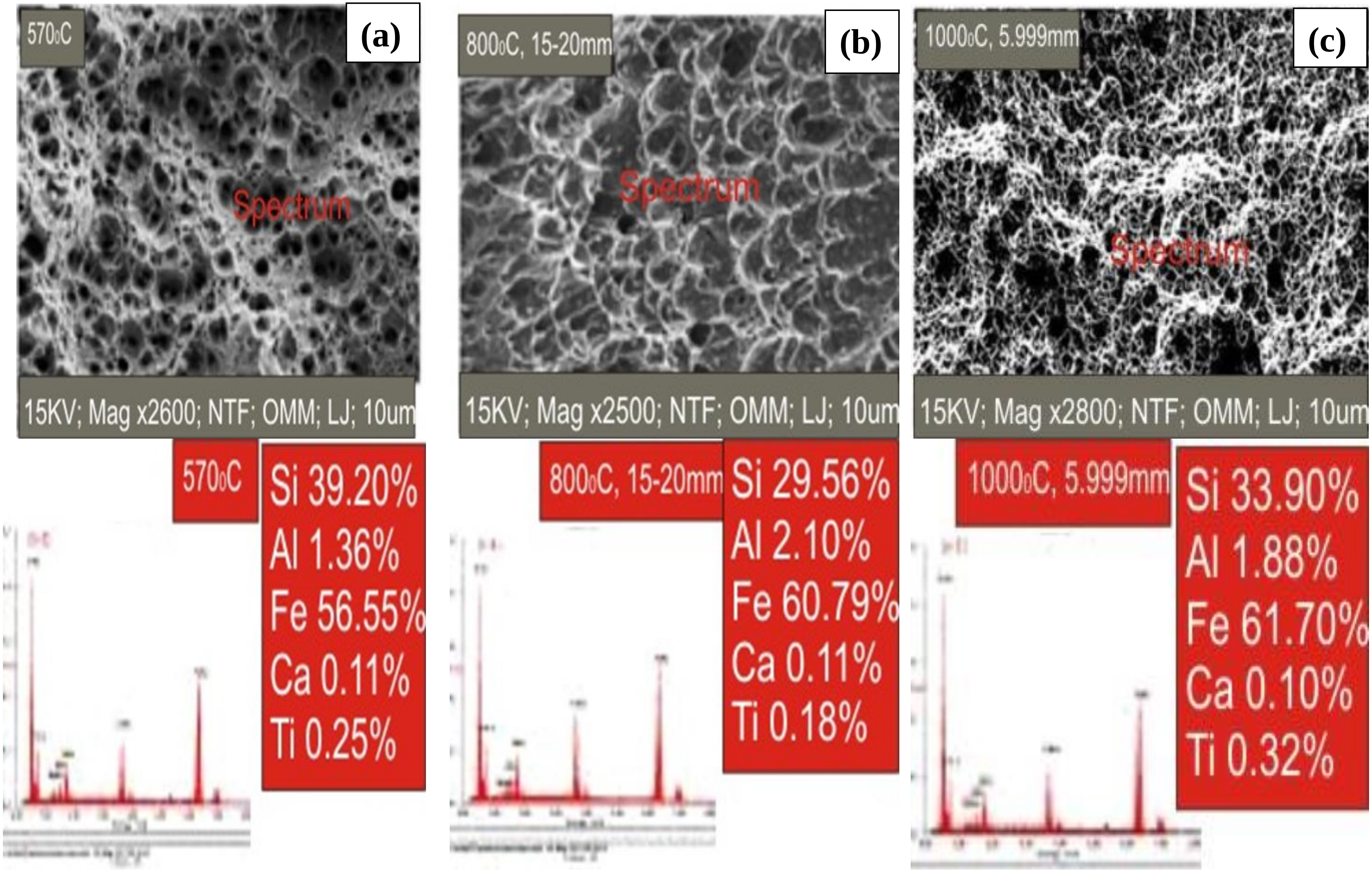


Fig. 5.8: SEM/EDX Micrograph view at 570, 800 and 1000^{o}C at different size ranges

5.9 SEM/EDX Analysis and Degree of Metallization

Table 5-1: Reduce Ore-Carbon mixture from SEM/EDX analysis for metallic components

