

Effect of Change the Percentage of Mill Scale on the Reduction of Briquettes Made from El-Baharia Iron Ore by Hydrogen

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Abstract— The demand of iron for the manufacture of different types of steel is increasing continuously and new solid reductant-based sponge iron plants are being commissioned. In the existing blast furnace, an increase in production by at least 25% to 35% can be achieved by using reduced iron ore. Also, the majority of fines which are generated during the course of handling, mining and transportation are exported at a through away price which needs to be utilized by making iron ore briquettes for sponge iron making.

A lot of investigations have been carried out on direct reduction of iron oxides by using hydrogen gas.

In the present work, an attempt has been made to study the reduction behavior and kinetics of fired mill scale added to iron ore pellets.

The effect of different reduction parameters such as temperature and hydrogen flow rate also, the effect of drop damage resistance, applied pressure and compressive strength was studied.

Reduction of briquetted fine mill scale added to iron ore by hydrogen is carried out in the temperature range 700 to 1000°C. In the reduction kinetic study, the most satisfactory model is to take the slope of the initial linear region of fractional reduction vs. time curve as a measure of rate constant (k) and $\ln k$ vs. $1/T$ plots are straight line from which activation energy was calculated.

In kinetic studies relating to reduction of ores, a mechanism is assumed that correlates time (t) to conversion (R):

$$R=F(t)$$

The most satisfactory model is that which gives the higher R^2 coefficient on plotting $F(R)$ against (t).

Keywords— Briquetting, mill scale, reduction kinetics, diffusion model, energy of activation.

I. INTRODUCTION

Metals have been used in human society for thousands of years and the amount of metal production continuously increased. In modern society, the use of metals became inevitable in our daily life throughout society. The source of metals was shifting from high concentrations of ores to low concentrations or industrial wastes.

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 nature in free form because it has a high tendency to oxygen. and to obtain pure elemental iron, the impurities

must be removed by chemical reduction (Mishra and Baliarsingh 2008)

Heihachi and M.S 1932 Indicated that iron oxides and oxide iron ores are easily reducible by hydrogen at low temperature And also confirmed that more compact the ore, the more difficult the reduction. Easily reducible ores were nearly completely converted to the metallic state at 900° to 950°C. in 3 to 4 hr. Magnetite sands were most difficult to reduce, requiring temperatures above 1,100° or 1,150°C. When melting the product in a crucible no difficulty was encountered when more than 95 % of the iron in the sponge iron was in the metallic state. No chemical reaction occurs which would bring about evolution of gas as is the case in the melting of ordinary iron and steel containing carbon. The ores containing phosphorus and sulfur below 0.03 and 0.07 per cent respectively, gave iron which had less than 0.02 per cent of these two elements combined. If we start with an ore low in P, S, Mn, etc., it is not difficult to keep the total amount of impurities in the melted iron under 0.1 per cent. The physical properties of hydrogen reduced melted iron depend upon the impurities present but when these are low the elastic limit and tensile strength are about the same as those for electrolytic iron,. The oxides of phosphorus are more difficult to reduce than the oxides of iron. At any constant temperature the percentage reduction of phosphorus is much lower than that of iron as is demonstrated in the case of the reduction of Taihei and Johole ores at temperatures ranging between 600°C. and 1,150°C. At 600°C., the percentage of reduction for iron is between 50 and 60 and for phosphorus is less than 30. At 900°C., the percentage for iron is 90 to 95; and for phosphorus 60 to 70.

(McKewan 1958) studied the reduction of magnetite by hydrogen at temperatures less than 570°C. And (McKewan 1960) found the rate of weight loss due to the removal of oxygen from magnetite/iron interface in spherical pellets done at temperature lower than 570°C is proportional to the area of the iron/iron oxide interface.

More than 90% of iron is produced in the blast furnace process while the balance is produced by the direct reduction processes [Yearbook and Association, (2010)].

Fruehan et al. 2005 A high degree of reduction or metallization of products, such as hot briquetted iron, used in steelmaking is desirable. For many ores it is difficult to achieve this goal because the rate of reduction slows significantly after 70–90% reduction. This study shows that this happens for several types of ores and oxides because a shell of dense iron forms around wustite grains requiring atomic diffusion of oxygen through iron, for reduction to proceed. This rate is slow because of the low driving force and diffusion coefficient. Examination of the rate equations for gaseous reduction and oxygen diffusion indicate that if the wustite grains are about 1 μm, gaseous reduction will govern the rate up to 95% reduction or greater, but for 2-μm-sized grains the rate will slow significantly earlier when atomic diffusion controls the rate. The present work also indicates that if the equilibrium gas pressure at the Fe/FeO exceeds 1 atm, the iron shell may fracture allowing for faster gaseous reduction. Also, annealing or holding the ore at magnetite (Fe₃O₄) can also cause the rate of reduction to slow at lower degrees of reduction.

Damien et al (2006) 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 (Fe₂O₃) is first transformed into magnetite (Fe₃O₄), then into wustite (Fe_{1-y}O), and finally into metallic iron while at temperatures below 570°C, magnetite is directly transformed into iron as wustite is not thermodynamically stable

El-Husseiny et al. 2015 concluded the following:- 1- The reduction of iron ore briquette by hydrogen depends on the flow rate of hydrogen and temperature of the reduction pressure of the briquetting. 2- As the temperature increased the reduction increased. 3- As the flow rate of hydrogen increased the reduction rate increased 4- The reduction of the iron ore briquette is controlled by one of the following models:- a- Diffusion through thin ash layer (jander equation) b- Diffusion controlled c- Diffusion through ash layer (crankincslling-Broushten equation)

Ezz and Wild [1960] indicated that an increase in temperature exerts a major influence on increasing reduction rate, while ore characteristics, such as porosity, shape factor, and surface condition also affected reduction rate also the ore/gas ratio has a major influence on the reduction rate.

Moo [2010] and Haitao [2011] indicated that the kinetics feasibility tests showed that 90 - 99% reduction of iron ore concentrate by hydrogen was obtained within 1 - 7 seconds at 1200 – 1400 °C, depending on the amount of excess hydrogen supplied with iron oxide. This reduction rate is fast enough for a flash reduction process. The activation energy of hydrogen reduction of iron ore concentrate was determined to be 463kJ/mol, which demonstrates that this process has greater temperature effect on the reduction rate than most reactions.

