

Sintering of the Briquette Egyptian Iron Ore with Lime and Reduction of it via Hydrogen

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Abstract: This investigation studies the effect of lime addition to iron ore raw material on the physicochemical properties of its green briquette forms and indurate forms. Also the effect of this addition on the degree of reduction was studied.

The results indicated that the addition of (2-8%) lime improve the mechanical properties of the briquettes in both green and indurate forms. Also the reduction of these briquettes via hydrogen was studied and the model of reduction was putted in this paper.

Keywords:- Indurate briquettes, lime addition to iron ore, model of reduction.

1. Introduction

The using of fluxed pellets as blast furnace iron-bearing burden material is very important. The reason is suitably produced fluxed pellets can meet progressively stringent quality requirements in terms of physical strength and reduction behavior at low and high temperatures. In general, the quality of pellets is affected by the type and nature of ore, concentrate, gangue and other additives and their subsequent treatment to produce pellets. These factors result variation in the physicochemical properties of coexisting phases, structure, distribution, number of pores, etc., in the pellets. The properties of the pellets are largely governed by the form and degree of bonding achieved between ore particles and also by the stability of these bonding phases during the reduction of iron oxides [1]. In general, the bonding in fluxed pellets is achieved primarily through melt formation during indurations. The bonding phase consists mainly of silicates formed from the melt. The various components contributing to melt formation are the gangue of the concentrate, lime and magnesia of the fluxes and iron oxides. Lime and magnesia react with the gangue and/or with the iron oxides. When they react with the gangue, they form part of the intergranular melting phase. The lime also simultaneously reacts with Fe_2O_3 to form different calcium ferrites. These melting phases interact with each other and dissolve a

are attacked at the acute angles and faces, causing a certain amount of surface smoothing. On cooling, the iron oxides and their compounds precipitate from the melt, and calcium ferrites and silicates of various compositions are formed depending on the local chemistry [1].

Ebrahimzadeh [1964] indicated that $Ca(OH)_2$ has a positive influence on the drop resistance and compressive strength of green and dry pellets. Also the influence of calcium hydroxide on the final strength of burned pellets is remarkable [2].

Turkdogan et al. [1973] indicated that the addition of lime is lowering the reducibility of sintered hematite and magnetite ore pellets [3].

Wynnyckyj and Fahidy [1974] found that the strength index of iron oxide pellets is directly proportion with the shrinkage that takes place during burning of these pellets and the addition of lime increases pellet shrinkage and hence increases pellet strength. They attributed this behavior to the interaction between lime, silica and iron oxide forming calcium silicate and calcium ferrites [4]. Thomas et al. [1974] concluded that with increasing both temperature and lime concentration more slag was formed, thus consolidating the structure and lowering the accessible porosity [5].

Hamilton [1976] found that with the addition of CaO the improvement in cold compressive strength of pellet at 1000–1200°C was probably due to the sintering of fine hematite particles supported by much localized secondary mineral bonding near original lime particle sites. More substantial increase in strength at 1200–1400°C was correlated with the formation of slag in the porous structures and consolidation of the pellets. The decreases in the pellet strength reported for

variable amount of iron oxides. While very fine particles of the ore components are easily dissolved, the larger ore particles

pellet burned at 1400–1500°C was due to the excessive formation of thermally sensitive slag and severe shrinkage cracking [6].

Shalabi et al. [1994] reported that the addition of CaO to the iron ore change slightly decreases in the productivity of green pellets, whereas average drop number and compressive strength of green pellets increases [7].

In this paper, the effect of lime as a fluxing material on both physical and reduction properties of briquettes produced from Egyptian iron ores with using molasses as binding materials will discuss.

2. Materials and Method

Iron ore and lime samples were supplied by the Egyptian Iron and Steel Company, The chemical composition of these raw materials is as the following:-

Chemical analysis of lime: CaO= 91.48%, SiO₂= 4.41% and MgO= 4.11%. While the chemical analysis of El-Baharia iron ore: 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%

The X-ray analysis of El-Baharia iron ore is illustrate in figure (1). From which it is clear that El-Baharia iron ore mainly consists of hematite and quartz. While the X-ray analysis of lime mainly consists of calcite and syn.Ca(OH)₂ as shown in figure (2).

