

The Effect of Addition of Fine Mill Scale (M) on Reduction of El-Baharia Iron Ore (O) Briquettes via Hydrogen

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Abstract—In this investigation, the effect of addition of mill scale (M) fine to El-Baharia iron ore (O) on the physical properties of briquettes in wet and dry form were studied. The effect of this addition on the degree of reduction was also studied.

Keywords— Iron ore, mill scale, briquette, Reduction by hydrogen, kinetic model of reduction.

I. INTRODUCTION

Hughes et al. (1982) studied the rate of reduction of particles of Carol Lake and Kiruna ores using pure hydrogen and pure carbon monoxide and mixtures of these two gases in the temperature range of 500 – 870°C and throughout this range the reduction rate with hydrogen was greater than that with carbon monoxide. And retracting core model was found to best fit the experimental data even when granules of 9×10^{-4} m diameter were used. Reduction with gas mixtures of hydrogen and carbon monoxide gave rates intermediate between those of the pure gases.

Zhang and Ostrovski (2002) investigated the reduction iron ore and iron cementation by H₂ - CH₄ - Ar gas mixtures in a laboratory isothermal fixed bed reactor in the temperature range of 600 - 925°C. Iron ore was first reduced to metallic iron by hydrogen, and then metallic iron was carburized to cementite by methane. Increasing the temperature and the hydrogen content accelerated the reduction process. However, for vol > 55 %, the effect of H₂ content was not significant. Methane had almost no effect on the reduction process. Increasing the temperature increased the rate of iron cementation and also the rate of free carbon deposition. The optimal conditions for cementite formation were temperature 750°C and reducing carburizing gas contents of 40 - 55 vol H₂ and 35 vol CH₄. Under these conditions, reduction of iron ore to cementite was completed in ~15 min. A two interface grain model and a volume reaction model were used to simulate the process of iron ore reduction and iron cementation.

Wagner *et al.* (2006) indicated that the reduction of synthetic hematite samples is a multi-stage reaction with one or two intermediate oxides depending on temperature. Thermo gravimetric experiments and analyses of partially reduced

samples have shown that the longest step is the last transformation, i.e. from wüstite to iron.

The first two reduction reactions, hematite to magnetite and magnetite to wüstite, were successive and well separated since hematite has completely disappeared when the first grains of wüstite are detected. On the contrary, the reduction of wüstite into metallic iron began before the total consumption of magnetite. An increase in temperature accelerates the reaction. Experiments with three types of hematite samples have shown differences in reactivity. With the sintered pieces and the nano powder, the final iron structure can be quite dense, making a gaseous diffusion very difficult. The solid state diffusion thus probably became the limiting step of the kinetics and the reaction rate was lowered even if the initial specific area of the sample was high.

Yunyun (2012) found that when iron lump ores were reduced by direct reduction method the reduced sample kept its shape without breaking into small fragments at temperature 900°C. Also, the reduction degree increases with the raise of the reaction temperature. Reduced iron ore at high temperature 900°C had higher reduction degree in comparison with reduced samples at 700 - 850°C. At 900°C, H₂ worked as the most effective reducing gas to give higher reduction degree and faster process. Microstructure strongly influenced reduction degree, smaller grain size samples being reduced faster and more completely. He also found that samples reduced at high flow rate (one L / min) and high temperature (900°C) took longer reduction time although the sample weight was smaller.

Pineau *et al.* (2006) studied the reduction of Fe₂O₃ by H₂ in the temperature range of 220 – 680°C, to examine the rate controlling processes of this reaction in the widest and lowest possible temperature range. Reduction of hematite to magnetite with H₂ was characterized by an apparent activation energy of 76 kJ/mol and apparent activation energy of the reduction of magnetite to iron is 88 and 39 kJ/mol for temperatures lower and higher than 420°C, respectively. They found that the mathematical modeling of experimental data suggested that the reaction rate was controlled by two- and three-dimensional growth of nuclei and by phase boundary

reaction at temperatures lower and higher than 420°C, respectively. Morphological study confirmed the formation of compact iron layer generated during the reduction of Fe₂O₃ by H₂ at temperatures higher than 420 °C.

Asima and Itishree (2007) found that with Increase in temperature for the percentage reduction increases with the increase in time. Lower the binder percentage, greater the reducibility. Reduction of pellets with Dextrine binder is faster as compared to Bentonite.

Longbottom and Kolbeinsen (2008) found that when the iron ore reduced by CO and H₂ gas mixture the hematite is reduced to magnetite quickly, which in turn is reduced fairly quickly to wüstite. The reduction of wüstite to metallic iron seems to be the limiting stage in the reduction of the pellets which is in line with what would be expected.

Pati and Vinay (2008) indicated that with increase in temperature degree of reduction increases from 850 - 1000 °C With increase in time degree of reduction of pellets increases from 15 - 120 minutes.

Mohamed *et al.* (2008) concluded that the recycling of some iron oxide waste characterized by high iron oxide content such as El-Dekhilla iron oxide pellets waste during the sintering of iron concentrate. The results showed that, replacement of iron ore concentrate with 10% iron oxide pellets fine increases the amount of readymade sinter, sinter strength and productivity of both sinter machine and blast furnace yard.

More than 90% of iron is currently produced by the blast furnace (BF) process, while the balance is produced by the Direct Reduction (DR) processes (World steel Committee on Economic Studies, 2010).