Wenguang et al. 2017, Found that the surplus coke oven gases which contain substantial amounts of H₂, CH₄, and CO and low grade hematite ores are abundant in Shanxi, China. In this work, low-temperature hydrogen reduction of hematite ore fines was performed in a fixed-bed reactor with a stirring apparatus, and a laboratory Davis magnetic tube was used for

the magnetic separation of the resulting magnetite ore fines. The experimental results indicated that, at temperatures lower than 400°C, the rate of reduction of the hematite ore fines was controlled by the interfacial reaction on the core surface. However, at temperatures higher than 450°C, the reaction was controlled by product layer diffusion. With increasing reduction temperature, the average utilization of hydrogen initially increased and tended to a constant value thereafter. The conversion of Fe₂O₃ in the hematite ore played an important role in the total iron recovery and grade of the concentrate. The grade of the concentrate decreased, whereas the total iron recovery increased with the increasing Fe₂O₃ conversion.

II. EXPERIMENTAL WORK

2.1. Raw Material

2.1.1 Iron ore

Iron ore ore samples was supplied by the Egyptian Iron and Steel Company, The chemical composition of iron ore is as follows:-

Fe total = 52.35 %, MnO= 2.92%, SiO₂= 10.84%, CaO= 0.39%, MgO= 0.18%, Al₂O₃= 1.44%, S= 0.74%, TiO₂= 0.16%, BaO= 1.17%, ZnO= 0.15%, K₂O= 0.27%, Na₂O= 0.25%, P₂O₅= 0.5 %.

A representative sample of mill scale was provided from iron and steel Company

The chemical analysis of mill scale shows that it contains Fe total 69.33% in the form (Fe₂O₃ 70%, Fe₃O₄ 17.26% and FeO 7.83%). Sulphur 0.33%, Phosphorus 0.22%, MnO 0.66%, SiO₂ 1.92% and carbon 0.04%.

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.

The X- Ray analysis of mill Scale is illustrated in figure (2) From which it is clear that mill Scale mainly consists of magnetite, wustite, iron, quartz and hematite.

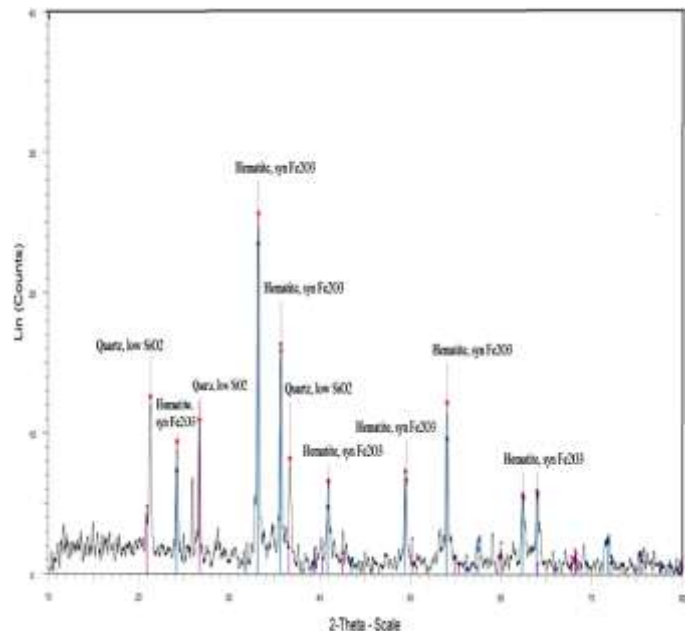


Fig. 1. X-ray of El-Baharia iron ore.

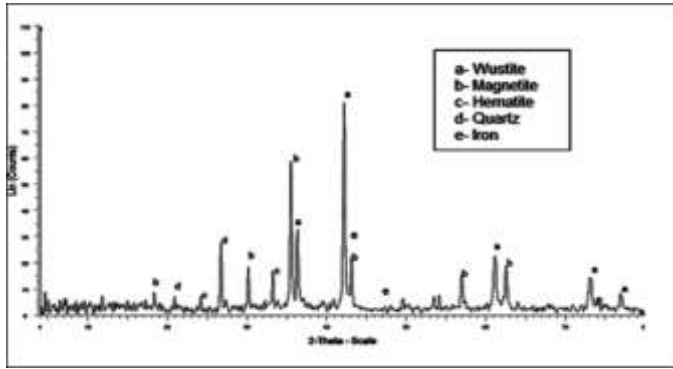


Fig. 2. X-ray of Mill Scale Sample.

2.2. Reduction Procedures

The reduction of the briquette by hydrogen were done on thermo gravimetric apparatus (A schematic diagram of thermo gravimetric apparatus is shown in Fig. 3. It consists of a vertical furnace, electronic balance for monitoring the weight change of reacting sample and temperature controller. 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 °C) and maintained constant to ± 5 °C. Then samples were placed in hot zone. The nitrogen flow rate was 0.5 l/min on all the experiments was passed at initial time and after the end of reduction only, 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 the desiccators. The amount of removable oxygen and carbon monoxide was determined by the weight loss from the sample (Wo-Wt) during the experiment of reduction .The percentage of losses was calculated according to the following equation:-

$$\text{Percentage of loss} = [(W_o - W_t) / W_o] * 100 \tag{1}$$

Where W_o the initial mass of sample, g.
 W_t mass of sample after each time, g.

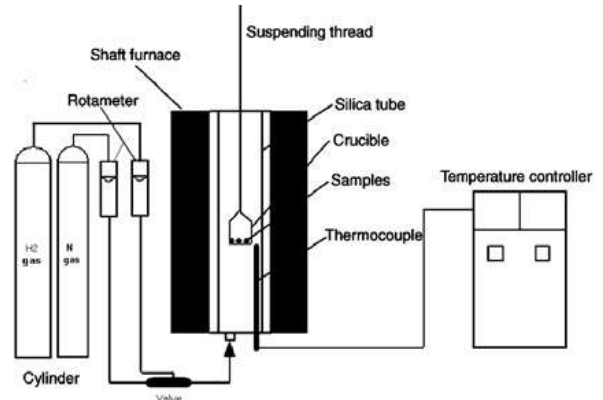


Fig. 3. Schematic diagram of the reduction apparatus.