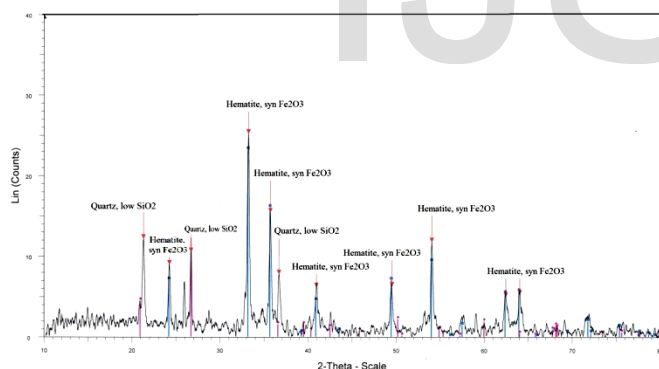


Fig.(1) X-ray analysis of El-Baharia iron ore

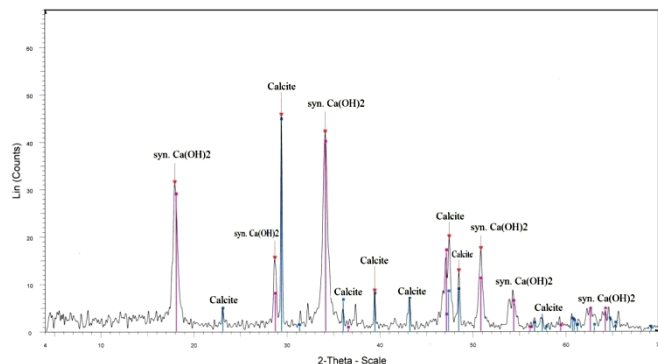


Fig.(2) X-ray analysis of lime

2.1 Preparation of the briquettes and its physical properties

The iron ore and lime were grinding in vibrating mill to powder with size less than 75μm. The mixture of iron ore with certain amount of lime powder (10g) are pressed under pressure 196.133MPa using MEGA.KSC-10hydraulic press figure (3). The briquette subjected to drop damage resistance test and compressive strength test. The drop damage resistance indicates how often green briquette can be dropped from a height 46cm before they show perceptible cracks or crumble. Ten green briquettes are individually dropped on to a steel plate. The number of drops is determined for each briquette. The arithmetical average values of the crumbing behavior of the ten briquettes yield the drop number. The average compressive strength is done by compressed 10 briquettes between parallel steel plates up to their breaking [8]. Then the green briquette burned in the muffle furnace in different temperature from 900 to 1200°C. Then 10 sinter briquette subjected to compression test.



Fig. (3) MEGA.KSC-10 hydraulic press.

2.2. Reduction process

The reduction of sintered iron ore with lime by hydrogen was done in a thermo balance apparatus. A schematic diagram of thermo balance apparatus is shown in figure (4) [9-10]. 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 crucible which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the required temperature (650-950°C) and maintained constant to $\pm 5^\circ\text{C}$ then samples were placed in hot zone. The nitrogen flow rate was 0.5 L/min in all the experiments (at the initial time in order to remove air before each experiment and

also after the end of reduction). The weight of the sample was continuously recorded 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:-

$$\text{Percentage of reduction} = \frac{W_0 - W_t}{\text{Oxygen (mass)}} \times 100 \quad \text{----- (1)}$$

Where:- W_0 : the initial mass of sample after removal of moisture.

W_t : mass of sample after each time, t .

Oxygen (mass): indicates the mass of oxygen percentage in the sample in form FeO & Fe_2O_3 .