II. EXPERIMENTAL WORK

2.1. Materials

A representative samples of EL –Baharia iron ore (O), mill scale (M) were provided from iron and steel CO (Helwan, Cairo Egypt

2.2 Chemical Analyses of Raw Materials

The chemical compositions of raw Materials were analyzed by XRF apparatus and the chemical composition of raw Materials is as follows:

The chemical composition of El-Baharia iron ore is listed in Table I.

TABLE I. The chemical composition of El-Baharia iron ore

Compound	Weight %
Fe ₂ O ₃	74.79
MnO	2.92
SiO ₂	10.84
CaO	0.39
MgO	0.18
Al ₂ O ₃	1.44
S	0.74
TiO ₂	0.16
BaO	1.17
ZnO	0.15
K ₂ O	0.27

2.3 X- ray Diffraction of the Raw Materials

X-ray diffraction analyses for raw Materials were conducted to determine qualitatively its phase composition. This analysis was carried out using Broker AXS-D8 Advance. The investigated samples were finely ground to pass through 0.076 mm sieve to remove the effect of particle size on the obtained X-ray diffraction pattern. The mineral composition of the analyzed samples was qualitatively determined from their XRD pattern using XRD data of minerals given by ASTM which are stored in the memory of the computer of the apparatus.

The X- Ray analysis of El-Baharia iron ore is illustrated in figure 1. From which it is clear that El-Baharia iron ore mainly consists of hematite and quartz

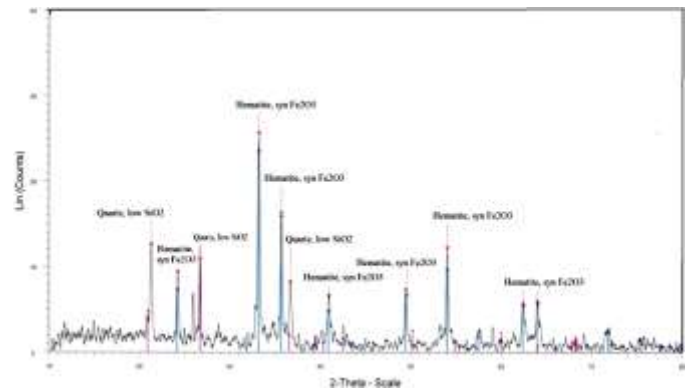


Fig. 1. X-ray diffraction analysis of El-Baharia iron ore sample.

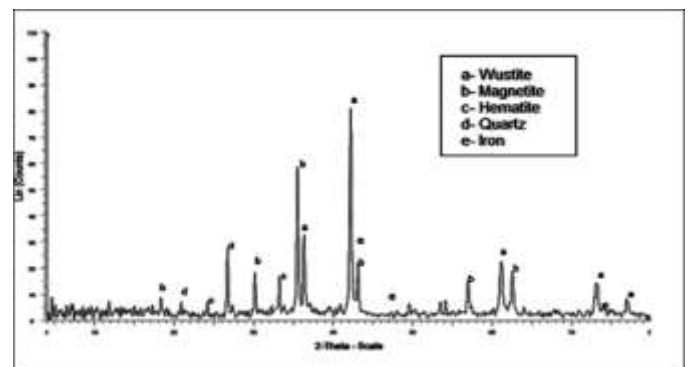


Fig. 2. X-ray of Mill Scale Sample

2.4. Methods

2.4.1. Preparation of samples in the form of briquette for reduction by hydrogen

Preparation of samples for the briquetting process was carried out by mixing of iron ore with fine or the mill Scale with 3% molasses (binding material) was pressed in the mould (12mm diameter and height 22 mm) using MEGA.KSC-10 hydraulic press Fig. 3.

2.5 Determination of the Quality of Briquettes

2.5.1 Drop Damage Resistance Test

The produced green or dry briquettes were subjected to Drop damage resistance test (Mayer, 1980; Forsmo *et al.*, 2006; Forsmo *et al.*, 2008). The drop damage resistance indicates how often briquette can be dropped from a height of

46cm before they showed perceptible cracks or crumbed. Ten briquettes were individually dropped on a steel plate until their breaking. The mean value of the tested briquettes gave their average drop number.



Fig. 3. MEGA. KSC - 10 hydraulic press

2.5.2 Compressive Strength Test

The average compressive strength tests of briquettes wet or dried (ASTM E 382-12 / 2012 standards) controlled by compressing at least 10 of briquettes between parallel steel plates up their breaking. The mean value of the tested briquettes gave their compressive strength.

2.6 Reduction Procedure by Hydrogen

The reduction of EL-Baharia iron ore with mill scale briquette by hydrogen was done in the thermo gravimetric apparatus Fig. 4. It consists of vertical furnace, electronic balance for monitoring the weight change of reacting sample and temperature controller. The sample was placed in a Ni - Cr crucible which was suspended under the electronic balance by Ni - Cr wire. The furnace temperature was raised to the required temperature and maintained constant to ± 5°C. Then the sample was placed in the hot zone. The nitrogen flow rate was 0.5 L / min in all experiments at initial time and after the end of reduction by hydrogen only. The weight of the sample was continuously recorded at the end of the run; the samples were withdrawn from the furnace and kept in the desiccators.



Fig. 4. Thermo gravimetric apparatus used for reduction.

