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Hydrogen Reduction Kinetic of High Barite Iron Ore Briquettes

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Abstract: Reduction of high barite iron ore briquettes by hydrogen is carried out in the temperature range 700 to 1000 oC. In the reduction kinetic study, the most satisfactory model is to take the slope of the initial linear region of fractional reduction vs. time curve as a measure of rate constant (k) and In k vs. 1/T plots are straight line from which Activation Energy was calculated.

Introduction

The reduction of iron ore by hydrogen was widely studied in the 60s to 80s. Most of the reaction features are very similar to that of the reduction by carbon monoxide and many mechanisms are common to both of them [1-6]. The reduction of synthetic hematite samples is a multi-stage reaction with one or two intermediate oxides depending on temperature. The first two reactions, hematite to magnetite and magnetite to wustite, are successive and well separated since hematite has completely disappeared when the first grains of wustite are detected. On the contrary, the reduction of wustite into metallic iron begins before the total consumption of magnetite. Experimentally , in the range of 550-900°C, an increase in temperature accelerates the reaction.

When Kinetic of the hydrogen reduction of pure α-Fe_2O_3 doped with foreign metal oxides is employing a sensitive micro-gravimetric technique, the results show that the reduction of pure Fe_2O_3 proceeds by a consecutive two-step mechanism via Fe_3O_4. The overall rate being controlled by the topochemical reduction of Fe_3O_4 while that of doped oxides and hematite ore takes place by a different mechanism involving the mixed ferrite formed. In addition, the reduction of pure Fe_2O_3 is catalysed by metal additives in the presence of water vapour. This enhancement in reduction rate is attributed to a "hydrogen spill-over" effect.[7]

Experimental measurements of the rate of reduction of particles of Carol Lake and Kiruna ores have been made using pure hydrogen and pure carbon monoxide and mixtures of these two gases. The temperature range covered was 773–1143 K and throughout this range the reduction rate with hydrogen was greater than that with carbon monoxide. A retracting core model was found to best fit the experimental data even when granules of 9×10^{-4} m diameter were used. Reduction with gas mixtures of hydrogen and carbon monoxide give rates intermediate between those of the pure gases.[8]

The aim of this work is to study the briquetting the high barite iron ore and reduce it in static bed by hydrogen

Keywords: High barite iron ore , reduction kinetics, diffusion model, Energy of activation , briquettes

2- EXPERIMENTAL WORK

The chemical analysis of high barite Egyptian iron ore present in Table 1. and it is clear that iron ore contains 16.9 % barium oxide.

Table 1 Chemical analyses of Iron with high Barite percentage

Compounds or elements	Percentage %
Fe_2O_3	43.72 %
SiO_2	4 %
CaO	0.8 %
TiO_2	0.14 %
Al_2O_3	0.42 %
MnO_2	0.99 %
S	4.09 %
P_2O_5	0.52 %
Cl^-	0.38 %
BaO	16.9 %
ZnO	0.14 %
Li	8.07 %

