ISSN 2229-5518

Reduction Kinetics of El-Baharia iron ore (Egypt) via charcoal

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Abstract— Reduction kinetics of El-Baharia iron ore via solid charcoal briquettes in nitrogen atmosphere were carried out at different temperatures ranging from 700˚C to 950˚C. It was found that the best reduction properties were found at 950˚C, where the kinetic models were determined.

Also the main crystalline phases of reduced briquettes at 950˚C were found to be metallic iron (syn. Fe).

Index Terms— El-Baharia iron ore , charcoal, Reduction Kinetics, briquettes. Metallic iron

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.

Goksel (1981) [1] indicated that the SR-pellets are produced when carbon is incorporated in the mixture with iron ore and binders. Then an internal solid-solid reduction occurs according to the following general reactions :

Fe,O, + 3C - --------------2Fe + 3CO

Fe,O, t 3CO-------------- 2Fe + 3C0, (secondary reaction)

Charcoal has been used as a source of thermal energy since the beginning of the steel industry in Brazil [2]. Charcoal is used in the production of metallic iron from ore. Due to non-existence of sulphur in its composition, charcoal improves the quality of pig iron and steel produced. This phenomenon allows the steel industry to command attractive prices, Today, Brazil produces about 10 million tons of pig iron using charcoal; 60% are exported, generating an income of US$ 2.0 billion per year.

Kris , [3] indicated that the use of charcoal as a fuel for iron manufacturing declined in Canada between 1870 and 1890 only to increase again between 1890 and 1913. Although this old method of iron manufacture is generally believed to have become obsolete in North America during the mid nineteenth century, it survived in Canada at the end of the nineteenth century because the price of charcoal declined the technology of smelting improved. Charcoal iron manufacturers successfully responded to the challenge of the late nineteenth century by adapting for their own use a series of innovations pioneered by the competing technologies of coke manufacture and coke iron smelting.

Attempts to innovate and develop direct reduction methods using solid reductants have become an important prime in iron making. The main goal of these attempts is to replace the current polluting methods with more environment-friendly ones. Several studies have been carried out to investigate the use of wood and coal as solid reductant for iron oxide [4, 5]. In addition to the environmental consequences, however, their low performances challenge the applicability of these methods [6]. Since volatile matter (VM) of coal is a source of pollution, its utilization decreases environmental problems while contributes to the process of reduction of iron oxide. Potential reducing ability of VM can be particularly effective at lower temperatures [7]. When coal is heated, a substantial weight loss occurs because of the evolution of volatile matter [8]:

Coal ---------------Coal char + Volatile Matter (hydrogen, water, hydrocarbons)

Sandeep and Barun (2008)[9] concluded that the percentage of reduction of iron ore increased with increase in temperature and time, because this increase in temperature and time increased the rate and quantity of diffusion and chemically controlled reactions included in the mechanism of step wise reduction of iron ore pellets. Use of charcoal increased the percentage of reduction of pellets as compared to coals, because of higher fixed carbon content of charcoal. The activation energy for the reduction of pellet by coal was found to be more than that of in case of charcoal. This indicates that the reduction of pellet starts at a lower temperature for charcoal as compared to the coal and the extent of reduction in case of charcoal will be higher. They also indicated that, the increase in fixed carbon content of reductant increases the percentage of reduction and less is the activation energy of reaction; more will be the extent of reaction.

Kazuta et al , (2013) [10]indicated that the charcoal have higher reactivity and less strength than coke and utilization of charcoal as substititon for nut coke is effective and realistic..

Gireesh (2014)[11] concluded that in carbon type reductant, the volatile matter present, fixed carbon value and moisture content present are playing key role for in the reduction process.

Hemmati et. al (2015)[12] reported that reduction degree of 45 percent 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 affect Yokota, Jun Okazakid 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 charcoal 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%, SiO2; 10.84%, CaO; 0.39%, MgO; 0.18%, Al2O3; 1.44% , S; 0.74%, TiO2; 0.16% , BaO; 1.17%, ZnO; 0.15%, K2O; 0.27%, Na2O; 0.25%, P2O5 ; 0.5 % [13].