III. RESULT AND DISCUSSION

3.1 The Effect of Percentage of Mill Scale Added to Iron Ore on the Physical Properties of the Produced Briquettes in Green, Dry and Burning Forms

Figs 4 and 5 show the relationship between the change of amount of mill scale added to iron ore and the drop damage resistance and compressive strength of the wet briquettes, dry samples and burning at 1000°C, at constant amount of molasses (2.5%) as binder From these figures, it is clear that when the amount of mill scale increases, both the drop damage resistance and compressive strength decreased.

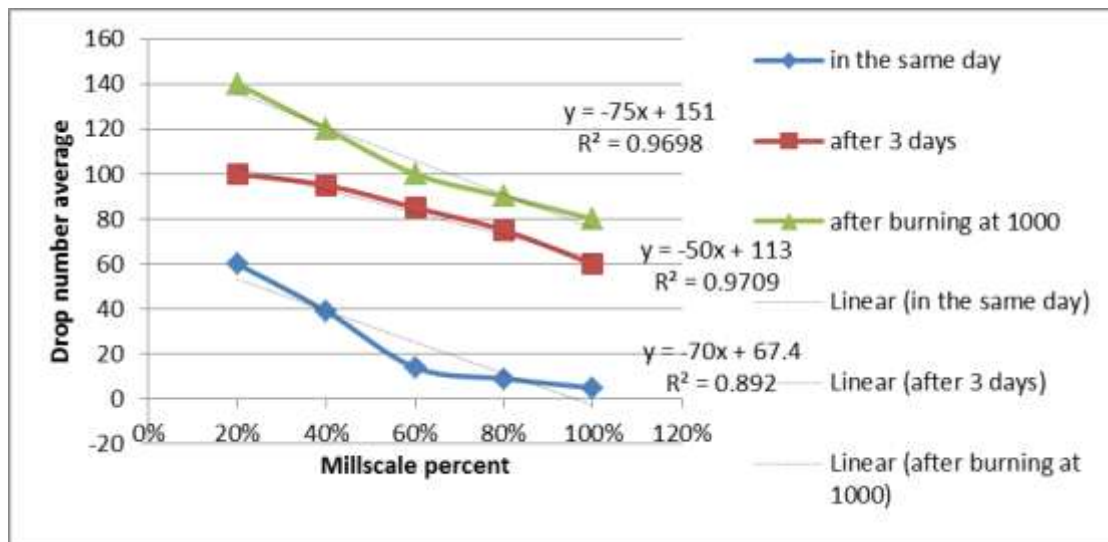


Fig. 4. The relationship between the change of amount of mill scale added to iron ore and the drop damage resistance of the wet briquettes, dry samples and burning at 1000°C

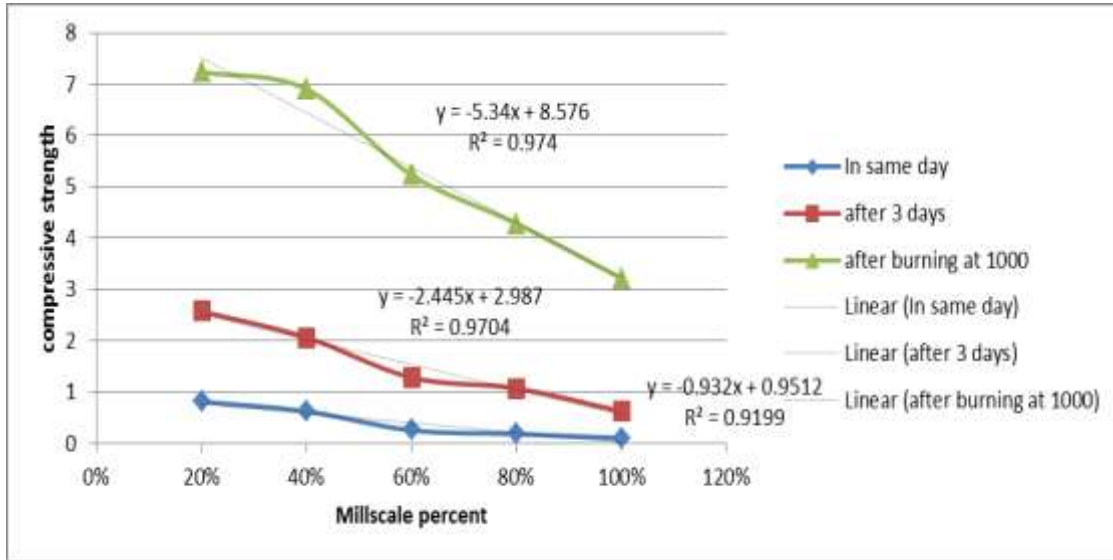


Fig. 5. The relationship between the change of amount of mill scale added to iron ore and the compressive strength of the wet briquettes, dry samples and burning at 1000°C

The Effect of temperature upon the reduction percentage

In order to examine the effect of temperature upon the reduction of briquettes formed, the experiments were carried out at 700 – 1000°C and under 1.5 L/min hydrogen flow rate. The plots of the reduction percentage versus time are shown in Figures 6 and 7 from these figures, it was observed that the temperature 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. (Sayed *et al.*, 2001; Sayed *et al.*, 2002; El -Hussiny *et al.*, 2014).

Zuo *et al.* (2015) indicated that the rate constant of the chemical reaction speeds depend on the 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.

