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Kinetics reduction of El-Baharia iron ore (Egypt) via coke breeze

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Abstract: Kinetics reduction of El-Baharia iron ore via solid coke breeze briquettes in nitrogen atmosphere were investigated at different temperatures ranging from 700˚C to 1050˚C. It was found that the best reduction properties were found at 1050˚C, so the kinetic models were determined. Also the main crystalline phases of reduced briquettes at 1050˚C were metallic iron (syn. Fe).

Keywords: Iron ore, coke breeze, Reduction Kinetics, briquettes. Metallic iron

I-Introduction

Iron ores have been reduced in the solid state in a variety of reactors such as retorts, shaft furnaces, rotary kilns and fluidized beds to produce Direct Reduced Iron (DRI) [1].

Bryk and Lu [2] studied the reduction behavior of commercial magnetite concentrate and carbon mixture in the temperature of 900-1300 °C. They concluded that the reaction kinetics was affected by furnace temperature, heat transfer, particle size of coal, coal: ore ratio and the type of reducing agent.

Sun [3], indicated that The rate of the overall reaction of iron ore oxide with carbon increases with the increase of several experimental parameters such as furnace temperature, carbon/ iron oxide ratio, reactivity of carbon, and specific surface of both iron oxide and carbon.

Reijiro et al. [4] ,studied reaction rates for the reduction of iron oxide, the gasification of coke and the thermal decomposition of the binder in oxidized iron-scrap briquettes containing pulverized coke under the conditions of increasing and fixed temperatures in the nitrogen atmosphere. They indicated that the weight decreases in the reduction reaction of the briquette in the temperature range of 1270 to 1500 K. and the results showed high reaction rate at higher temperature and the retardation of reaction rate at later stage of reaction. In iron making system, carbon acts as reductant which removes the combined oxygen from iron oxides as well as the fuel and it reacts with molecular oxygen to generate heat .The reduction of iron oxide in iron ore-carbon mixture [5-7] in a retort is used for making high quality sponge iron for decades. Carbon reacts with O2 and CO2 as the intermediate reactants to form CO as the reductant. In the overall reaction of hematite reduction by carbon, there are five solid phases i.e. Hematite(H),Magnetite (M),Wustite (W),Metallic Iron (Fe) and Carbon (C), and the gaseous phase.

Ünal et al [8] studied the production of sponge iron by direct reduction of oxides and the effect of reductants on metallization and they concluded that (i) direct reduction using both solid and gas reductants caused higher metallization compared to using only solid reductants, (ii) as the reduction time and ratio of fixed C/Fe total increase, reduction percentage of ore increased.

Hashem et al [9], found that the reduction of iron ore by coal was: (1) increased with increase in stochiometric amount of coal (up to certain value 1.75), temperature and time.

(2) The reduction reaction follows either by model:,

$$R+ (1-R)\ln(1-R) = kt \quad \text{or} \quad - \ln (1-R) = kt$$

(3) The value of activation energy in the temperature range 973-1223 K are = 68.411 k J/mole or 81.024 kJ/mole.

Gaballah et al [10] indicated that the reduction rates of mill scale by coke breeze increased with increasing temperature and at high reduction temperatures (more than 900 and up to 950°C), with increasing temperature, the oxygen removal increased and the activation energy of this reaction ≈ 61.5 kJ/mole for reduction of mill scale with coke breeze in the form of briquettes with 2% molasses, where chemical reaction at interface is applicable.

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The aim of this work is reduction of Egyptian iron ore by coal to determine the model of reaction and the activation energy for reduction in the form of briquette.

2- Experimental Work

2.1. Materials and sample characterization

El-Baharia iron ore samples was supplied by the Egyptian Iron and Steel Company, The chemical composition of iron ore is as follows:- Fe total ; 52.35 %, MnO; 2.92%, SiO_2; 10.84%, CaO; 0.39%, MgO; 0.18%, Al_2O_3; 1.44% , S; 0.74%, TiO_2; 0.16% , BaO; 1.17%, ZnO; 0.15%, K_2O; 0.27%, Na_2O; 0.25%, P_2O_5 ; 0.5 % [9].