The percentage of reduction was calculated according to the following equation

$$\% \text{ reduction} = \frac{(W_o - W_t)}{W_o} \times 100 \quad (1)$$

Where (W_o) is the initial mass of sample in g and (W_t) is the mass of the sample in g after time (t) min and The oxygen mass indicated the mass of oxygen present in the briquette in the form Fe_2O_3 .

III. RESULTS AND DISCUSSION

The effect of pressure on the physical properties of the produced in green briquettes forms of mill scale added to iron ore

Figures (5–8) show the relationship between the change of pressure load versus the drop damage resistance and compressive strength of the wet and dry briquettes with M/O ratio of 0.0526 and 0.25, respectively, at a constant amount of molasses (3%) as binder from these figures, it is clear that when the pressure load increases, both the drop damage resistance and compressive strength increased. This may be due to the fact that increasing the pressure leads to an increase in the briquette compaction which leads to an increase in the inherent Vander Waals forces present (Mohamed *et al.*, 2004; El - Hussein *et al.*, 2015).

As well, increasing the pressure load may have progressively crushed and decreased the macro pores present within the briquettes (Gaballah *et al.*, 2014; El - Hussein *et al.*, 2015).

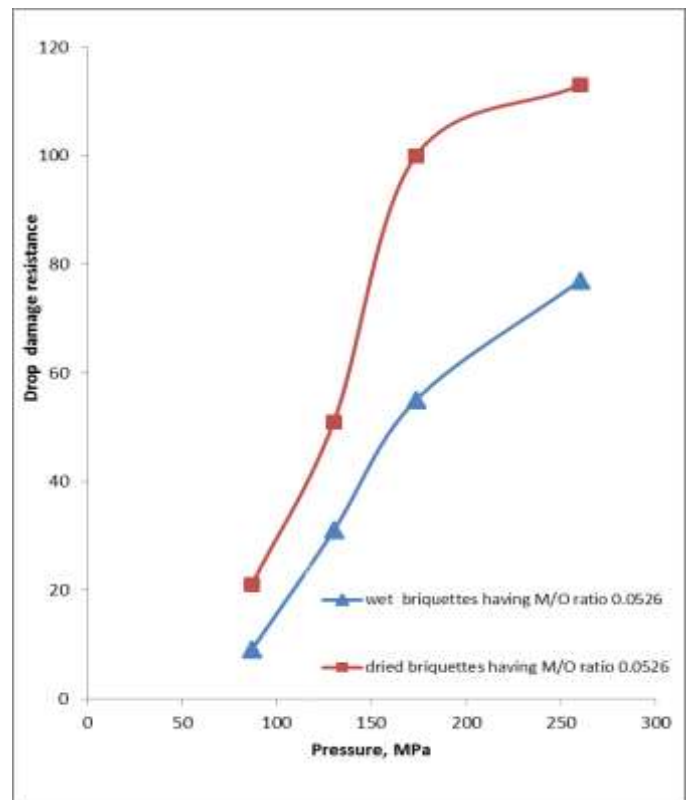


Fig. 5. The relationship between the change in pressure load vs. the drop damage resistance of the wet and dry briquettes having E/O ratio of 0.0526 at constant amount of molasses (3%) binder.

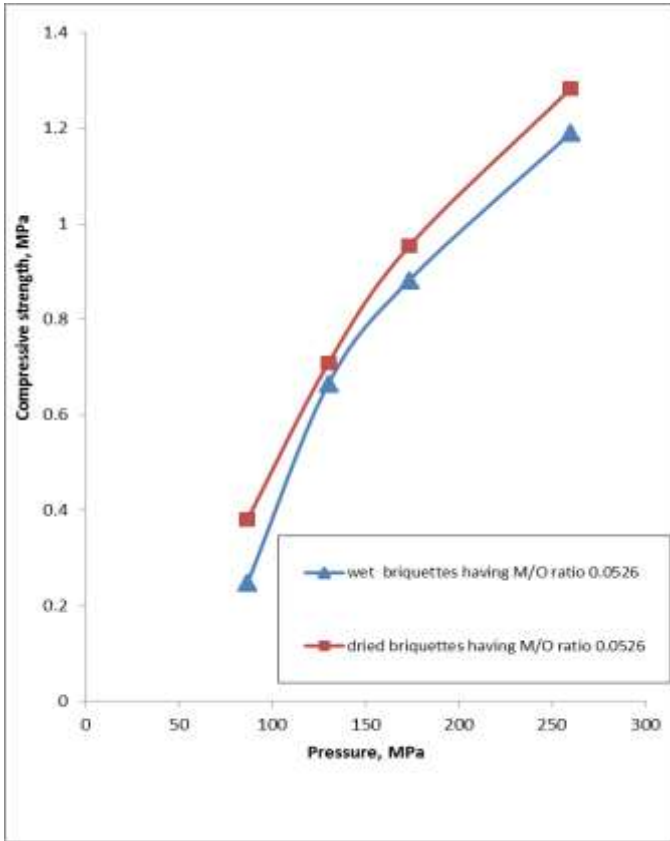


Fig. 6. The relationship between the change in pressure load vs. the compressive strength of the wet and dry briquettes having E/O ratio of 0.0526 at constant amount of molasses (3%) as binder.

