Reduction of Egyptian El-Baharia iron Ore briquettes with bentonite as binding material by Hydrogen gas in static bed

F.M.Mohamed (1,2) , Hala H. Abd El-Gawad(3), N.A. El-Hussiny (1), M.E.H.Shalabi (1*)

1-Centeral Metallurgical Research and Development Institute, (CMRDI). Cairo, Egypt.
2- King Khalid University, Faculty of science and Arts For Girls. Sarat Abida . Saudi Arabia
3-Faculty of Science and arts Mohail Asser king khalid university, Saudi Arabia
* corresponding author: e.mail : mehshalabi@hotmail.com

Abstract .

Reduction of Egyptian El-Baharia iron ore briquettes was carried out in the temperature range 700 °C to 1000°C. On studying the reduction kinetics, the most satisfactory model was obtained upon measuring the reaction rate constant (*k*) as being the slope of the initial linear region of fractional reduction vs. time curve. From ln *k* vs. 1/*T* plots, straight lines were obtained from which the activation energy of reduction was calculated.

Key words

El-Baharia iron ore, briquette, bentonite ,Reduction, hydrogen, kinetics

1-INTRODUCTION

Hydrogen has been reported to be the best reducing medium from both environmental and speed of reaction points of view. Its use is however hampered by its high cost. (1).

On the other hand, the blast furnace is still widely used worldwide for producing pig iron (2) mainly because it has very high production rate and possesses an elevated thermal efficiency owing to the countercurrent heat exchange principle utilized.

As early as the late sixties of the last century, it has been common practice to increase production and decrease the coke consumption each by about 18 per cent by charging pre-reduced pellets (69 % Fe, 58 % metallization) amounting to 40 % of the total charge. In addition to the above mentioned advantages, the use of pre-reduced pellets or briquettes is further justified in view of the scant reserves of good quality coking coal and utilization of large quantity of ore fines resulting from mechanized mining (3).

The reduction behavior of Fe_2O_3 is greatly affected by various factors such as temperature,
concentration of the reducing gas used, particle size, crystallinity and possible additives (4-7). The reduction of iron oxide is a complex gas–solid reaction influenced by a complicated structural changes in the intermediate oxides which may include several steps or possibilities including a two-step mechanism $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$ or a three-step reaction, i.e. $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$ in which reactions usually occur simultaneously (8, 9).

Damien et al (10) concluded that the reduction of iron ores by hydrogen is a gas-solid reaction that occurs in two or three stages. At temperatures higher than 570°C, hematite (Fe_2O_3) is first transformed into magnetite (Fe_3O_4), then into wüstite ($Fe_{1-y}O$), and finally into metallic iron while at temperatures below 570°C, magnetite is directly transformed into iron as wüstite is not thermodynamically stable.

On the other hand, El-Husseiny et al (11) found out that the reduction of El-Baharia iron ore briquette by hydrogen mainly depends on the flow rate of hydrogen and temperature of the reduction process

In this paper, the effect of addition of bentonite as a binding material on the physical properties of briquettes produced from Egyptian iron ores will be discussed as well as and also the reduction of the produced briquettes with1.5 % bentonite content.

2- EXPERIMENTAL WORK

2.1. Raw material

Iron ore samples were kindly supplied by the Egyptian Iron and Steel Company. The chemical composition of iron, as determined by XRF (12), is shown in Table 1 which also displays the composition of bentonite used.

Table 1: XRF analysis of iron ore and bentonite

Oxide%	Iron ore	Bentonite
Fe total	52.35	9.55
SiO_2	10.84	53.4
MnO	2.92	---
Al_2O_3	1.44	18.66
BaO	1.17	---
CaO	0.39	1.23
MgO	0.18	2.6
SO_3	0.74	---
P_2O_5	0.50	---
K_2O	0.27	1.23
Na_2O	0.25	4.41
TiO_2	0.16	---
ZnO	0.15	---
LOI	29.5	10.26

On the other hand, the XRD pattern of El-Baharia iron ore is illustrated in Figure 1 from which it is clear that the ore mainly consists of hematite and quartz. The X- Ray analysis of bentonite is shown in Figure 2, the main phases being quartz, kaolinite and montmorillonite. Its very small crystal size and poor crystallinity reflected in the lack of sharpness of its peaks.