The chemical composition of coke breeze used contains 84.75 % fixed carbon, 1.25% volatile matter, 14% ash. About 96.5% of the coke breeze fines used in this work have size in range -0.25 + 0.125 mm.

The X- Ray analysis of El-Baharia iron ore and coke breeze are illustrated in figures 1 and 2. From which it is clear that El-Baharia iron ore mainly consists of hematite and quartz. While the X- ray analysis of coke breeze mainly consists of carbon and quartize [11]

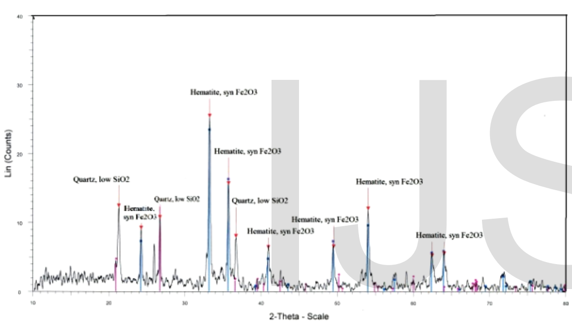

Fig. 1. X-ray of iron ore

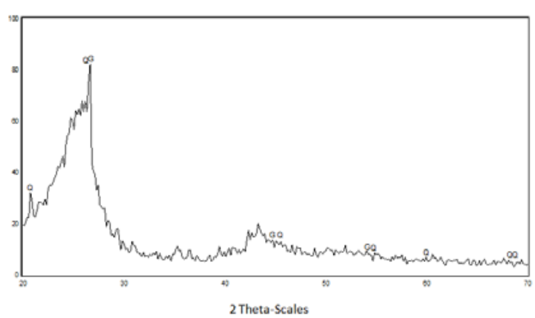

Fig.2. X-ray of coke breeze.
G: - Graphite Q: - Quartz SiO_2

2.2 Preparation of the briquettes and its physical properties

The preparation of samples for the briquetting process was carried out by the grinding iron ore with different stoichiometric ratios of coke breeze in a vibrating mill to powder with size less than 75 μm. The stoichiometric ratios of carbon to convert all Fe_2O_3 to Fe, is according to the following equations:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \qquad (1)$$

10 grams of the mixture of iron ore with different stoichiometric coke breeze with 2% molasses binder was pressed under pressure; 196.133 Mpa in the mould (12 mm diameter and a height 22 mm using MEGA.KSC-10 hydraulic press). Fig.3[10]

The stoichiometric amount of carbon

$$(X) = Y.Z/100 \qquad (2)$$

Where Z = Stoichiometric amount of coke breeze
Y = Percentage of carbon in coke.

The produced briquette subjected to drop damage resistance test and compressive strength tests. The drop damage resistance indicates how often green briquette 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 where the number of drops is determined for each briquette. The arithmetical average values of the crumbing behavior of the ten briquettes yield the drop number. The average compressive strength is done by compressed 10 briquettes between parallel steel plates up to their breaking [12-15].

Fig.3. MEGA.KSC-10 hydraulic press

2.3. Reduction process

The reduction of iron ore with coke breeze was done in a thermo balance apparatus. (a schematic diagram of thermo balance apparatus is shown in figure 4 and present in references[10- 11, 16- 18]. It consisted of a vertical furnace, electronic balance for monitoring the weight change of 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 (950, 975, 1000, 1050 ºC) and maintained constant to ± 5 °C. Then samples were placed in hot zone. The reduction experiments were carried out using an inert atmosphere (0.5 l/min nitrogen in all experiments). 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 equations:-

Percentage of reduction = (W_o-Wt/)x 16/28x Oxygen (mass) --------------------- (1)

Where:

W_0: the initial mass of sample after removal of moisture, gm.

