Reduction Kinetics of Egyptian Iron Ore by Non Coking Coal

Nagwa Mohamed Hashem (1) , Bahaa Ahmed Salah (1), , Naglaa Ahmed El-hussiny(2) , Said Anwar Sayed (1) , Mohamed Gamal Khalifa (3) . Mohamed El-Menshawi Hussein Shalabi (2) *

Chemical department , Faculty of Science , Helwan University , Cairo , Egypt

Central Metallurgical research and Development Institute, (CMRDI), Cairo , Egypt

El-Tabbin Metallurgical Institute, Cairo, Egypt

*Corresponding another , shalabimeh@hotmail.com

Abstract: Reduction kinetics of El-Baharia iron ore by solid coal briquettes in 0.5 liter/min nitrogen flow rate were investigated at different temperatures ranging from 700˚C to 950˚C. It was found that the best reduction properties were found at 950˚C, so the kinetic models were determined. Also the main crystalline phases of reduced briquettes at 950˚C were metallic iron (syn. Fe),.

1-Introduction

Iron is believed to be the tenth most abundant element in the universe, and the fourth most abundant in the earth's crust. Iron is the most used of all the metals, comprising 95% of all the metal tonnage produced worldwide. Iron is extracted from its ore, and is almost never found in the free elemental state. In order to obtain elemental iron, the impurities must be removed by chemical reduction (1).

Several investigators (2-5) attempted to the rates of true "direct" reduction, viz., the solid-solid reaction between iron oxide and carbon, by continuous evacuation of the chamber in the overall temperature range of 700 to 1150 ºC and pressure range of $5(10^{-4}-10^{-2})$ ton. They assumed that the gas phase was substantially eliminated by evacuation and hence the rates obtained represented those of solid-solid reaction while Rao (6), who employed inert gas flushing when coal is heated to char, a substantial weight loss occurred because of the evolution of volatile matter (7).

The kinetic aspects and the effect of process variables on the reduction of mill scale by coal were studied at four different temperatures from 900 to 1050 ºC, particle sizes from 0.51 to 2.03 mm, coal/mill scale ratios from 0.5 to 1.00, and bed depths from 25 to 51 mm. The kinetic data of reduction fit the Ginstling-Brounstein kinetic model. The activation energy for the reduction was found to be 147 kJ mol^{-1}. Within the range of variables studied an increase of reaction temperature and coal/mill scale ratio results in a high reduction rate, whereas an increase of average particle size and bed depth decreases the reduction rate. Optical micrographs of the reduced masses show the distinct appearance of metallic phase and the disappearance of wustite phase with time and temperature (8).

Stanley(1997) (9), 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.

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) (10-11).

Ladin et al (2002) (12) found that higher reduction rates were attained by utilizing coke powder, where another form of solid waste produced in integrated plants, as compared to the use of graphite powder. With increasing temperature, the degree of reduction was increased, so in comparison, equal degrees of reduction were obtained in low reduction times. In order to reach a high degree of reduction, the temperature should be higher than 1000 ºC. For the economics of the process and from the environmental point of view, the reduction should be carried out at the optimum time and Cfix /Fe total ratio.

Sandeep and Barun (2008) (1) indicated that the percentage of reduction of iron ore by char coal or coal increased with increasing the fixed carbon content of reductant, increase in temperature and increase in time, increases the percentage of reduction while less in the activation energy of reaction; more will be the extent of reduction. The kinetic model of the reaction was Chemically Controlled. i.e. $-\ln(1-f) = Kt$

Konishi et al.(2008) (13) studied the effect of residual VM on reduction of iron oxide in composite pellet and concluded that the VM have an important role in the reduction at low temperatures.

