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The Effect of Addition of Mill Scale Oxide Fine and El Dekhilla Fine Pellets on Reduction of El-Baharia Iron Ore Pellets Via Hydrogen - Reaction Controlled Kinetics

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Abstract— *In this work, the effect of addition of fine El Dekhaila pellets and mill scale to El-Baharia iron ore on the degree of reduction was studied and also the model of reduction was proposed.*

I. Introduction

Iron is the tenth element in the universe, and the fourth in the earth's crust. Iron is extracted from its ore, and is not found in the free elemental form and to obtain elemental iron, the impurities must be removed by chemical reduction (Mishra and Baliarsingh, 2008)

Human society used metals for thousands of years, and the amount of metal production continuously increased. In modern society, and the use of metals becomes inevitable in our daily life throughout society. The source of metals change from high concentrations of ores to low concentrations or industrial wastes (Lee and Kim, 2011)

The Egyptian iron ores of El-Baharia oasis are the main raw materials for the blast furnaces of the Egyptian iron and steel Co. and El-Dekhaila iron Co. During the transportation of the imported pellets from outside of Egypt to the companies, a lot of fine substances formed which are not suitable for reduction inside the furnace. (El-Hussiny, et al., 2015)

The pelletization of fine ores and the quality of produced pellets depend on many factors such as particle size, amount of water added during pelletization , disc rotating speed, inclination angle of the disc and residence time of materials in the disc. The effect of these parameters on the mechanical properties of green, dried and fired iron ore pellets has been the subject of much research (Knepper, 1962, Mayer, 1980, Ahmed et al. 2005).

The reduction of iron ores by hydrogen is a gas-solid reaction which occurs in two or three stages. At temperatures higher 570°C, hematite is transformed into magnetite, then into wustite, and finally into metallic iron while at temperatures below 570°C, magnetite is directly transformed into iron since wustite is not thermodynamically stable (Bogdandy and Zngle, 1971)

Baolin, et al. (2012) found that the kinetic parameters for reducing Fe_2O_3 by hydrogen were represented mainly by the reaction temperatures in the range 440°C and 490°C. However, in order to distinguish the reduction of Fe_3O_4 to FeO from that of FeO to Fe, the reaction temperature was set to be greater than 570°C.

Wang, H. (2011) found that within 1-7 seconds at 1200 – 1400^{o}C, 90 - 99% reduction of iron ore concentrate by hydrogen occurred depending on the amount of hydrogen supplied. This reduction rate is fast enough for a flash reduction process. The nucleation and growth kinetics was found to describe the kinetics.

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This study aims to investigate the reduction kinetic via hydrogen gas of the pellets of El-Baharia iron ore mixed with El-Dekhaila pellets waste and mill scale.

II. Experimental Procedures

2.1. Preparation of Samples in the form of Pellets for Reduction by Hydrogen

Preparation of samples for the pelletizing process was carried out by mixing of iron ore with El-Dekhaila fine and the mill scale were prepared in a disc pelletizer of diameter 400 mm, collar height 100 mm figure 1, angle of inclination 60^{o}C, disc rotating speed 17 rpm and residence time 10 min. The materials were feed to the pelletizer. The predetermined moisture amount (10% water + 2% 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

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out to dry in a drying oven at 110^{o}C for 2h, to ensure the evaporation of all water used during the process.


Fig. 1. Disc pelletizer equipment.

2.2 Method of Determination of the Quality of Pellets to Produce Suitable Pellets

2.2.a. Drop damage resistance test

The produced pellets were subjected to mechanical tests (Drop damage resistance test) (Mayer, 1980, Forsmo et al., 2006, Forsmo et al., 2008). The drop damage resistance indicates how often pellets can be dropped from a height of 45 cm before they show perceptible cracks or crumbed. Ten pellets are individually dropped on a steel plate until their breaking. The mean value of the tested pellets gives their average drop number.

2.2.b. Compressive strength test

The average compressive strength tests of pellets; (Annual book of ASTM E382-12/2012 Standards) is controlled by compressing at least 10 of pellets between parallel steel plates (Figure 2) up their breaking. The mean value of the tested pellets gives their compressive strength.

Fig. 2. MEGA.KSC-10 hydraulic press.