Wt: mass of sample after each time, gm.

Oxygen (mass): indicates the mass of oxygen percent in the sample in form Fe_2O_3.

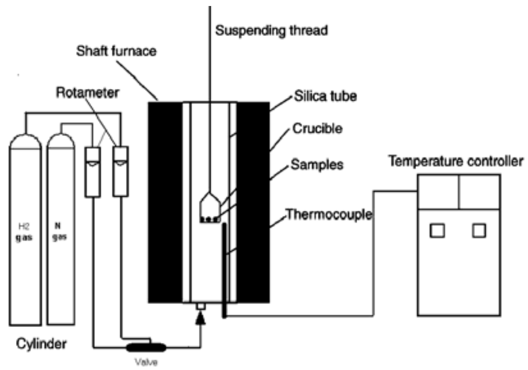

Fig.4 Schematic diagram of the reduction apparatus

3-Result and Discussion

3.1. Effect of stoichiometric amount of coke breeze on the physical properties of the produced briquette

Figs 5 and 6 illustrate the effect of stoichiometric amount of coke breeze in the mixture with iron ore on the drop number and strength of the briquette of iron ore and coke breeze mixture with 2 % molasses. From these figures it is clear that the drop number of the briquettes and its strength decreased as the amount of coke breeze increased.

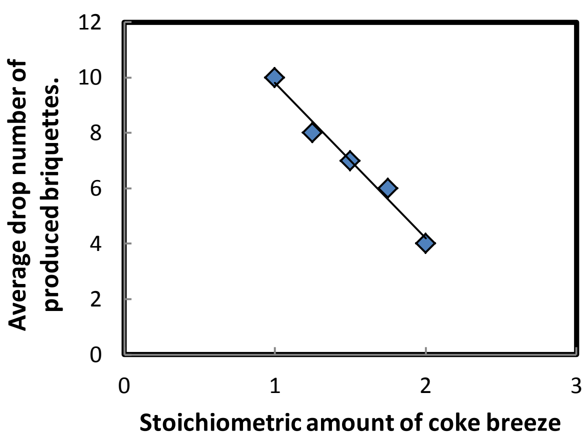

Fig. 5 Effect of the amount of coke breeze on the drop no. of the briquette consists of mixture iron ore with coke breeze.

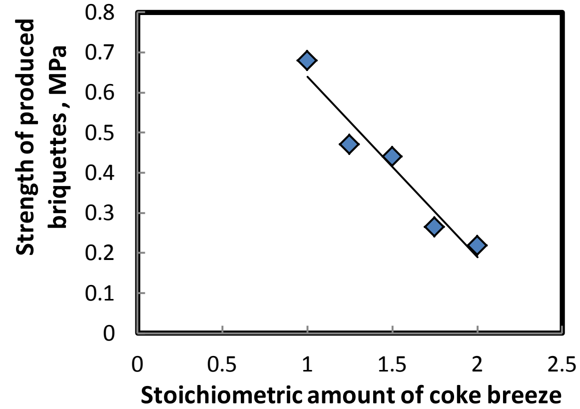

Fig. 6 Effect of the amount of coke breeze on the strength of the briquette consists of mixture iron ore with coke breeze

3.2. Effect of stoichiometric amount of coke breeze on the degree of reduction of iron ore briquettes

From Fig 7 it is clear that at 950 °C, there is not much difference in reduction at time up to 30 min. after which the reduction increases as stoichiometric amount of coke breeze increased. Also it is clear from the same figure that the reduction increases with increase in time.

