ISSN 2229-5518

Shalabi

Reduction Kinetic of Mill Scale Briquettes by Hydrogen

Eisa M.G.M.H.[(1)], Salah B.A[(1)], Sayed A.S[(1)],Kalifa,M.G. [(2)],Shalabi M.E.H.[(3)]

[1] Chemistry department, Faculty of Science, Helwan University, Helwan, Cairo 11795 Egypt
[2] El-Tabbin Metallurgical Institute, Cairo, Egypt
[3] Central Metallurgical research and Development Institute, (CMRDI), Cairo, Egypt

Abstract: Reduction of mill scale briquettes was carried out within the temperature range 700 to 1000 oC. In reduction kinetic study the most satisfactory model was to take the slope of the initial linear region of fractional reduction vs. time curve as a measure of rate constant (k). In k vs. 1/T plots were straight line from which Activation Energy was calculated.

1-Introduction

About 500 kg/ton of solid wastes of different nature are generated in several iron and steel making processes; one of these wastes is the mill scale which represents about 2% of produced steel [1]. Mill scale is a very attractive waste because it contains about 70 % Fe with traces of non- ferrous metals and alkaline compounds [2].

About 13.5 million tons of mill scales are generated annually in the whole world [3]. Mill scale is suitable for direct recycling to the blast furnace via sintering plant [4]. Approximately, 90% of mill scale is directly recycled within steel making industry and small amounts are used for ferroalloys, petrochemicals industry and in cement plants [5-9].

ISSN 2229-5518

corresponding author mehshalabi@hotmail.com

Mill scale is a steel making by-product from the rolling mill in the steel hot rolling process; contains both iron in elemental form and three types of iron oxides: Wustite (FeO), Hematite (α-Fe_2O_3) and Magnetite (Fe_3O_4). The chemical composition of mill scale varies according to the type of steel produced and the process used. The reduction of rolling mill scale to sponge iron powder is a new way to take advantage of a cheap by-product of the steel making industry, can be re-used in the electric furnace as metallic charge for steel making to obtain a product with a lower residual content and improved properties [9-14].

The aim of this work is to study the reduction kinetic of iron briquetting mille scale waste in static bed by hydrogen.

2-EXPERIMENTAL :

In previous study the chemical analysis of mill scale was tested that shows contents of : Fe total 69.33 weight % in the form (Fe_2O_3 70 weight %, Fe_3O_4 17.26 weight % and FeO 7.83 weight %). Sulphur 0.33 weight %, Phosphorus 0.22 weight %, MnO 0.66 weight %, SiO_2 1.92 weight % and carbon 0.04 weight %.[14]

The X- Ray analysis of mill scale is illustrated in figure 1. From which it is clear that mill scale mainly consists of magnetite, wustite, iron, quartz and hematite [14]

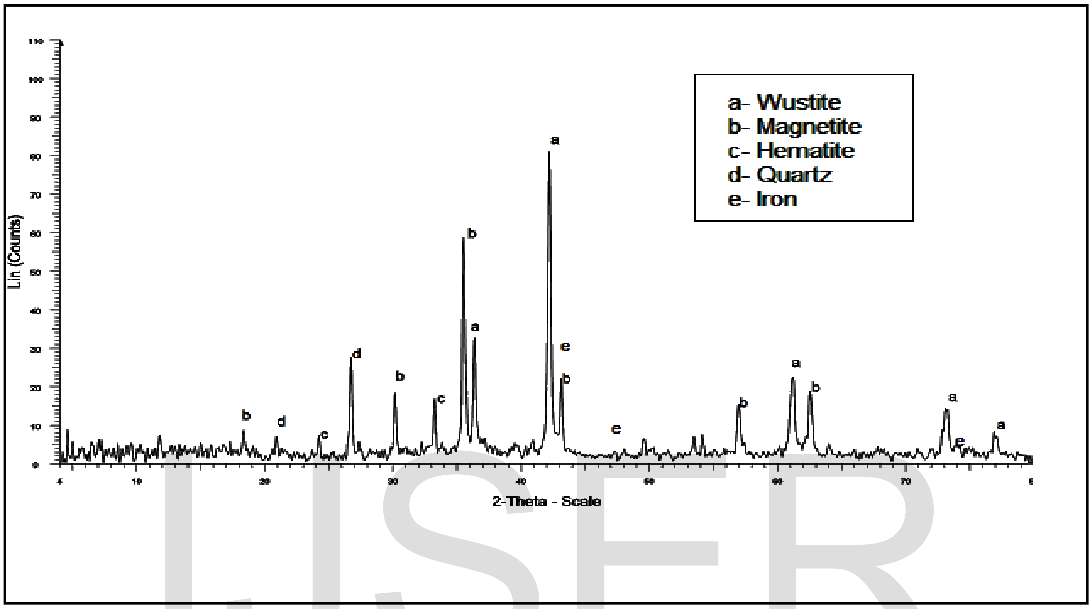


Fig. 1. X-ray diffraction analysis of mill scale sample

2.2. Preparation of the briquettes and its physical properties

The fine mill scale particles (10 g) after grinding for different time in laboratory ball mill are mixed with 2% molasses and then pressed in the mould ;12 mm diameter and a height 22 mm using MEGA.KSC-10 hydraulic press; Fig2. and under different pressure (75 MPa up to 250 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 46 cm 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 damage resistance for these briquettes, while the average compressive strength is done by compressing 10 briquettes between parallel steel plates up to their breaking according to (15-18).

