Pelletization of El-Dekhila iron oxide waste and reduced it by hydrogen gas

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Abstract -Reduction of El-Dekhaila iron oxide waste in the form pellets was done in the temperature range 700 to950 °C. In reduction kinetics study the most satisfactory model was done to take the slope of the initial linear region of fractional reduction vs. time curve as a measure of rate constant (k). In k vs. 1/T plots were straight line from which Activation Energy was calculated.

Key words - Pellets of El-Dekhaila iron oxide waste , Reduction of pellets by hydrogen . kinetic reduction model, energy of activation

1. INTRODUCTION

El-Dekhaila iron Co. imported the pellets from the outside of Egypt, during the transportation from outside to Company, a lot of fine (waste pellets fine) formed, this fine was not suitable for the reduction inside the furnace of reduction [1].

Hydrogen has been proven to be a good reductive agent as well as an environment-friendly material because it uses innocuous H2O as its reducing product [2–5].

Hsin-Yu Lin et al [6] indicated that when hematite ore used by H_2as the reduction agents , the two-stage reduction was observed: Fe_2O_3 was reduced to Fe_3O_4 and then reduced to metallic Fe. The activation energy for the two reduction steps of iron oxide are 89.13 and 70.412 (kJ mol^{-1}), respectively , and the reduction models are unimolecular model for $Fe_2O_3 \rightarrow Fe_3O_4$ reduction and two-dimensional nucleation according to Avarmi–Erofeev model for $Fe_3O_4 \rightarrow Fe$.

Damien et al [7] concluded that the reduction of iron ores by hydrogen is a gas-solid reaction which occurs in two or three stages. For temperatures higher than 570°C, hematite (Fe_2O_3) is first transformed into magnetite (Fe_3O_4), then into wustite (Fe_{1-y} O), and finally into metallic iron whereas at temperatures below 570°C, magnetite is directly transformed into iron since wustite is not thermodynamically.

Pineau et al [8] found that the reduction of iron oxides with hydrogen in the temperature range of 200–680 ◦C leads to the following conclusions:

1. The reduction of hematite to magnetite byH2 is characterized by an apparent activation energy of about 76 kJ/mol.
2. The reduction path of magnetite to iron is function of the reaction temperature. At temperatures lower than 420 ◦C, Fe3O4 is reduced directly to iron. At 450 < *T* < 570 ◦C, magnetite and w¨ustite are present with iron. At *T* > 570 ◦C, magnetite is fully reduced to w¨ustite before its reduction to Fe.
3. The apparent activation energy for the reduction of Fe3O4 by H2 decreases from 88 to 39 kJ/mol for temperatures lower and higher than 420 ◦C.
4. Mathematical modeling of experimental data suggest that the controlling mechanism is the two- and three-dimensional growth of nuclei and by phase boundary reaction at higher temperature.
5. The decrease of *E*a around 420 ◦C could be attributed to the annealing of defects of the crystalline structure of magnetite.
6. The reduction rate of magnetite with hydrogen is higher than that obtained with CO.

ASIMA & ITISHREE [9] indicated that with increase in temperature, reduction percentage of iron ore pellets increases and . with increase in time the reduction percentage of pellets increases and Iron ore reduction kinetics follow topochemical reaction nature and the reduction reaction is temperature dependant

Raymond and Leiv [10] indicated that The reduction of wüstite to metallic iron seems to be the limiting stage in the reduction of the iron ore pellets with H2 and CO mixture .

Mohamed et al [11] concluded that the recycling of some iron oxide waste characterized by high iron oxide content such as El-Dekhaila iron oxide pellets waste during the sintering of iron concentrate. The results show that, replacement of iron ore concentrate with 10% iron oxide pellets fine increases the amount of ready made sinter, sinter strength and productivity of both sinter machine and blast furnace yard.

Siyi , et al [12] found that when green pellets of iron ore were prepared by blending iron ore powder with biomass, dolomite and bentonite; and then the green pellets were firstly preheated under oxygen-free atmosphere and then reduced by syngas produced from catalytic gasification of biomass. Heat energy for pellet reduction was provided by biomass combustion. The results showed that the improvement of DRI quality can be achieved by increasing preheating temperature, decreasing pellet size and the addition of dolomite. Under optimum operation conditions

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(900 °C of preheating temperature, 8–10 mm of pellet size), 90.1% total iron and 94.9% metallization rate were achieved .,