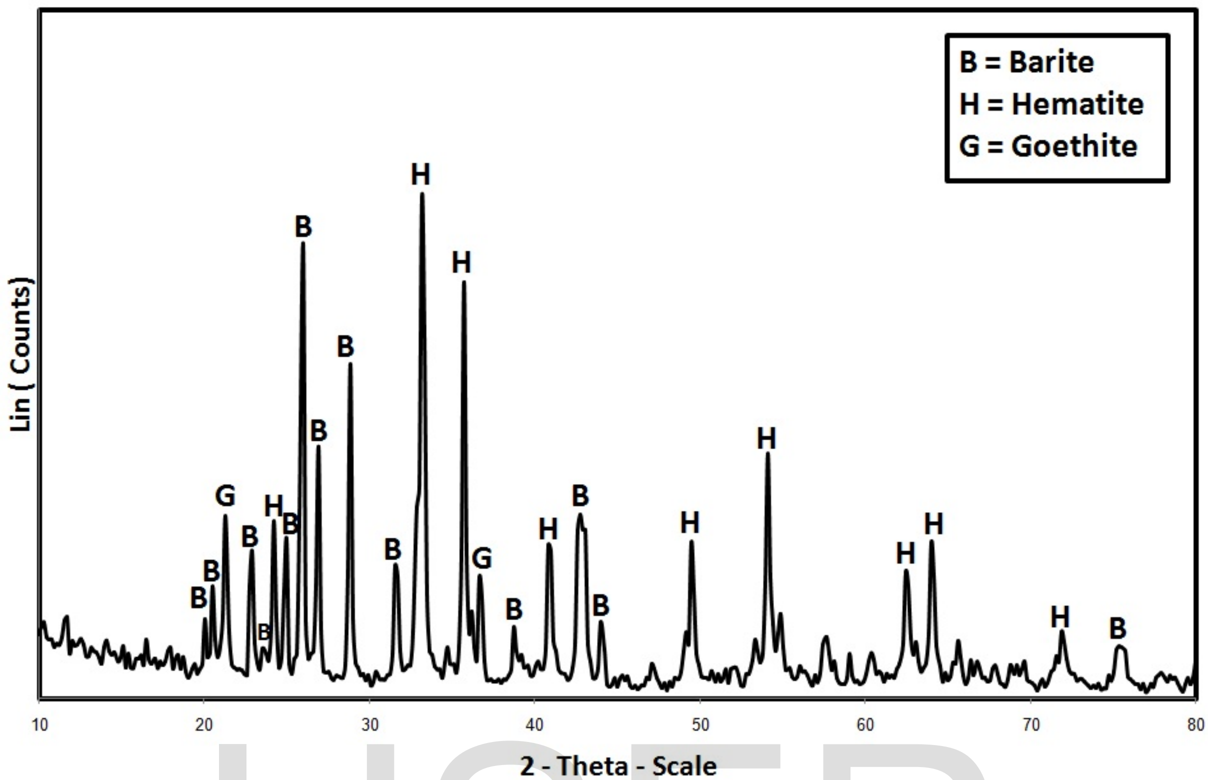


Fig.1 X-Ray of high barite iron ore contains barium oxide ,hematite and goethite

2.2. Preparation of the briquettes and its physical properties

The fine high barie iron ore particles (10 g) after grinding for different time in laboratory ball mill are mixed with 2% molasses and then pressed in the mould (12 mm diameter and a height 22 mm using MEGA.KSC-10 hydraulic press

{Fig2}. Under different pressure (the pressure ranges from 75 MPa up to 250 MPa). The produced briquettes were subjected to drop damage resistance tests and compressive strength tests. The drop damage resistance indicates how often green briquettes can be dropped from a height 46 cm before they show perceptible cracks or crumble. Ten green briquettes are individually dropped on to a steel plate. The number of drops is determined for each briquette. The arithmetical average values of the crumbing behavior of the ten briquettes yield the drop damage resistance for these briquettes, while the average compressive strength is done by compressing 10 briquettes between parallel steel plates up to their breaking according to (9-12).

Fig2. **MEGA.KSC-10 hydraulic press**

2.3. *Reduction Procedures.*

The reduction of high barite iron ore briquette with hydrogen was performed in thermo gravimetric apparatus similar to that present elsewhere (12) (Figure 3). It consisted of a vertical furnace, electronic balance for monitoring the weight change2of reacting sample and temperature controller. The sample was placed in a nickel chrome crucible which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the required temperature (650°C - 950°C) and maintained constant to ±5°C. Then samples were placed in hot zone.

The nitrogen flow rate was 0.5 l/min pass through furnace in all the experiments at initial time air should be removed before each experiment and also after the end of reduction. The weight of the sample was continuously recorded at the end of the run; the samples were withdrawn from the furnace and put in the desiccators.

The percentage of reduction was calculated according to the following equation [1]:

Percentage of reduction = [(Wo −Wt) x100/ Oxygen mass] -------------------

-- [1]

Where: Wo: The initial weight of high barite iron sample after removal of moisture.

Wt: Weight of sample after each time, t.