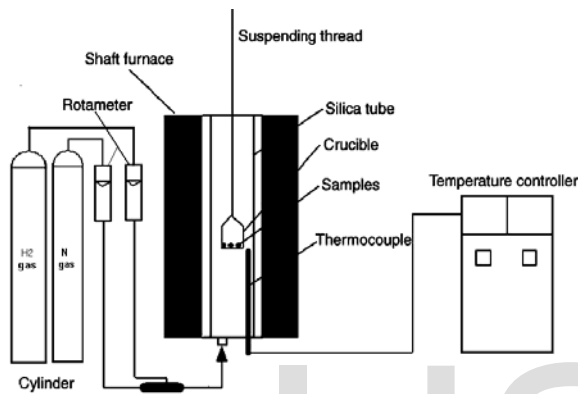


Fig.(4) Schematic diagram of the reduction apparatus

3. Result and Discussion

3.1 Effect of lime addition on physical properties of green briquettes before burning

The effect of adding varying percentage of lime on the green iron ore briquette properties (briquettes pressed under pressure = 196.133 MPa.) is shown in figures (5) and (6). From which it is clear that increase lime addition leads to increase both the drop damage resistance (drop/briquette) and compressive strength of green briquettes. Increasing these properties may be due to the fact that lime increased the coagulation between particles and improved the specific area of the mix, which subsequently lead to an increase in the growth of formed briquettes thus increasing the briquettes strength (8 and 11).

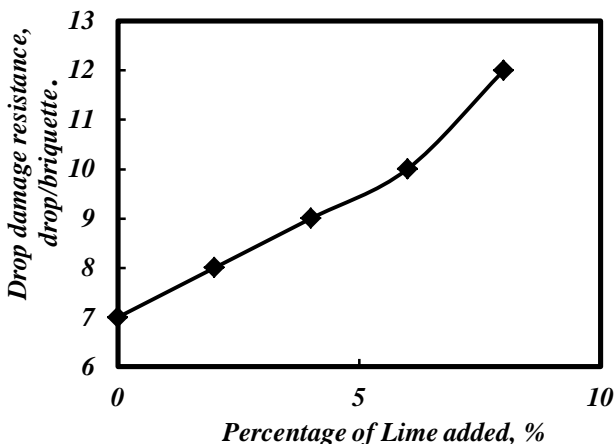


Fig.(5) Effect of lime addition on drop damage resistance of green iron ore briquette pressed

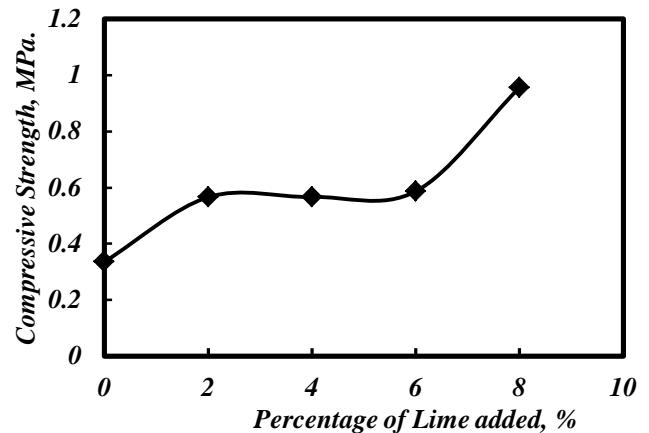


Fig.(6) Effect of lime addition on compressive strength of green iron ore briquette pressed under pressure = 196.133 MPa.

3.2 Effect of lime addition on physical properties of the briquettes burned at different temperatures.

The effect of adding varying percentage of lime on the iron ore briquette properties (briquettes pressed under pressure = 196.133 MPa.), after burning in the muffle furnace at different temperatures from 900 to 1200°C is shown in figure (7). From which it is clear that at any constant amount of lime addition the increase of burning temperature leads to an increase in the compressive strength of briquettes, this may be due to the formation of mono and di calcium ferrite [12].

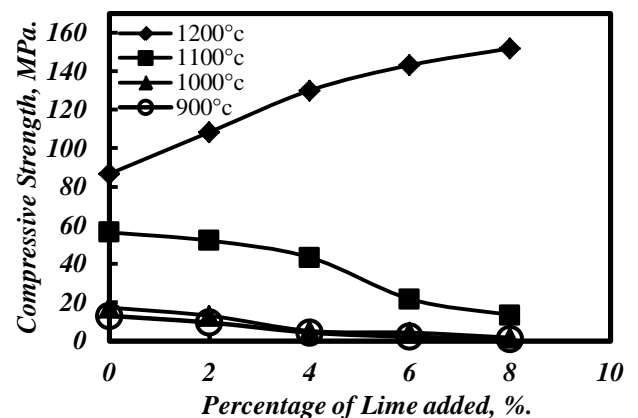


Fig.(7) Effect of different percentage of lime addition on the compressive strength of the briquette sample sintered at different temperature.