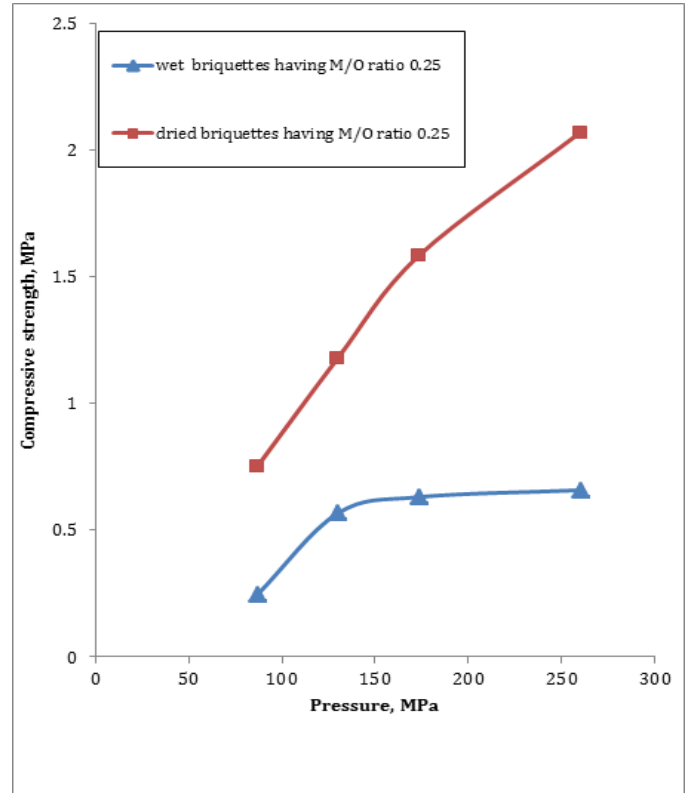


Fig. 8. The relationship between the change in pressure load vs. the compressive strength of the wet and dry briquettes having E/O ratio of 0.25 at constant amount of molasses (3%) as binder

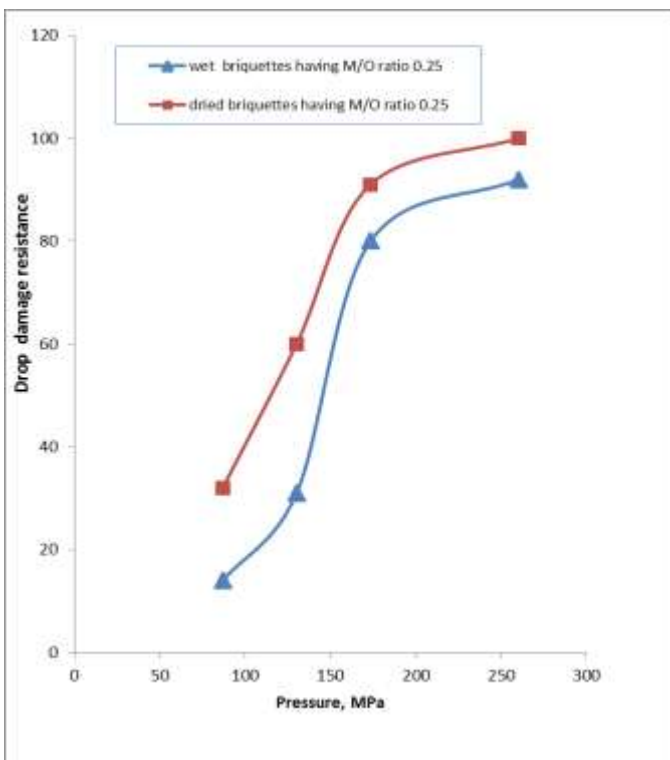


Fig. 7. The relationship between the change in pressure load vs. the drop damage resistance of the wet and briquettes having E/O ratio of 0.25 at constant amount of molasses (3%) binder.

Effect of ratio M/O on the reduction percentage

Figure 9 illustrates the effect of ratio M/O on the reduction percentage by hydrogen flow rate 1.5 L/min for the briquette which compressed at 261 MPa. From this figure, it is clear that as the M/O ratio increased the reduction percentage decreased, which may be attributed to the loss of porosity in briquette due to the increase in melt within its.

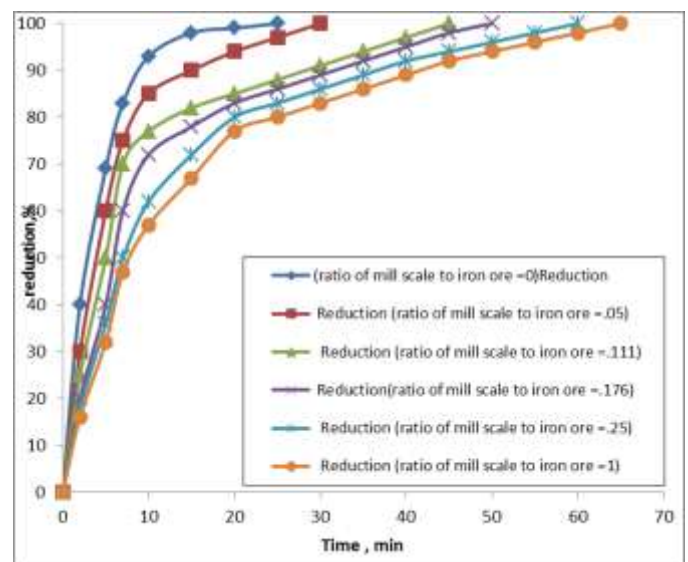


Fig. 9. The effect of varying the M/O ratio upon the ore reduction process at 900°C.

