

# Reduction of Iron Ore Contain Phosphorous

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**Abstract**—A lot of investigations have been carried out on direct reduction process of iron oxides by using hydrogen gas at different flow rate. In the present work, an attempt has been made to study the reduction behavior and kinetics of fired high phosphorous iron ore briquettes. The effect of different reduction parameters such as temperature and hydrogen flow rate, also, the effect of drop damage resistance, applied pressure, compressive strength was studied. Reduction of high phosphorous iron ores briquettes by hydrogen was carried out in the temperature range 800 to 1200°C.

**Keywords**— High phosphorous iron ore, reduction kinetics, diffusion model, Energy of activation, briquettes.

## I. INTRODUCTION

Iron cation exists as two different valences ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) in oxides forming three different iron oxides, i.e. hematite, magnetite and wüstite in descending order of oxidation. In addition to hematite,  $\text{Fe}_2\text{O}_3$  has also another crystalline form called maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), but that form is very unstable

The reduction of iron ores used hydrogen is a gas-solid reaction which occurs in two or three stages. For temperatures more than 570 °C, hematite ( $\text{Fe}_2\text{O}_3$ ) is first transformed into Magnetite ( $\text{Fe}_3\text{O}_4$ ), then into wustite ( $\text{FeO}$ ), and finally into metallic iron whereas at temperatures less 570 °C, magnetite is directly transformed into iron since wustite is not thermodynamically stable (Hughes *et al*, 1982).

In direct reduction of iron ore, the mechanisms are complex because the oxide must go through a series of step which changes before the conversion is complete (Raymond and Leiv, 2008).

Reduction by Hydrogen occurs in three stages as follows

1.  $3\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$
2.  $\text{Fe}_3\text{O}_4 + \text{H}_2 \rightarrow 3\text{FeO} + \text{H}_2\text{O}$
3.  $\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$

The reduction of iron oxide to metallic iron proceed through various kinetic steps and one of them is the slowest step, which controls the overall reaction rate (Bonalde *et al*, 2005).

The reduction of  $\text{Fe}_2\text{O}_3$  by  $\text{H}_2$  in range of temperatures 220 – 680°C, was found that the reduction of hematite to magnetite with  $\text{H}_2$  was characterized by an apparent activation energy ‘ $E_a$ ’ of 76 kJ/mol while  $E_a$  of the reduction of magnetite to iron is 88 and 39 kJ/mol for temperatures lower and higher than 420°C, respectively. Also it was found that the reaction rate was controlled by two- and three-dimensional growth of nuclei and by phase boundary reaction at temperatures less and higher than 420°C, respectively. The morphological examination confirmed the formation of

compact iron layer generated during the reduction of  $\text{Fe}_2\text{O}_3$  by  $\text{H}_2$  at temperatures higher than 420 °C (Pineau *et al.*, 2006).

Asima and Itishree suggested that reduction increases with increase in temperature and time of reduction. Also a greater reducibility was observed when lower binder percentage. Greater pellets with Dextrine binder showed faster reduction as compared to Bentonite (Asima and Itishree, 2007).

It was found out that the briquettes retain their strength up to reduction temperature of 700°C-750°C. Due to the cement stone. On future reduction at high temperature, strength is retained due to the formation of metallic iron on the briquette’s surface, as the iron oxide on the briquette surface is reduced to metallic iron (Kurunov *et al.*, 2007).

It was found that when the iron ore was reduced by a mixture of carbon monoxide and hydrogen, hematite is reduced to magnetite quickly, which in turn is reduced quickly to wüstite. The reduction of wüstite to metallic iron is the limiting stage in the reduction of the pellets (Longbottom and Kolbeinsen, 2008).

Singh *et al* state that the percentage of reduction increases when both temperature and time increases and the reduction activation energy of depends on the type of binder (Singh and Krishnan, 2008).

Ranzani *et al* state that reduction with hydrogen was faster than that with carbon monoxide, making it possible to use a more compact reactor than Midrex and HYL shafts (e.g.4.5m instead of 9 m, with almost 100 % FeO) and also decreasing the size of pellet to the process is accelerated (Ranzani *et al.*, 2009).