Abdul Wahab and Sahar (2009) (14) investigated the reducibility of AL-HUSSAINIYAT pisolitic iron ore (Iraq iron ore) with coke and some alkali carbonate additives ,the experimental results show that, reduction temperature, reduction time and additive amount substantially influence the reducibility and higher degree of reduction was accordingly yielded. The best results were obtained at 5% additive at 1000°C .The effect of additives was found in the following order: $CaCO_3 > K_2CO_3$.

Sinha et al (2014) (15), indicated that the reduction of iron ore fines (Size -212 μ + 75 μ, having about 65% Fe content) with non coking coal fines Size -212μ, Ash 22.4%,VM 24.1%)show the following results ::

(1) Degree of reduction increases with increase in Fe_2O_3 : C ratio, temperature and time. Maximum degree of reduction was observed at Fe_2O_3 : C ratio of 1:1.75 .

(2) The reduction reaction follows first order shrinking core model for mono sized particle: - $1-(1-f)^{1/3} = K\,t$

(3) The value of activation energy in the temperature range 900-1050 ºC is 203.2 KJ/mole.

Man et al (2014) (16) observed that the reduction rate of iron ore with coal increased obviously as the temperature raised and the particle size decreased. The reaction activation energy increased from 53.04 kJ /mol to 131.72 kJ /mol when the particle size of iron ore increased from 38μm to 163μm. The increase of activation energy means the decrease of reacting moles which lead to the decrease of adsorption rate. Also increasing activation energy means that the mass diffusion and chemical reaction become more difficult.

Hemmati et al (2015) (17) concluded that a reduction degree of 45% was obtained by utilizing VM in a non-isothermal heating condition up to 950ºC. Reduction of iron oxide by VM at a multilayered array was influenced by thermodynamics and kinetics of the iron oxide reduction. Devolatilization of the non-coking coal and the reduction of the iron oxide are both thermal activated processes which can be greatly affected by heat transfer. It can be concluded that the most probable rate-controlling step in both volatilization of the coal and reduction of the iron oxide by VM is the heat transfer to the materials.

The aim of this work is reduction of Egyptian iron ore by coal to determination the model of reaction and determination 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 %.

The chemical analysis of coal used in this experiments is as follows :- fixed carbon 58 %, Volatile mater 25 % , ash 16.5% , and water 0.5 %.

The X- Ray analysis of El-Baharia iron ore and coal 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 coal mainly consists of carbon and quartize

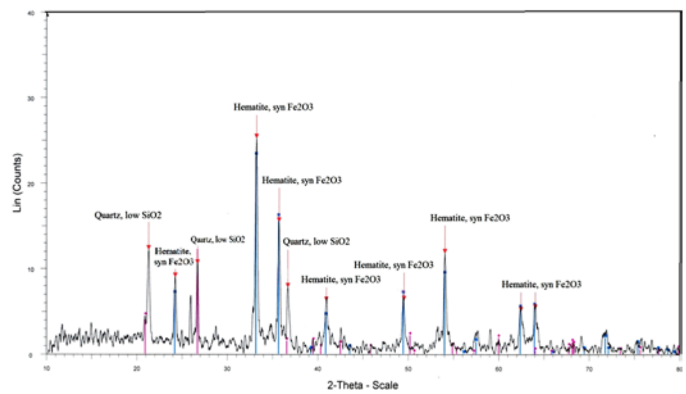

Fig.1. X-ray analysis of El-Baharia iron ore

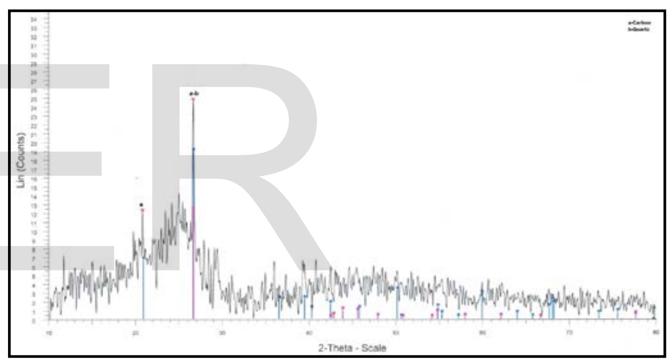

Fig 2 x-ray of coal

2.2 Preparation of the briquettes and its physical properties

The iron ore and coal is grinded in a vibrating mill to powder with size less than 75 μm. The mixture of iron ore with certain amount of coal powder (10 g) are pressed under pressure = 196.133MPa in the mould (12mm diameter and height 22 mm) using MEGA.KSC-10hydraulic press Fig.(3)(18).