2.2. Preparation of the Briquetting and Its Physical Properties

El-Baharia iron ore samples were ground in a vibrating mill to less than 75 μm. 10 g of the fine powder were then mixed with different percents bentonite then pressed in moulds (12 mm diameter and 22 mm height using MEGA.KSC-10 hydraulic press) under different pressure loads ranging from 75 MPa up to 275 MPa. The briquettes were then subjected to drop number and crushing strength tests. The drop number indicates how often a green briquette can be dropped from a height of 460 mm before showing any perceptible cracks or crumbling. Ten green briquettes are individually dropped on to a steel plate and the number of drops determined for each briquette. The arithmetical average of the crumbing behavior of the ten briquettes yields the drop number. The average crushing strength was obtained by compressing 10 briquettes between parallel steel plates up to their breaking, according to the procedure adopted by Meyer (13).

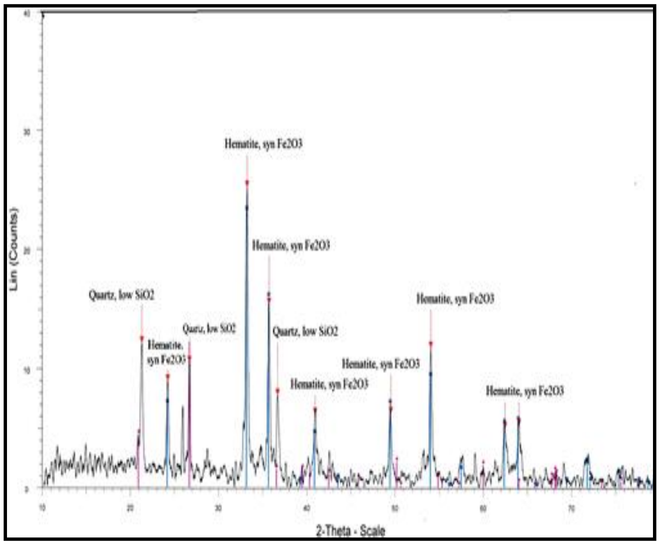

Fig.1 X-ray analysis of El-Baharia iron ore

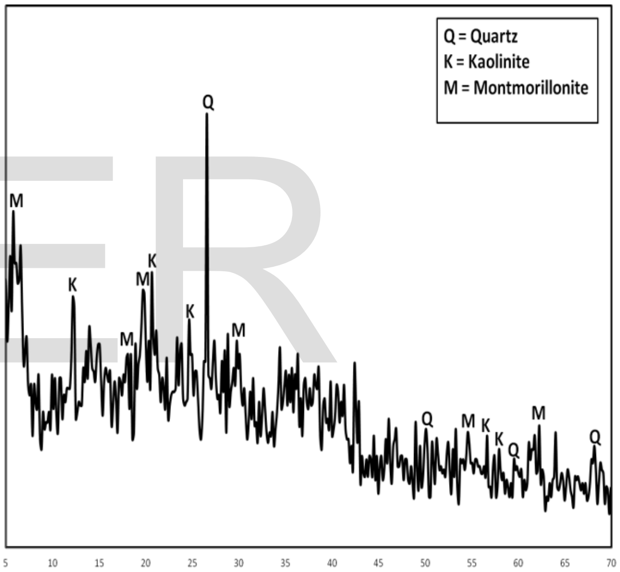

Fig.2 X-ray of bentonite

2.3. Reduction Procedures

The reduction of El-Baharia iron ore with bentonite briquette by hydrogen was performed in a thermogravimetric apparatus, a schematic diagram of which is shown in Fig.3. This kind of apparatus has been repeatedly used to the same aim (14-18). It consists of a vertical furnace, an electronic balance for monitoring the weight change of reacting sample and a temperature controller and indicator. The 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 ^{o}C) and maintained constant to ± 5 ºC. Then samples were suspended in the hottest zone of the furnace. The weight of the sample was continuously recorded and at the end of the run, the samples were withdrawn from the furnace and putted in desiccators. The amount of removable oxygen was determined by the weight loss from the sample (W_0-W_t) during reduction.The percentage of reduction was calculated according to the following equation (19-20)

% reduction = $(Wo\text{-}Wt)/W_{O2}$ ×100% (1)

Where: W_0 is the initial mass of sample (g).