The X-ray analysis of iron ore briquettes with 8% lime which give maximum compressive strength for sample burned at 1200°C is illustrated in figure (8). From which it is clear that

the briquettes mainly consists of Dicalcium ferrite, hematite, syn. Fe_2O_3 and $CaO.Fe_2O_3$ phases. While the X-ray analysis of sample burned at $900^\circ C$ and has minimum compressive strength at 8% lime is illustrated in figure (9). From which it is clear that it is mainly consists of Dicalcium ferrite, calcium ferrite, hematite- syn. Fe_2O_3 and some traces of quartz, low (SiO_2) phases as shown in the following figures:-

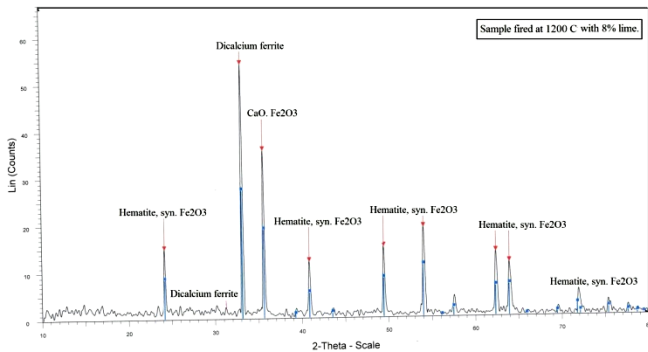


Fig.8 X-ray of iron ore briquette sample with 8% lime and burned at $1200^\circ C$

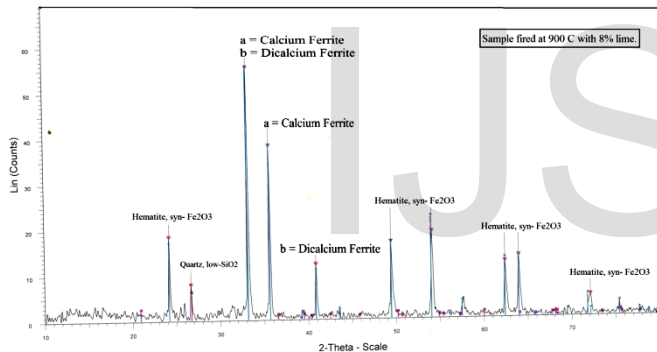


Fig.(9) X-ray of iron ore briquettes sample with 8% lime and fired at $900^\circ C$

3.3 Effect of lime addition and burning temperature on the degree of reduction

Figures (10-13), illustrate the reduction percentage at temperature $900^\circ C$ for different briquetted samples sintered at different temperature (the weight of samples was constant and hydrogen flow rate was 1.5 l/min.).

From these figures, it is clear that the percentage of reduction decreased as the percentage of lime increased for all samples sintered at different temperature. Also it clear that the reduction decreased for all samples as sintering temperature increased, this may be due to the porosity decreased as the sintering temperature increased.

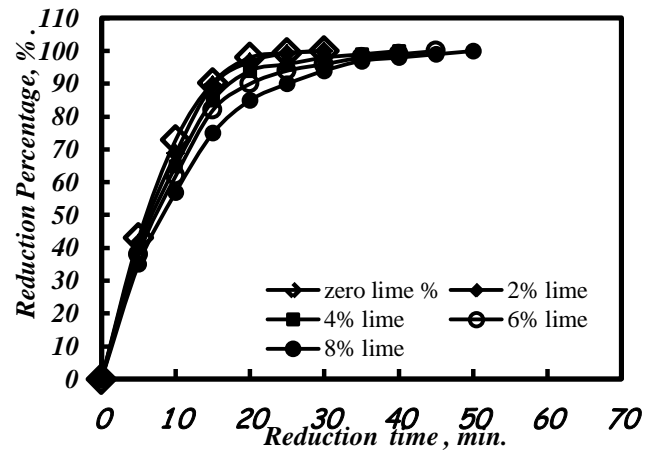


Fig.(10) Reduction of the briquettes burned at $900^\circ C$ with different amount of lime. (Reduction temperature $900^\circ C$)