The Effect of hydrogen flow rate upon the reduction of M/O mixture

Figures (10 and 11) show the effect of changing the hydrogen flow rate upon the reduction of the briquettes pressed at 261 MPa at 900 °C for both M/O ratios 0.0526 and 0.25, respectively. From these figures, it is clear that as the flow rate increased the reduction percentage increased.

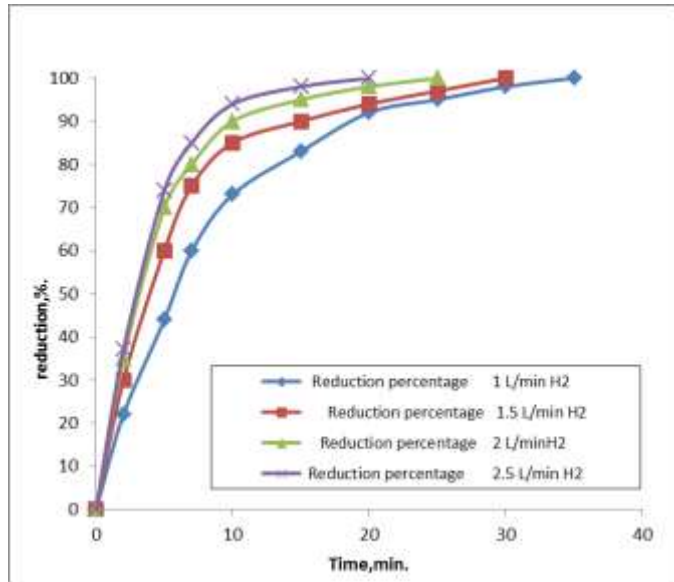


Fig. 10. The effect of changing the hydrogen flow rate upon the reduction of the briquette pressed at 261 MPa at 900 °C containing M/O ratio of 0.0526.

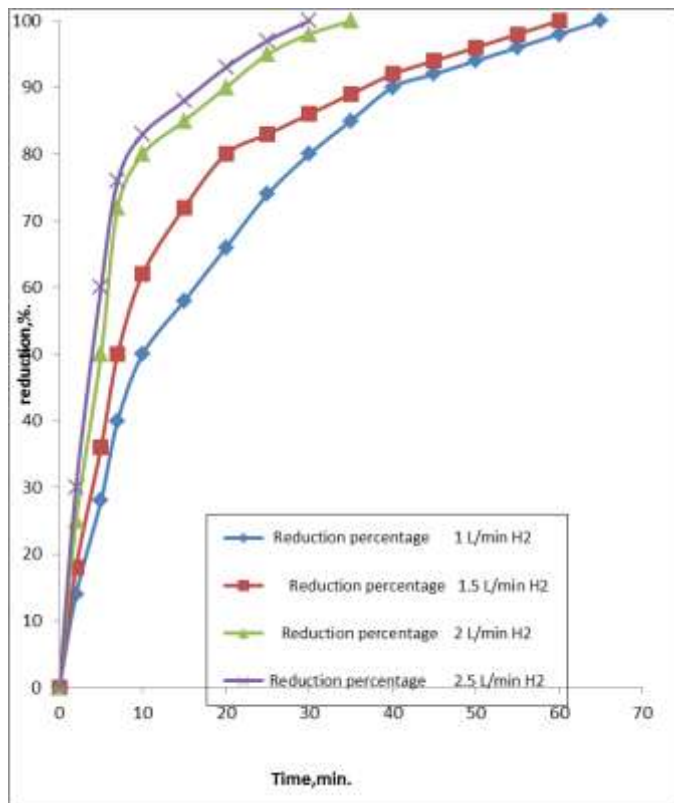


Fig. 11. The effect of changing the hydrogen flow rate upon the reduction of the briquette pressed at 261 MPa at 900 °C containing M/O ratio of 0.25.

The increase in flow rate may increase the gas diffusion across the boundary layer increasing the rate of the reaction. (Mohamed *et al.*, 2004; Gaballah *et al.*, 2014). This may be attributed to the fact that increasing the flow rate leads to the increase in the number of hydrogen moles passing through the bulk phase, which in turn leads to an increase in hydrogen adsorption onto the briquette material.

Zuo *et al.* (2015) also indicated that the reaction rate increases gradually with the increase of H₂ content which may be attributed to the higher penetration capacity of H₂. As well, there was a decline in diffusion resistance as H₂ becomes a dominating factor. On the other hand, the prevailing increase in flow rate in the reaction zone enhances the rate of hydrogen absorption and subsequently the rate of chemical reaction increases (Mohamed *et al.*, 2004; El - Hussiny. *et al.*, 2014 a; Gaballah *et al.*, 2014).

The Effect of temperature upon the reduction percentage

In order to study the effect of temperature upon the reduction of M/O briquettes formed, the experiments were carried out at 700 – 950°C and under 1.5 L/min hydrogen flow rate. The plots of the reduction percentage versus time are shown in Figures (12 and 13). From these figures, it was observed that the reduction temperature did significantly influence the reduction percentage. This may be due to the fact that as the reduction percentage increases with increase in temperature as the number of reacting moles having excess of energy increased. Moreover, the raise of temperature may lead to an increase of the rate of mass transfer through diffusion as well as the rate of desorption. (Shalabi, 1973; Sayed *et al.*, 2002; Sayed *et al.*, 2001; El - Hussiny *et al.*, 2014 b).