W_t is the mass of sample after time t (g)

W_{O2} is the mass of total oxygen in the initial sample (g).

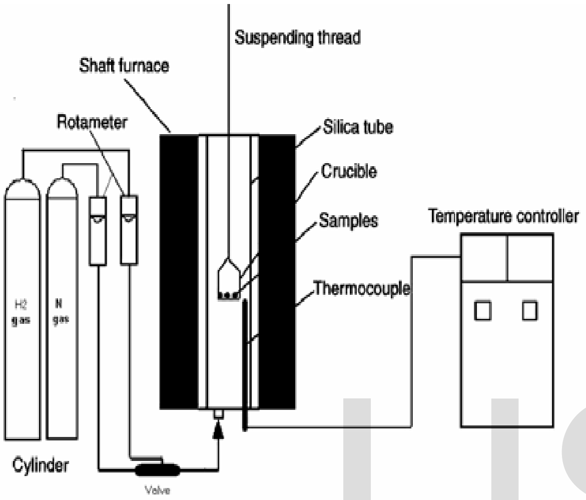

Fig.3 Schematic diagram of the apparatus

3-RESULTS AND DISCUSSIONS

3.1. Effect of adding bentonite as binding materials on the quality of the produced green, dried and firing briquette (applied pressure 216.75 MPa)

Tables 2 to 4 illustrate the effect of the percent bentonite added on the drop number (drop damage resistance) and cold crushing strength of the green, dried and fired (at 1150°C) briquettes of iron ore. It is clear that as the percentage of bentonite increased both the drop damage resistance and crushing strength increased due to its obvious binding material effect.

Table 2: Effect of bentonite added on the drop number and strength of green iron ore briquettes.

% Bentonite	Drop N^o	Strength , MPa
1	48	0.065
1.5	55	0.082
2	70	0.089
2.5	80	0..12

Table 3: Effect of bentonite added on the drop number and strength of iron ore briquette dried in air for 3 days.

% Bentonite	Drop N^o	Strength , MPa
1	48	0.95
1.5	72	1.1
2	80	1.25
2.5	> 100	1.37

Table 4: Effect of bentonite added on the drop number and strength of iron ore briquettes fired at 1150 °C

% Bentonite	Drop N^o	Strength , MPa
1	> 100	50
1.5	> 100	72
2	> 100	85
2.5	> 100	90

3.2. Effect of pressing load on the quality of the produced briquettes

The drop damage resistance and compressive strength of the produced iron ore br6quettes with respect to different pressing load at constant level of bentonite (2.5%) are shown in tables 4 to 7. From these tables, it was found that as the pressing load increased from 86.7 to 216.75 MPa the drop damage resistance and the compressive strength for green , dried (for 3 days) and fired briquettes (at 1150°C) increased and reached maximum values at 216.75 MPa. This is attributed to the fact that increasing pressing load leads to increasing the number of contact points between particles and subsequently the Vander Waals force (21-23).

Table 5: Effect of pressing load on the drop number and strength of green iron ore briquettes.

Load, M.Pa	Drop N^o	Strength, MPa.
86.7	7	0.051
130.05	30	0.068
173.4	60	0085
216.75	80	0.12

Table 6: Effect of pressing load on the drop number and strength of dried iron ore briquettes.

