

Relationship between grinding time of mill scale and the physicochemical properties produced briquettes and its kinetic the reduction via Hydrogen.

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ABSTRACT

This study deals with the grinding of mill scale in a laboratory ball mill at different milling times, then

briquetting with 2% molasses as binder material. The effect of grinding of mill scale at different times on

the physicochemical properties and the degree of reduction of mill scale briquettes via hydrogen was investigated. This reaction was found to be controlled by diffusion through reduced layer and experimental data could be fitted by the equation $(1 - (1 - R)^{1/3})^2 =$

1. INTRODUCTION

In integrated steelmaking processes, some dusts, sludges, mill scale...etc. commonly called residual materials, are inevitably generated along with the production of steel. Steelmaking by-products very rich in iron ($\approx 72\%$ Fe), are currently produced in large quantities and represent a potential of almost 5 million tons in the world [1,2]. Dumping of residual materials is not allowed by environmental protection regulations [3]. Generally, these by-products are recycled in metallurgical processes such as the blast furnace or the direct reduction reactors that use coal as reducing agent to produce pre-reduced pellets intended for remelting in electric steel plant. Besides the steelmaking, recycling part of these by-products is already applied in powder metallurgy where

kt. The energy of activation was consequently calculated and found to be 28.04 kJ / mole

Key words :- Grinding time , kinetic of reduction vi hydrogen, Energy of activation , mill scale

the economic recovery is more favorable [1, 2].

Mill scale is a steelmaking by-product from the rolling mill in the steel hot rolling process. Mill scale contains both iron in elemental form and three types of iron oxides: Wustite (FeO), Hematite (α -Fe₂O₃) and Magnetite (Fe₃O₄). The chemical composition of mill scale varies according to the type of steel produced and the process used. The iron content is normally around 70 %, with traces of non-ferrous metals and alkaline compounds. The reduction of rolling mill scale to sponge iron powder is a new way to take advantage of a cheap by-product of the steelmaking industry, yielding sponge iron that can be re-used to the

electric furnace as metallic charge for steelmaking to obtain a product with a lower residual content and improved properties [3-5].

Mechanical activation pretreatment of minerals by intensive milling can improve the efficiency of subsequent processes such as leaching, reduction, chemical synthesis, etc. Consequential benefits of mechanical activation, besides higher efficiencies, may include lower reaction temperatures and enhanced kinetics. As a result, the subsequent processing can be performed in simpler and less expensive reactors with shorter reaction times [6–8]. Several factors, most importantly the formation of new and additional surface area as well as creation of lattice defects, are responsible for the mentioned improvements [6, 9-14]. Different types of milling apparatus such as ball mills, planetary mills, vibratory mills,

pin mills and rolling mills may be used for milling operations [15].

Mechanical treatment in a high energy mill generates a stress field within solids. Stress relaxation can occur via several channels: (1) heat release, (2) development of surface area as a result of brittle fracture of the particles, (3) generation of various sorts of structural defects and (4) stimulation of chemical reaction within solids. All relaxation channels cause changes in the reactivity of the solid substance under treatment, which is why the resulting action is called mechanical activation [16]. The concentration of the mechanically induced defects and their spatial distribution depend upon the condition of the energy transfer in the mill. These can also be influenced by varying the external conditions of stress. The creation of defects enhances the stored energy (enthalpy) in the solids and consequently causes a decrease of activation

barrier for the process and/or subsequent processes [17]. A large number of studies have been devoted to the understanding of the influence of the grinding variables and conditions on the structural changes of mechanically-activated material. Structural changes of inorganic oxides have been shown to be intensified with increasing grinding media density, acceleration and duration of milling in a planetary mill [18].

It has been further reported that the crystallite size decreased exponentially with

2. EXPERIMENTAL WORK:

2.1. Characterization of mill scale:

2.1.1. Sieve analysis:

Mill scale used in this experiment was delivered from Egyptian Iron and Steel Company. This mill scale was ground in laboratory ball mill for different times (from 1 hour up to 4 hours). This mill scale was

increasing milling time and the strain increased by extending activation time during mechanical activation of ilmenite [19]. A comparative study of the influence of attritor, ball vibratory mills on the reactivity of sulphide minerals was carried out by Balaz et al. [20]. $\gamma\text{-Fe}_2\text{O}_3$ samples ground with smaller amplitude in a vibratory mill showed higher reactivity [21]. The aim of this work is to investigate the effect of grinding duration on the quality and the reduction behaviour of mill scale briquettes.

subjected (before and after grinding) to sieve analysis using Tyler standard sieve set with electric shaker. The results are shown in Figure 1 and the mean size of mill scale is illustrated in Table 1.