The chemical composition of charcoal contains 65.26 % fixed carbon, 24.88% volatile matter, 9.86% ash and sulphur % 0.13

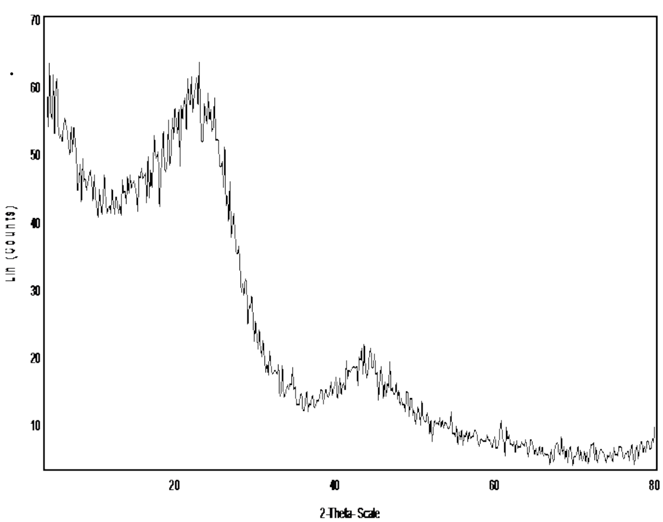

Fig.2. X-ray of charcoal

The X- Ray analysis of El-Baharia iron ore and charcoal 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 charcoal has amorphous structure [14].

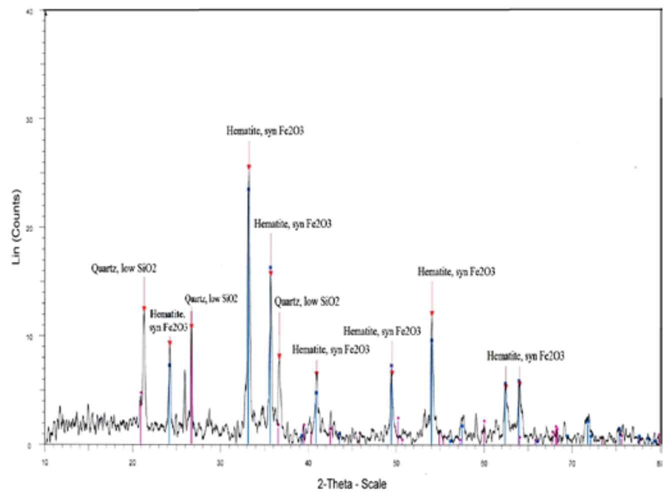

Fig. 1. X-ray of iron ore

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 charcoal in a vibrating mill to powder with size less than 75 µm. The stoichiometric ratios of carbon to convert all Fe2O3 to Fe is according to the following equations:

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

10 grams of the mixture of iron ore with different stoichiometric amount of charcoal

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 [14]

The stoichiometric amount of carbon

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

Where Z = Stoichiometric amount of char coal

Y = Percentage of carbon in char coal

The produced briquette was 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 [15-18].

Fig.3 MEGA.KSC-10 hydraulic press.

2.2. Reduction process

The reduction of iron ore with char coal was done in a thermo balance apparatus. (a schematic diagram of thermo balance apparatus is shown in figure 4 and postulated in references [13- 14, 19- 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 (700-950 °C) 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 = (Wo-Wt/)x 16/28x Oxygen (mass) --------------------- (1)

Where:

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

Wt: mass of sample after each time, t, g.

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

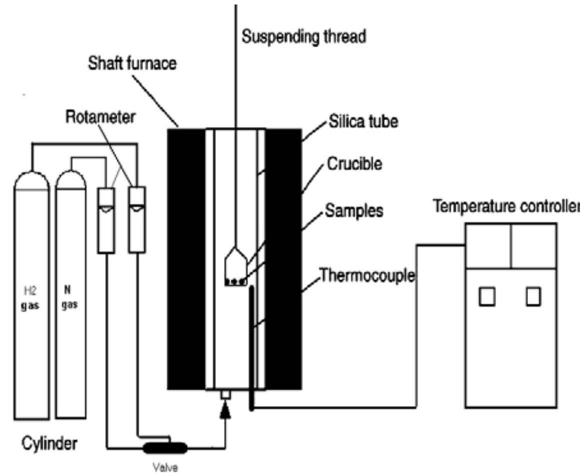

Fig.4 Schematic diagram of the reduction apparatus

3-Result and Discussion

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

Figs 5 and 6 illustrate the effect of stoichiometric amount of charcoal in the mixture with iron ore on the drop number and strength of the briquette of iron ore and charcoal 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 charcoal increased .