Temp. (^{o}C)	**%W_o of O_2 at XRD**	**%W_o of O_2 at EDX**	**%W_i of Fe at EDX**	**Degree of Metallization (%)**
0	**0**	**0**	**0**	**0**
570	**30.2**	**2.53**	**56.55**	**91.62**
800	**30.2**	**7.26**	**60.79**	**75.96**
1000	**30.2**	**2.10**	**61.70**	**93.05**

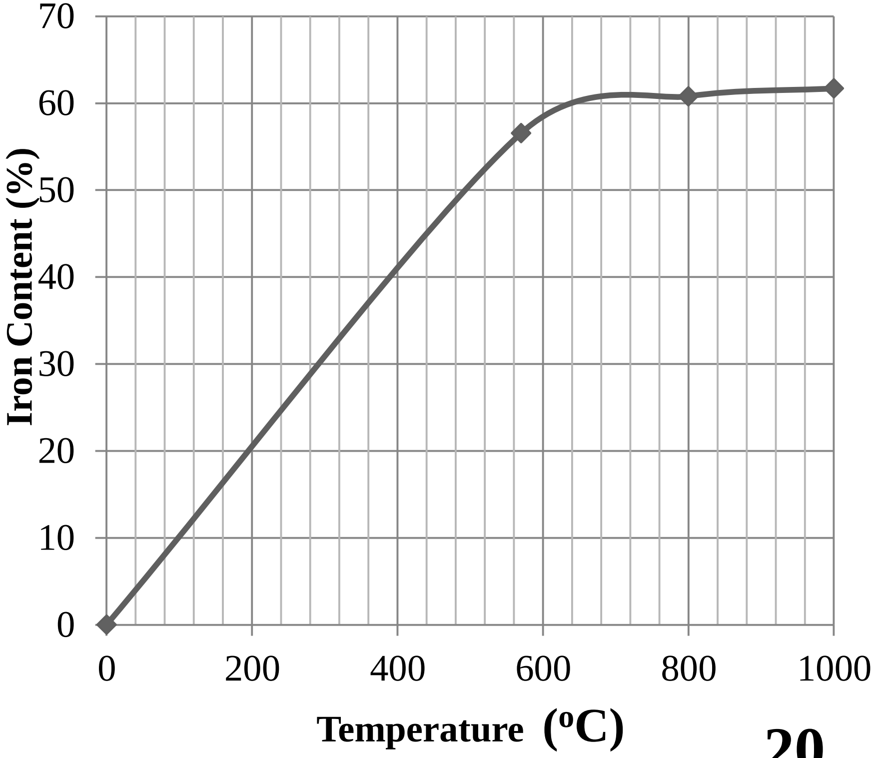


Fig. 5.9: Metallization degree as function of inlet temperature from SEM/EDX micrograph