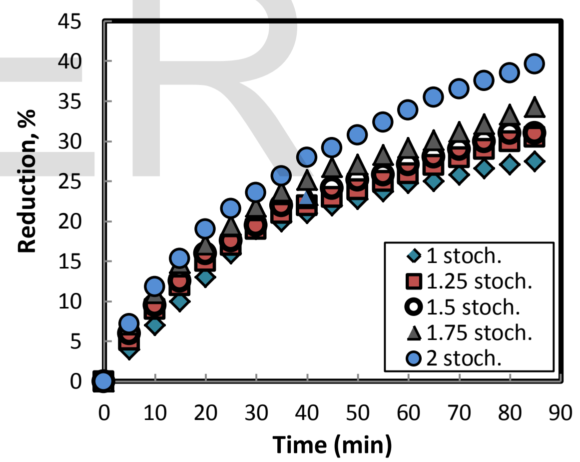

Fig.7 Effect of stoichiometric amount of coke breeze on the reduction of iron ore at 950°C

3.3. Effect of temperature on the reducibility of iron ore briquettes

The reduction was carried out at different temperatures ranging from 700 to 1050°C, where the weight of the briquette and the stoichiometric of coke breeze to iron ore; 2 were constant and the nitrogen flow rate 0.5 liter/min. The results of the reduction investigation at temperature range 950 to 1050 °C are shown in Fig.8. From this figure, it is clear that with increase in temperature of the reduction of the briquette, the percentage of reduction increases with the increase in time. The increase of reduction percentage

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with rise of temperature may be due to the increase of number of reacting moles having excess energy which leads to the increase of reduction rate [11, 19- 23].

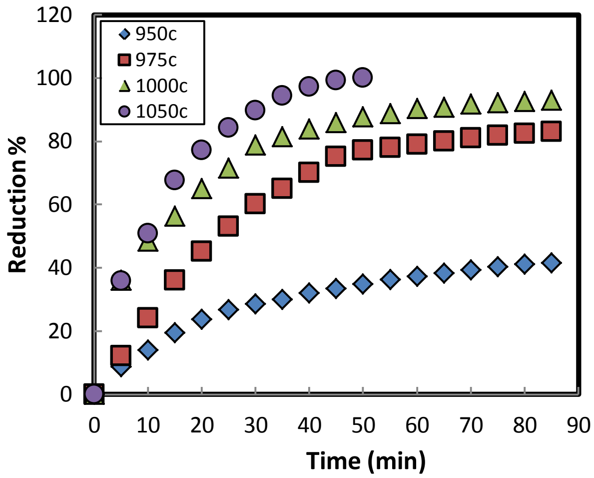

Fig.8. Effect of temperature on the degree of reduction of the briquette consists of mixture of iron ore with coke breeze

3. 4. Reduction Kinetics

Kinetic studies for estimation of apparent activation energies were carried out for El-Baharia iron ore with coal briquettes at four different temperatures of 950ºC, 975ºC, 1000ºC and 1050°C for different time intervals in the range of 5 – 85 minutes.

The following models have been used to interpret experimental results demonstrated in Fig. 9.

1) When chemical reaction controls the following equation is used [24].

$- \ln (1-R) = kt$ Chemically Controlled (2)

Where: R is fractional reduction.

t is time of reduction and k is the rate constant.

The results show that this model gave fair straight lines at all temperatures (as shown in Fig.9); the slopes of these straight lines gave the constant rate for each reduction temperature.

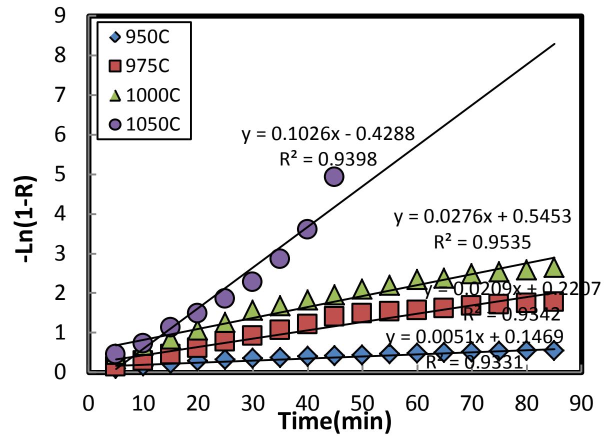

Fig.9 Relationship between [- ln (1-R)] and reduction time of briquette consists of mixture of iron ore with coke breeze.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction by using the calculated rate constant *k*.