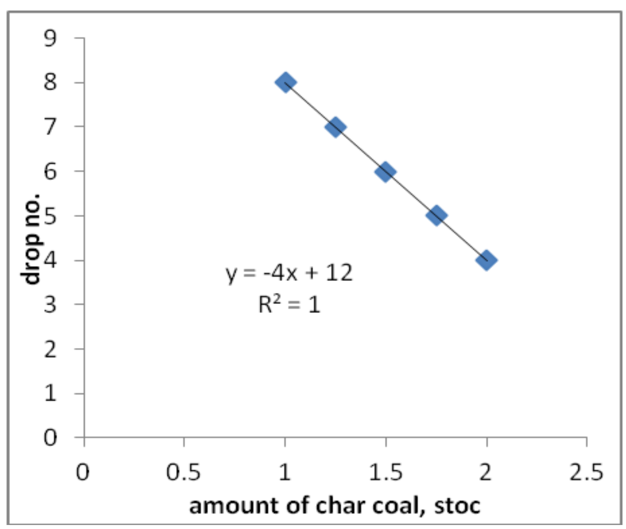

Fig. 5 Effect of the *stoichiometric* amount of charcoal on the drop No. of the briquette of mixture iron ore with charcoal

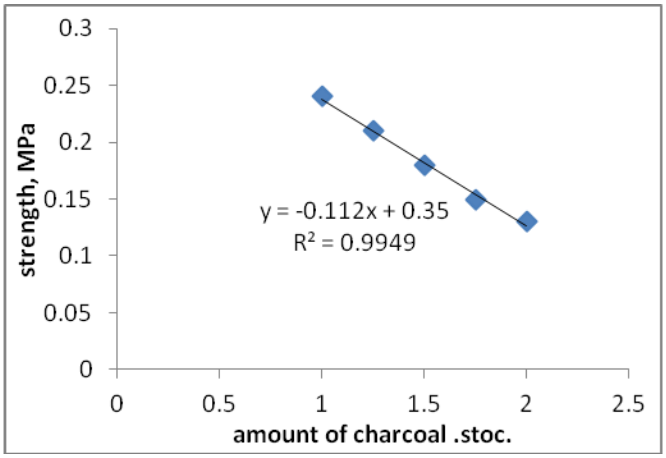

Fig. 6 Effect of the *stoichiometric* amount of charcoal on the strength of the briquette of mixture iron ore with charcoal

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

From Fig 7 it is clear that at 900oC, the reduction increases as stoichiometric amount of char coal increased Also it is clear from the same figure that , the reduction increases with increase in time.

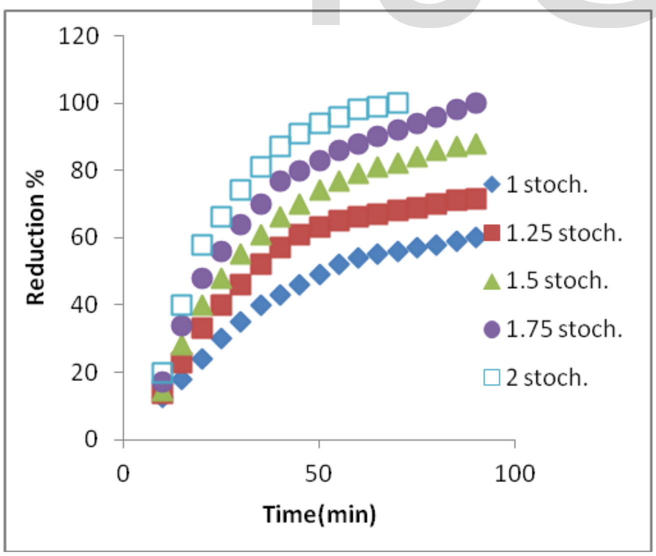

Fig.7 Effect of stoichuometric amount of charcoal on the reduction of iron ore at 900oC

3-3- Effect of temperature of reductio*n*

The reduction was carried out at different temperatures ranging from 700 to 950oC,where the weight of the briquette and the stoichiometric of char coal to iron ore ; 2 was constant and the nitrogen flow rate 0.5 liter/min. The results of the reduction investigation at temperature range 700oC to 950 oC 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 energy which leads to the increase of reduction rate [14, 22- 26].