Haitao indicate that the reduction of 90 – 99 % iron ore concentrate by hydrogen at 1200 - 1400 °C was obtained by 1 - 7 seconds depending on the amount of hydrogen supplied with iron oxide. The rate of reduction depends on hydrogen partial pressure size of particle, and temperature. The reduction rate has 1/2 - order dependence on the hydrogen partial pressure and increase in partial pressure of reducing gas had effect on rate of reduction than at the 1200 - 1400°C 1st - order reaction (Haitao, 2011).

Hai-bin *et al.* indicated that the reduction reaction increased by increase the content of hydrogen in the reducing gas mixture or by increasing the temperature of reaction since the reaction of hydrogen is endothermic reaction, partly overcoming the exothermic reaction of carbon monoxide reduction. They also found that the effective diffusion coefficient and the rate constant of chemical reaction were enhanced with increasing temperature or increasing the content of hydrogen in the mixture. Adding just a small amount of carbon monoxide into hydrogen leads to the gas

diffusion coefficient decreasing compared with pure hydrogen. Also the reduction of iron oxide pellets using an hydrogen and carbon monoxide mixture is a complex kinetic system. The rate reaction is dominated by chemical reaction at the very beginning, subsequently competing with diffusion during the reduction process and internal gas diffusion at the end. The transition of the rate-control step varies with the reducing agent composition and reaction temperature. Lowering the hydrogen content in mixture and increasing temperature takes the transition point of the rate control step from chemical reaction to internal gas diffusion to a high degree of reduction (Hai-bin *et al.*, 2011)

1.1. The Aim of the Work

The study aims at investigating the kinetics of reduction of briquette formed from high phosphorous from El-Baharia iron.

II. EXPERIMENTAL WORK

2.1 Chemical Analysis of High Phosphorous Iron Ore

The chemical analysis of high phosphorous iron ore presents in Table I. From which it is evident that iron ore contains 1,84 % P<sub>2</sub>O<sub>5</sub> and weight lose equal 14.2 %.

TABLE I. Analyses of high phosphorous iron ore percentage

Compounds or elements	Percentage
Fe <sub>2</sub> O <sub>3</sub>	44.82 %
SiO <sub>2</sub>	20.65 %
CaO	8.96 %
MgO	0.23 %
Al <sub>2</sub> O <sub>3</sub>	3.88 %
MnO <sub>2</sub>	0.18 %
S	0.3 %
P <sub>2</sub> O <sub>5</sub>	1.84 %
Cl <sup>-</sup>	0.15 %
BaO	0.2 %
ZnO	0.4 %
Li	4.19 %
Weight lose	14.2 %
Total	100 %

2.2. X-ray Diffraction of High Phosphorous Iron Ore

The XRD pattern of high phosphorous iron ore contains, hematite, quartz, kaolinite, calcite and anhydrite are shown in Figure 1. In this figure no phosphorous appear because its amount less than 5%.

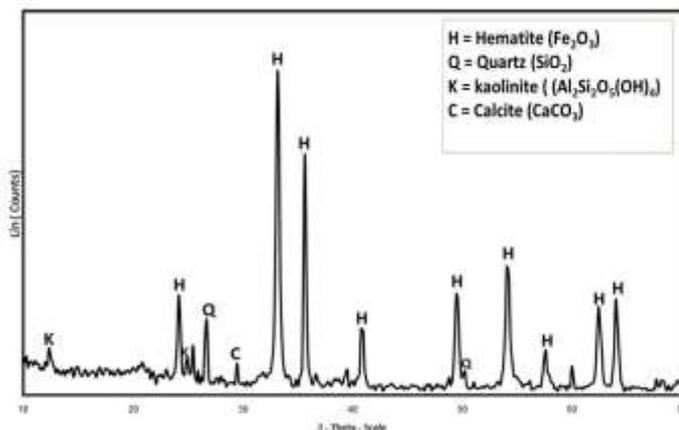


Fig. 1. X-Ray of high phosphorous iron ore.

2.3. Experimental Procedures

a. Preparation of samples in the form of briquette

Preparation of samples for the briquetting process was carried out by mixing 10 g of fine of high barite iron ore or high phosphorus iron ore fine with 2% molasses (binding material) was pressed in the mould (12 mm diameter and height 22 mm) using MEGA.KSC-10 hydraulic press Fig. (2).