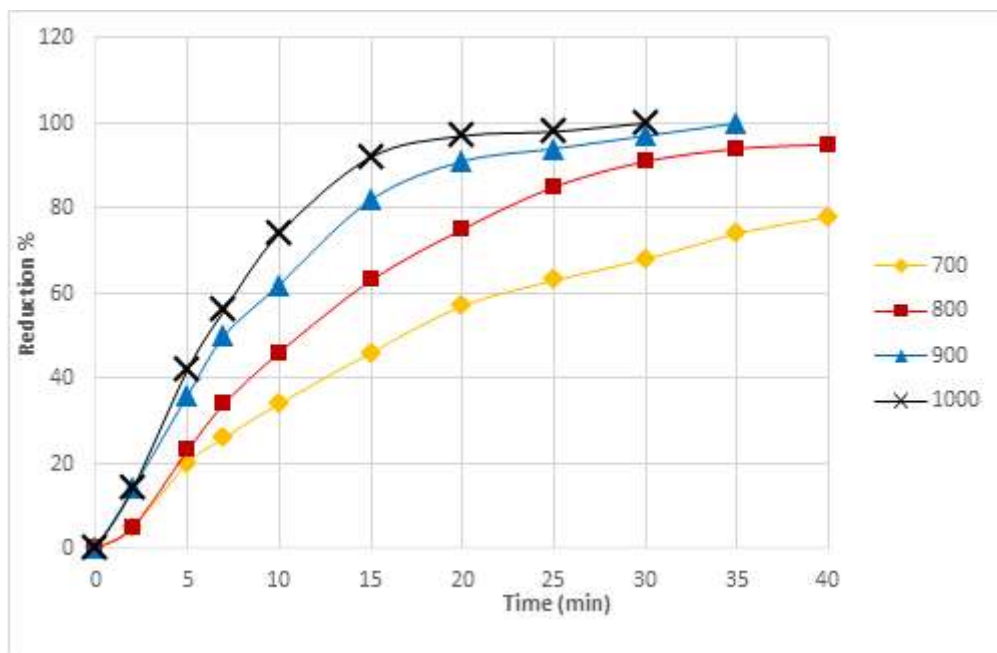


Fig. 6. Effect of temperature on the reduction percentage of mill scale briquette.

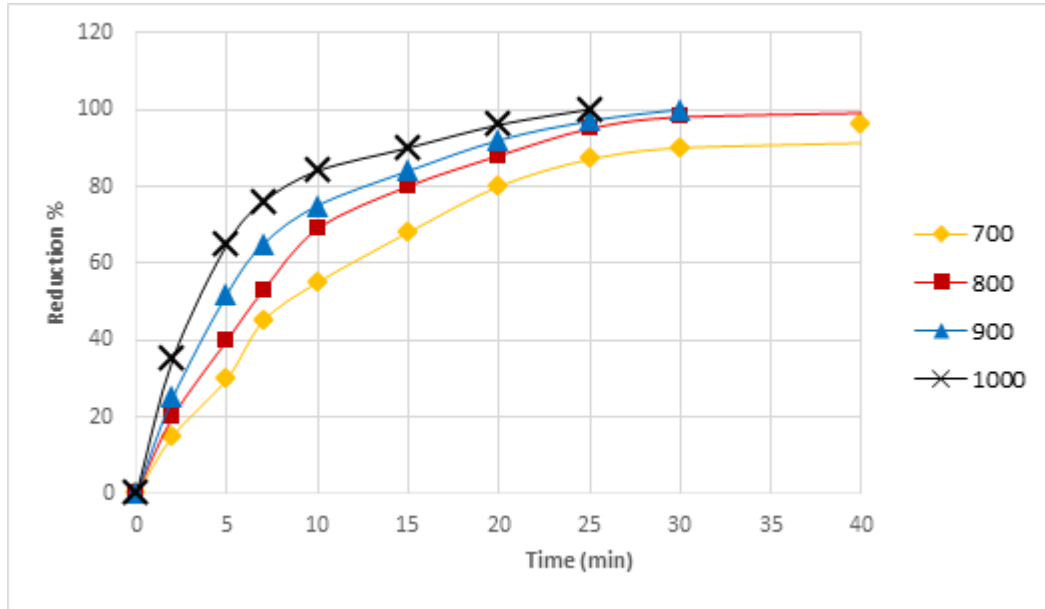


Fig. 7. Effect of temperature on the reduction percentage of 40% iron ore and 60% mill scale briquette.

Effect of the change of the ratio of mill scale to ore on the reduction process

Figure (8) Illustrate the effect of change amount of mill scale to iron ore ratio on the reduction process by hydrogen from which it is clear that as amount of mill scale /amount of iron ore increased the reduction percentage increased

3.2. Kinetics Reduction of the Briquette

Kinetic studies for estimation of apparent activation energies were carried out for the briquette at different temperatures range from 700°C up to 1000°C for different time intervals in the range of 0 - 60 min. Using equation diffusion model

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

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

Figures (9-11) illustrate the relationship between $1-2/3 R - (1-R)^{2/3}$ and reduction time (t) for the different reduction temperatures for briquettes of mill scale and iron ore. From these figures, a linear relationship 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.10 -12, from which it is clear that the activation energy=45.8,23.9 kJ/ mole for 100 %mill scale and (40%iron ore and 60% mill scale) respectively.

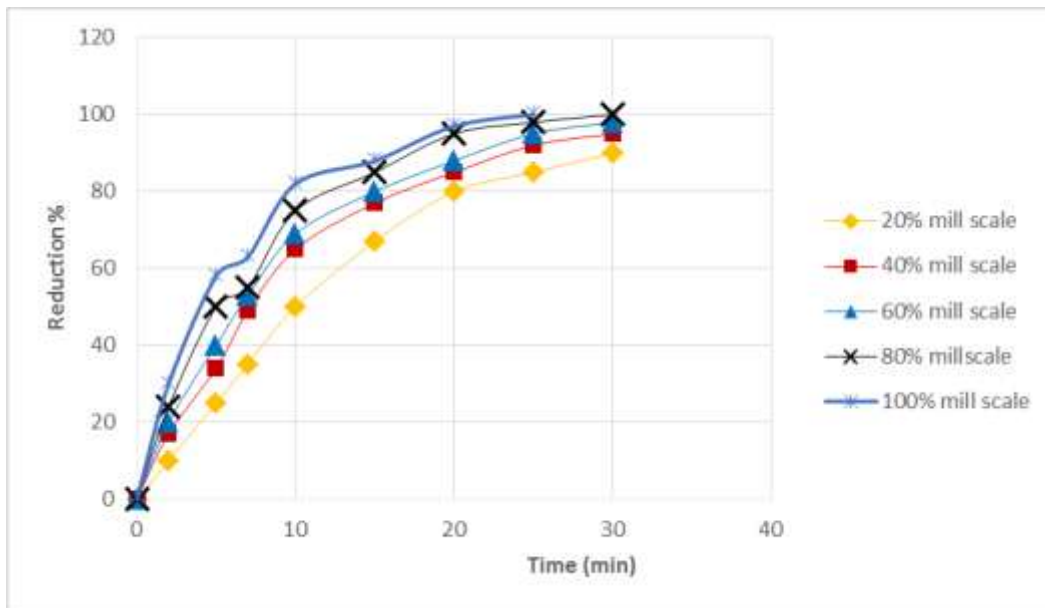


Fig. 8. The effect of change amount of mill scale to iron ore ratio on the reduction process by hydrogen.