5.9 SEM/EDX Analysis and Degree of Metallization (Cont'd)

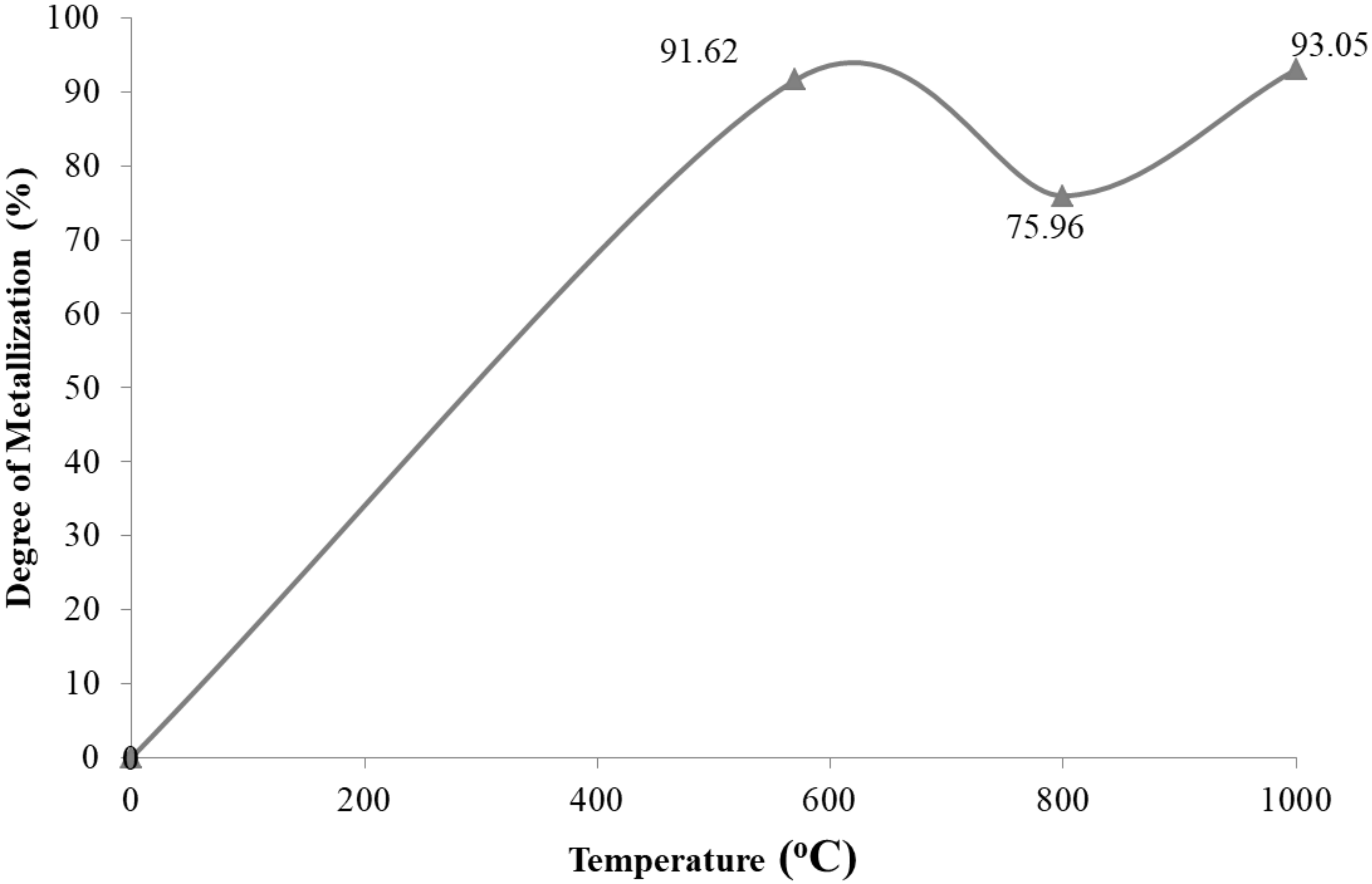


Fig. 5.10: Degree of metallization as a function of reducing gas temperature

6.0 CONCLUSION

The kinetics of reduction of commercially obtained Goethite iron ore have been successfully investigated using commercially acquired wood charcoal at specified reduction time. Other results achieved includes:

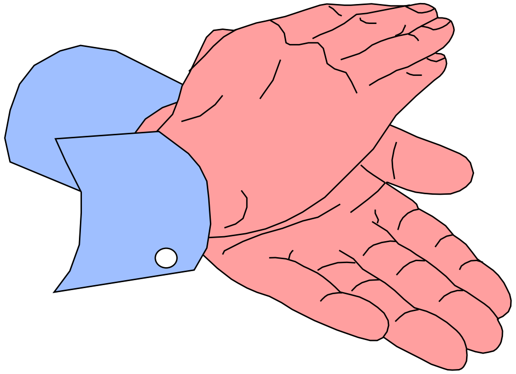
1. Derivation of all useful kinetic model and chemical equations needed for result analysis have been achieved.
2. The relationships between residence reaction time, conversion factor and control reaction have been attained.
3. The kinetic model for the percentage degree of reduction, swelling extent of the reduced iron ore by rate contact and resident time of reaction has been achieved.
4. The rate controlling resistance of the reduction reaction is the **Ash Layer Control**.
5. An increase in $CO\text{-}H_2$ composition produces higher metallization degree. Metallization degree is also increased with the gas inlet temperature.
6. Increase in temperature, increases the degree of reduction and swelling extent of reaction.
7. Increase in reduction time, increases the degree of reduction and swelling extent of reaction.
8. Increase in fixed carbon content of reductant, increases the degree of reduction and swelling extent.

7.0. RECOMMENDATION

- The phase and chemical compositions of layers of ore sameples can also be investigated in cases of incomplete reduction stages for complete metallization of the iron ore samples.

- Smelting of the DRI by introduction of quicklime (CaO) into the reduction process should be carried out to remove the high silicon content from reduced iron ore sample.

- Laboratory approach to solid-solid iron oxide reduction smelting process should be encouraged at the industrial level.



thank you!