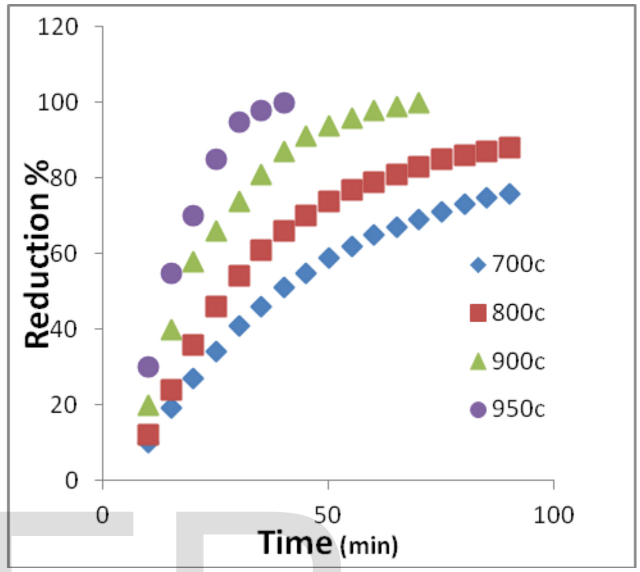

Fig. 8.Effects of temperature on the degree of reduction of the briquette of iron ore with charcoal.

3. 4 Reduction Kinitics

Kinetic studies for estimation of apparent activation energies were carried out for El-Baharia iron ore with char coal briquettes at four different temperatures of 700°C, 800°C 900°C and 950 oC 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.

When chemical reaction controls the following equation is used.

- ln (1-R) = kt Chemically Controlled [9] (2)

Where R is the fraction reduction and k is the rate constant

Where: R is fractional reduction.

t is time and k is 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.

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 = k0 exp- E /RT (3)

lnk= lnko- 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

ISSN 2229-5518

between the natural logarithm of reduction rate constant and the reciprocal of absolute temperature for iron ore briquettes reduced by char coal are shown in Figure 10 from which it is clear that briquette has activation energy = 2796.9 kJ/mole.

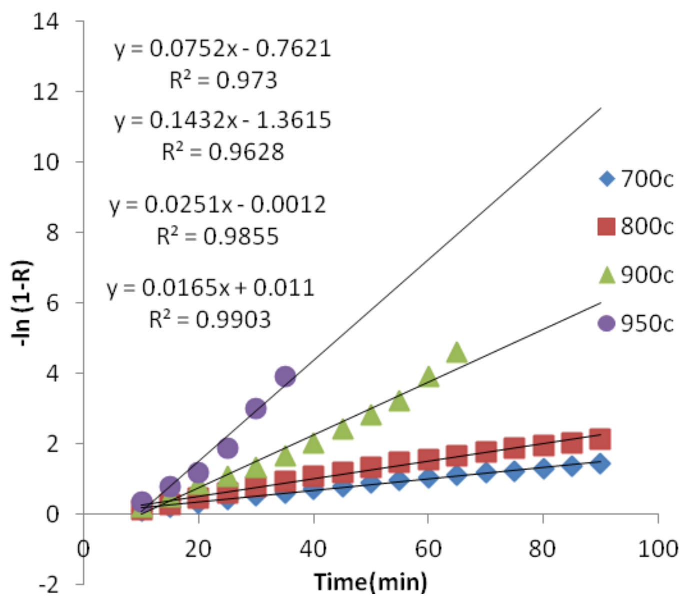

Fig.9 Relation between -Ln (1-R) and time of reaction

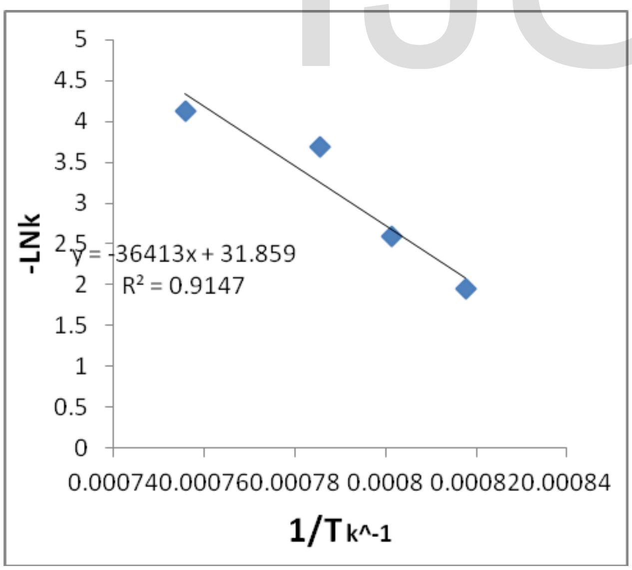

Fig.10 The relationships between the natural logarithm of reduction rate constant and the reciprocal of absolute temperature