$k = k_o \exp - E/RT$ (3)

$\ln k = \ln k_o - E/RT$ (4)

Where k_o is the coefficient; *E* is the apparent reduction activation energy; *R* is the universal gas constant [8.314 × 10−3 kJ/(mole ·K)]; T is the absolute temperature. The relationships between the natural logarithm of reduction rate constant and the reciprocal of absolute temperature for iron ore briquettes are shown in Figure 10 from which it is clear that briquette has activation energy = 381.53 kJ/mole.

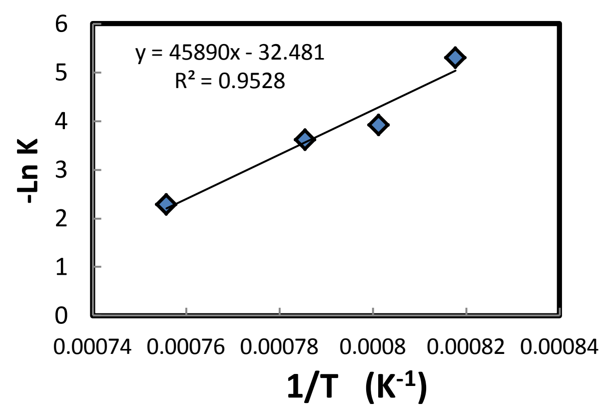

Fig.10 the relationship between the natural logarithm of reduction rate constant and the reciprocal of absolute temperature

2- Using the model .R+(1-R)ln(1-R) =kt which present in reference [25]

Where *R* is fractional reduction, *t* is time of reduction, *k* is the rate constant.

Fig.11 illustrates the relation between R+ (1-R)ln(1-R) against time of reduction for different reduction

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temperature. From which it is clear that the relationship is represented by straight line.

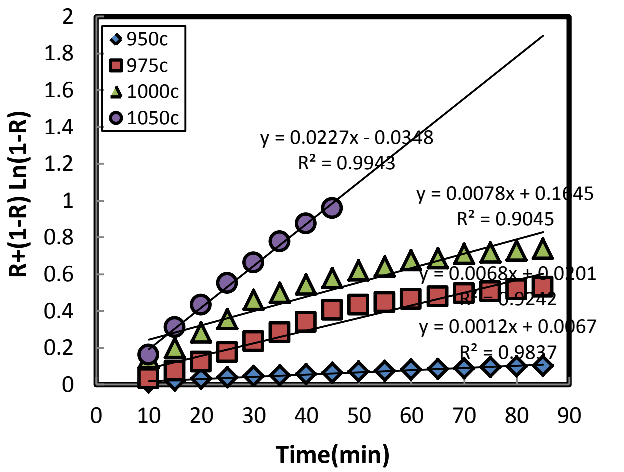

Fig. 11 Relationship between [R+(1-R)ln(1-R)] and reduction time of briquette of iron ore with coke breeze.

The relationships between the natural logarithm of reduction rate constant and the reciprocal of absolute temperature for iron ore briquettes are shown in Figure 12, from which it is clear that briquette reduction under the previous condition has activation energy = 378.42 kJ/mole.