The 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. 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 (18-19).

Fig.3 MEGA.KSC-10 hydraulic press.

2.2. Reduction process

The reduction of iron ore with carbon was done in a thermo balance apparatus. (A schematic diagram of thermo balance apparatus is shown in figure 4 (20 -21), 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 (650-950 °C) and maintained constant to ± 5 °C. Then samples were placed in hot zone. The nitrogen flow rate was 0.5 l/min in all the experiments during the 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 equations:-

Percent of reduction= (Wo-Wt/) x 16/28x Oxygen (mass) ---------(1)

Where:

W0: the initial mass of sample after removal of moisture.

Wt: mass of sample after each time, t.

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

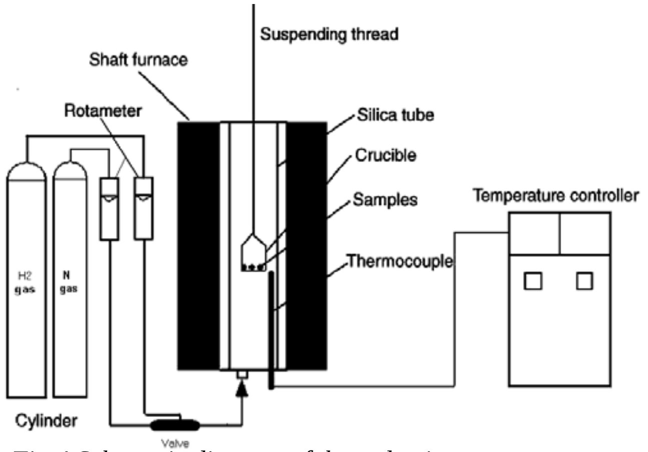

Fig.4 Schematic diagram of the reduction apparatus

3-Result and Discussion

3.1. Effect of stoichiometric amount of coal on the physical properties of the briquette

Figs 5 and 6 illustrate the effect of amount of stoichiometric amount of coal on the drop number and strength of the briquette if iron ore and coal mixture. From this figures it is clear that the drop number decreased as the amount of coal increased while the strength increased with rise of coal.

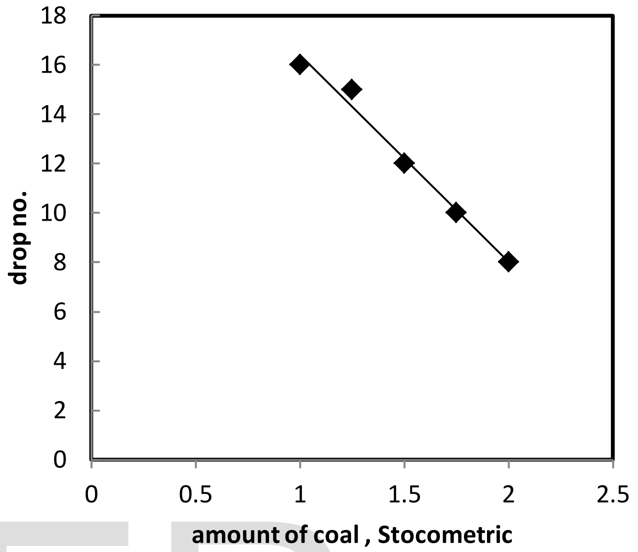

Fig.5 Effect of stoichiometric amount of coal on the drop number of the briquette

