Pelletization of El-Baharia iron ore (O) with different amount of El-Dekhaila waste pellets (E) and reduction kinetics of these pellets via hydrogen

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Abstract— The effect of the Addition of fine El-Dekhilla waste pellets(E) upon the quality and reduction kinetics of El-Baharia iron ore (O) pellets via hydrogen was carried out at different temperatures ranging from 700˚C to 950˚C and. the best reduction properties were found at 950˚C.The kinetic of the reduction process was studied using the best fit model determined was kt = - ln(1-R) . The main crystalline phases of reduced pellets at 950˚C were metallic iron (syn. Fe).

Index Terms— Iron ore, hydrogen, , Reduction Kinetics, pelletization . Metallic iron

1 Introduction

Iron is found in three key oxides: ferric oxide or wuestite (FeO), ferrous oxide or hematite (Fe_2O_3), and ferroferric oxide or magnetite (Fe_3O_4). Magnetite is also called lodestone, which was the first magnetic mineral to be discovered. The two next most important terrestrial ores, goethite ($HFeCO_3$) and siderite ($FeCO_3$), are not found on the Moon (despite certain contaminated lunar samples). As the lunar surface is underoxidised, however, significant quantities of metallic iron exist, which is quite rare on Rarth

Metalic iron is among these elements easily extracted using a mildly endothermic hydrogen reduction process:

$$Fe_2O_3 + H_2 = 2\ Fe_3O_4 + H_2O \quad (1)$$
$$Fe_3O_4 + H_2 = 3\ FeO + H_2O \quad (2)$$
$$FeO + H_2 = Fe + H_2O \quad (3)$$

The Egyptian iron ores of El-Baharia Oasis is the main feedstock for the blast furnace of Egyptian iron and steel Co.[1]
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Pelletization of the fine ore is one of the agglomeration processes which convert this fines into pellets of suitable size. Binders are important for holding the fine particles together during the pelletization process. Either organic or inorganic binders can be used. Organic binders burn or volatilize during movement of the flame front. Owing to the comparatively high prices of binders the only interest becomes feasible is that of using waste products such as molasses that is both cheap and locally available [2- 3].

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Ezz and Wild [4] indicated that an increase in temperature exerts a major influence on increasing reduction rate, while ore characteristics, such as porosity, shape factor, and surface condi-tion also affected re-duction rate also the ore/gas ratio has a major influence on the reduction rate.

Raymond and leiv [5] indicated that reduction of iron oxide with H_2 occurs in three steps when temperatures are over 570 c and two steps when the temperature is below 570 ^oC

For T>570°C

$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$ (g) ΔHo 298 =1.0 kJ/mol Fe

$Fe_3O_4 + H_2 \rightarrow FeO + H_2O$ (g) ΔHo 298 = +24.9 kJ/mol Fe

$FeO + H2(g) \rightarrow Fe + H2O$ ΔHo 298 = +25.4 kJ/mol Fe

For T<570°C

$Fe_3O_4 + 4H_2(g) \rightarrow 4Fe + 4H_2O$ ΔHo 298 = +50.4 kJ/mol Fe

$Fe_2O_3 + H_2(g) = 2Fe + 3H_2O(g)$ ΔHo 298 = +49.4 kJ/mol Fe

Baolin et al [6] , were evaluated the kinetics parameters of iron oxide reduction by hydrogen by the isothermal method in a differential micro-packed bed.. In the experiments, in order to correctly evaluate the intrinsic kinetics parameters for reducing Fe_2O_3 to Fe_3O_4, the reaction temperatures were set between 440 °C and 490 °C. In order to distinguish the reduction of Fe_3O_4 to FeO from that of FeO to Fe, the reaction temperature in the experiment was set to be greater than 570 °C.

Saikat et al [7] ,found that the experimental results of the reduction of magnetite fines took place in two stages:

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Fe_3O_4 to FeO and FeO to Fe. Each stage was controlled by pore diffusion kinetics. The activation energies in the two stages were found to be 42 kJ mol^{-1} and 55 kJ mol^{-1}, respectively.

The aim of this work is to study the pelletization the El-Baharia Oasis iron ore with waste pellets present in El-Dekhilla iron Co. and reduce its in static bed by hydrogen .