III. REDUCTION PROCEDURE BY HYDROGEN

The reduction of pellets by hydrogen was done in the thermo gravimetric apparatus figure 3. It consists of vertical furnace, electronic balance for monitoring the weight change of reacting sample and temperature controller, The pellets sample was placed in a Ni-Cr basket which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the required temperature (700-1000˚C) and maintained constant to ± 5˚C. Then the sample was placed in the hot zone. The nitrogen flow rate was 0.51/min in all experiments from initial time up to the end of reduction by hydrogen. The weight of the sample was continuously recorded during the reduction and at the end of the run; the samples were withdrawn from the furnace and kept in the desiccators.

The percentage of reduction was calculated according to the following equation:-

$$\text{Percent of the reduction } = \frac{\left(W_0 - W_t\right) \ *100}{\text{Oxygen }(\text{mass})}$$

Where: W_0 is the initial mass sample after removal of moisture and W_t: mass of sample after each time, t. Oxygen (mass) indicates the mass of oxygen percent in the sample in form FeO&Fe_2O_3.

3.1. Characterization of Raw Materials

El-Baharia iron ore was supplied by the Egyptian Iron and Steel Company and its chemical analysis is shown in table I.

The X-Ray analysis of El-Baharia iron ore is found in figure 4 which mainly consists of hematite and quartz (El-Hussiny et al., 2015)

El-Dekhaila waste fine pellets was delivered from El-Dekhaila steel Company (Alexandria, Egypt) and there chemical analyses is illustrated in table I.

X-ray pattern of the El-Dekhaila pellets waste is shown in figure 5, from which it is seen that the main compound of this waste is hematite (El-Hussiny, El-Gawad et al., 2015, El-Hussiny et al., 2016). Mill scale was delivered from Egyptian Iron and Steel Co. *The chemical analysis of mill scale is* presented in Table I. X-ray of the mill scale is presented in figure 6, it is clear that hematite is observed.


Fig. 3. Thermo-gravimetric apparatus used for reduction.

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TABLE I. The chemical compositions of the El Baharia Iron Ore, El-Dekhaila fine pellet waste and mill scale.

Compound	Iron ore, Weight,%	El-Dekhaila pellet waste weight,%	Mill Scale,%
Fe_2O_3	74.79	95	70
Fe_3O_4	-	-	17.26
FeO	-	-	7.83
SiO_2	10.84	1.5	1.92
MnO	2.92	-	0.66
S	0.74	-	0.33
CaO	0.39	0.7	
MgO	0.18		
P_2O_5	0.5		P=0.23
Al_2O_3	1.44		
TiO_2	0-16		
BaO	1.17		
ZnO	0.15		
Na_2O	0.25		
K_2O	0.27		
Cl^-	0.5		
C			0.04
L.O.I.	5.18		

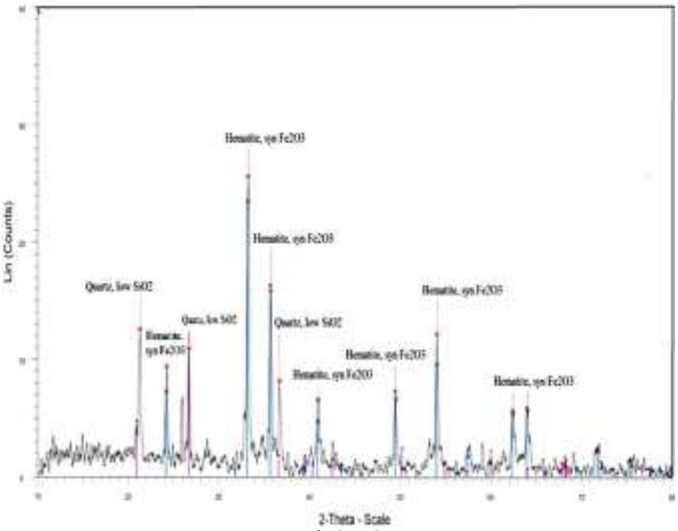

Fig. 4. X-Ray of El-Baharia iron ore.