Load, M.Pa	Drop N^{o}	Strength, MPa.
86.7	48	0.95
130.05	72	1.1
173.4	80	1.25
216.75	> 100	1.37

Table 7 Effect of pressing load on the drop number and strength of iron ore briquettes fired at 1150^{o}C

Load, M.Pa	Drop N^{o}	Strength, MPa.
86.7	> 100	60.4
130.05	> 100	80.7
173.4	> 100	90.76
216.75	> 100	94

3.3.1 Effect of hydrogen flow rate

Fig. 4 illustrates the relation between the degree of reduction of iron ore briquettes and time of reduction at different hydrogen flow rates when the reduction was undergone at constant temperature (900˚C), the weight of the briquette sample being kept almost constant. It is clear that as the flow rate of hydrogen increased the reduction percentage increased. This is due to the fact that increasing the flow rate leads to an increase in the number of hydrogen molecules in the bulk phase nad their diffusion across the boundary layer, which leads to a rise in hydrogen adsorption (23,25, 26).

3.3.2. Effect of Temperature on the Reducibility of Iron ore briquettes

Reduction was carried out at different temperatures ranging from 700˚C to 1000˚C, keeping the briquette weight and hydrogen flow rate constant (1.5 L.min^{-1}). The results of the investigation are shown on Figure 5, where it is obvious that an increase of temperature favors the reduction rate. These curves, relating the reduction percentage to time, show that for each single reduction curve the rate of reduction of iron ore briquette was highest at early stages then decreased as the time of reduction increased. The increase of reduction percentage with temperature is normally due to increase of number of reacting molecules having an excess energy (27-29) besides increasing the rate of mass transfer of the diffusion, rate of desorption and rate of chemical reaction (25, 27,29) .

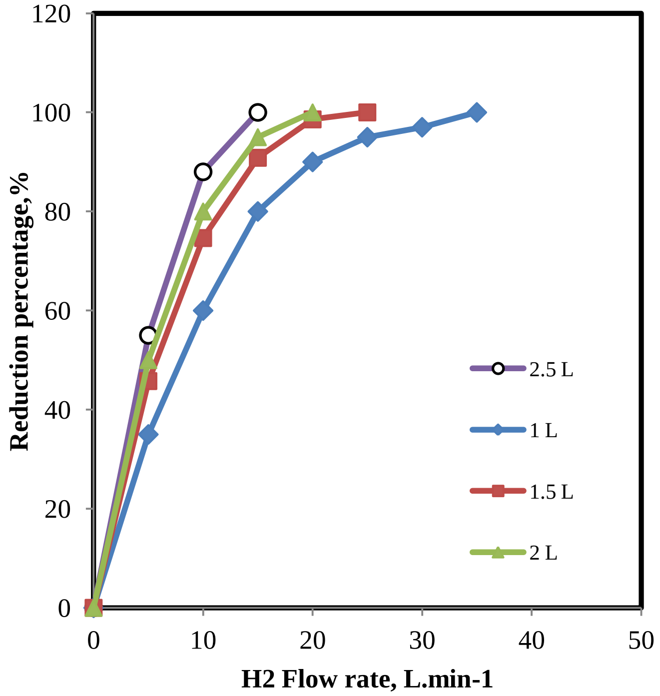

Fig.4 Effect of hydrogen flow rate on the percent reduction of iron ore briquettes at 900^{o}C