2-Experimental Work

2-1- Material used and its characteristics

El-Baharia iron ore was supplied by the Egyptian Iron and Steel Company, The chemical composition of this ore is as follows:- [8]

Chemical analysis of El-Baharia iron ore : 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 X- Ray analysis of El-Baharia iron ore is illustrated in figures 1 . From which it is clear that El-Baharia iron ore mainly consists of hematite and quartz[8].

El-Dekhaila waste pellets 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%.. [9-10]

X-ray of the El-Dekhaila pellets waste illustrated in Fig.2, from which it is clear that the main compound of this waste is hematite.[9-10].

2.2. Preparation of the pellets and Its Physical Properties

The iron ore and El-Dekhila waste pellets were grinding separate in vibrating mill to powder with size less than 75 micrometers. After which the pellitization of iron ore with the predetermine of El-Dekhila waste pellets were done in a disc pelletizer of diameter 400 mm, collar height 100 mm Fig. 3 [10] , angle of inclination 60 °C, disc rotating speed 17 rpm and residence time 30 min. The materials were feed to the pelletizer. The predetermined moisture amount (12% water) and different % of the charge molasses) was then sprayed onto the rolling bed of material in the disc pelletizer. The green pellets in the size range 5-7 mm diameter were screened out to dried in the air for 3 days, to ensure the evaporation of all water used during the granulation process.

The green and dry pellets subjected to drop number test and crushing strength tests. The MEGA.KSC-10 hydraulic press used for crushing strength test Fig.4 The drop number indicates how often green and dry pellets can be dropped from a height 46 cm before they show perceptible cracks or crumble. Ten green and dry pellets are individually dropped on to a steel plate. The number of drops is determined for each pellet. The arithmetical average values of the crumbing behavior of the ten pellets yield the drop number[11-14] .The average compressive strength tests of at least 10 pellets; between parallel steel plates of MEGA.KSC up their breaking then the mean value of the tested pellets gives their compressive strength. [11-14]

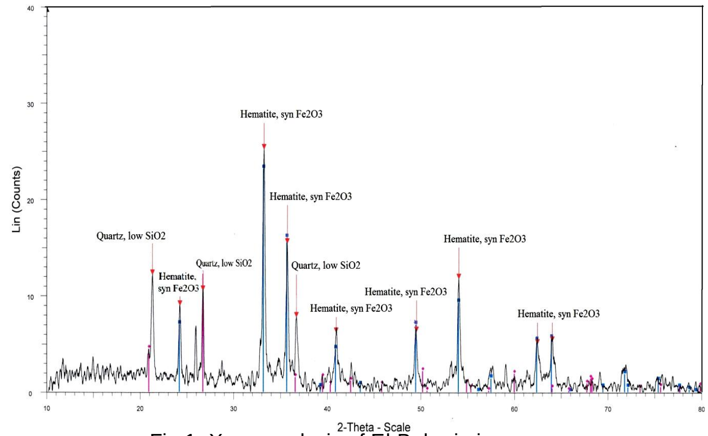

Fig.1. X-ray analysis of El-Baharia iron ore

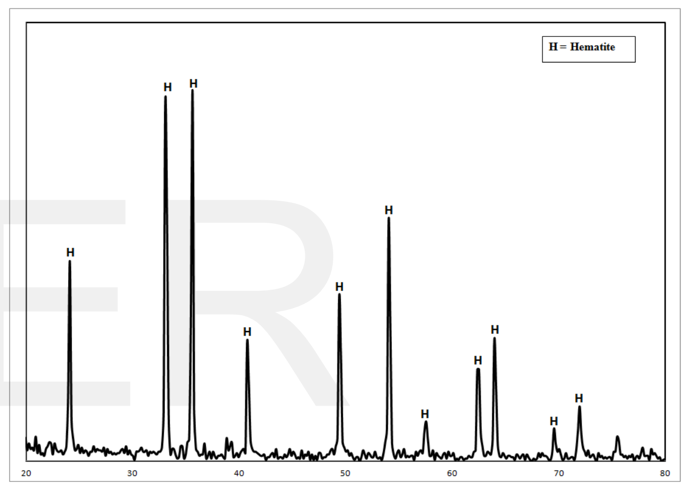

Fig.2. X-ray of El-Dekhaila Pellets waste


Fig. 3 Disc pelletizer equipment

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2.3. Firing of pellets in muffle furnace

The dried pellets was fired in muffle furnace at temperature 800 – 1150 ^{o}C

2.4 Reduction Procedures

The reduction of pellets was performed in thermogravimetric apparatus. This scheme is similar to that present elsewhere [9,15-22] (Figure 5). 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 basket which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the required temperature (700°C - 950°C) and maintained constant to ±5°C. Then samples were placed in hot zone. The nitrogen flow rate was 0.5 l / min pass through furnace during initial and final time of reduction. The weight of the sample was continuously recorde, 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) x100 / Oxygen mass]

Where:

Wo: the initial mass of the sample, g.