Table 1: Mean size of mill scale after grinding for different times

Time of grinding, hr	0	1	2	3	4
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Mean size, mm	0.88	0.341	0.295	0.213	0.125
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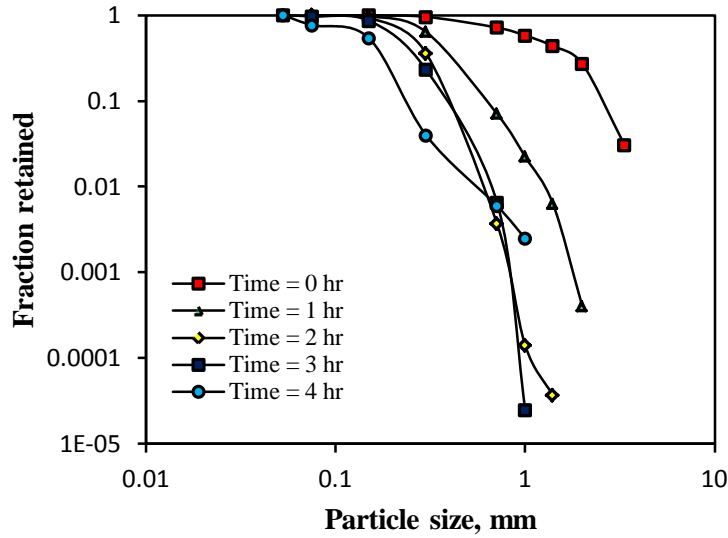


Figure 1. Sieve analysis of mill scale after grinding in ball mill for different times.

2.1.2. Chemical analysis of mill scale:

Table 2. Chemical composition of mill scale:

Compounds	Fe total	Fe ₂ O	Fe ₃ O	FeO	S	P	MnO	SiO ₂	C
		3	4						
Weight %	69.33	70	17.26	7.83	0.33	0.22	0.66	1.92	0.04

2.1.3. X- ray analysis:

The X- ray analysis of mill scale is illustrated in Figure 2. It is clear from this figure that it mainly consists of magnetite, wustite, iron, quartz and hematite

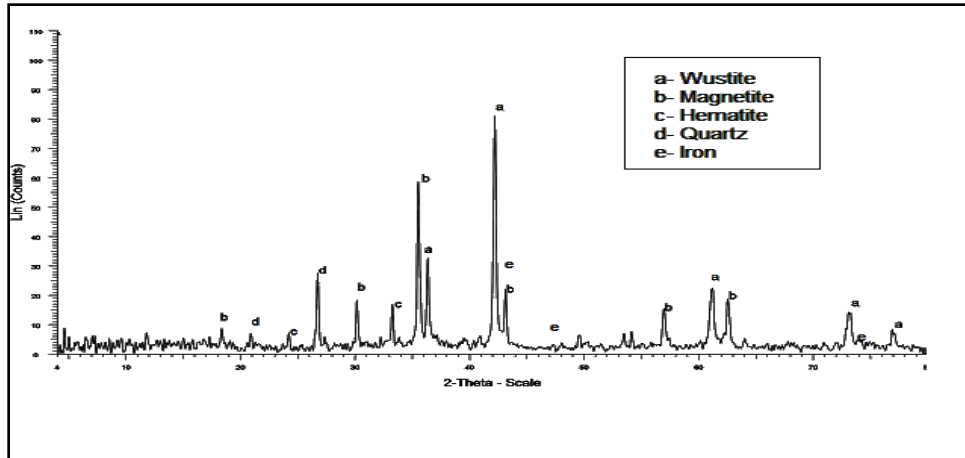


Figure 2. X-ray analysis of mill scale sample

2.2. Preparation of the briquettes and its physical properties:

After grinding for different times, 10 g of fine mill scale particles were mixed with 2% molasses then pressed in the mould (12 mm diameter 22 mm height) using MEGA.KSC-10 hydraulic press, under different pressures (from 86 up to 260 MPa). The produced briquettes were subjected to drop damage resistance tests and compressive strength tests. The drop damage resistance indicates how often green briquettes can be dropped from a height of 46 cm

before they show perceptible cracks or crumble. Ten green briquettes were individually dropped onto a steel plate. The number of drops was determined for each briquette. The arithmetical average values of the crumbing behavior of these ten briquettes yield their drop damage resistance, while the average compressive strength is obtained by compressing 10 briquettes between parallel steel plates up to their breaking[22].