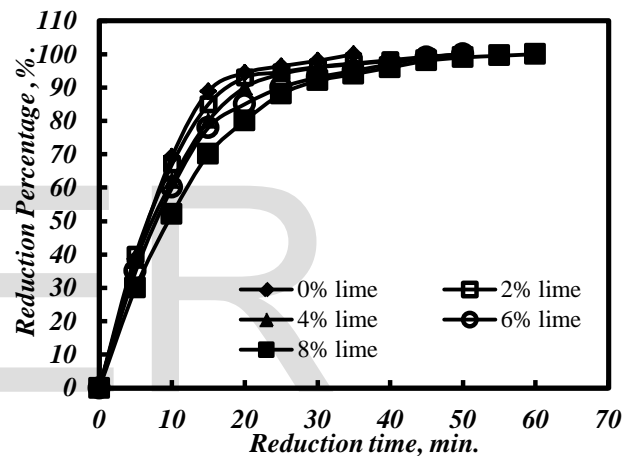


Fig.(11) Reduction of the briquettes burned at $1000^\circ C$ with different amount of lime. (Reduction temperature $900^\circ C$)

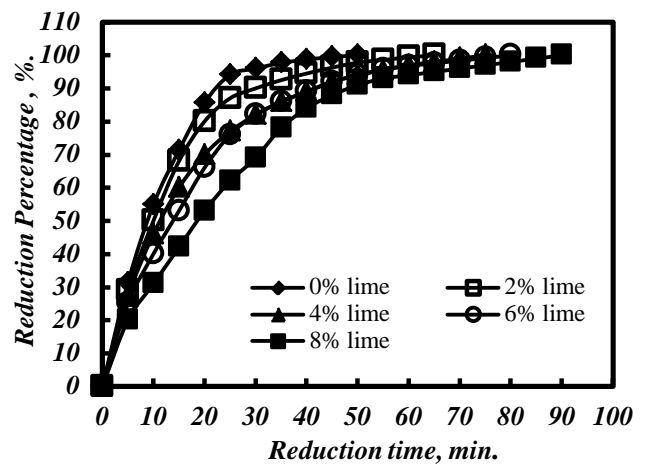


Fig.(12) Reduction of the briquettes burned at $1100^\circ C$ with different amount of lime. (Reduction temperature $900^\circ C$)

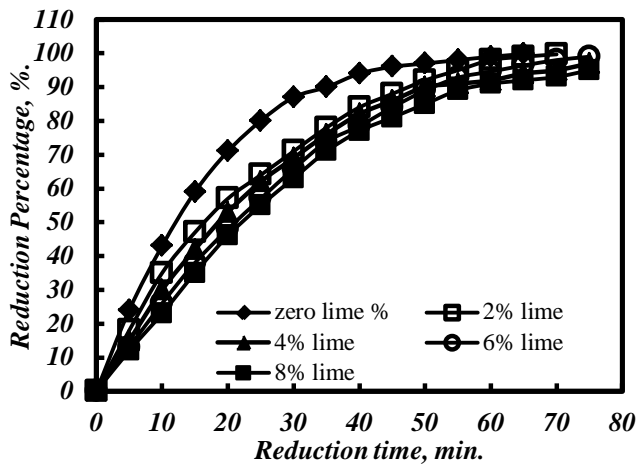


Fig.(13) Reduction of the briquettes burned at 1200°C with different amount of lime. (Reduction temperature 900°C)

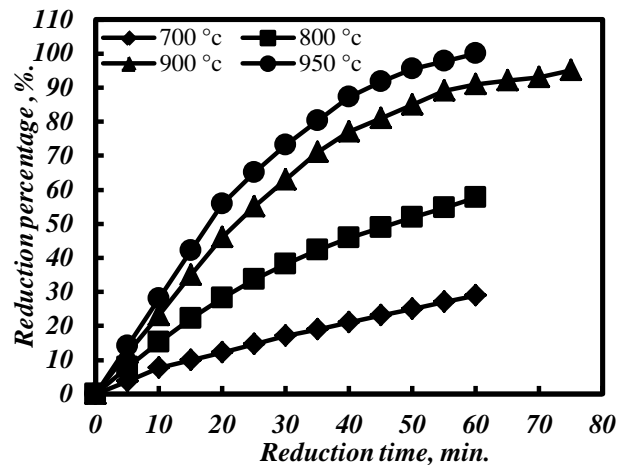


Fig.(15) Reduction of iron ore briquette with 8 % lime at different temperature by hydrogen flow rate 1.5 l/min.