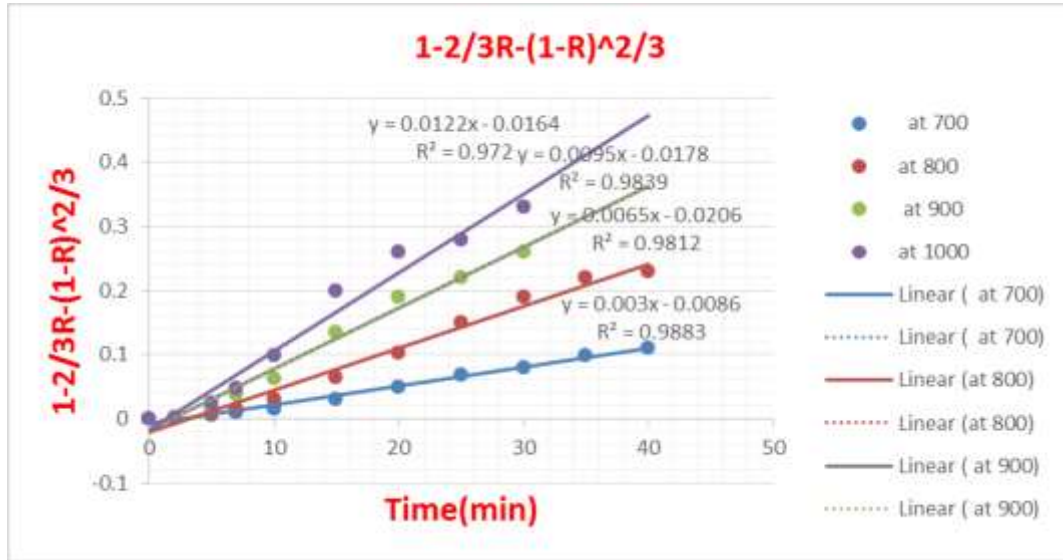


Fig. 9. The relation between $[1 - \frac{2}{3} R - (1-R)^{\frac{2}{3}}$ and time of reaction for 100% Mill scale.

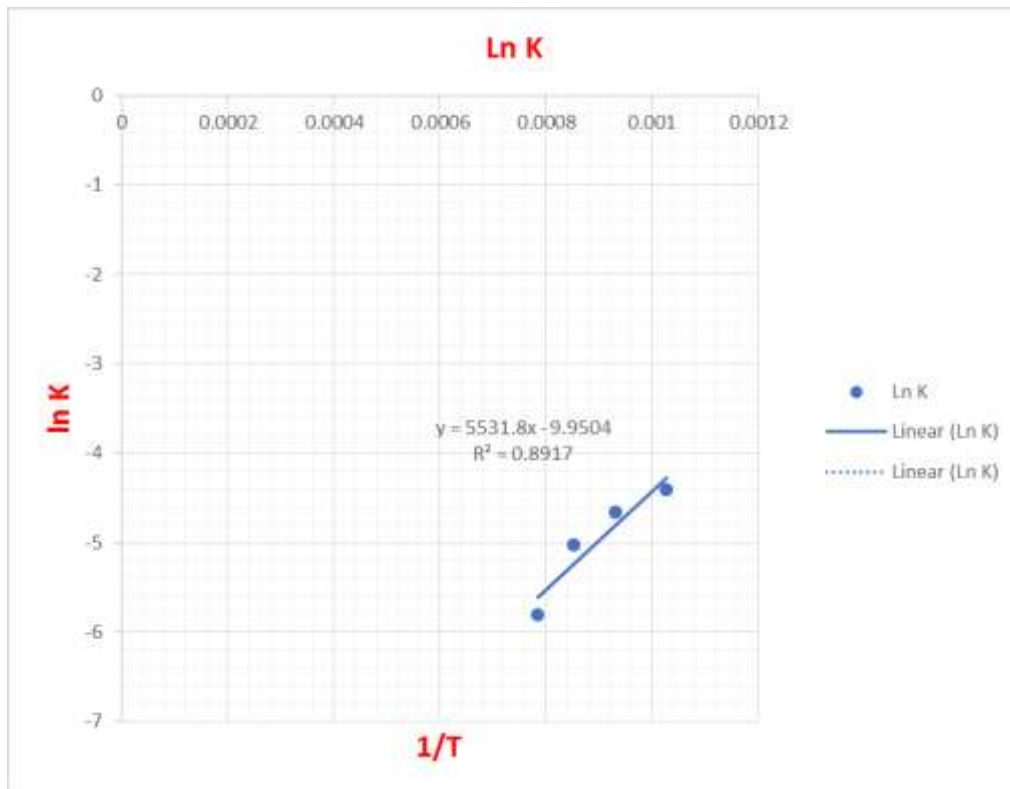


Fig. 10. Relation between ln k and 1/T for mill scale.

Figures (13-15) illustrate the relationship between $1 - (1-R)^{1/3}$ and reduction time (t) for the different reduction temperatures for briquette. From these figures, a linear relationship 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.14 -16, from which it is clear that the activation energy=46.03.25.56 kJ/ mole for 100 %mill scale and (40% iron ore and 60% mill scale) respectively.