2- The using the model .R+(1-R)ln(1-R) =kt [27]

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 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 reduction undr the previous condition has activation energy = 2640.8 kJ/mole.

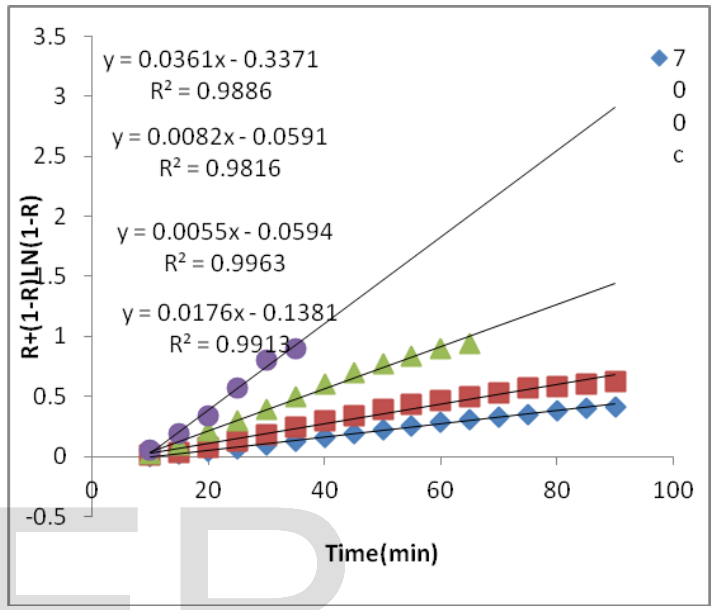

Fig. 11 Relationship between [R+(1-R)ln (1-R)] and reduction time of briquette of iron ore with charcoal

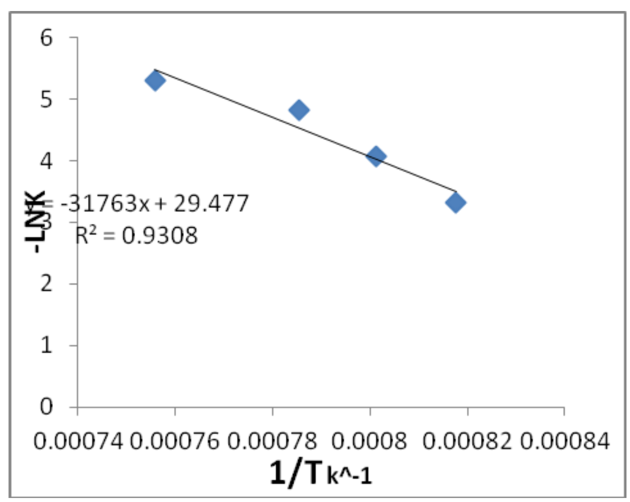

Fig.12 the relationships between the natural logarithm of reduction rate constant and the reciprocal of absolute temperature

4.6. X-ray Analysis of Sample Reduced by charcoal at 900oC

Fig. 13illustrates x-ray analyses of a reduced iron ore briquette contain 2 stoichiometric amount of char coal in nitrogen atmosphere at (900oC). From which it is clear that the reduction of iron ore by char coal at 900oC not completed reached to 100% metallic iron and the sample stay contain hematite and, magnetite