Fig. 2. MEGA.KSC-10 hydraulic press.

b. Determination of the quality of briquettes

i. Drop damage resistance test

The produced briquettes were subjected to the (Drop damage resistance test). Which indicates how often briquette can be dropped from a height of 45 cm before they show perceptible cracks or crumbed. Ten the produced briquettes are individually dropped on a steel plate until their breaking. The mean value of the tested briquettes gives their average drop damage resistance (Mayer, 1980; Forsmo *et al.*, 2006; Forsmo *et al.*, 2008).

ii. Compressive Strength Test

The average compressive strength tests of briquettes are controlled by compressing at least 10 of briquettes between parallel steel plates up their breaking. The mean value of the tested briquettes gives their compressive strength.

2.4 Reduction Procedure by Hydrogen

The reduction of briquette by hydrogen was done in the thermo gravimetric apparatus (A schematic diagram of thermogravimetric apparatus is shown in Fig. 3.

It consists of vertical furnace, electronic balance for calculate the weight change of reacting sample and temperature controller. The sample was placed in a Ni-Cr basket which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the temperature required (700-1000 °C) and maintained constant to ± 5° The sample then was placed in the hot zone. The weight of the sample was continuously recorded, at the end of the run; the samples were withdrawn from the furnace and kept in the desiccators.

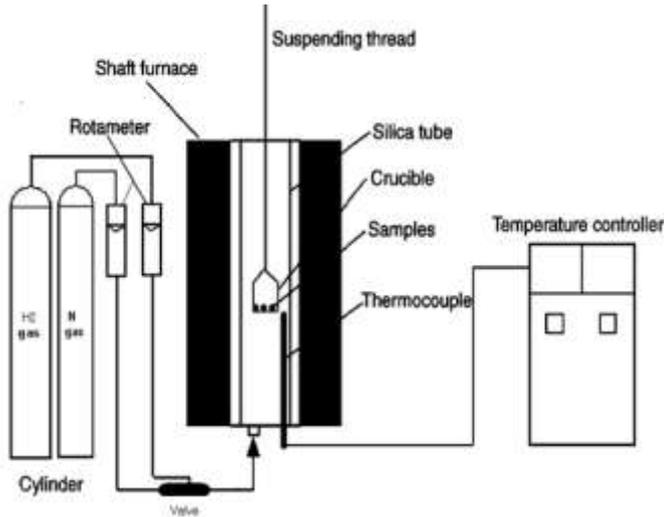


Fig. 3. Schematic diagram of thermo balance apparatus.

The percentage of reduction was calculated according to the following equation:

$$\% \text{ Reduction} = \frac{(W_0 - W_t) * 100}{\text{oxygen (mass)}}$$

Where,  $W_0$ : the initial mass of iron ore sample after removal of moisture,  $W_t$ : mass of sample after each time of reduction, t, Oxygen (mass): indicates the oxygen mass percent in from  $Fe_2O_3$ .

### III. RESULTS AND DISCUSSION

#### 3.1. Drop Damage Resistance of the Wet and Dry Briquette of High Phosphorus Iron Ore

The effect of applied pressure on the wet high phosphorus iron ore briquette and after 3 days properties is shown in Figures (4 and 5). From which it is clear that increase applied pressure leads to an increase both the drop damage resistance (drop damage resistance of briquette) of dry briquette and after 3 days

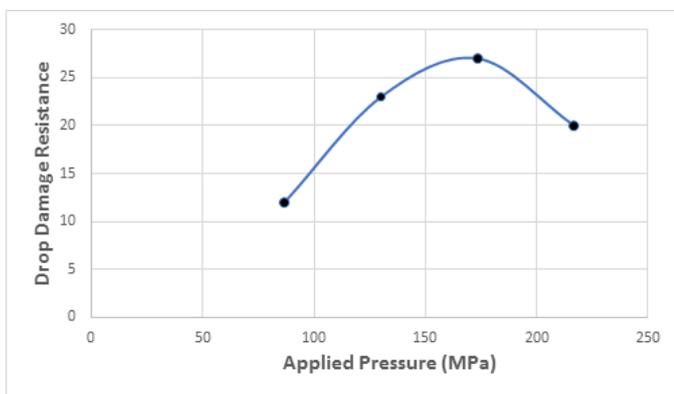


Fig. 4. Relation between drop damage resistance of wet high phosphorus iron ore briquette and applied pressure.