Oxygen mass: is the total weight of oxygen percent present in high barite ore in form FeO& Fe_2O_3

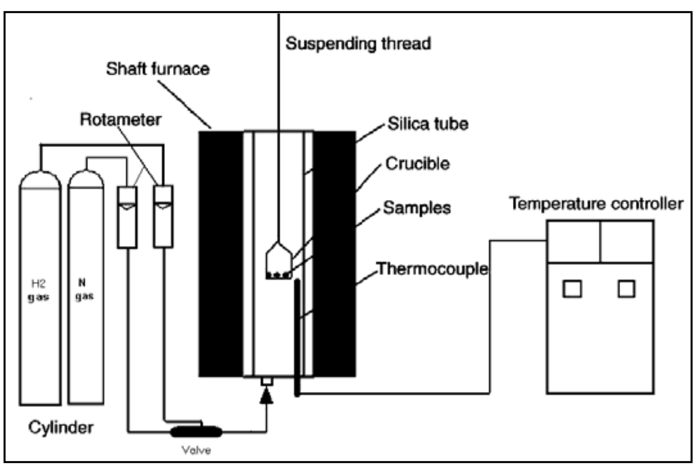


Fig. 3.Schematic diagramof the reduction apparatus

3.Results and Discussion

3.1-Drop damage strength of the wet and dry briquette **of high barite iron ore**

The effect of pressing pressure on the green and dry iron ore briquette properties is shown in figures (4-5) . From which it is clear that increase pressing pressure leads to an increase both the drop damage resistance (drop number of briquette) and compressive strength of green and dry briquettes. Increasing these properties may be due to the fact that lime increased the coagulation between particles and improved the specific area of the mix, which subsequently resulted an increase in the growth of formed briquettes thus increasing the briquettes strength .

3.2. Compressive strength of fire high barite briquette at 700^{o}C-1200^{o}C

Fig 6 show the Compressive strength of fire high barite briquette at 700^{o}C-1200^{o} C .from this figure it is evident that the compressive strength increased as the temperature of fired sample increase.

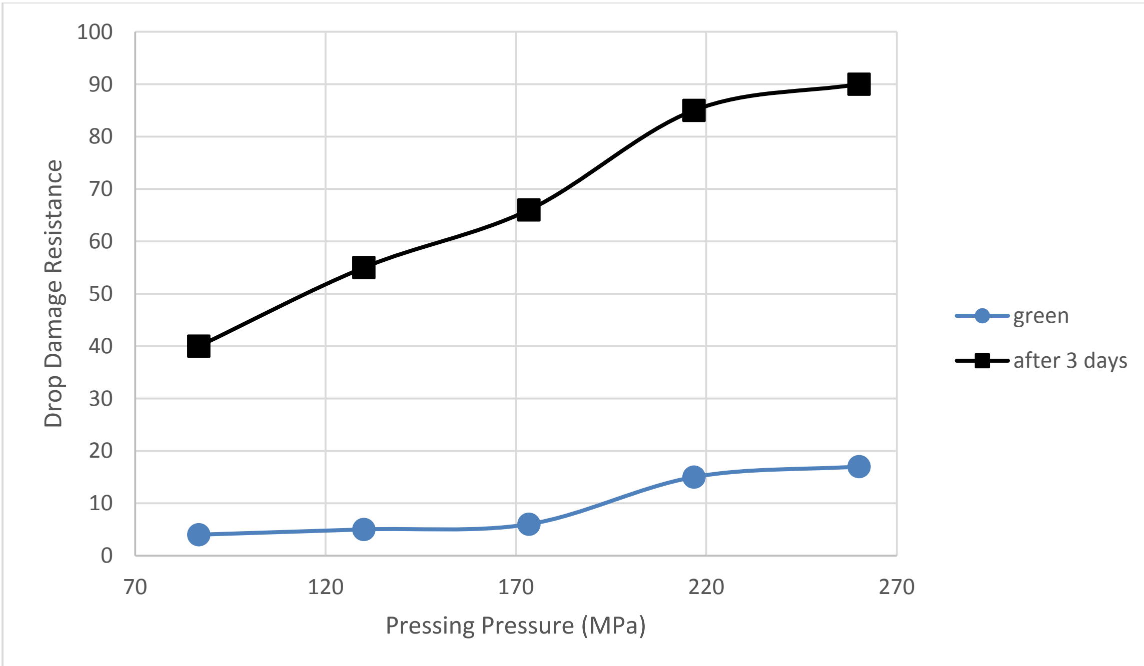


Fig. 4 Relation between drop number of wet and dry briquette and pressing pressure