Hai-bin et al [13] indicated that: (1) Increasing hydrogen or increasing reaction temperature can accelerate reduction reactions, due to the endothermal reaction of hydrogen
2- Adding just a little CO into the H_2 would decrease the gas effective diffusion coefficient drastically compared with pure hydrogen.
El-Hussiny et al [1] found that: 1- the reduction rates of briquette of El-Dekhaila iron oxide waste increased with increasing temperature of the reduction from 700 up to 950°C.
2- The reduction rate increased with increased of hydrogen flow rate at constant temperature.
3- The diffusion processes through the produced briquettes is the reduction control step and the briquettes have activation energy = 36.12 kJ/ mole.
This work aimed pelletization the iron oxide pellets waste which present in El-Dekhaila iron Co. and reduced it in static bed by hydrogen (hydrogen is best as a reductant from the environmental and reduction kinetics points of view

2. EXPERIMENTAL Work

2.1. Raw Materials

El-Dekhaila waste pellets fine which used in this work was delivered from El-Dekhaila steel Company (Alexandria, Egypt) the chemical analyses of this fine are, Fe total = 66.5%, Fe_2O_3 = 95%, SiO_2 = 1.5% and CaO = 0.7%.. [1].
X-ray of the El-Dekhaila pellets waste fine illustrated in Fig.1, from which it is clear that the main compound of this waste is hematite.[1]

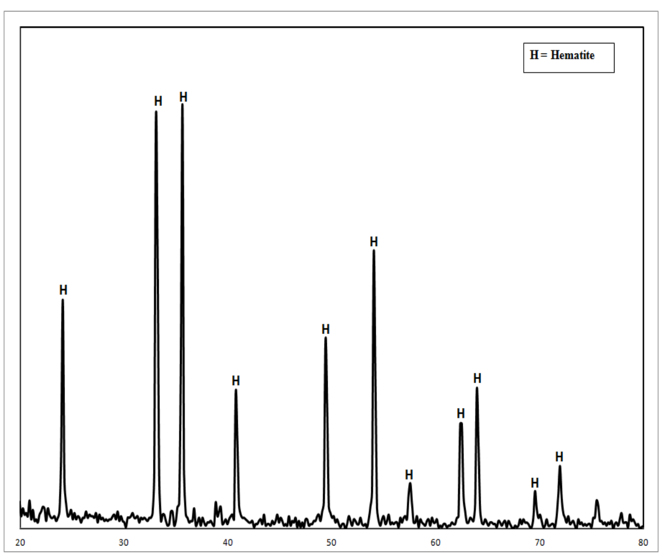

Fig.1. X-ray of El-Dekhela Pellets waste

2.2. Preparation of the Pellets and Its Physical Properties.

El-Dekhaila waste pellets was grinding in vibrating mill to powder with size less than 75 micrometers. After which the pellitization of the El-Dekhila waste pellets were done in a disc pelletizer (Fig.2) of diameter 400 mm, collar height 100 mm , angle of inclination 60 °C, disc rotating speed 17 rpm and residence time 30 min. After the materials were feed to the pelletizer the predetermined moisture amount (8.5% water + 2.5% of molasses) was then sprayed onto the rolling bed of material in the pelletizer. The green pellets in the size range 5-7 mm diameter were screened out to dry in air for 3 day, to ensure the evaporation of all water used during the granulation process.
The green and dried produced pellets subjected to drop number test from 46 cm height and crushing strength tests. The crushing strength test used MEGA.KSC-10 hydraulic press)Fig.3 The drop number indicates how often green or dried pellets can be dropped from a height 46 cm before they show perceptible cracks or crumble. Ten green or dried pellets are individually dropped on to a steel plate. The number of drops is determined for each pellets and the arithmetical average values of the crumbing behavior of the ten pellets yield the drop number .The average crushing strength is done by compressed 10 pellets by MEGA.KSC-10 hydraulic press up to their breaking [14-17].

Fig. 2. Disc pelletizer equipment

Fig.3. MEGA.KSC-10 hydraulic press

2.3. Reduction Procedures

The reduction of El-Dekhaila pellets by hydrogen were done on thermo gravimetric apparatus (A schematic diagram of thermo gravimetric apparatus is shown in Fig. 4 [1,18 -24] It consisted of a vertical furnace, electronic balance for monitoring the weight change of reacting sample and temperature controller. The sample was placed in an Ni –Cr basket which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the required temperature (700-950 ^{o}C) and maintained constant to ± 5 ºC. Thensamples were placed in hot zone. The nitrogen flow rate was 0.5 l/min on all the experiments. at initial time and after the end of reduction only The weight of the sample was continuously recorded At the end of the run, the samples were withdrawn from the furnace and putted in the desiccators. The amount of removable oxygen was determined by the weight loss in the sample (Wo-W) during the experiment of reduction with H_2 in the furnace .The percentage of reduction was calculated according to the following equations [1, 25-26].