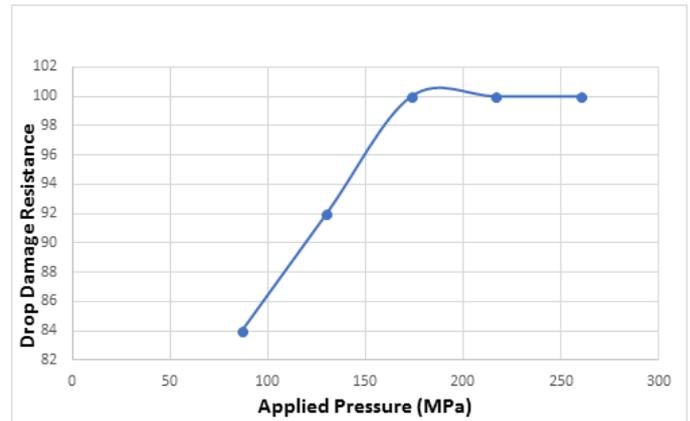


Fig. 5. Relation between drop damage resistance of dry briquette and applied pressure after 3 days.

#### 3.2. Compressive Strength of Fired High Phosphorus Iron Ore Briquette at 900- 1200 °C

Fig. 6 shows the compressive strength of fired high phosphorus iron ore briquette at 900-1200 °C. From this figure it is evident that the compressive strength increased as the temperature of fired increase.

The relation between compressive strength and applied pressure (up to 220 MPa) and firing temperature was found to take the form:

$$\sigma = -258.2 + 0.289 T + 0.32P$$

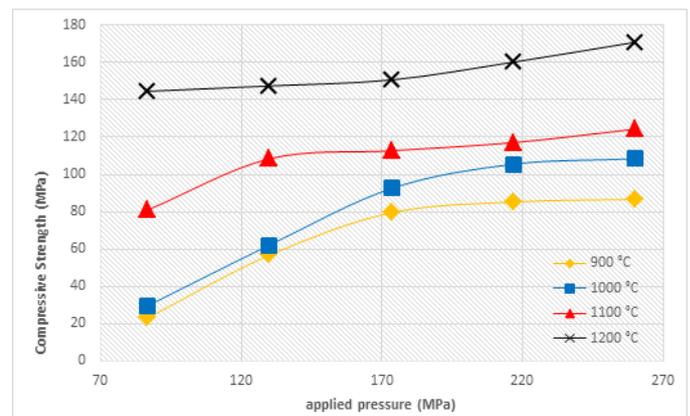


Fig. 6. The compressive strength of fire high phosphorus iron briquette at 900-1200°C.

#### 3.3 Reduction of High Phosphorus Iron Ore Briquette

Reduction was carried out at different temperatures range from 900°C to 1200°C, keeping the briquette weight and hydrogen flow rate constant (1.5 L.min<sup>-1</sup>). The results of the investigation are shown on Figures 7, where it is obvious that an increase of temperature increased the reduction rate.

Fig. 8 illustrated that X-ray of sample after reduction at 1200°C from which it is clear that the mean compound of sample is metallic iron quartz and some iron oxide

#### 3.3. Kinetic of Reduction of Fired High Phosphorus Briquette

Fig. 9 illustrates the relation between  $(R+(1-R)\ln(1-R))$  against time of reduction for different reduction temperature (900-1200°C). From which it is clear that the

relationship is represented by straight line. The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results were illustrated on Figure 10. From which it is clear that high phosphorus iron ore briquette has activation energy= 11,06 kJ/ mole.