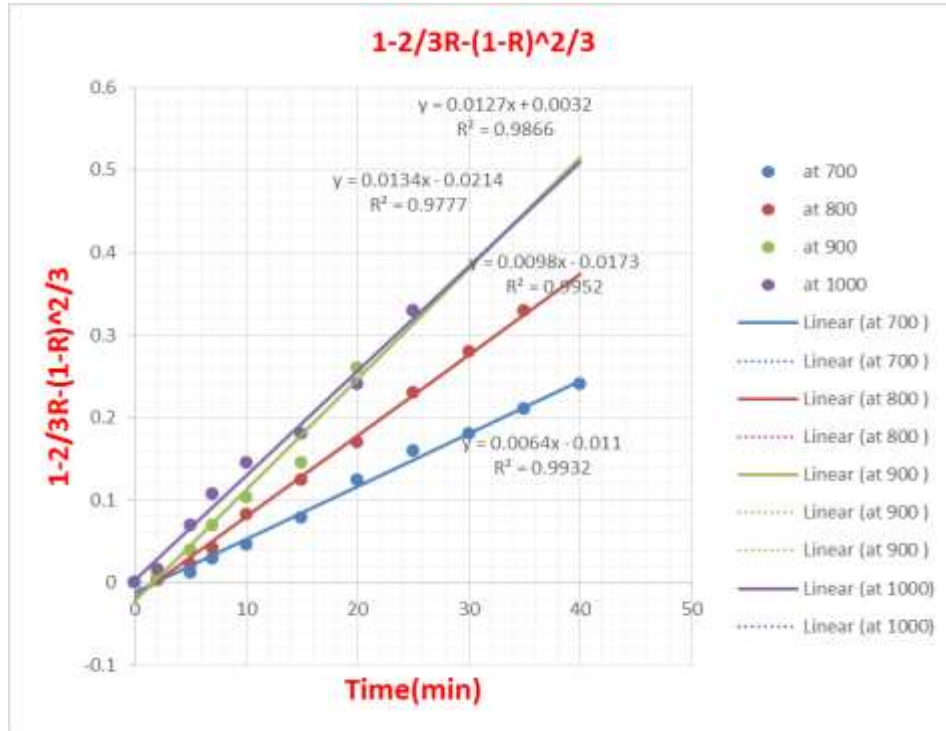


Fig. 11. The relation between $[1 - 2/3 R - (1-R)^2/3]$ and time of reaction for 60% Mill scale. and 40% iron ore.

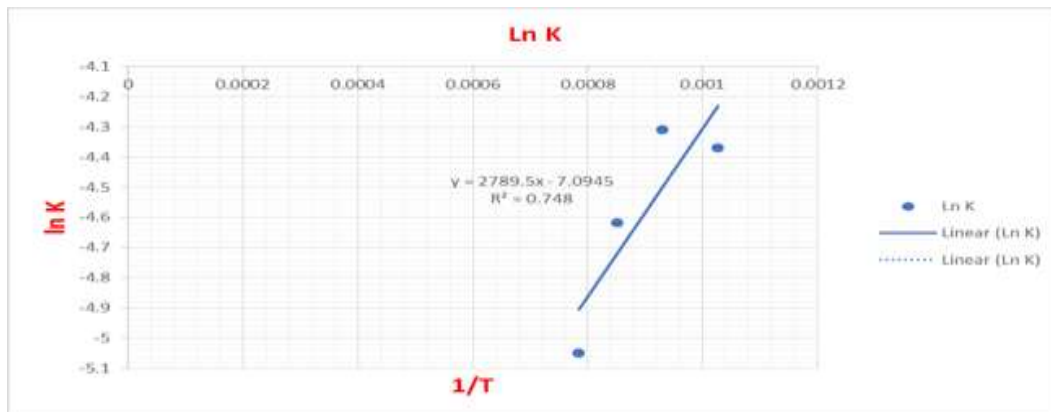


Fig. 12. Relation between $\ln k$ and $1/T$ for 60% mill scale and 40% iron ore.

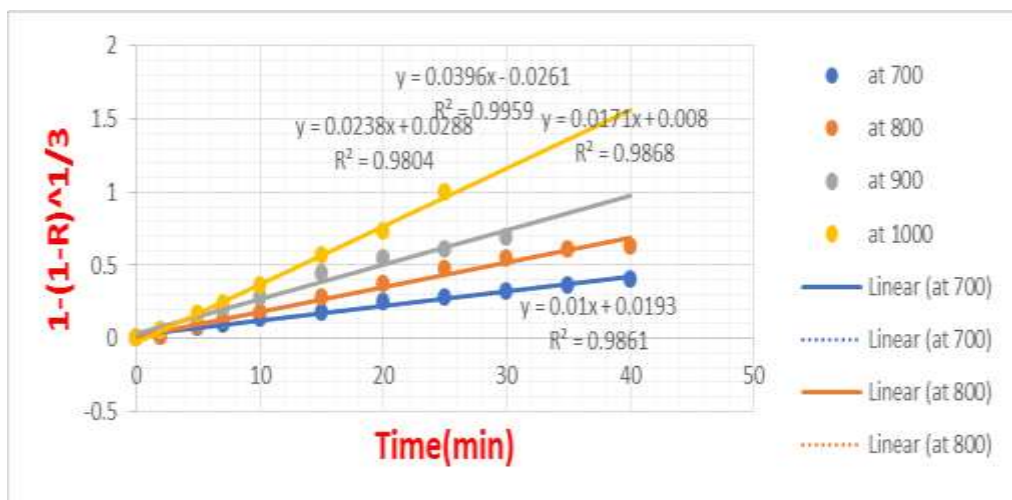


Fig. 13. The relationship between $1 - (1-R)^{1/3}$ and reduction time (t) for the different reduction temperatures for mill scale briquettes.

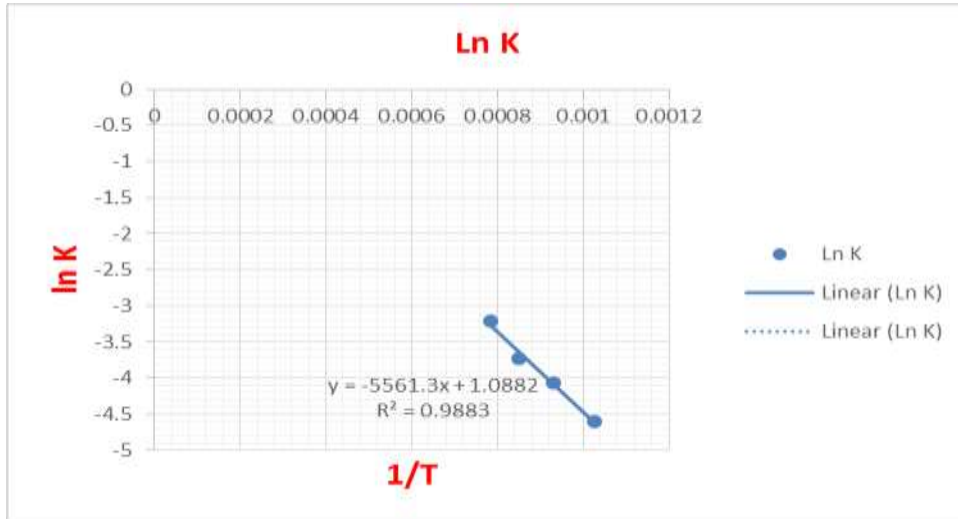


Fig. 14. Relation between ln k and 1/T for reduction of mill scale by hydrogen.