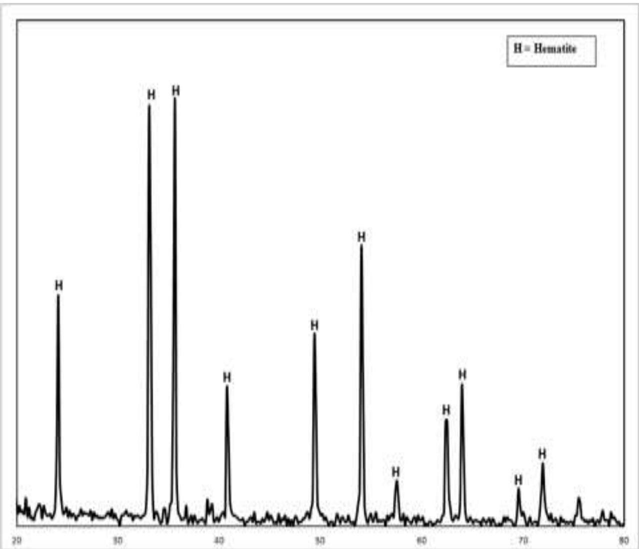

Fig. 5. X-ray of El-Dekhaila Pellets waste.

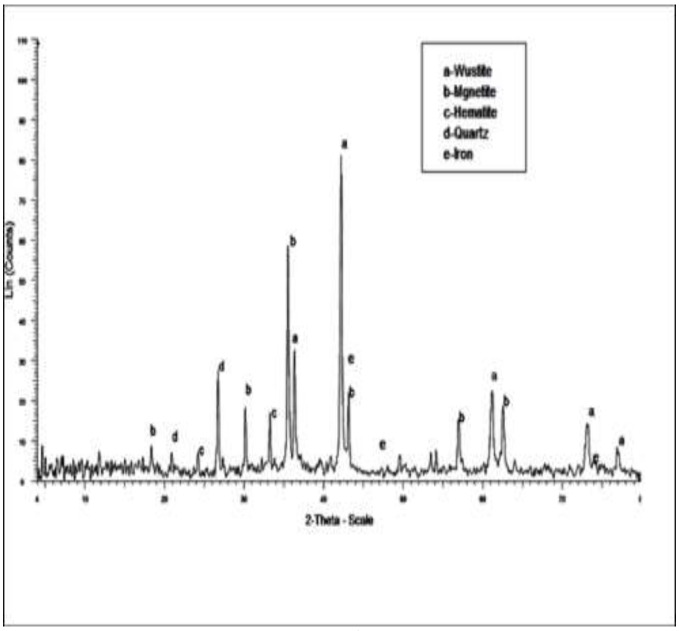

Fig. 6. X-ray of mill scale.

IV. Results and Discussion

3.1 Effect of Hydrogen Flow Rate on Adding Different Amounts of Mill Scale and Mill Scale +fine El-Dekhaila Pellets to Iron Ore

It is clear that as the flow rate of hydrogen increased the fraction of reduction increases, as shown for both mixed mill scale, fine pellets and iron ore figs 7-8.

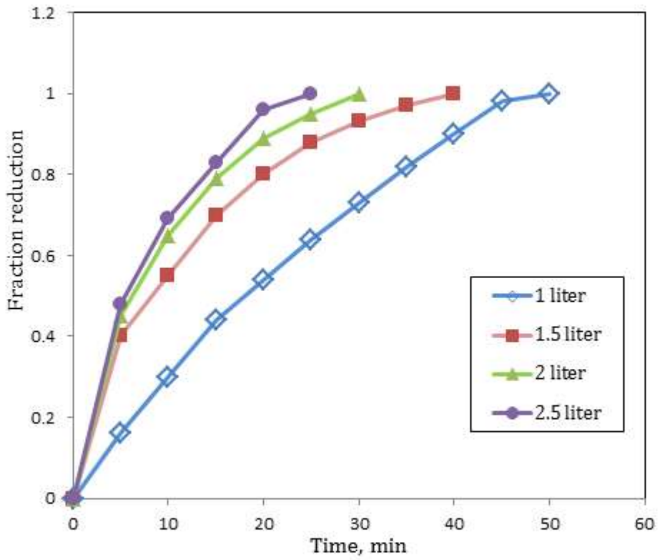

Fig. 7. The effect of change of hydrogen flow rate on the reduction of the pellets which fired at 1150°C mill scale/fine pellets/iron ore ratio 5/15/80.