Percentage of reduction =(Wo-Wt) x100/ Wo

Where Wo the initial mass of sample after removal of moisture , g.Wt mass of sample after each time, t. Oxygen (mass) indicates the mass of oxygen percent in El-Dekela waste fine in form Fe_2O_3 , g.

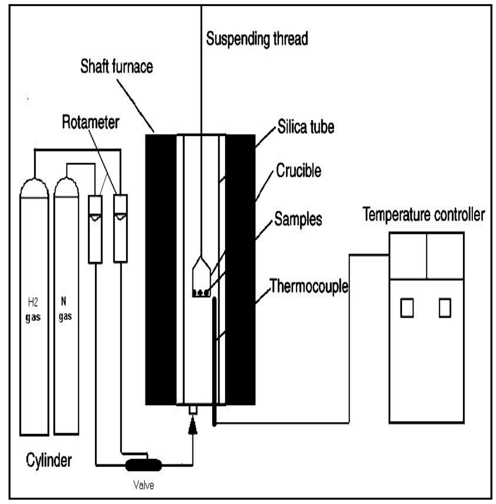

Fig. 4. Schematic diagram of the reduction apparatus

3. RESULTS AND DISSECTIONS

3.1. Quality of the Produced Green and Dried Pellets

The drop damage resistance and compressive strength of the produced green and dried pellets are shown in Table 1 . From this table, it was found that the the drop damage resistance and the compressive strength for green equal 4 and 0.017 MPa respectively while for the dried pellets (drying time 3 day) the drop damage resistance and compressive strength equal to 27 and 0.31MPa respectively

Table.1. Characterization of the produced pellets.

Type of pellets	Green pellets	Dried pellets
Average drop number	4	27
Average crushing strength, MPa.	0.017	031

3.2. Effect of Hydrogen Flow Rate on The Reducibility of The El-Dekhila Waste After The Pelletization at 900 ^{o}C

Fig. 5. shows the effect of different flow rate on the percentage of reduction of the pellets of El-dekhela iron oxide waste when the reduction were done at constant temperature (900°C), and the weight of the sample was constant . . It is clear that as the flow rate of hydrogen increased the reduction percentage increased. This may be due to the fact that increase of flow rate leads to increasing the number of hydrogen moles in the bulk phase, which in turn leads to the raise of hydrogen adsorption. In this way, the rate of reaction increased [24, 27-28] or the increase of flow rate increased the gas diffusion across the boundary layer subsequently increased [24 ,27 -29] . Also may be the higher flow rate prevailing in the reaction zone which enhances the rate of hydrogen absorption and subsequently the rate of chemical reaction steps increased [27,30] .

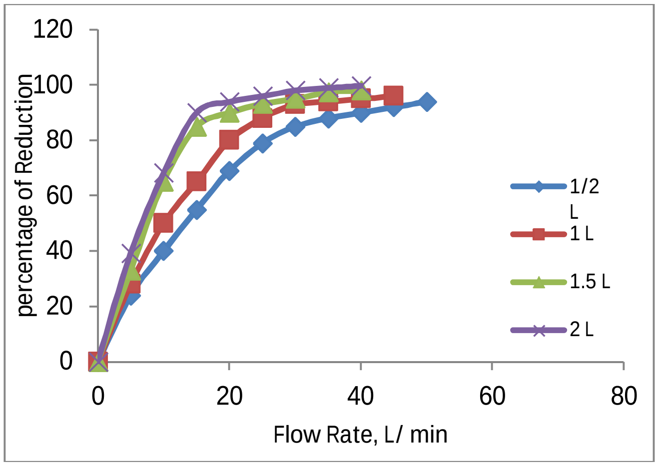

Fig. 5 - Effect of hydrogen flow rate on the reduction of pellet of El-Dekaila waste.

3.3. Effect of Change of Temperature on The Reduction Percentage

In order to examine the effect of temperature on the reduction of pellets of El-Dekhaila waste (5-7 mm) by 2 L/min hydrogen flow rate , experiments were carried out at 700 – 950°C.Plots of the reduction percentage as function of time are shown in Fig. 6. From this figure it is clear that the increase in temperature causes an increase in the extent of reduction as observed previously [1. 31.32]The increase of reduction percentage with temperature could be due to increase number of reacting moles having excess energy which leads to the increase of adsorption rate. Also increasing temperature leads to increase the rate of mass transfer of the diffusion and rate of chemical reaction (1.23.29,30, 33).