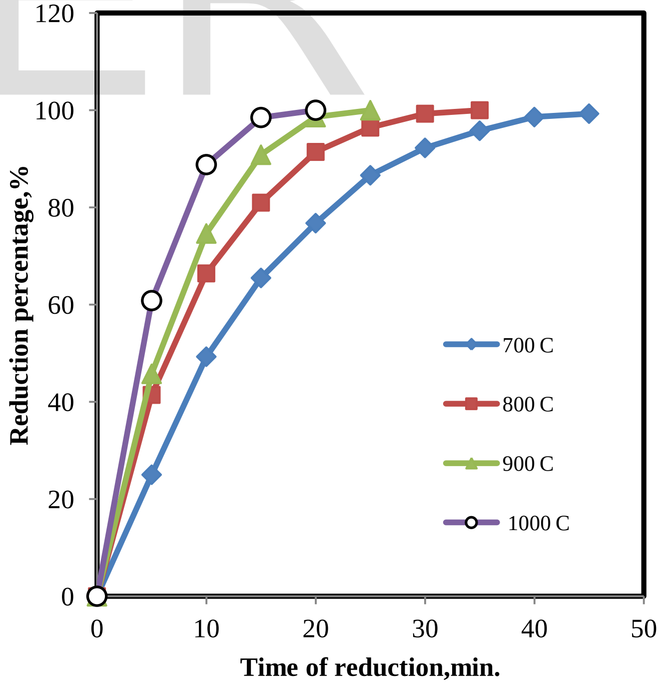

Fig.5. Effect of temperature on the percent reduction of iron ore briquette (Hydrogen flow rate = 1.5 L/min)

3.3.3. Kinetics of reduction of iron ore briquette.

Kinetic calculations aiming at estimating the apparent activation energies of the process was carried out at different temperatures from 700˚C to 1000˚C for briquettes fired at different time periods (0 - 60 min) using the equations relating fractional reduction (R) to time (t) for cylindrical bodies (30, 31):

$$Kt=1-(1-R)^{1/2} \qquad (2)$$

Where, the controlling step is the reaction at interface between reduced and unreacted core.

$$k.t = R + (1 - R).\ln(1 - R) \qquad (3)$$

Where, the controlling step is the diffusion of gases across the reduced shell.

In both equations, k is the reaction rate constant.

Figure 6 illustrates the relationship between $1 - (1 - R)^{1/2}$ versus reduction time (t) at different reduction temperatures. Straight lines are obtained, the slopes of which correspond to the reaction rate constant k.

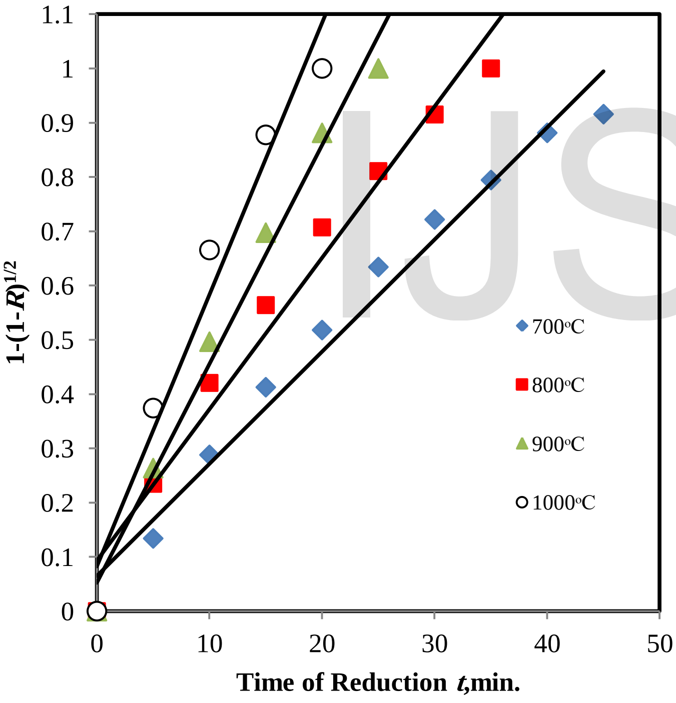

Fig.6. Plots of conversion function assuming reaction controlled mechanism

Natural logarithms of k were plotted against the reciprocal of temperatures according to the Arrhenius equation to calculate the activation energy of the reduction process of briquettes. The results are illustrated in Figure 7. The activation energy calculated for this process assuming an interface reaction controlling was 31.24 kJ.mol^{-1}.