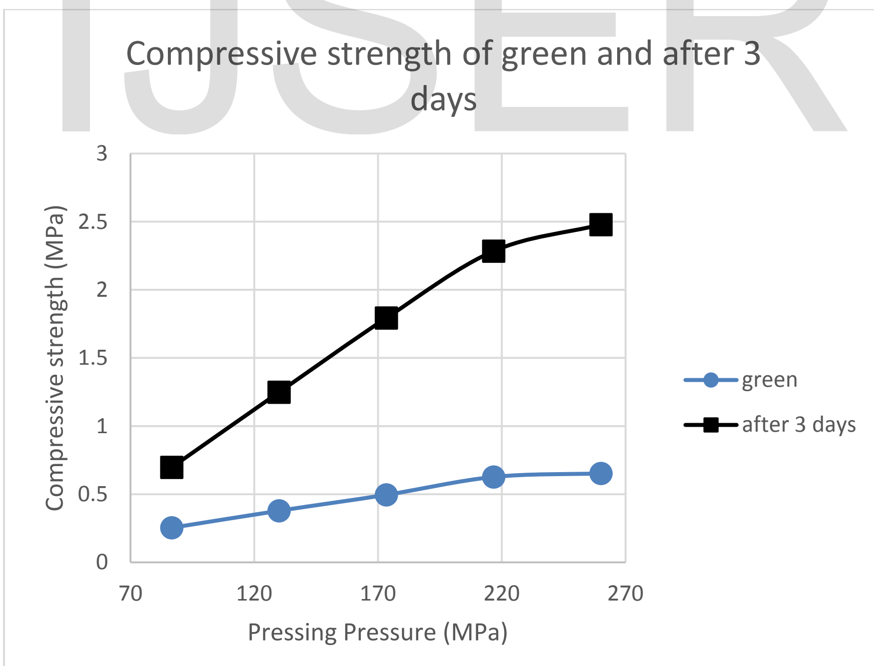


Fig 5 . Relation between strength of wet and dry briquette and pressing pressure

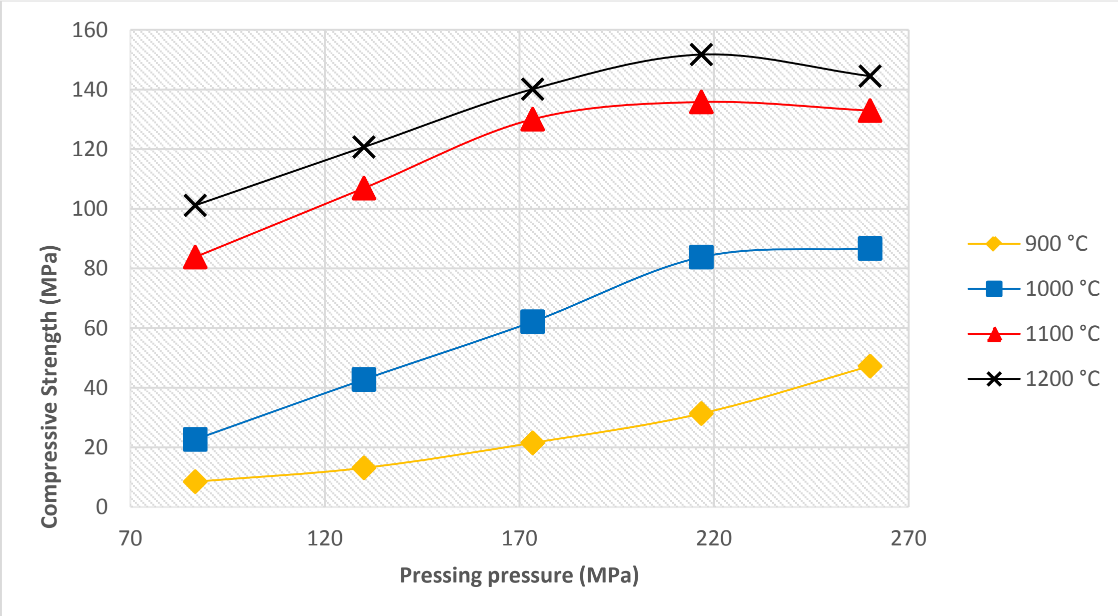


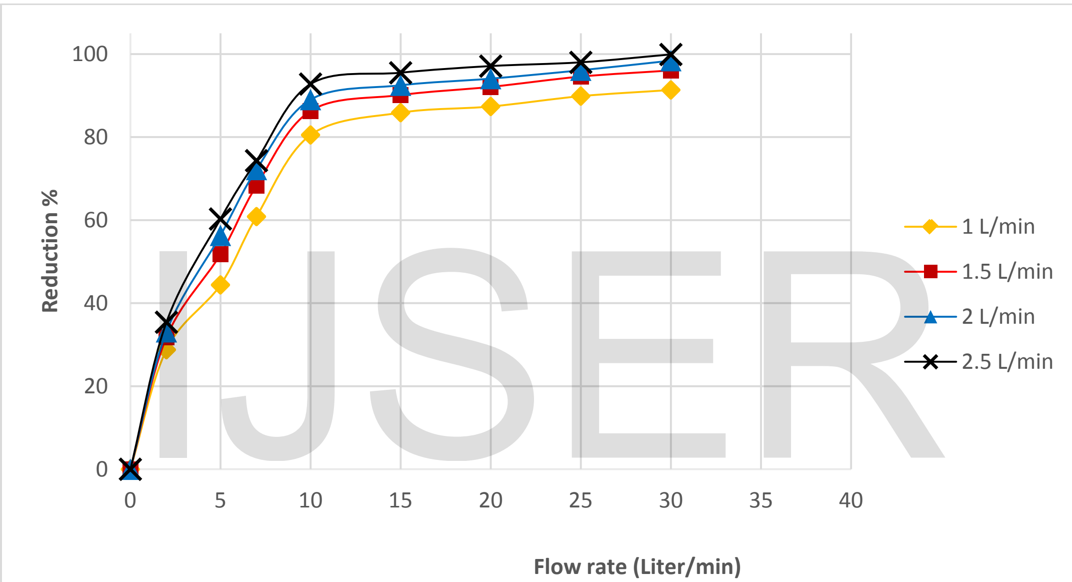
Fig 6 The Compressive strength of fired high barite briquette at 700oC-1200o C

3.3 Effect of Hydrogen flow rate

Fig,7 illustrate relation between reduction percentage and hydrogen flow rate .From figure 7 it is clear that as flow rate of hydrogen increase the reduction percentage increase.

3.4. Reduction of high barite briquette

Reduction was carried out at different temperatures ranging from 700˚C to 1000˚C, keeping the briquette weight and hydrogen flow rate constant (1.5 $L.min^{-1}$). The results of the investigation are shown on Figure 8, where it is obvious that an increase of temperature favors the reduction rate. These curves, relating the reduction percentage to time, show that for each single reduction curve the rate of reduction of iron ore briquette was highest at early stages then decreased as the time of reduction increased. The increase of reduction percentage with temperature is normally due to increase of number of reacting molecules having an excess energy (13-15) besides increasing the rate of mass transfer of the diffusion, rate of desorption and rate of chemical reaction (13-16)



Fig,7 Relation between reduction percentage and hydrogen flow rate

3.5. Kinetic of reduction of high barite iron ore **briquette**

Figure 9 illustrates the relation between (R+(1-R)ln(1-R) against time of reduction for different reduction temperature(800 -850C^{O}). 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 Figures 10 from which it is clear that briquette has activation energy = 22.12 kJ/ mole.