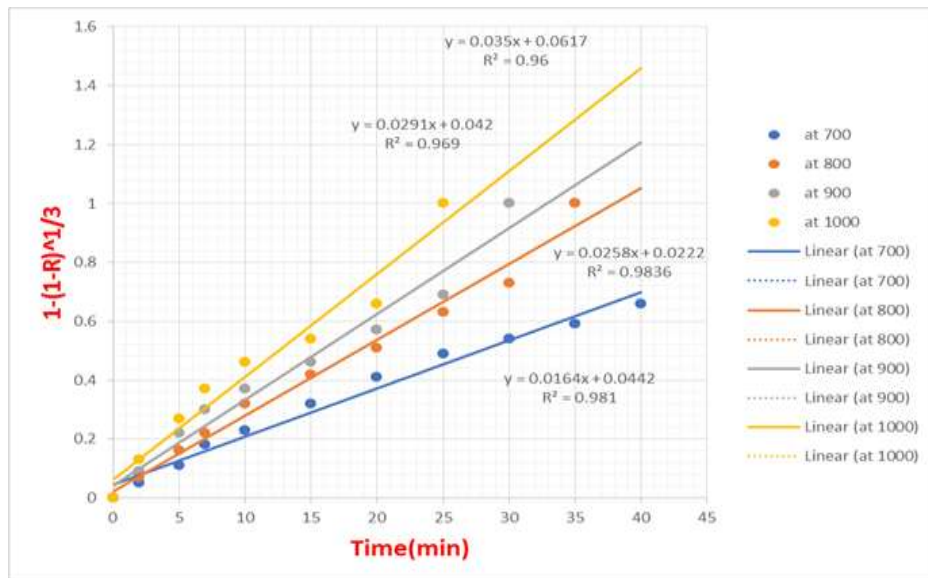


Fig. 15. The relationship between $1 - (1 - R)^{1/3}$ and reduction time (t) for the different reduction temperatures for (60% mill scale + 40% iron ore) briquettes.

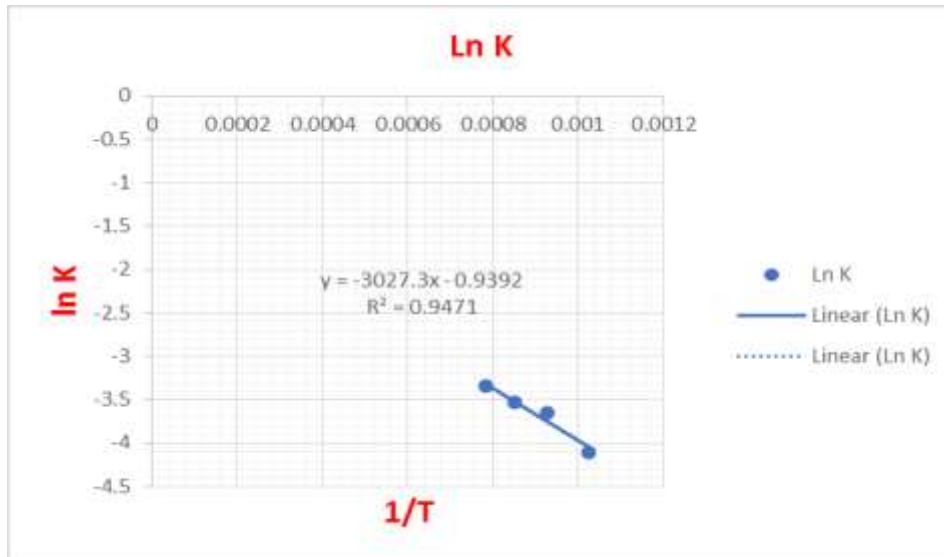


Fig. 16. Relation between ln k and 1/T for reduction of 60% mill scale and 40% iron ore by hydrogen.

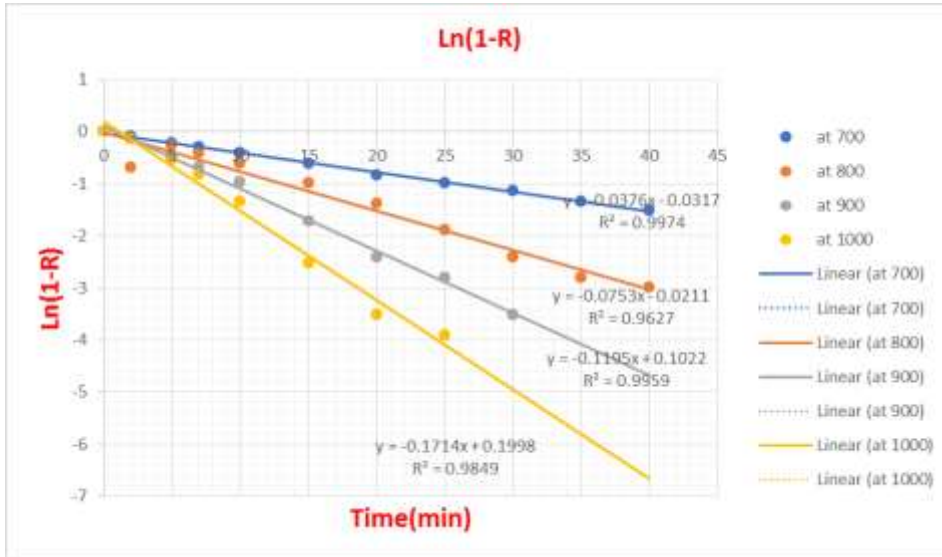


Fig. 17. The relationship between ln (1-R) and reduction time (t) for the different reduction temperatures for mill scale briquettes.