Fig.2. **MEGA.KSC-10 hydraulic press**

2.3. *Reduction Procedures.*

The reduction of mill scale briquette with hydrogen was performed in thermo gravimetric apparatus similar to that present elsewhere (18) (Figure 3). 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°C - 950°C) and maintained constant to ±5°C. Then samples were placed in hot zone.

The nitrogen flow rate was 0.5 l/min pass through furnace in all the experiments at initial time where air should be removed 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.

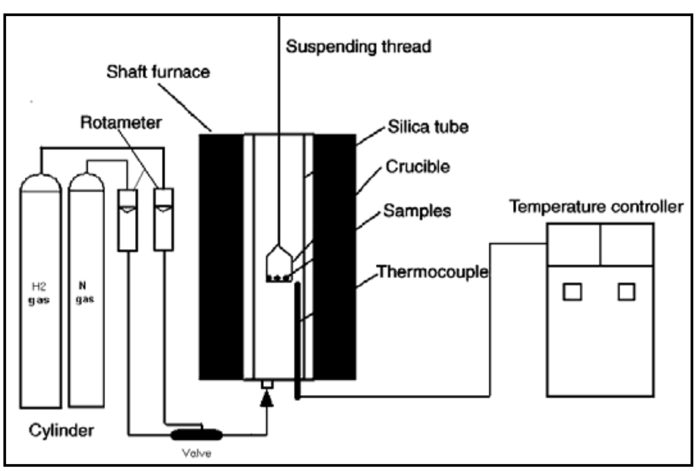
The percentage of reduction was calculated according to equation [1]:

Percentage of reduction = [(Wo –Wt) x100/ Oxygen mass] -------------------- [1]

Where: Wo: The initial weight of mill scale sample after removal of moisture.

Wt: Weight of sample after each time, t.

Oxygen mass: is the total weight of oxygen percent in mill scale in form FeO& Fe_2O_3



ISSN 2229-5518

Fig. 3.Schematic diagramof the reduction apparatus

3.Results and Discussions

3.1Drop damage resistance and pressing pressure

Drop damage resistance at the same day of production and after 3day present in Fig.4, from which it is clear that as pressing pressure increase the drop number increase.