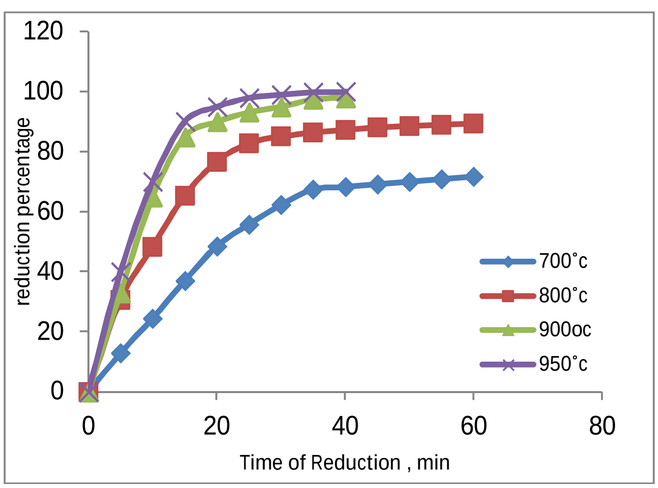

Fig.6. Effect of reduction temperature on the reduction of pellets of El-Dekaila waste

3.4. Kinetics Reduction of Reduction of Pellets of El-Dekhaila Waste

Kinetic studies for estimation of apparent activation energies were carried out for the pellets at different temperatures range from 700˚C up to 950˚C for different time intervals in the range of 0 - 60 min.

Using 1- diffusion process control equation (Jander and Anorg Equation) [1,24, 34-35].

$$[1 - (1-R)^{1/3}]^2 = kt$$

2- Avrami-Erofeev n=1

$$[-\ln(1-R)] = kt$$

Where R is fractional reduction, t is time of reduction, k is the rate constant. Fig.7. illustrate the relation between $[1- (1-R)^{1/3}]^2$ against time of reduction for different reduction temperature . From which it is clear that the straight line was observed.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrate in Fig.8 , from which it is clear that the activation energy= 93.43 kJ/ mole.

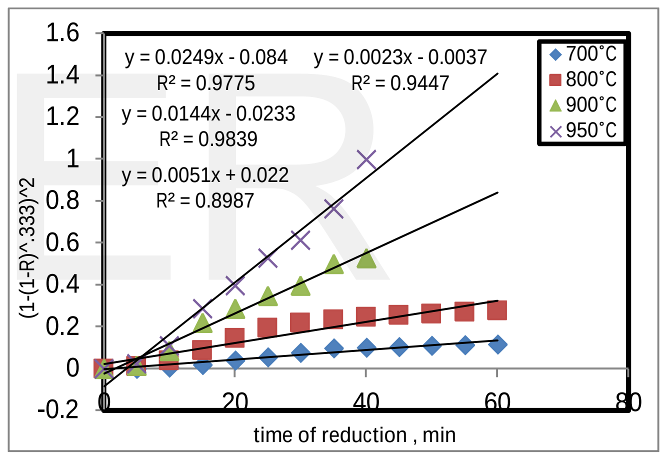

Fig.7. The relation between $[1 - (1-R)^{1/3}]^2$ and time of reduction

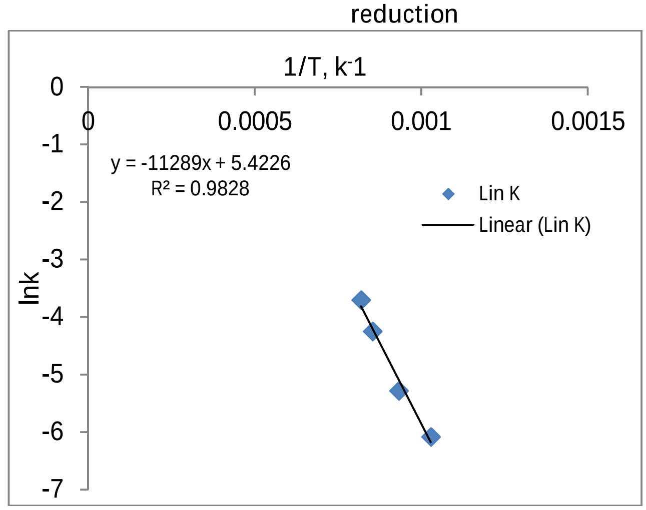

Fig.8. Relation between In k and 1/T , , K^{-1}

Fig.9. illustrate the relation between -ln (1-R) against time of reduction for different reduction temperature . From which it is clear that the straight line was observed. The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrate in Fig.10 , from which it is clear that the activation energy= 80.8 kJ/ mole .