Zuo *et al.*, 2015 indicated that rate constant of the chemical reaction speeds up with the increase in the reaction temperature in the presence of hydrogen gas. Moreover, using pure H₂ as the reducing agent decreases both the resistance of diffusion and chemical reaction with the rise of temperature due to the endothermal reaction of the gas. This leads to a higher reducing potential at high temperatures which enhances the reaction rate.

Kinetics of the reduction process

Kinetic studies for estimation of the apparent activation energies of the process were carried out at different temperatures from 700°C - 950°C for briquettes formed at different time intervals (0 - 60 min). Using a pseudo first order equation $kt = - \ln (1-R)$ for both briquettes of M/O ration 0.0526 and 0.25 respectively.

Figures (14 and 15) illustrate the relationship between $-\ln (1 - R)$ versus reduction time (t) for the different reduction temperatures for briquettes from with M/O ratio of 0.0525 and 0.25, respectively. From both figures, a linear relationship was observed from 0 to 35 min for M / O ratio 0.0525 and from 0 to 55 min for M / O ratio 0.25.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of the reduction process of briquettes from with M/O ratio of 0.0526 and 0.25, respectively. The results are illustrated in Figures (16 and 17).

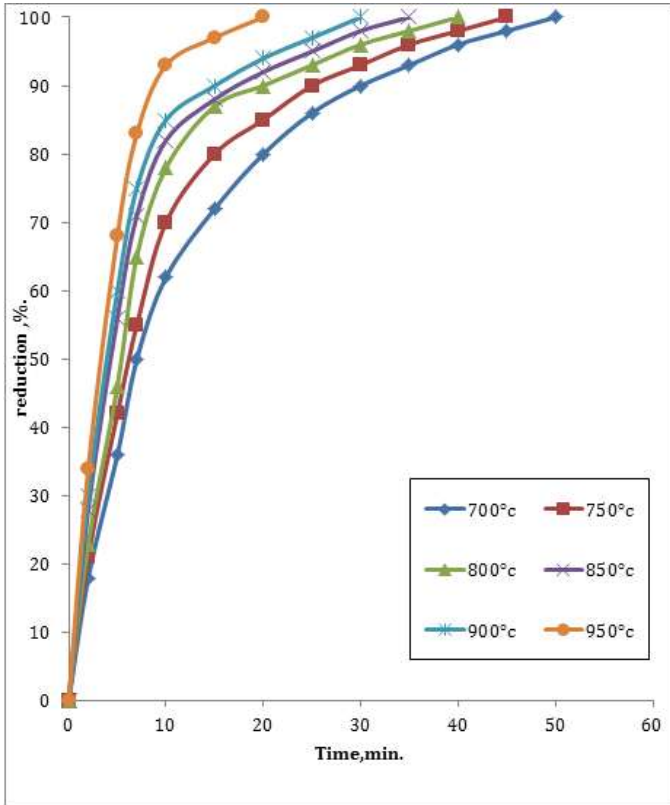


Fig. 12. The effect of temperature upon the reduction percentage of briquettes containing M/O ratio of 0.0526

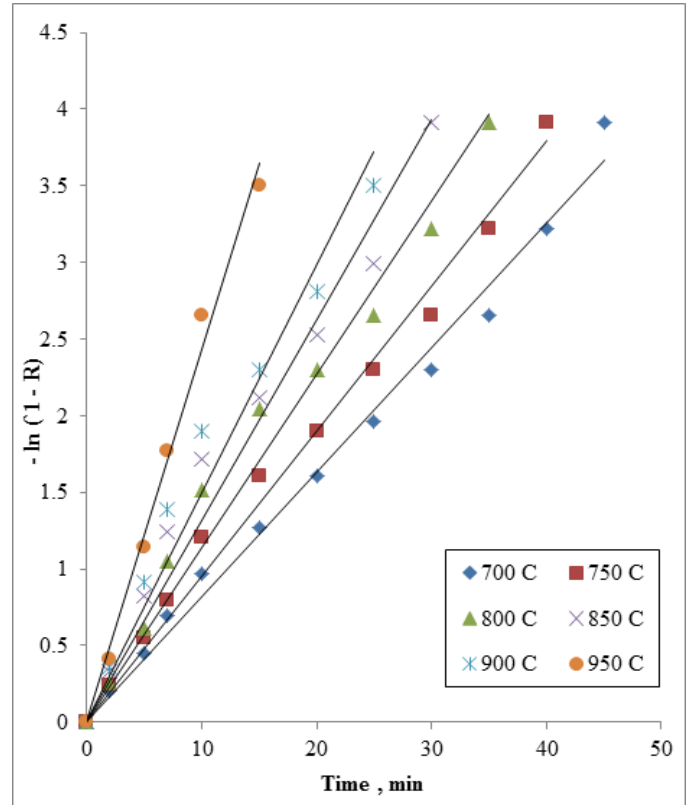


Fig. 14. The relationship between $-\ln(1-R)$ vs reduction time (min) at the different reduction temperatures for briquettes from with ratio of M/O of 0.0525.