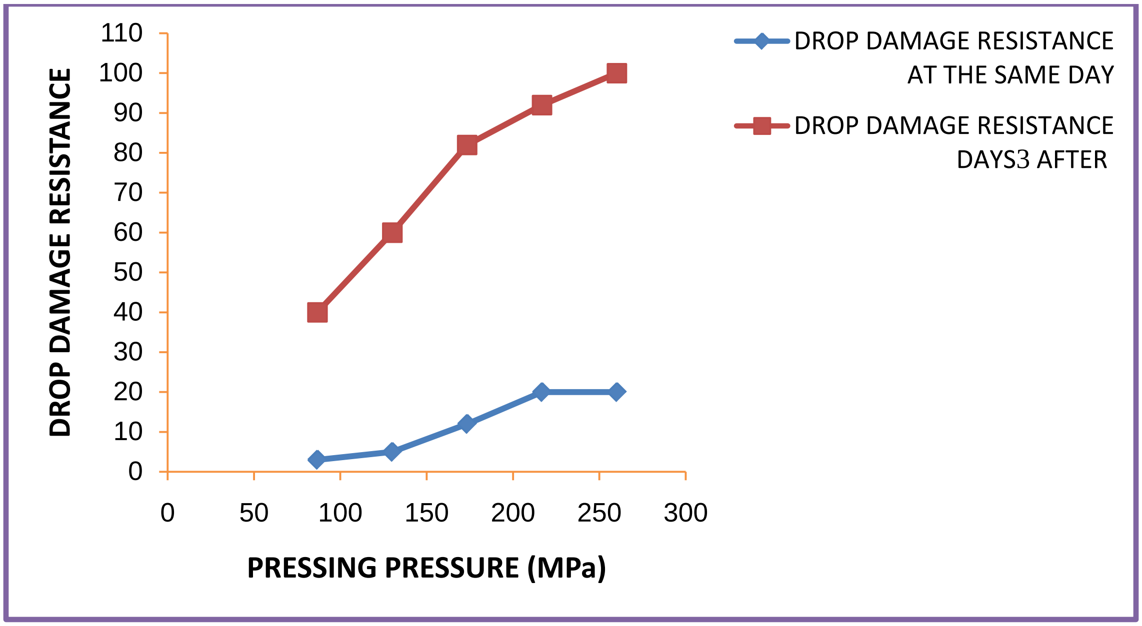


Fig. 4.Schematic diagram of **drop damage resistance and pressing pressure**

3.2.The strength of the wet and dry briquette

Fig . 5 shows increasing strength of the wet and dry bruquites where as

pressure press increase the strength of the briquette in wet and dry form

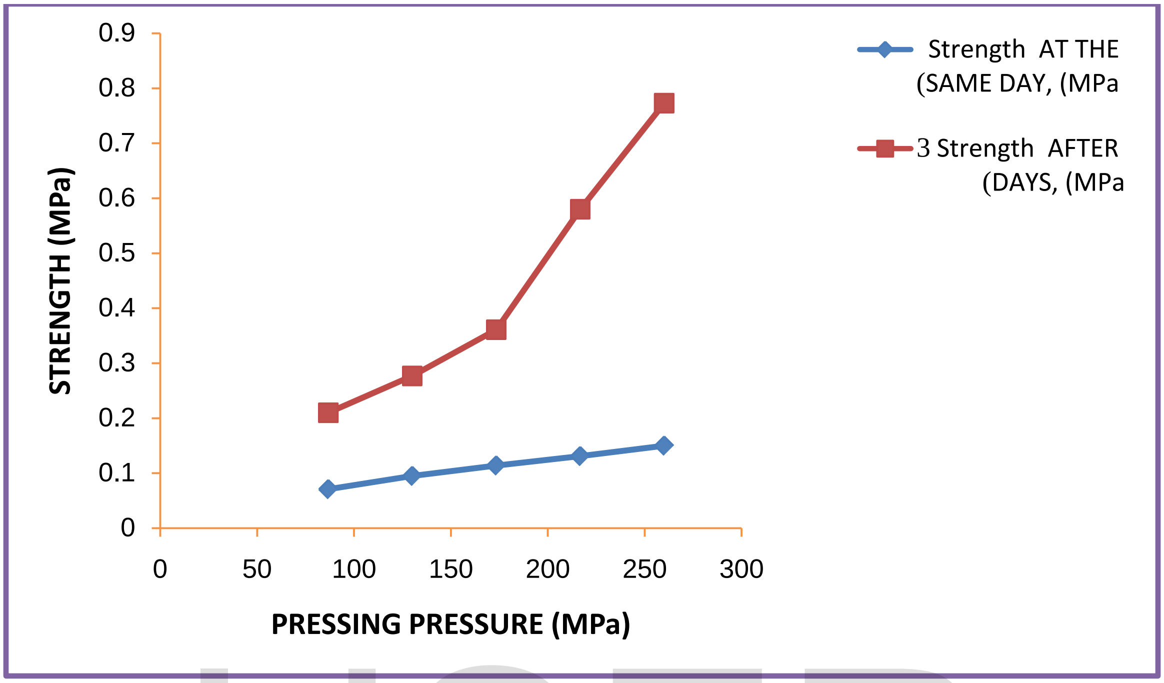
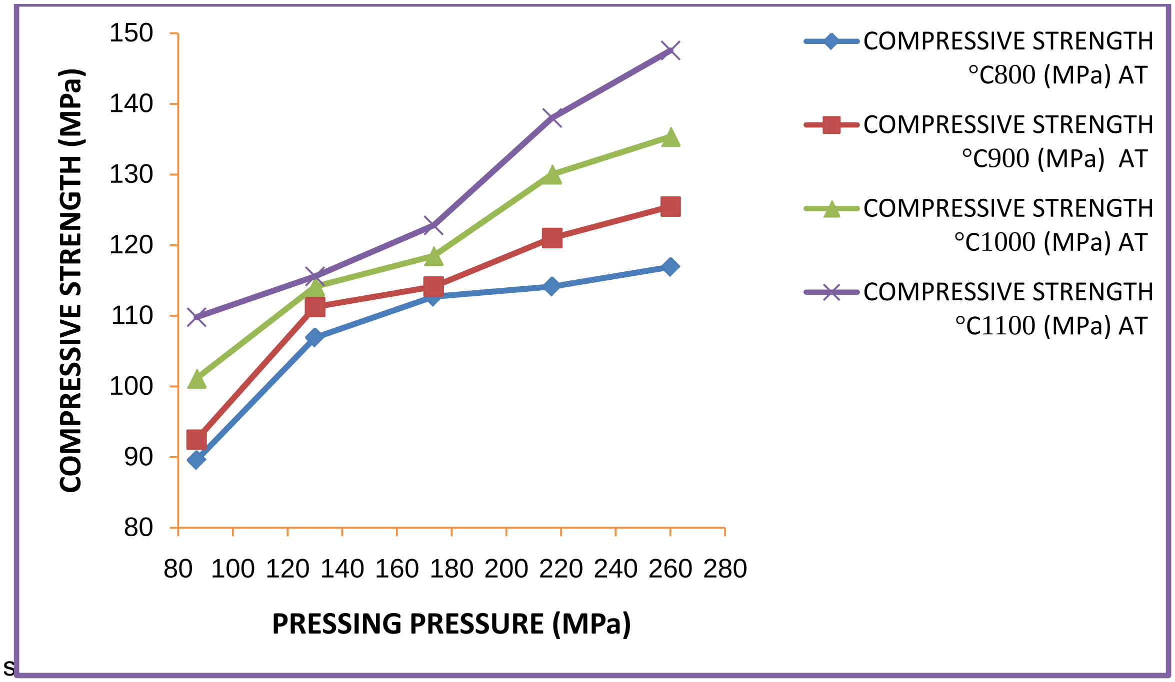