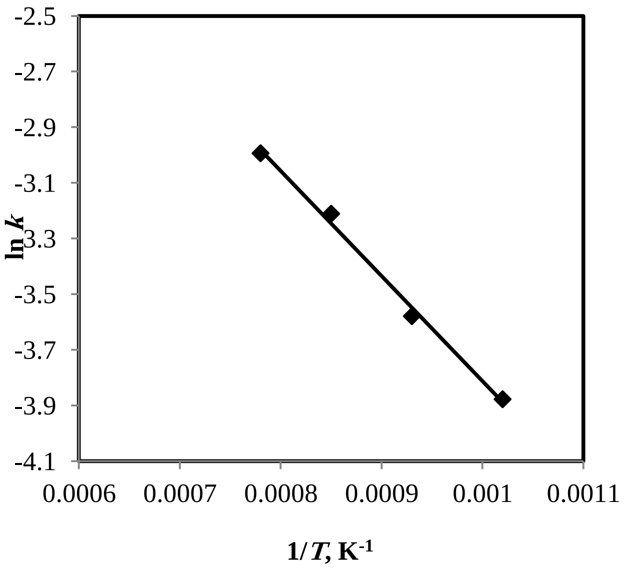

Fig.7. Arrhenius plot for the reduction process of briquettes [the controlling step is the reaction at interface]

On the other hand, when a diffusion mechanism is assumed, Figure 8 illustrating the relationship between $R + (1 - R).\ln(1 - R)$ and reduction time (t) for the different reduction temperatures used reveals that here also straight lines were obtained.

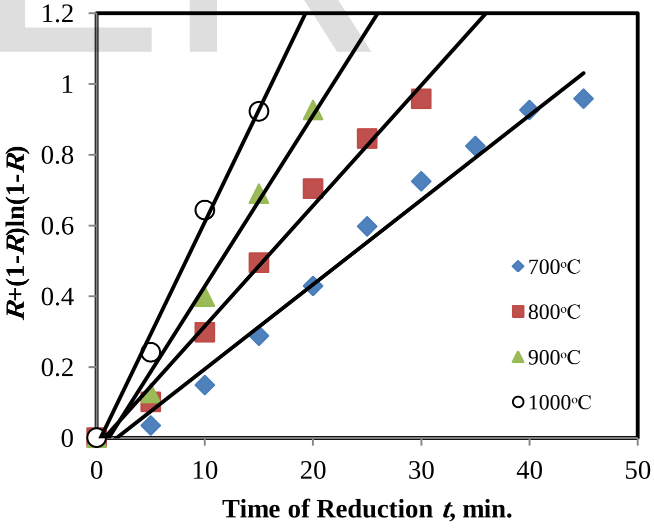

Fig.8. Plots of conversion function assuming diffusion controlled mechanism

The corresponding Arrhenius plot is shown in Figure 9 where calculation of the slope of the straight line obtained revealed an activation energy of 33.88kJ/ mol.

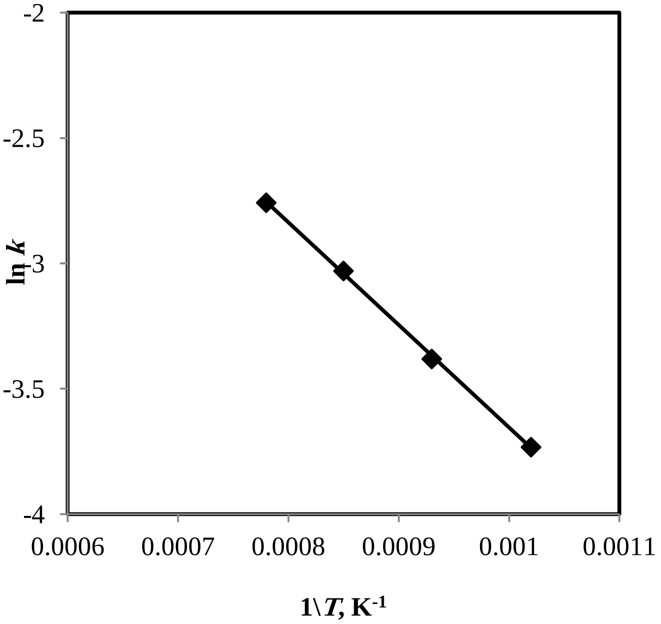

Fig.9. Arrhenius plot for the reduction process of briquettes (assuming diffusion controlling)