2.3 Reduction Procedure:

The reduction of mill scale briquette with hydrogen was performed in thermo gravimetric apparatus. This

scheme as shown in Figure 3 is similar to that described elsewhere [23]. The reduction apparatus 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 (600 – 950 °C) and maintained constant within $\pm 5^\circ\text{C}$. Then samples were placed in the hot zone of the furnace and nitrogen flown at a rate of 0.5 L/min.. Air was removed before each experiment and also after the end of reduction. The weight of each sample was continuously recorded till the end of the run; then samples were withdrawn from the furnace and put in the desiccators.

The percentage of reduction was calculated according to the following equation:

$$\text{Percent of reduction} = \frac{[(W_0 - W_t) \times 100 / \text{Oxygen mass}]}{\dots\dots\dots} \quad (1)$$

Where:

W_0 : the initial mass of mill scale sample after removal of moisture, g;

W_t : mass of sample after time (t), g;

Oxygen mass: indicates the mass of oxygen percent in mill scale in the form of FeO and Fe_2O_3 , g.

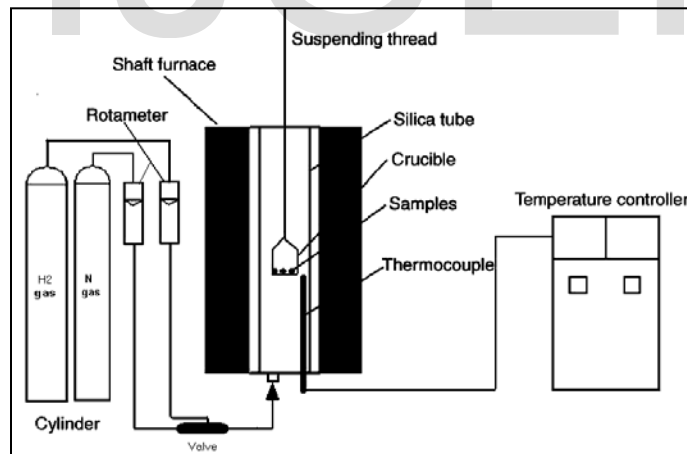


Figure 3. Schematic diagram of the reduction apparatus

3. RESULTS AND DISCUSSION

3.1. Effect of pressing load (with constant amount of molasses) on the quality of wet and dry mill scale briquettes:

Figures 4 to 7 show the relation between the effect of pressing load at constant percentage of molasses (2 %) on the drop damage resistance and compressive strength of both wet and dry briquettes. It is evident that as the pressing pressure load increased both drop damage resistance and compressive strength increased. This is due to the fact that increase of pressure load increases the compaction of briquette

and subsequently the Vander Waals forces [24, 25]. Also the increase of briquetting pressure leads to progressive crushing of macrospores [26]. These figures also reveal that as the size of mill scale decreases by increasing the grinding time, both drop damage resistance and compressive strength of wet and dry briquette increase.

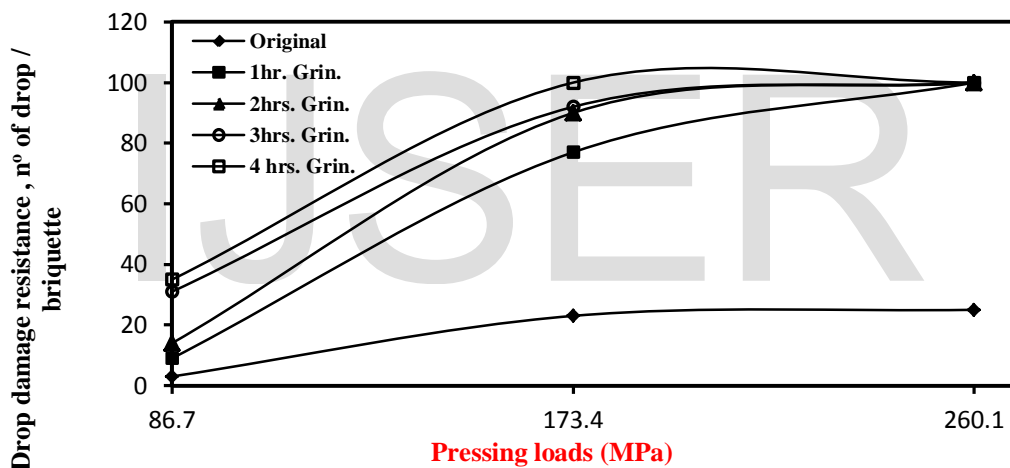


Figure 4. Effect of grinding time on drop damage resistance of mill scale briquette in green state under different pressing loads .