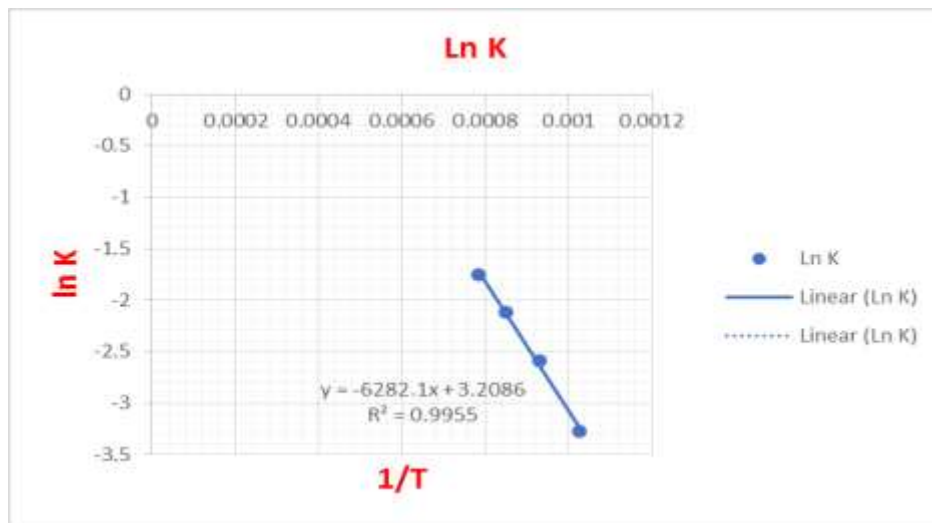


Fig. 18. Relation between ln k and 1/T for reduction of mill scale by hydrogen.

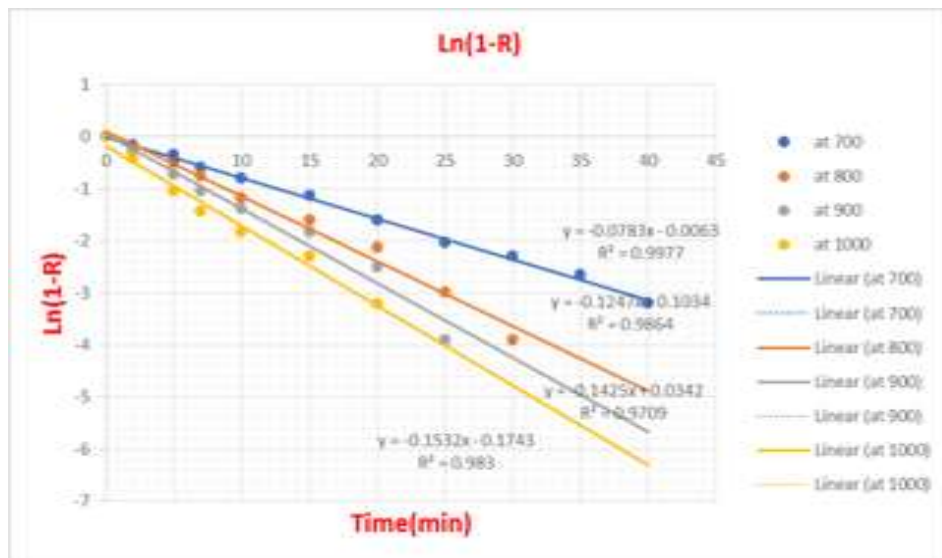


Fig. 19. The relationship between ln (1-R) and reduction time (t) for the different reduction temperatures for (60% mill scale + 40% iron ore) briquettes by hydrogen.

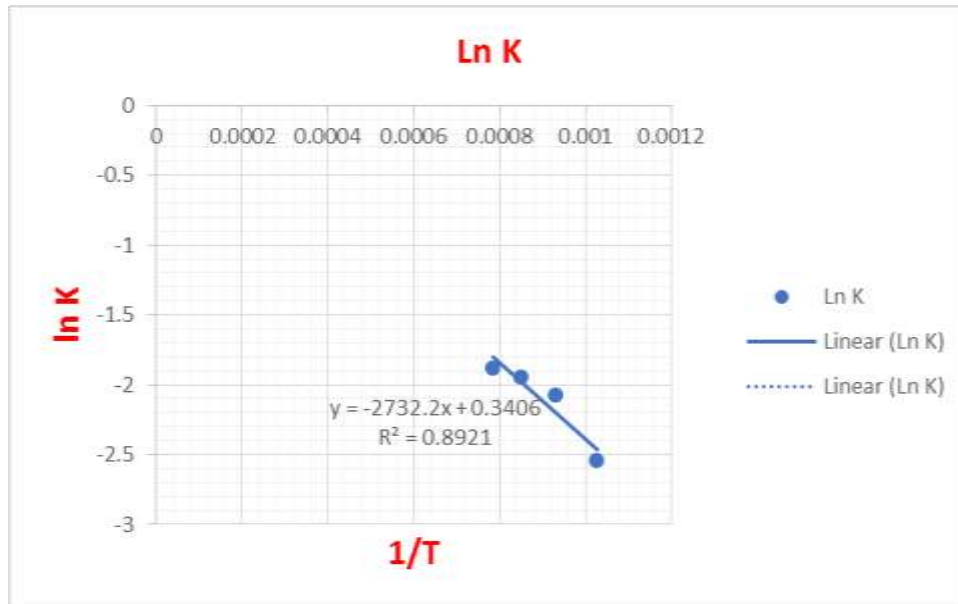


Fig. 20. Relation between Ln k and 1/T for reduction of 60% mill scale and 40% iron ore by hydrogen.

Figures (17-19) illustrate the relationship between $\ln(1 - R)$ versus reduction time (t) for the different reduction temperatures for briquettes. From these figures, a linear relationship 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. 18 and 20, from which it is clear that the activation energy = 51.395, and 23.613 kJ/ mole for 100 % mill scale and (40% iron ore and 60% mill scale) respectively.

IV. CONCLUSIONS

- 1-Iron is the most used of all metals, it extracted from its ores as it is not found in the elemental form by reduction. In this work hydrogen was used in reduction of El-Baharia iron ore with mill scale to remove oxygen and obtain iron.
- 2-Increasing hydrogen flow rate have the effect to increase the reduction rate of of El-Baharia iron ore with mill scale.
- 3- Increasing the temperature of reduction have the effect to increase the rate of reduction of El-Baharia iron ore with mill scale.

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