3.8-Conclusions:

From the obtained results, the following can be concluded:

1. Increase the pressing pressure leads to an increase both the drop number and compression strength of the green, dried and fired briquette.
2. Reduction of the briquettes formed increased applying a higher hydrogen flow rate.
3. The activation energy calculated for this process for the briquettes formed using equation **kt=R+ (1-R)ln(1- R)** is = 22.12kJ/ mole

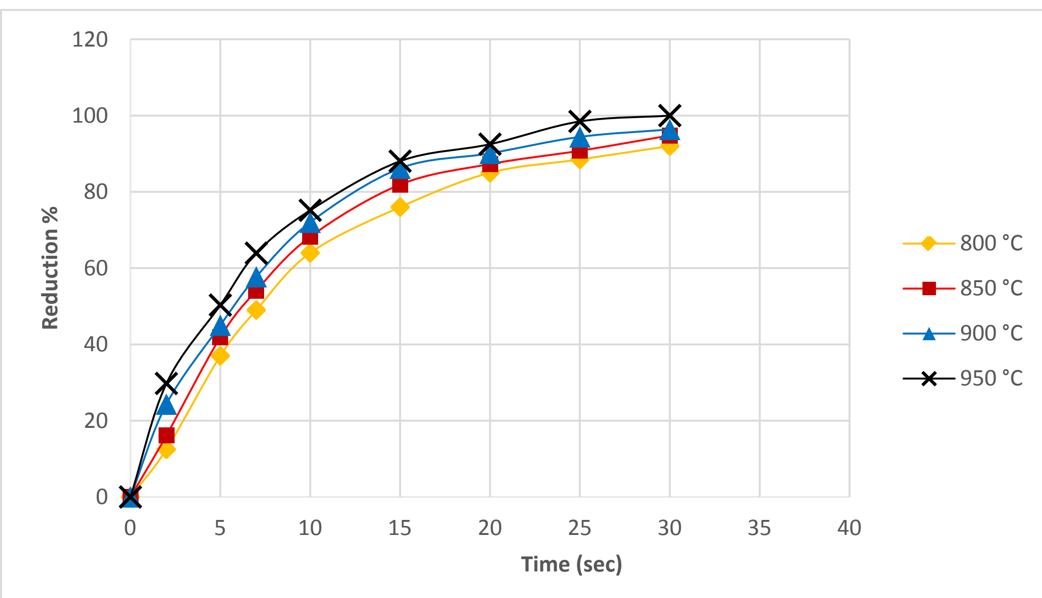


Fig. 8.Schematic diagram of **Reduction percentage at 800, 850, 900, 950 °C**

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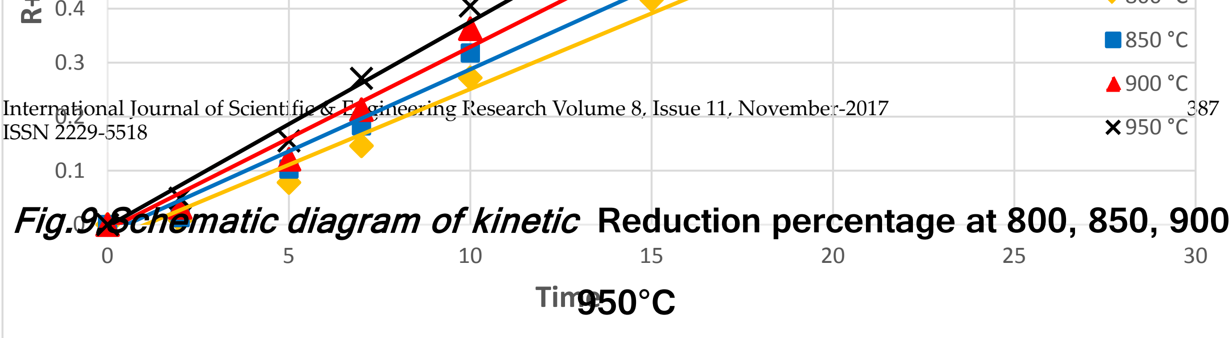

Fig.9 Schematic diagram of kinetic **Reduction percentage at 800, 850, 900, 950°C**

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

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