3.4 Effect of different reduction temperature on the percentage of reduction of the briquetted sample burned at 1200°C

Figures (14) and (15), illustrate the reduction percentage of the briquetted iron ore sample burned at 1200°C with hydrogen gas (flow rate 1.5 l/min.) at different temperatures from 700°C up to 950°C. From these figures, it is clear that the increase of temperature favors the reduction rate and degree. At high reduction temperature, with increasing temperature, the oxygen removal 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 an increase in reduction rate [12 - 14]. Also the raise of temperature leads to an increase in the rate of mass transfer of the diffusion and rate of desorption, [13- 17]

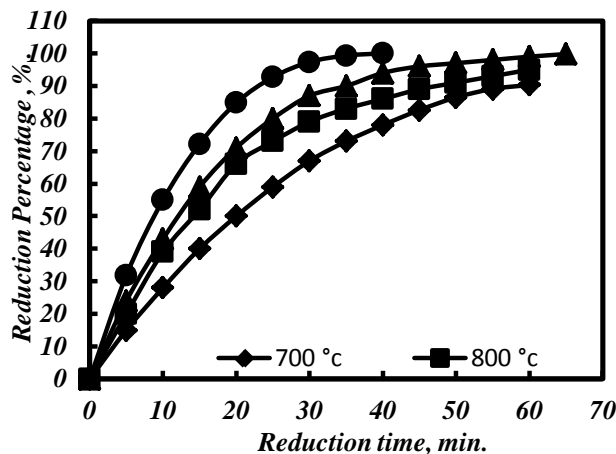


Fig.(14) Reduction of iron ore briquette without lime addition at different temperature by hydrogen flow rate 1.5 l/min.

3.5 Kinetics reduction of iron ore briquette without lime and with 8%lime burned at 1200°C

With using diffusion process controls equation [18]:-

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

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

Figures (16 & 17), illustrated the relation between $1 - (1-R)^{1/3}$ against time of reduction for different reduction temperature for iron ore briquette without lime and with 8% lime respectively, from which it is clear that the straight line was observed.

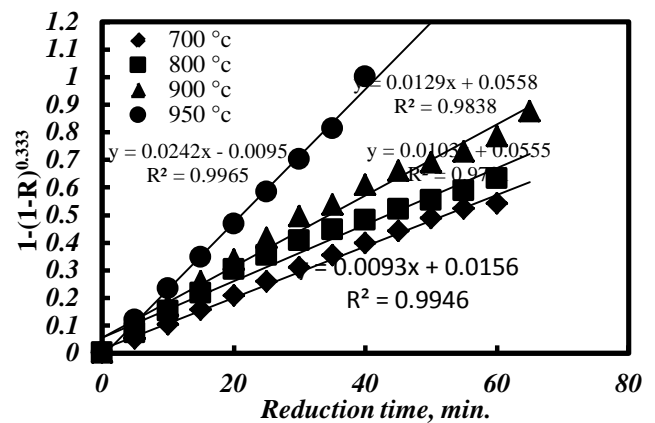


Fig.(16) Relation between different time of reduction and $1 - (1-R)^{0.333}$ of the briquettes contained 0% lime at different reduction temperature .

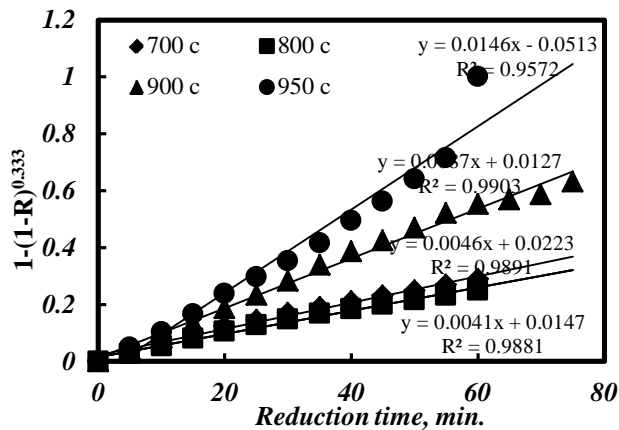


Fig.(17) Relation between different time of reduction and $1-(1-R)^{0.333}$ of the briquettes contained 8% lime at different reduction temperature .