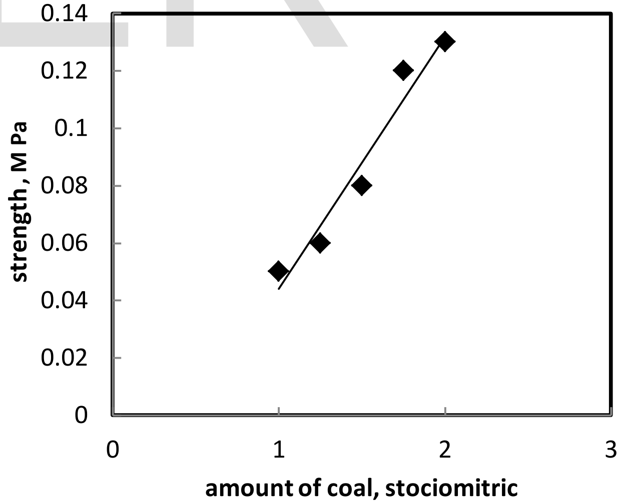

Fig.6 Effect of stoichiometric amount of coal on the strength of the briquette

3-2-Effect of stoichiometric amount of coal on the degree of reduction of iron ore

From Fig 7 it is clear that at 900°C, there is not much difference in reduction at time up to 30 min. this may be due to the reduction done by volatile matter (17) after which the reduction increase as stochometric amount of coal increased up to 1.75 after that the reduction decreased slightly as

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stoichiometric amount of coal increased to 2 , this me be due to the increase of coal decreased the contact of coal with iron ore or it may be due to re-oxidation of freshly reduced iron by carbon dioxide (15) .Also it is clear from the same figure that , the reduction increases with increase in time.

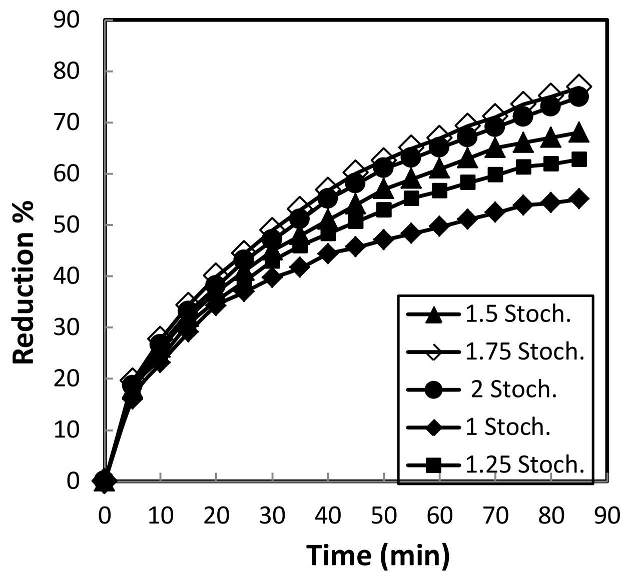

Fig. 7 Effect of stoichiometric amount of coal on the degree of reduction of iron ore

3-3- Effect of temperature of reduction

The reduction was carried out at different temperatures ranging from 700 to 950ºC, where the weight of the briquette and the stoichiometric of coal to iron ore =1.75 were constant and the nitrogen flow rate 0.5 liter/min. The results of the investigation 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 with rise of temperature may be due to the increase of number of reacting moles having excess of energy which leads to the increase of reduction rate (21-22). Also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rate of desorption (23-26).