3.4 X-Ray analyses of the reduced briquette

The results of the X-ray analyses of briquette samples reduced at 700°C and 1000^{o}C are shown in Figures 10-11, respectively. They indicate a dominant phase of metallic iron with some lines of magnetite [M] (Fe_3O_4) and wüstite present in the sample reduced at 700^{o}C (Fig.10) while for the sample reduced at 1000^{o}C the main phase is metallic iron with some traces of magnetite (Fig.11)

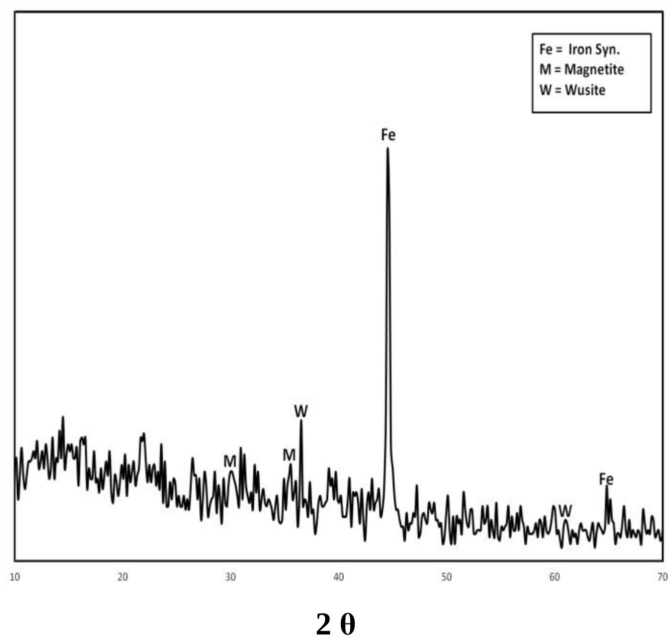

Fig.10. X-ray analysis of a briquette sample reduced at 700°C

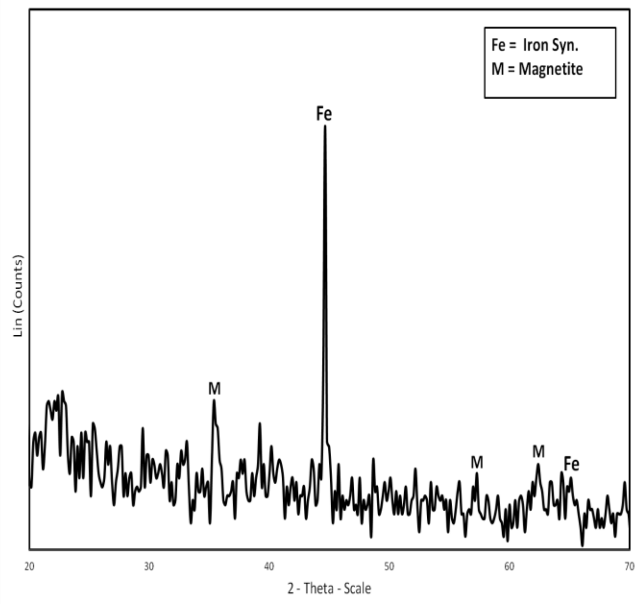

Fig 11. X-ray analysis of a briquette sample reduced at 1000°C

4. CONCLUSIONS.

From the obtained results, the following conclusions could be drawn:

1. As the percentage of bentonite added to iron ore increased, both the drop number and compression strength of green, dried and fired briquettes increased
2. Increasing the applied pressure leads to an increase both the drop number and compression strength of green, dried and fired briquettes.
3. Reduction of the briquettes formed increased applying a higher hydrogen flow rate.
4. The kinetics of reduction of iron ore briquettes using hydrogen could be interpreted either by assuming a reaction or a diffusion controlled mechanism. In either case, the values of calculated activation energy were close: 31.24 and 33.88 kJ.mol^{-1} respectively.

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