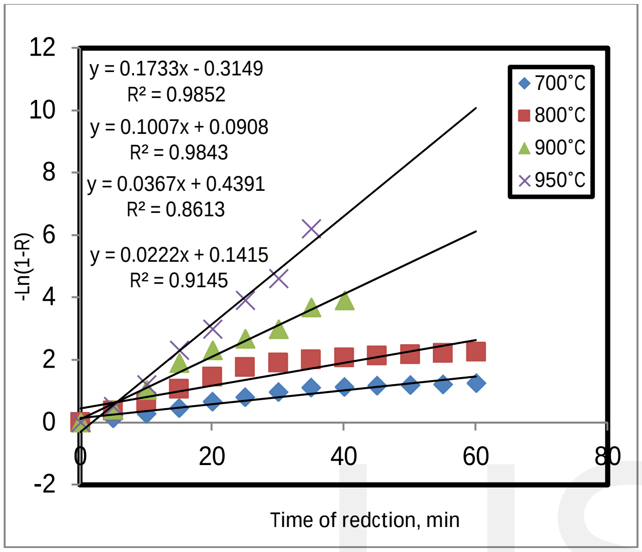

Fig.9. The relation between -ln (1-R) against time of reduction for different reduction temperature.

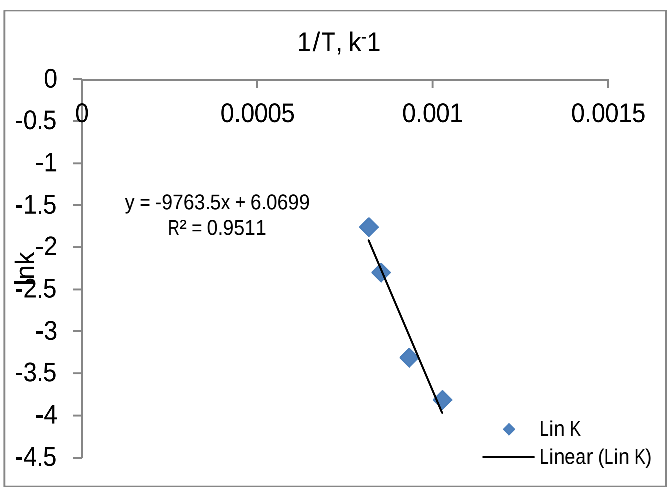

Fig.10. Relation between ln k and 1/T , K-1

3.5. X-Ray Analysis of The Reduced Briquettes

Figs. 11. shows the phases produced after reduction by hydrogen at 700 and 950 °C. From these figure it is clear that at temperature 950 °C the reduction is nearly completed and all hematite nearly converted to metallic iron .

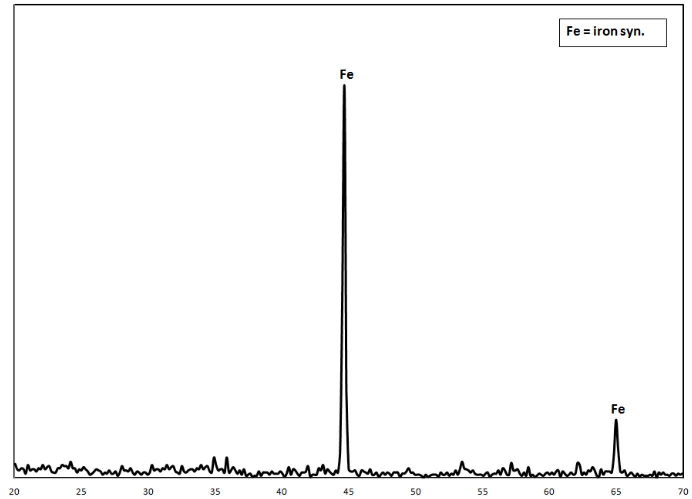

Fig.11. ray analyses of the sample of pellets reduced by hydrogen at 950 °C

4. CONCLUSIONS

1) The reduction rates of pellets with hydrogen increased with increasing temperature of the reduction from 700 up to 950°C.
2) The reduction rate increased with increased hydrogen flow rate at constant reduction temperature.
3) The diffusion processes through the produced briquettes or Avrami-Erofeev n=1 are the reduction controler steps for the reduction of El-Dekhila iron oxide waste pellets El-Dekhila iron oxide waste reduced it by hydrogen gas

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