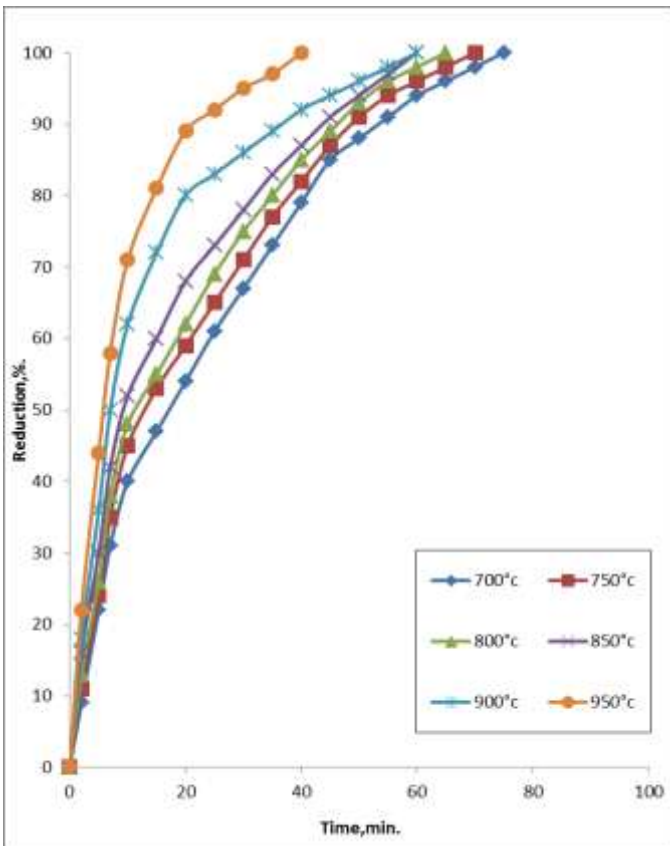


Fig. 13. The effect of temperature upon the reduction percentage of briquettes containing M/O ratio of 0.25

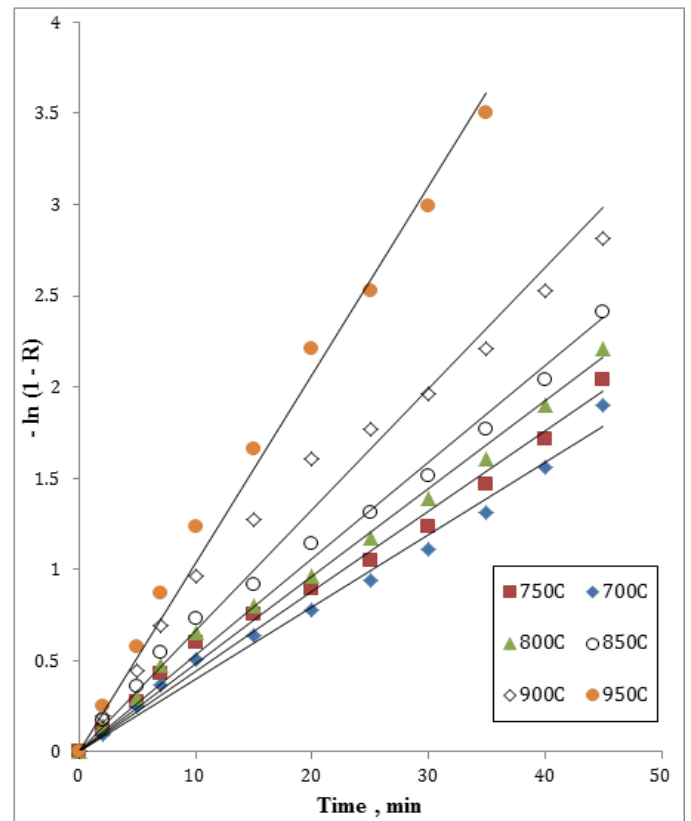


Fig. 15. The relationship between $-\ln(1-R)$ vs reduction time (min) at the different reduction temperatures for briquettes from with ratio of M/O of 0.25.

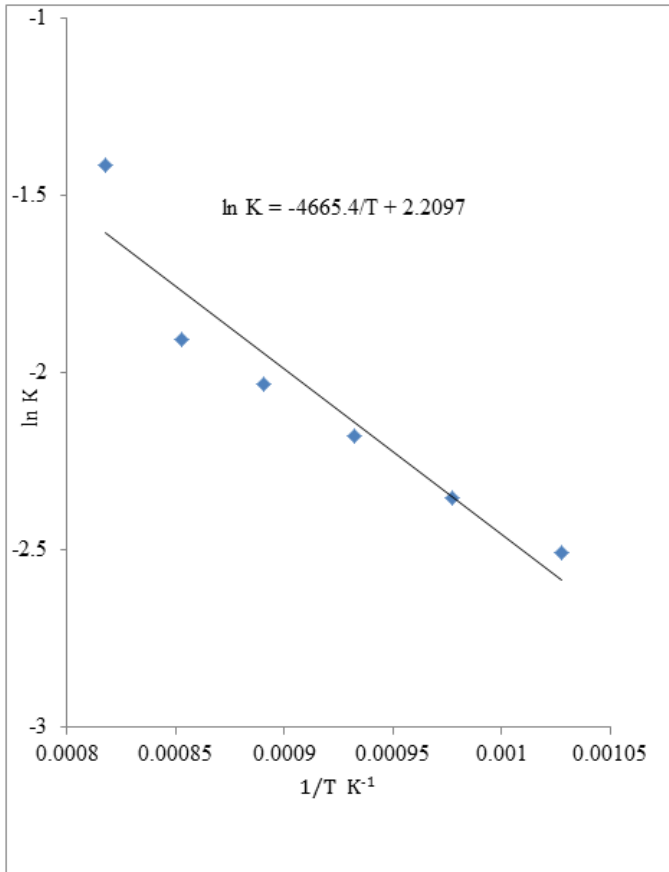


Fig. 16. The Arrhenius plot for the reduction process of briquettes from with ratio of M/O of 0.0526