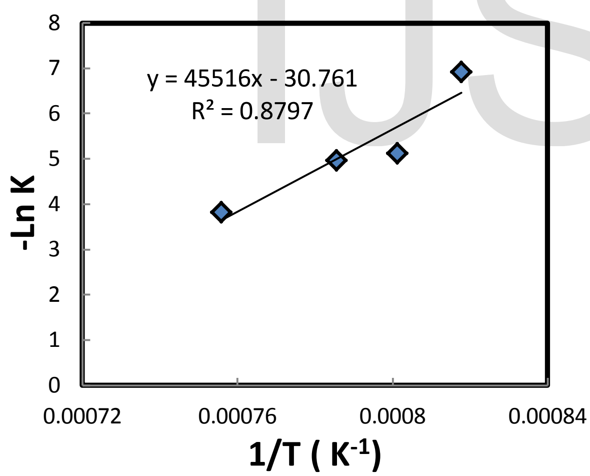

Fig.12 The relationships between the natural logarithm of reduction rate constant and the reciprocal of absolute temperature

3.5. X-ray Analysis of Sample Reduced by Coke Breeze at 950 °C and 1050 ºC.

Figs. 13-14 illustrate x-ray analyses of a reduced iron ore briquette contain in stoichiometric amount of 2; coke breeze in nitrogen atmosphere at (950°C and 1050ºC). Fig.13, from which it is clear that the reduction of iron ore by coke breeze at 950ºC not completed reached to 100% metallic iron and the sample contain iron, quartz, hematite and magnetite. While Fig .14 which shows the X-ray analyses of the briquette reduced at 1050 ºC contains high percentage of iron and hematite.

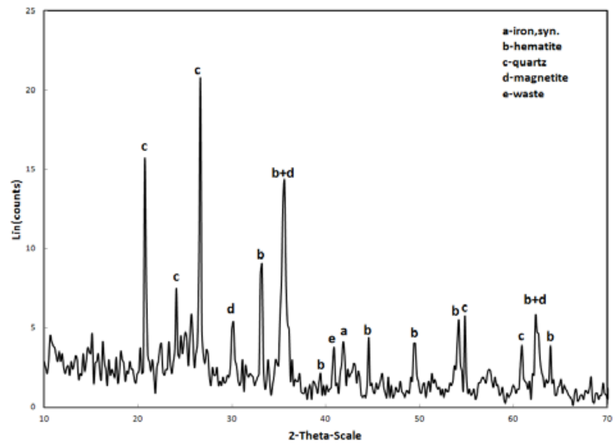

Figure13. XRD analysis of reduced iron ore by coke breeze briquettes at 950°C

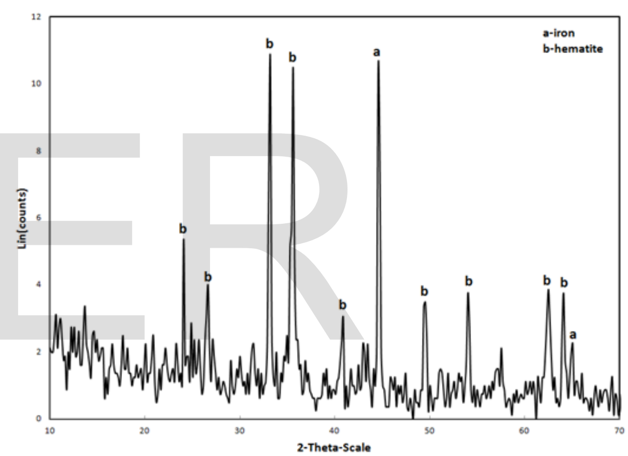

Figure14. XRD analysis of reduced iron ore by coke breeze briquettes at 1050°C

4-Conclusions

Based on the results of the reduction of iron ore by coke breeze briquettes in nitrogen atmosphere obtained the following conclusions have been drawn:,

(1) Degree of reduction increases with increase in stochiometric amount of coke breeze up to 2, temperature and time of reduction.

(2) The reduction reaction follows either by these models

1) - ln (1-R) =*kt*

or 2) R+ (1-R) ln (1-R) = kt

(3) The value of activation energy in the temperature range 950 – 1050 ºC are = 381.53 kJ/mole for model (1) or 378.42 kJ/mole for model (2).

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