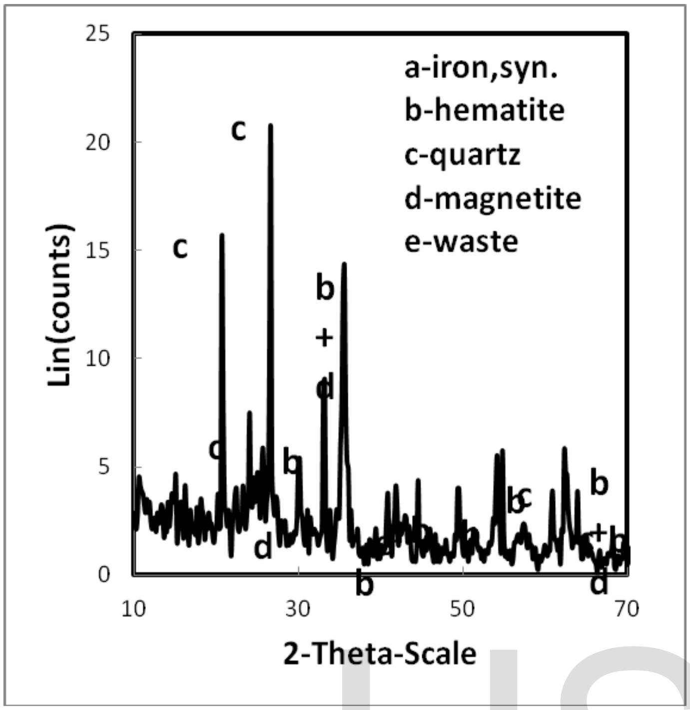

Figure13. XRD analysis of reduced iron ore by charcoal briquettes at 900˚C

CONCLUSIONS

Based on the results of the reduction of iron ore by char coal briquettes in nitrogen atmosphere obtained the following conclusions have been drawn.

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

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

(3) The value of activation energy in the temperature range 700-950 oC are =2640.8 kJ/mole or 2796.9 kJ/mole.

REFERENCES

1- Goksel M. A., Agglomeration, ASM, Vol. 1, Chap. 52, 877, 1981

2- *Luiz Augusto Horta Nogueira; Suani Teixeira Coelho & Alexandre Uhlig, Criteria and indictors for sustainable wood fuels* , Sustainable charcoal production in Brazil *case studies from Brazil,Guyana, Nepal, Philippines and Tanzaniam , PP 1-46.*

3- **Kris E. Inwood, The Decline and Rise of Charcoal Iron: The Case of Canada, BUSINESS AND ECONOMIC HISTORY, Second Series, Volume Fourteen, 1985., 237-243**

4- Fortini, O., "Renewable energy steelmaking: On a new process for ironmaking", (2004).

5- . Gupta, R., "Woodchar as a sustainable reductant for ironmaking in the 21st century", ***Mineral Processing Extractive Metall. Rev.***, Vol. 24, No. 3-4, (2003), 203-231.

6- . Shivaramakrishna, N., Agrawal, B., Ray, A., Prasad, K., Bandopadhyay, P. and Gupta, S., "Production of high carbon sponge iron from ore--coal composite pellets", ***Transactions of the India6-n Institute of Metals***, Vol. 43, No. 2, (1990), 91-101.

7- . Dey, S.K., BISWANATH, J. and Basumallick, A., "Kinetics and reduction characteristics of hematite-noncoking coal mixed pellets under nitrogen gas atmosphere", ***ISI J international***, Vol. 33, No. 7, (1993), 735-739.

8- Sampaio, R., Coal devolatilization in bath smelting slags, (1990), Carnegie Mellon University PhD thesis, Pittsburgh.

9- Sandeep Kumar Baliarsingh & Barun Mishra , Kinetics of iron ore reduction by coal and charcoal , A Thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Technology in metallurgical and materials Engineering , Department of Metallurgical and Materials Engineering. National Institute Of Technology. 769008 , 2008

10- Kazuya Kunitom , Ko-ichiro Ohamd , Kyohei Yokota , Jun Okazaki , Tsunehisa Nishimura , Satoshi Kogure, Reduction behavior of iron oxide using woody biomassm IEAGHG/IETS iron &steel Industry , CCUS & Process Inegration workshop , Nov.7.2013

11- V. S. Gireesh , V. P. Vinod, S. Krishnan Nair, Georgee Ninan , Ilmenite Reduction Studies Using charcoal and Petroleum Coke as Reductant , Indian Journal of Advances in Chemical Science 2(4) (2014) 275-27