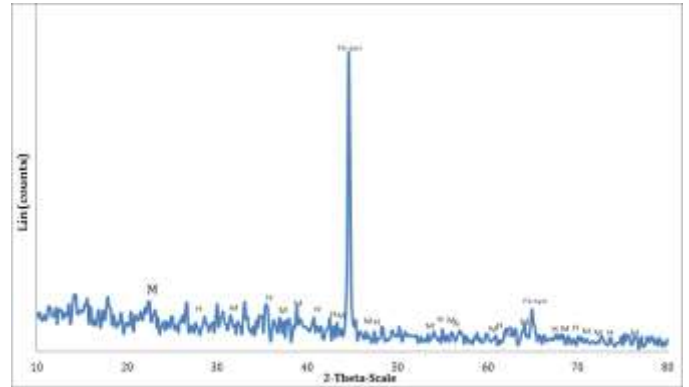


Fig. 18. X-ray analysis of the samples reduced at 950°C for briquettes formed with ratio of M/O = 0.0526

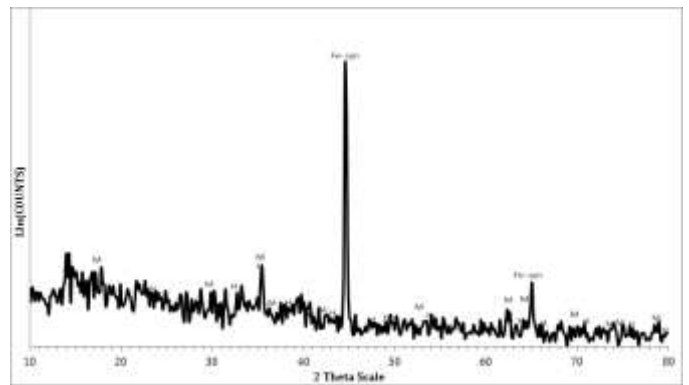


Fig. 19. X-ray analysis of the samples reduced at 950°C for briquettes formed with ratio of M/O of 0.25

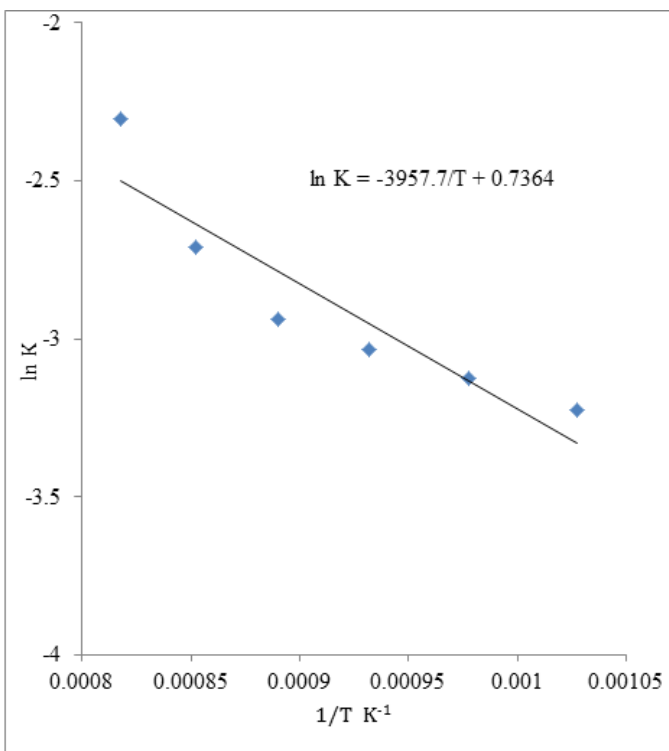


Fig. 17. The Arrhenius plot for the reduction process of briquettes from with ratio of M/O of 0.25

The activation energies calculated for this process for the briquettes formed with M/O ratio of 0.0525 and 0.25 was = 38.8 kJ/ mole and 32.9 kJ/ mole, respectively.

X-Ray analyses of the reduced briquette

The results of the X-ray analyses of the samples reduced at 950°C for briquettes formed with M/O ratio of 0.0526 and 0.25 are shown in Figures (18- 19), respectively. The results indicate the dominant phase was metallic iron (syn. Fe).

IV. CONCLUSIONS

1. As M/O ratio increased, both the drop number and compression strength increased in the briquettes formed from mill Scale fines (M) and El-Baharia iron ore (O).
2. As the M/O ratio increased the reduction percentage decreased
3. Reduction of the briquettes formed increased applying a higher hydrogen flow rate.
4. Reduction of the briquettes formed increased with increasing the temperature.
5. The activation energies calculated for this process for the briquettes formed with M/O ratio of 0.0526 and 0.25 Using equation $kt = -\ln(1 - R)$ was = 38.8 kJ/ mole and 32.9 kJ/ mole, respectively.

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