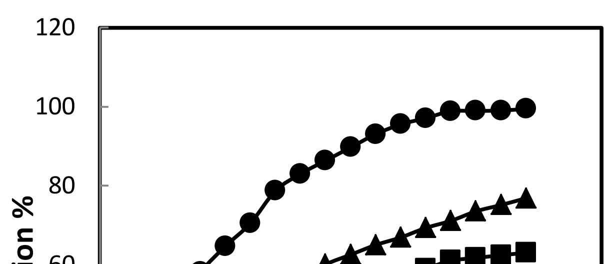

Fig. 8 Effect of temperature on the reduction percentage of iron ore when the amount of coal equal 1.75 stoichiometric amount of coal required completing reduction

3-4- Kinetic reduction

Different kinetic models studies for estimation of apparent activation energies were carried out for El-Baharia iron ore with coal briquettes at four different temperatures of 700˚C, 800˚C, 900˚C and 950˚C for different time intervals in the range of 0 – 85 minutes.

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

Where *R* is fractional reduction, *t* is time of reduction, *k* is the rate constant (27).

Fig.9 illustrates the relation between R+ (1-R)ln(1-R) against time of reduction for different reduction temperature. 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 by using the calculated rate constant *k.*

$k = k_0 \exp - E/RT$ (3)

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

Where *ko* is the coefficient; *E* is the apparent reduction activation energy; *R* is the universal gas constant [8.314×10^{-3} kJ/(mol.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 = 68.411 kJ/mole.

2) By using chemical control Equation [15]
- ln (1-R) = kt Chemically Controlled (5)

Fig.11 illustrates the relation between ln (1-R) against time of reduction for different reduction temperature. From which it is clear that the relationship is represented by straight line. 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 has activation energy = 81.024 kJ/mole.

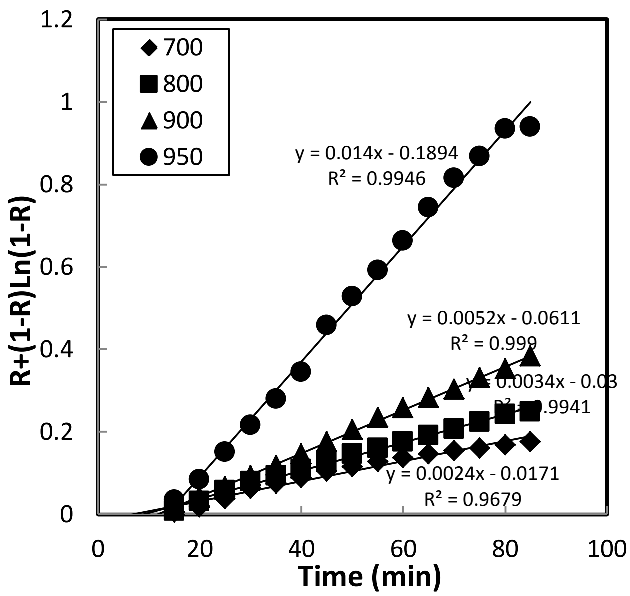

Figure 9 The relationship between time of reduction and R+(1-R) ln (1-R) at different temperature

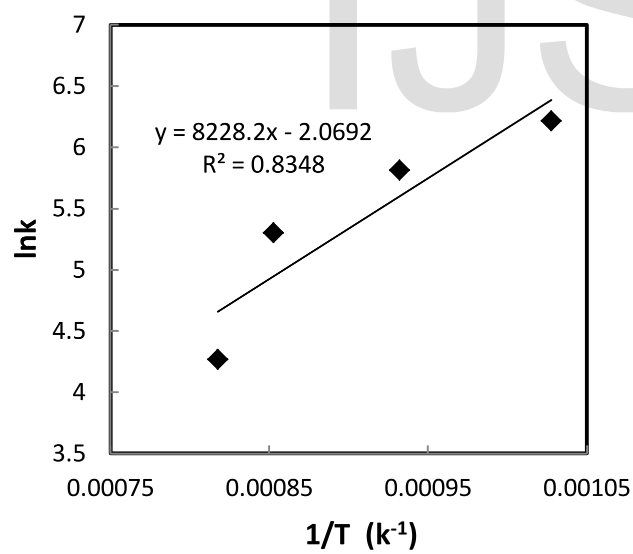

Figure 10. The relation between the reciprocal of absolute temperature $1/T$ and $\ln K$ (Arrhenius plot for reduction reaction) for model R+ (1-R)ln(1-R)= kt