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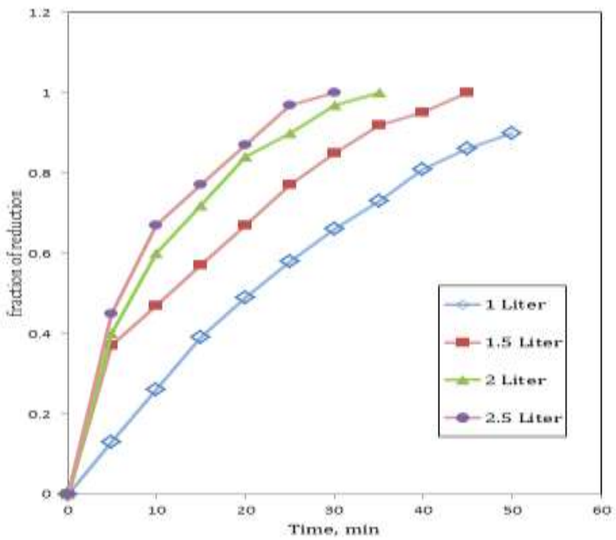

Fig. 8. The effect of change of hydrogen flow rate on the reduction of the pellets which fired at 1150°C mill scale / fine pellets/iron ore ratio15/5/80.

3.2-Effect of Change of Temperature on the Reduction Degree of the Pellets Produced from a Mixture of 80% Iron Ore with of 10% Mill Scale 10% Fine Pellets of Constant Hydrogen Flow Rate

The effect of temperature on the reduction of the 80% mixture of iron ore with 10% mill scale, 10% fine pellets and fired at 1150°C of 1.5 L/min hydrogen flow rate, was studied at 700–950°C. The plots of the reduction percentage as function of time are shown in figure 9. From this figure, it is evident that the reduction percentage increased as the temperature increased. 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. Also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rate of desorption.

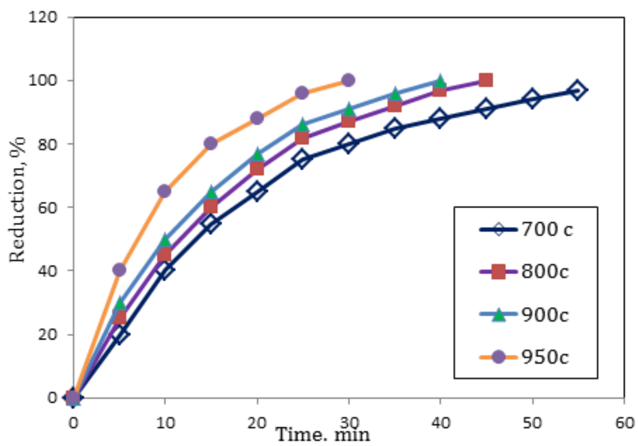

Fig. 9. Effect of temperature on the reduction of the mixture of 80% iron ore with 10% mill scale + 10% fine pellets and fired at 1150°C by 1.5 L/min hydrogen flow rate.

3.3-Kinetics Reduction of Pellets

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 unimolecular decay law equation (Shalabi, Mohamed et al. 1997)

$$-\text{Ln}\,(1-R) = kt$$

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

Figure 10 illustrates the relation between *-ln (1-R)* against time of reduction for different reduction temperatures, it is clear that straight line was observed.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results are illustrated in figure 11, from which it is clear that the activation energy is 25.4 kJ/mole.