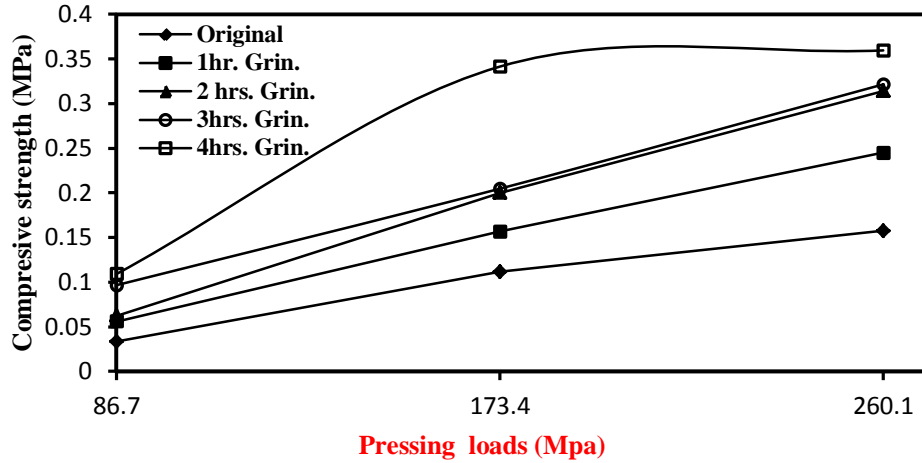


Figure 5. Effect of grinding time on compressive strength of mill scale briquette in green state under different pressing loads.

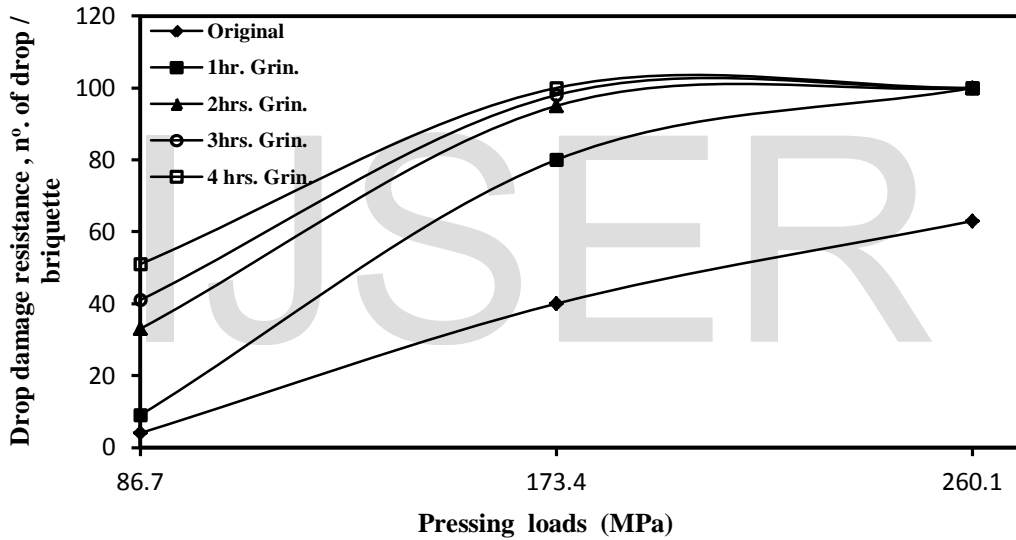


Figure 6. Effect of grinding time on drop damage resistance of mill scale briquette in dry state under different pressing loads.