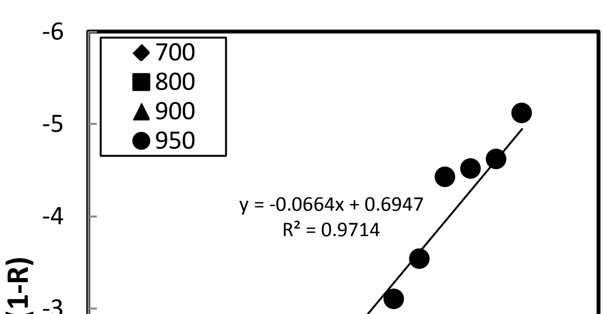

Figure 11 The relationship between time of reduction and ln (1-R) at different temperature

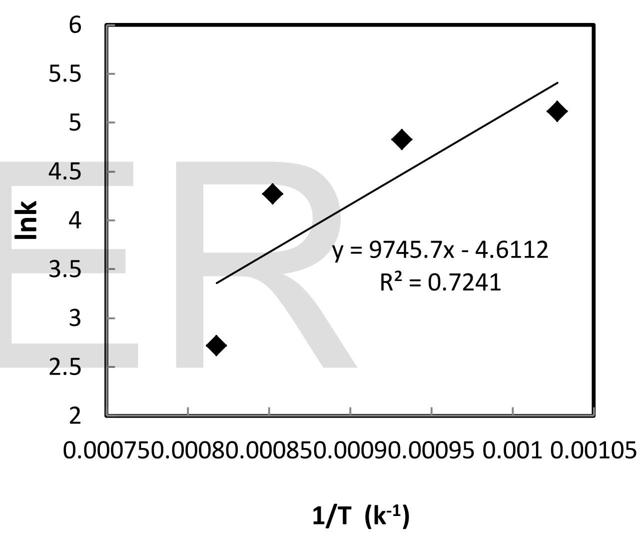

Figure 12. The relation between the reciprocal of absolute temperature $1/T$ and $\ln K$ (Arrhenius plot for reduction reaction) for model - ln (1-R) = kt

1- X-ray analysis of iron ore with coal briquette reduced at 900°C

The X- ray analysis of iron ore with coal briquette reduced at 900oCis illustrated in figure (13). From which it is clear that the briquettes mainly consists of Iron (syn. Fe) and Magnetite (syn. Fe_3O_4).

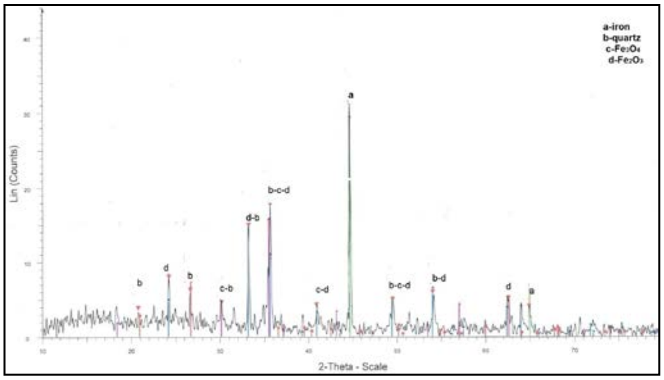

Figure13. XRD analysis of reduced iron ore briquettes at 950˚C

Conclusions

Based on the results obtained and observation made, the following conclusions have been drawn.

(1) Degree of reduction increases with increase in stochiometric amount of coal up to certain value 1.75, temperature and time.

(2) The reduction reaction follows either by this model R+(1-R)ln(1-R) $=kt$ or - ln (1-R) = kt

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

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