12- M. H. Hemmati , J. Vahdati Khaki , A. Zabett , An Investigation on Devolatilization of Non-coking Coal and Non-isothermal Reduction of Iron Oxide, IJE TRANSACTIONS A: Basics Vol. 28, No. 1, (January 2015) 109-114
13- Naglaa.A.El-Hussiny, ,Ahmed.A. Khalifa , Ayman.A. El-Midany , Ahmed.A.Ahmed , Mohamed.E.H.Shalabi ,(February-2015) , Effect of replacement coke breeze by charcoal on technical operation of iron ore sintering International Journal of Scientific & Engineering Research, 6, 2, 681 -686.
14- N. M. Gaballah , A. A. F. Zikry, N. A. El-Hussiny, M. G. El-D. Khalifa, A. El-F. B. Farag, M. El-M. H. Shalabi. (2015) , Reducibility Mill Scale Industrial Waste Via Coke Breeze at 850-950 °C, *Science of Sintering*, 47 103-113
15- . K. Mayer, "Pelletization of Iron Ores", Springer-Verlag Berlin Heidelberg, (1980).
16- S.P.E. Forsmo , A.J. Apelqvist , B.M.T. Björkman , and P.O. Samskog (2006)., “Binding mechanisms in wet iron ore green pellets with a bentonite binder”, Powder Technology 169 , p. 147-158.
17- S.P.E. Forsmo , P.O. Samskog , and B.M.T. Björkman , (2008),”A study on plasticity and compression strength in wet iron ore green pellets related to real process variations in raw material fineness”, Powder Technology 181, p. 321-330.
18- Naglaa Ahmed El-Hussiny ,Inass Ashraf Nafeaa ,Mohamed Gamal Khalifa , Sayed Thabt.Abdel-Rahim,Mohamed El-Menshawi Hussein.Shalabi, (February-2015) .” Sintering of the Briquette Egyptian Iron Ore with Lime and Reduction of it via Hydrogen”, International Journal of Scientific & Engineering Research, 6, 2, 1318-1324
19- N.A. El-Hussiny . and M.E.H. Shalabi , (2011),”A self-reduced intermediate product from iron and steel plants waste materials using a briquetting process.”, Powder Technology. 205; 1–3 : p. 217–223.
20- N.A. El-Hussiny, M.E.H. Shalabi,(2012) ” Studying the Pelletization of Rosseta Ilmenite Concentrate With Coke Breeze Using Molasses and Reduction Kinetics of Produced Pellets At 800-1150 °C.”, Science of Sintering, p. 113-126.
21- Naglaa Ahmed El-Hussiny, Atef El-Amir , Saied Thabet Abdel-Rahim, Khaled El hossiny, Mohamed El-Menshawi Hussein Shalabi , Kinetics of Direct Reduction Titano-magnetite Concentrate Briquette Produced from Rossetta-Ilmenite via Hydrogen, OALibJ | August 2014 | 1 | e662, 1-11
22- M.E.H. Shalabi ,(1973) .Kinetic of reduction of El-Bharia iron ore and its sinter, M.Sc.thesis, El-Tabbin Metallurgical Institute for higher studies Cairo, Egypt,
23- M.E.H. Shalabi , O.A. Mohamed , N.A. Abdel-Khalek , and N.A. El-Hussiny , “The influence of reduced sponge iron addition on the quality of produced iron ore sinter”, proceeding of the XXIMPC, Aachen, 21-26 September 1997. pp 362-376.\
24- S.A. Sayed , G.M. Khalifa , E.S.R. El-Faramawy and M.E.H. Shalabi (2002) Kinetic Reduction of Low Manganes Iron Ore by Hydrogen. *Egyptian Journal of Chemistry*, 45, 47-66.
25- H.H.A. El-Gawad , M.M. Ahmed , N.A. El-Hussiny and Shalabi, M.E.H. (2014) Kinetics of Reduction of Low Grade SinaiManganese Ore Via Hydrogen at 800-950˚C. *Open Access Library Journal*, 1, e427.
26- S.A. Sayed , G.m. Khalifa , E.S.R. El-Faramawy and M.E.H. Shalabi , (2001) Reductions Kinetic of El-Baharia Iron Ore in a Static Bed. *Gospodarka Surowcami Mineranymi*, 17, 241-245. (*VII International Mineral Processingn Conference*, Szczyrk, 17-19 September 2001)
27- H. S. Ray, (1993) “Kinetics of metallurgical reactions”, Oxford & IBH Publ. C o . pp 22-24, 53-59