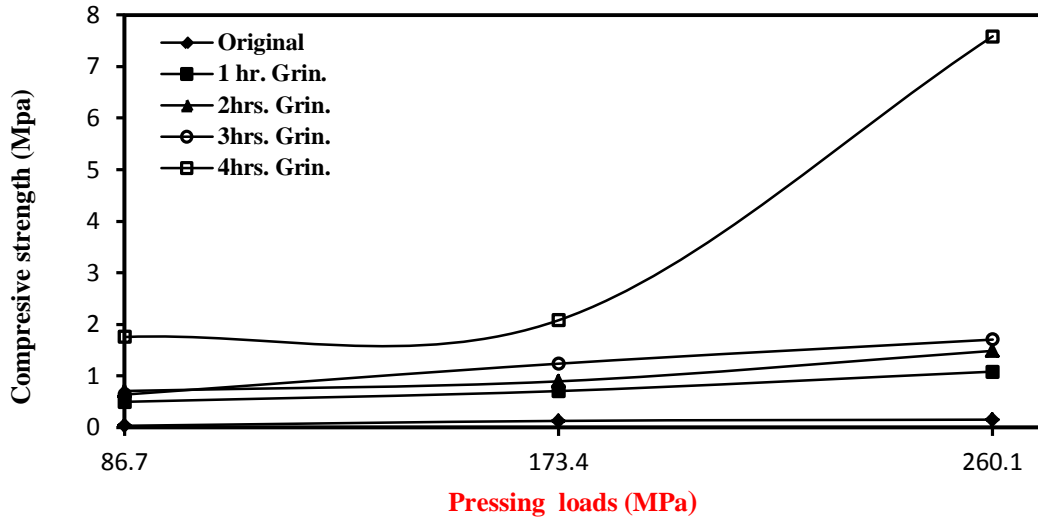


Figure 7. Effect of grinding time on compressive strength of mill scale briquette in dry state under different pressing loads.

3.2. Effect of the grinding time on the reduction percentage

Figure 8 illustrates the effect of increasing milling time on the degree of reduction of mill scale briquettes at 900°C under a pressing load of 260.1 MPa for different times and at 2 L/min. hydrogen flow rate. From this figure, it is clear that the extent of

the reduction increased as the milling time increased from 1 h. up to 4 h. This can be attributed to the creation of additional surfaces as well as the formation of lattice defects by the action of milling. [6, 9-14]

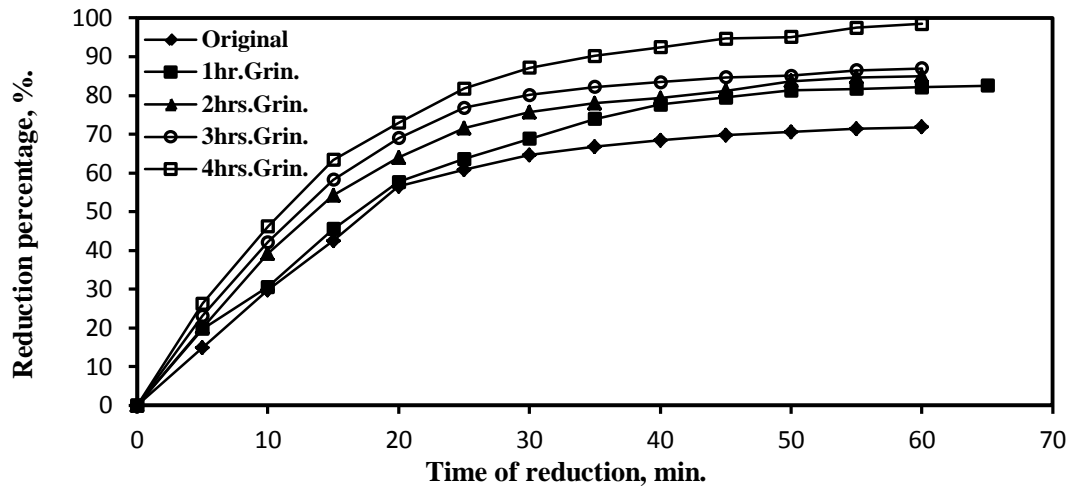


Figure 8. Effect of grinding time and reduction time on the reduction percentage of mill scale briquette (briquette pressing load=260.1 MPa) at 900°C and at 2 L/min. hydrogen flow rate during time progress.

3.3. Effect of hydrogen flow rate on the reduction percentage

Figure 9 illustrates the relation between the reduction percentage and hydrogen flow rate when the reduction was done at the following constant conditions: Temperature = 900°C, constant weight of the sample, three hours grinding and pressing load = 260.1 MPa). It is clear that as the flow rate of hydrogen increased the reduction percentage increased. The increase of flow rate leads to an increase of number of hydrogen mole in the bulk

phase, which in turn leads to the raise of hydrogen adsorption and a subsequent increase in the rate of reaction [27, 29]. Also the increase of flow rate increased the gas diffusion across the boundary layer subsequently increasing the extent of reduction [28]. However, from an economical point of view, it is preferable to restrict the flow rate to 1.5 L/min which was adopted in the rest of that investigation.