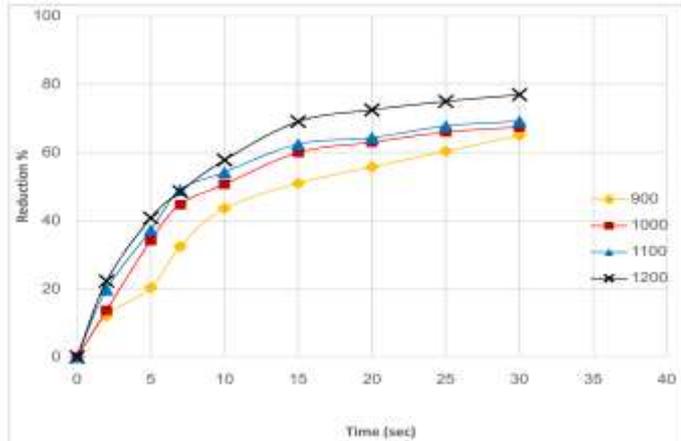


Fig. 7. Schematic diagram of reduction percentage at, 900- 1200°C

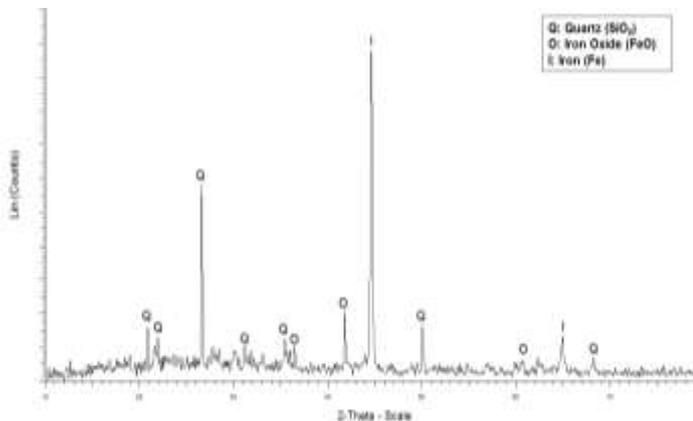


Fig. 8. X-ray of sample after reduction at 1200°C.

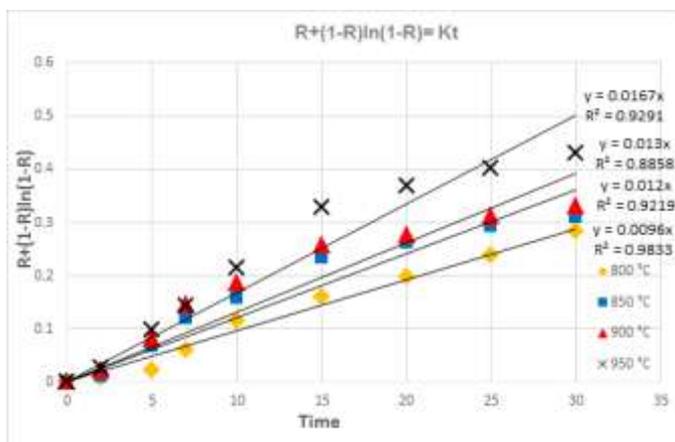


Fig. 9. The relation between  $(R+(1-R)\ln(1-R))$  against time of reduction for different reduction temperature (900-1200°C).

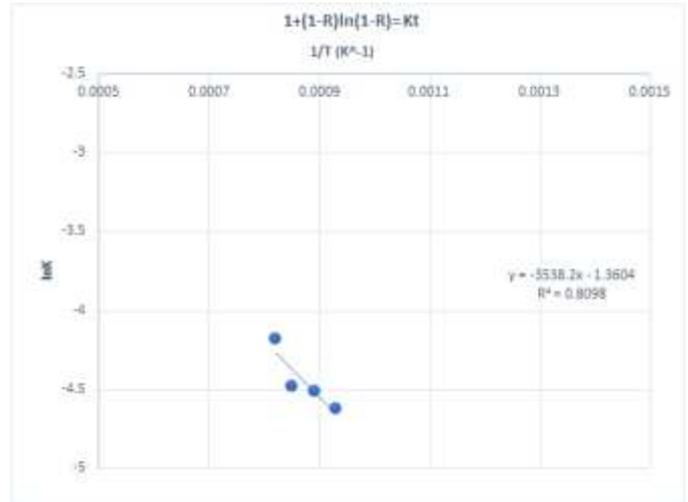


Fig. 10. Schematic diagram of the Arrhenius plot for the reduction process of high phosphorus iron ore briquettes.

#### IV. CONCLUSION

- 1- Increase applied pressure leads to an increase the drop damage resistance (drop damage resistance of briquette)
- 2- Compressive strength of fire high phosphorus iron ore briquette at 700-1200°C. strength increased as the temperature of fired increase.
- 3- An increase of reduction temperature increased the rate of reduction
- 4- The activation energies calculated for this process for the high barite iron briquettes formed using equation  $kt=R+(1-R)\ln(1-R)$  was = 11kJ/ mole

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