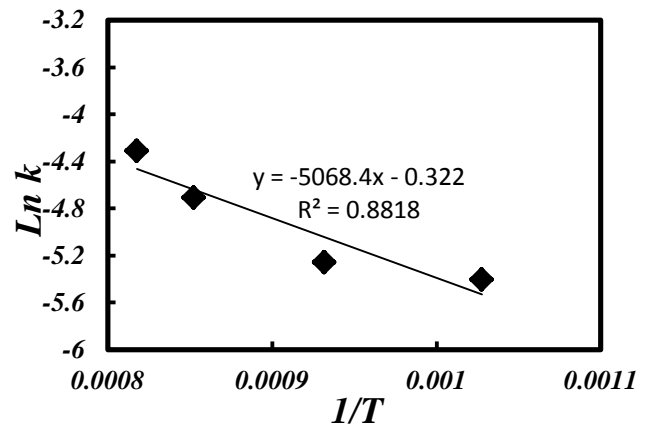


Fig.(19) The relation between the reciprocal of absolute temperature $1/T$ and $\ln K$ (Arrhenius plot for reduction reaction) of the briquettes contained 8% lime burned at 1200 °C.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrated in Figures 18-19, from which it is clear that the activation energy= 39.29 kJ/ mole and 45.25 kJ/ mole for briquettes contain zero lime and 8 % lime respectively.

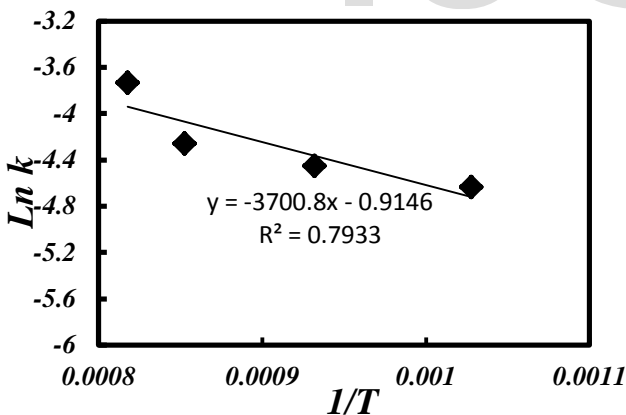


Fig.(18) The relation between the reciprocal of absolute temperature $1/T$ and $\ln K$ (Arrhenius plot for reduction reaction) of the briquettes contained 0% lime burned at 1200°C.

The X- ray analysis of iron ore briquettes with 8% lime which bured at 1200°C and reduced at 950°C is illustrated in figure (20). From which it is clear that the briquettes mainly consists of Iron (syn. Fe) and Magnetite (syn. Fe_3O_4).

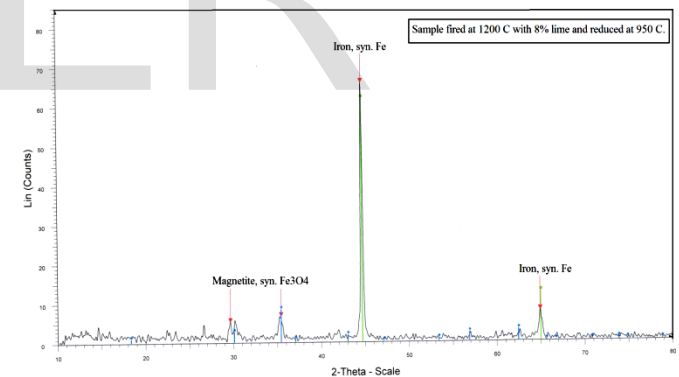


Fig.(20) X-ray of iron ore briquette sample with 8% lime burned at 1200°C and reduced at 950°C.

4. Conclusions

- 1- Addition of lime to iron ore and briquetted its improve the physical properties of the briquettes
- 2- The increase of amount of lime added to the iron ore leads to decrease the reduction degree of the briquettes.
- 3- The increase of reduction temperature leads to increase the reduction percentage.

- 4- *The kinetic reduction of iron ore briquettes with 8% lime or without lime addition briquettes shows that the reduction process is controlled by diffusion process and the activation energy= 39.29 kJ/mole and 45.25 kJ/mole for briquettes contain zero lime and 8%lime respectively.*

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