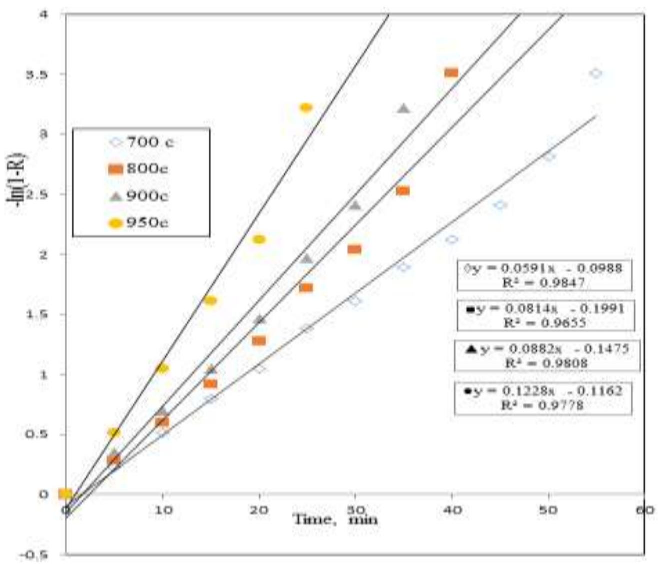

Fig. 10. Relation between –ln (1-R) and time of reduction at different reduction temperature.

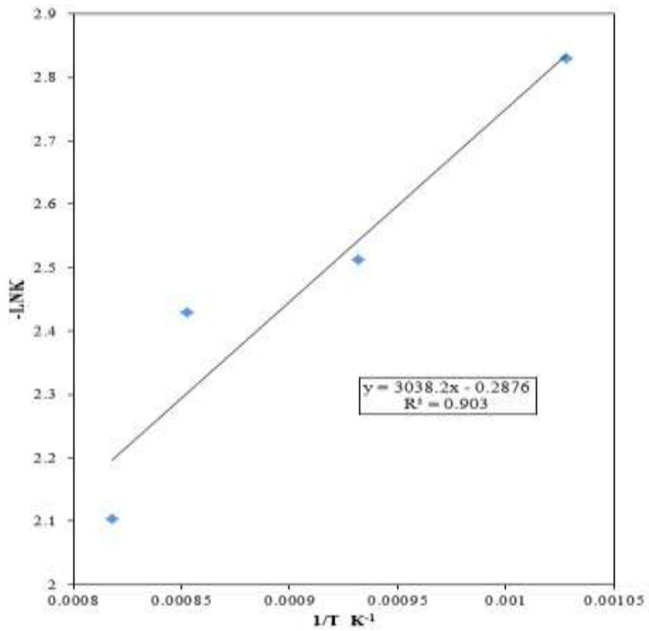

Fig. 11. The relation between natural logarithms an 1/T for reduction of mill scale/fine pellets/iron ore iron ore = 10/10/80 ratio

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3.4-X-Ray Analyses of the Reduced Pellets

X-ray analyses of the sample reduced at 950°C for 10% mile scale /10% fine pellets/80% iron ore shows that the present phases are metallic iron (syn. Fe), and some traces of magnetite (Fe_3O_4) as shown in figure 12.

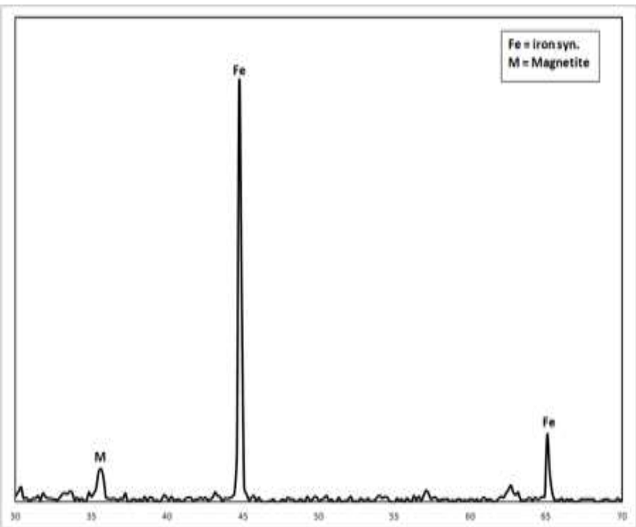

Fig. 12. X-ray analysis of the sample reduced at 950°C for 10% mill scale/10% fine pellets /80% iron ore.

V. CONCLUSION

1- The effect of temperature on the reduction of the 80% mixture of iron ore with 10% mill scale, 10% fine pellets and fired at 1150^{o}C by 1.5 L/min hydrogen flow rate, were done at 700–950^{o}C. The plots of the reduction percentage as function of time are shown. From this figure, it is evident that the reduction percentage increased as the temperature increased.
2- The activation energies of reduction reaction equal .25.4. KJ/mole.

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