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

Oxygen mass: indicates the total mass of oxygen percent in the sample in form FeO, Fe_2O_3 and manganese oxide. g.

Fig.4 MEGA.KSC-10 hydraulic press

3-RESULTE AND DISSICATION

3.1 Effect of binding material added on the pellet charcterstic (pellet consists of 5% E waste pellets and 95 % O)

Tables 1 and 2 illustrated the effect of the percentage of molasses added (+12 % water) on the drop number and crushing strength of the wet (green) and dried pellets after 3 day in air

From Table 1 it is clear that the increase of molasses added up to 2 % the drop number and crushing strength increase then more addition of molasses the drop damage resistance and crushing strength decreased While Table 2 shows that after 3 day both drop number and crushing strength of the pellets increases as the amount of molasses added increased**.**

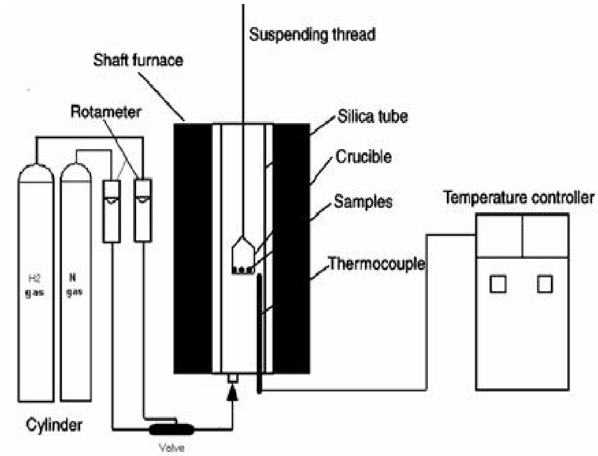

Fig. 5. Schematic diagram of the apparatus

Table 1 Effect of molass added on the drop number and strength of green pellets

Percentage of molasses added, %.	Drop No.	Strength, MPa.
1.5	11	0.0213
2	14	0.0328
2,5	10	0.0230
3	8	0.0220

Table 2 Effect of molasses added on the drop number and

Strength of dried pellets in air after 3

Percentage of molasses added, %.	Drop No.	Strength, MPa.
1.5	5	0.156
2	7	0.164
2,5	9	0.175
3	10	0.178

3.2 Effect of change the amount of E added to O on the produced pellets charcterstic

Tables 3 and 4 illustrated the effect of the change E added to O (amount of molasses =2% + 12 % water) on the drop number and crushing strength of the wet and dried pellets after 3 day in air From Tables 3 and 4 it is clear that the increase of E added

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to O the drop number and crushing strength of pellets increases .

Table 3 Effect of percen of E added to O on the drop number and strength of green pellets when 2 % molasses + 12 % water used during pelletization process

Percentage of El-Dekhila (E) added to iron ore (O), %.	Drop No.	Strength, MPa.
5	14	0.0328
10	15	0.0391
15	16	0.0397
20	17	0.0400

Table 4 Effect of percen of E added to O on the drop number and strength of dried pellets in air 3 day when 2 % molasses used during pelletization process

Percentage of El-Dekhila added to iron ore, %.	Drop No.	Strength, MPa.
5	7	0.146
10	8	0.149
15	10	0.151
20	11	0.153

3.3 Effect of change the amount of E added to O on the fireng produced pellets charcterstic

Table 5 illustrate the effect of the change E added to O (amount of water 12 % and molasses =2%) on the crushing strength of the fired pellets at different temperature of firing From Table 5 , it is clear that the increase of percentage of E in the mixure at any cinstant temperature of firing the crushing strength increase also at any constant amount of E in the pellets increase of firing temperature leades to an increase the crushing strength of fired pellets.