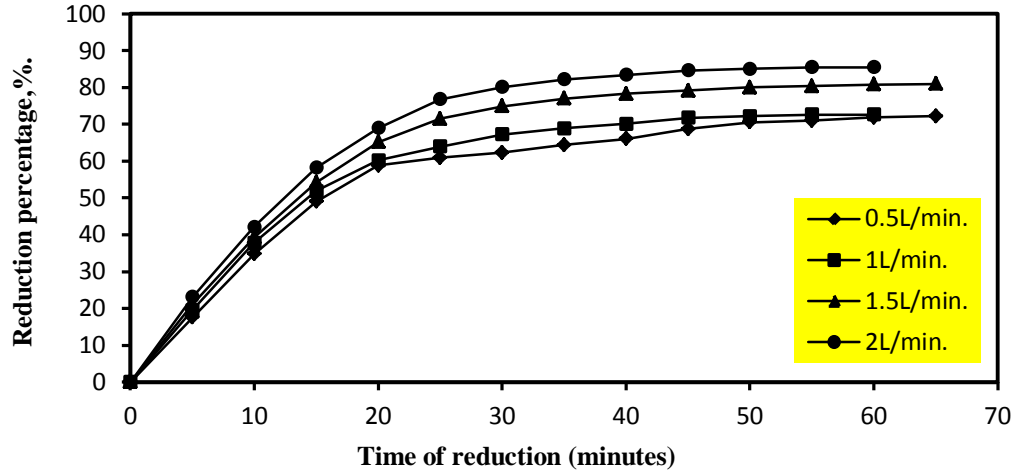


Figure 9. Effect of hydrogen flow rate on the reduction percentage of mill scale briquette (temperature = 900°C, constant weight of the sample, 3 hours grinding and pressing load=260.1 Mpa).

3.4. Effect of varying reduction temperature on the reduction percentage

Reduction was carried out at different temperatures ranging from 600 up to 950 °C, where the initial weights of briquettes were fixed at the same value, the hydrogen flow rate =1.5 liter /min., 3 hours grinding and pressing load=260.1 Mpa. The results are illustrated in Figure 10 for briquettes bound by 2% molasses. It is clear that the increase of temperature favors both reduction extent and rate. The curves

generally go through three phases: An initial rapid rate, a somewhat slower rate following and a third zone where reduction is slowest. The increase of reduction percentage with rise of temperature is due to the increase of number of reacting moles having excess energy [27, 30]. Also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rate of desorption [28- 31].

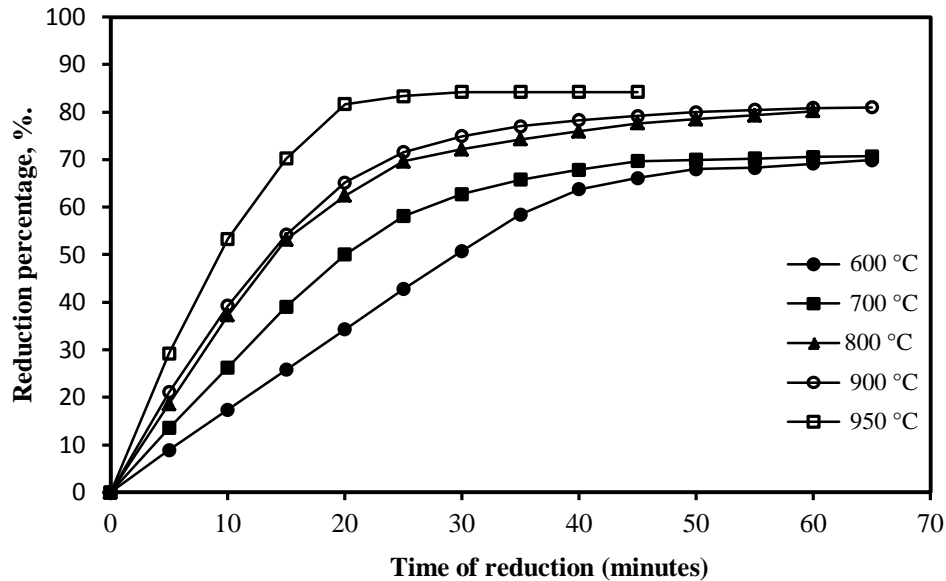


Figure 10- Effect of temperature change on the reduction percentage of mill scale briquette at constant condition (temperature = 900°C , 3 hours grinding and pressing load=260.1 MPa).

3.5. Kinetics of the reduction process

Kinetic studies for the estimation of apparent activation energies were carried out for mill scale briquettes at different temperatures from 600 up to 950°C for different interval times in the range of 0 – 65 minutes.