Table 5 Effect of percenage of E added to O on the strength of fired pellets at different temperature.

Percentage of El-Dekhila (E) added to iron ore, (O)%.	Strength , MPa , when firing temperature 800 OC.	Strength , MPa. when firing temperature 900 OC.	Strength , MPa. when firing temperature 1000 OC.	Strength , MPa. when firing temperature 1150 OC
5	0.3	0.543	1.3	7.37
10	0.4	0.57	2	10.16
15	0.46	0.74	3.03	19.42
20	0.52	o.78	4.16	20.8

3.4. Effect of different hydrogen flow rate on the reduction percentage of pellets containing mixture of E and O.

Figures 6 and 7 Show the effect of change of hydrogen flow rate on the reduction of the pellets produced using 2% molasses with 12 % water and dried in air 3 day and fired at 1150 °C. for both E/O ratio 0.0526 and 0.25 , from these figures it is shown that as the flow rate increased the reduction percentage increased . This results may be due to the 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 , thus , the rate of reaction increased or the increase of flow rate of hydrogen increased the gas diffusion across the boundary layer (23 -25).

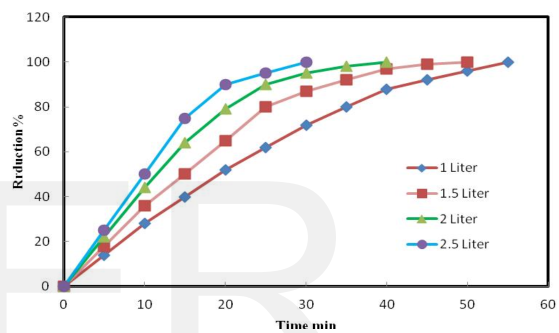

Figure 6 The effect of change of hydrogen flow rate on the reduction of the pellets which fired at 1150 °C. for E/O ratio 0.0526

3.5 Effect of the change of the ratio of E/O on the reduction process

Figure.8 illustrate the effect of change E/O ratio on the reduction of the pellets which fired at 1150 °C (reduction temperature = 900 °C, flow rate of hydrogen gas1.5 L/ min.), from which it is clear that as E/O increased the reduction percentage decreased, This may be due to the fact that the low porosity of the Eldekaila waste pellets.

3.6 Effect of change of temperature on the reduction degree of the mixture of iron ore with of El-Dekhaila waste pellets by constant amount of hydrogen flow rate

In order to examine the effect of temperature on the reduction of of the mixture of iron ore with El-Dekhaila waste pellets and fired at 1150°C by 1.5 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 Figs. 9and 10 From these figures it is observed that the reduction temperature influences significantly the reduction percentage 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.

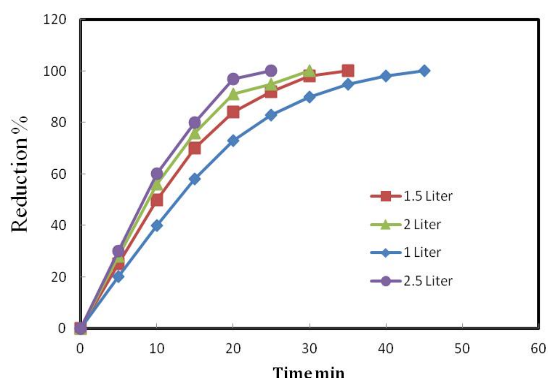

Figure 7 The effect of change of hydrogen flow rate on the reduction of the pellets which fired at 1150 °C. for E/O ratio 0.25

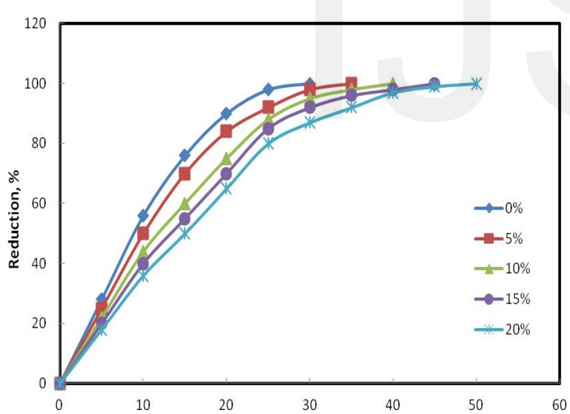

Figure.8 The effect of change E/O ratio on the reduction of the pellets which fired at 1150 oC

3.7. 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 equation unimolccuku decay law [24]

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

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

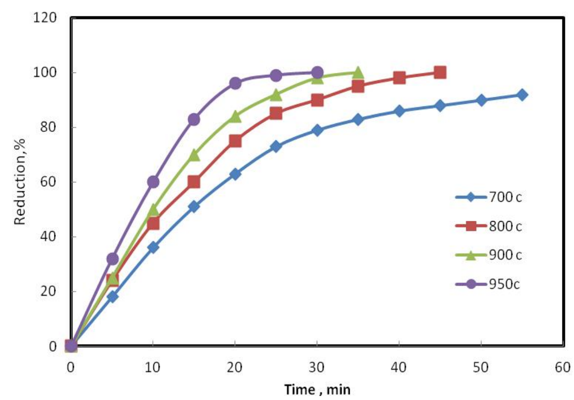

Fig.9 Effect of temperature on the reduction of the mixture of 95 % O with 5 % E and fired at 1150oC by 1.5 L/min hydrogen flow rate

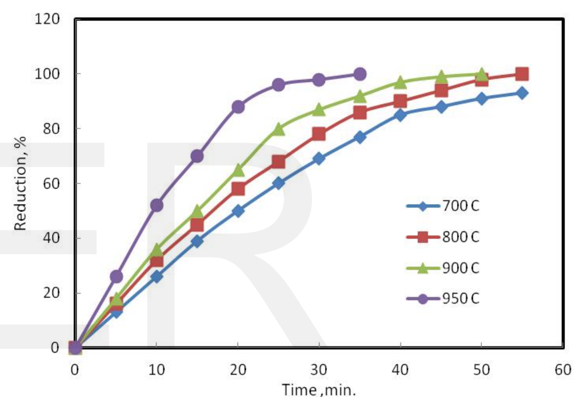

Fig.10 Effect of temperature on the reduction of the mixture of 80 % O with 20 % E and fired at 1150oC by 1.5 L/min hydrogen flow rate

Figs.11 and 13 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 Figs.12, 14 from which it is clear that the activation energy= 50.3 kJ/ mole .36.85 kJ/mole for 0.5 % E and 20% E added to on respectively.

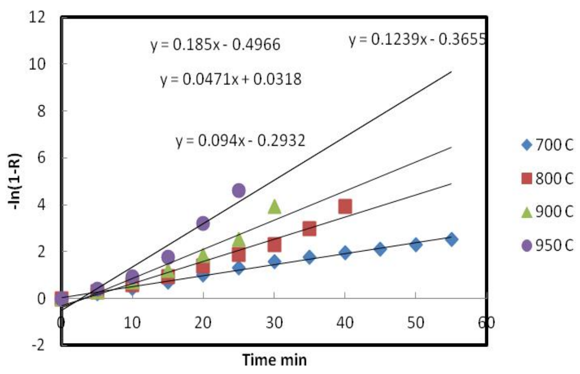

Fig. 11 Relation between -ln (1-R) and time of reduction at different reduction temperature for mixture of 95 % O with 5 % E and fired at 1150oC reduced by 1.5 L/min hydrogen flow rate

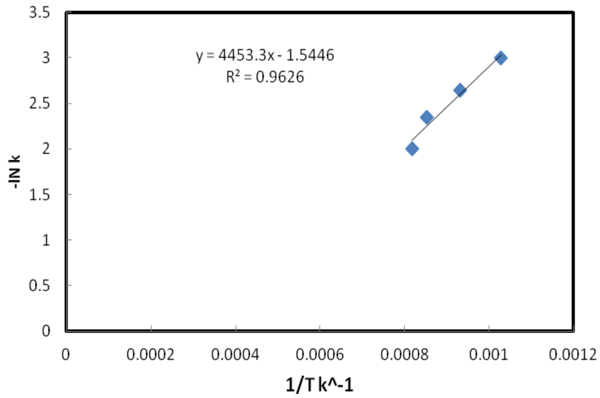

Fig. 14 The relation between natural logarithms an 1/ T for reduction of E/O = 0.25