- 1- By using diffusion process controls equation (Jander and Anorg Equation) [32]

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

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

Figure 11 illustrates the relation between $(1 - (1 - R)^{1/3})^2 = kt$ and time of reduction for different reduction temperatures. From this figure, it is clear that the relationship can be represented by straight lines.

The Arrhenius equation was used to calculate the activation energies of reduction reaction by using the calculated rate constant k .

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \text{ ----- (3)}$$

$$\ln k = \ln k_0 - \frac{E}{RT} \text{ ----- (4)}$$

Where k_0 is the pre-exponential coefficient, E is the apparent reduction activation energy (kJ/mol); R is the universal gas constant (8.314×10^{-3} kJ/ mol·K); T is the absolute temperature (K). The relationship between

the natural logarithm of reduction rate constant and the reciprocal of absolute temperature for mill scale briquettes is shown in Figure 12, from which it was found that the activation energy was about 28.04 kJ / mole.

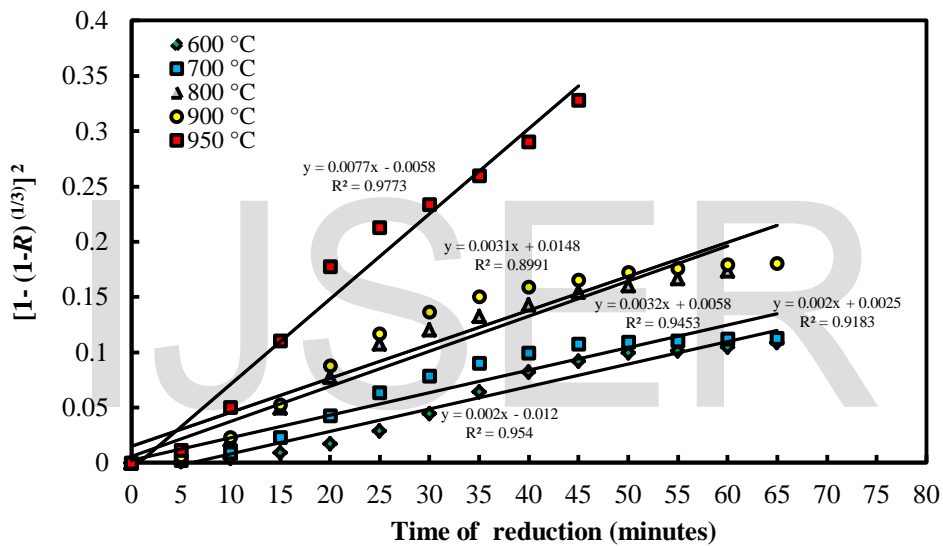


Figure 11. Relationship between time of reduction and $[1-(1-R)^{(1/3)}]^2$ at different temperatures.

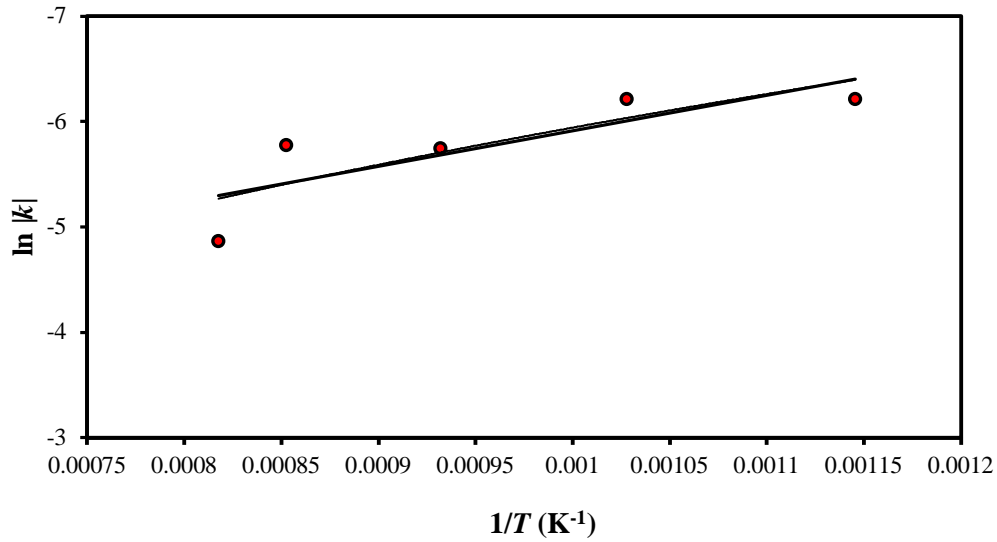


Figure 12. Relation between the reciprocal of absolute temperature $1/T$ and $|\ln k|$

3.6. X-ray analyses of reduced briquettes

Figure 13 and Figure 14 show the x-ray analyses of two reduced mill scale briquette at 600 and 950 °C respectively from which it is clear that the main

phases in the reduced briquette are Iron (Syn-Fe), Hematite and Magnetite. Iron oxide (FeO) phase is present at 950 °C rather than at 600 °C.

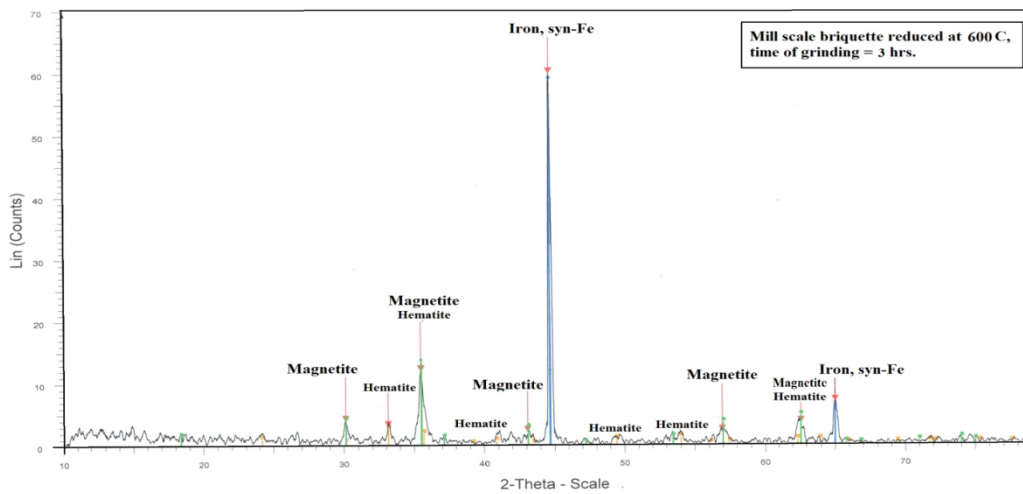


Figure 13. X-ray analysis of mill scale briquette reduced at 600 °C

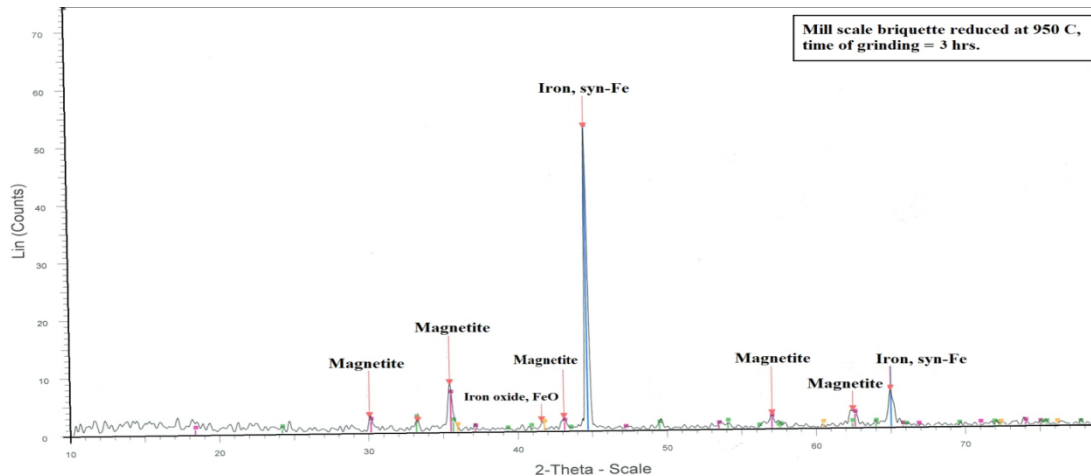


Figure 14. X-ray analysis of mill scale briquette reduced at 950 °C

Conclusion

Hydrogen reduction of mill scale ground for different times ranging from 1h to 4h in the form of briquettes (pressing load 260.1 MPa) at temperatures varying from 600 up to 950 °C and at 1.5 L/min. hydrogen flow rate for different times indicated that:-

1- The reduction rates increased with increasing temperature of the reduction up to 950 °C.

2- Diffusion process controls equation (Jander and Anorg equation) $(1 - (1 - R)^{1/3})^2 = kt$ describes the process and the energy of activation was calculated= 28.04 kJ / mole

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