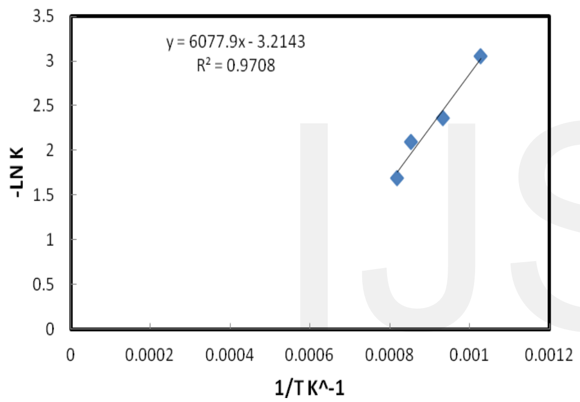

Fig. 12 The relation between natural logarithms an 1/ T for reduction of E/O = 0.052

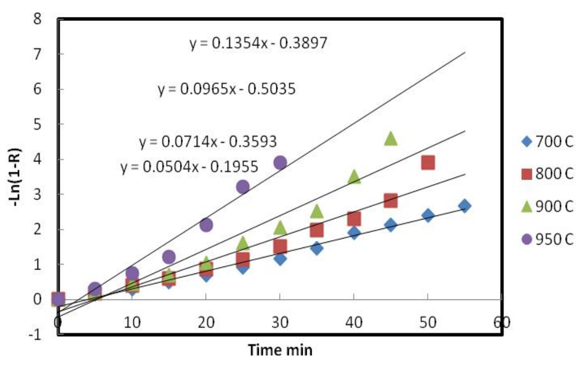

Fig. 13 Relation between -ln (1-R) and time of reduction at different reduction temperature for mixture of 80 % O with 20 % E and fired at 1150oC reduced by 1.5 L/min hydrogen flow rate

3.8. X-Ray analyses of the reduced pellets

X-ray analyses of the sample reduced at 950°C for E / O 0.0526 and 0.25 shows that the present phases are metallic iron (syn. Fe), and some traces of magnetite [M] (Fe_3O_4,) as shown in Figures 15-16

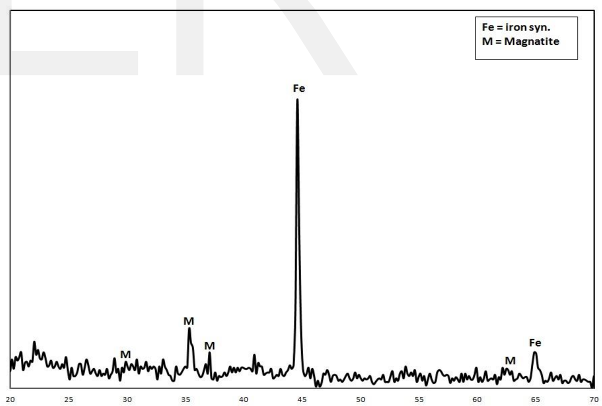

Fig. 15 X-ray analyses of the sample reduced at 950°C for E/O 0.0526

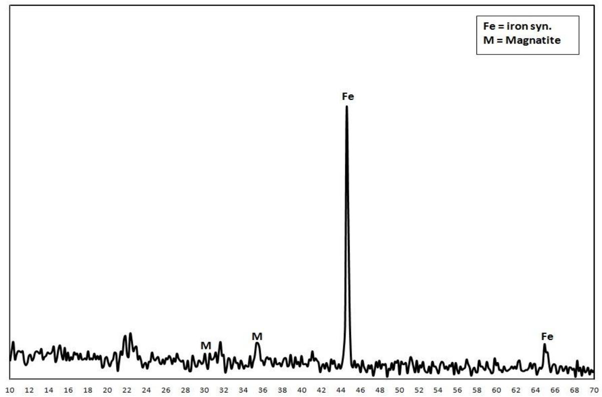

Fig. 16 X-ray analyses of the sample reduced at 950°C for E/O 0.25

4 Conclusion

1- As the E/O increase when the 2% molasses with 12 % water added during pelletization both drop number and compression strength of green pellet increased .
2- The increase of percentage of E in the mixture at any cinstant temperature of firing the crushing strength increase also at any constant amount of E in the pellets increase of firing temperature leads to an increase the crushing strength of fired pellets
3- As the E/O increased the reduction of the pellets decreased.
4- As the temperature increased the reduction of the pellets increased.
5- AS the hydrogen flow rate increased the reduction of the pellets increased.

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