***Fig. 5.Schematic diagram of* Pressing pressure and strength of wet and dry briquette.**

3.3. Compressive strength and pressing pressure for fired briquette

Fig.6 demonstrates the effect of compressive strength and pressing pressure for fired briquette at different temperatures. It is clear that as pressing pressure increased the compressive strength increased



s

Fig. 6.Schematic diagram of compressive strength and pressing pressure

3.4. Reduction percentage at different pressing pressure present

Reduction percentage at different pressing pressure present is illustrated in Fig.7.; from which it is clear that as pressing pressure increase the reduction percentage decreased.

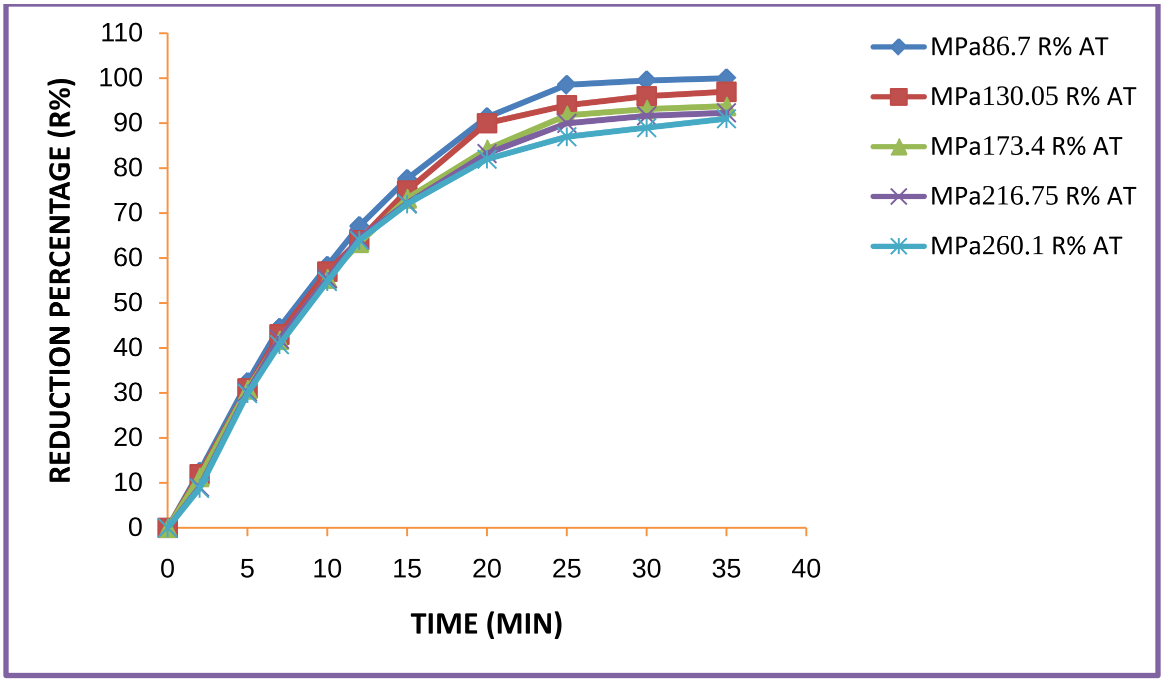


Fig. 7.Schematic diagram of reduction percentage at different pressing pressure

3.5. Reduction percentage at 0.5, 1, 1.5, 2 litre hydrogen

Fig.8 illustrates the relation between reduction percentage and hydrogen flow rate .and it is clear that as flow rate of hydrogen increase the reduction percentage increase.

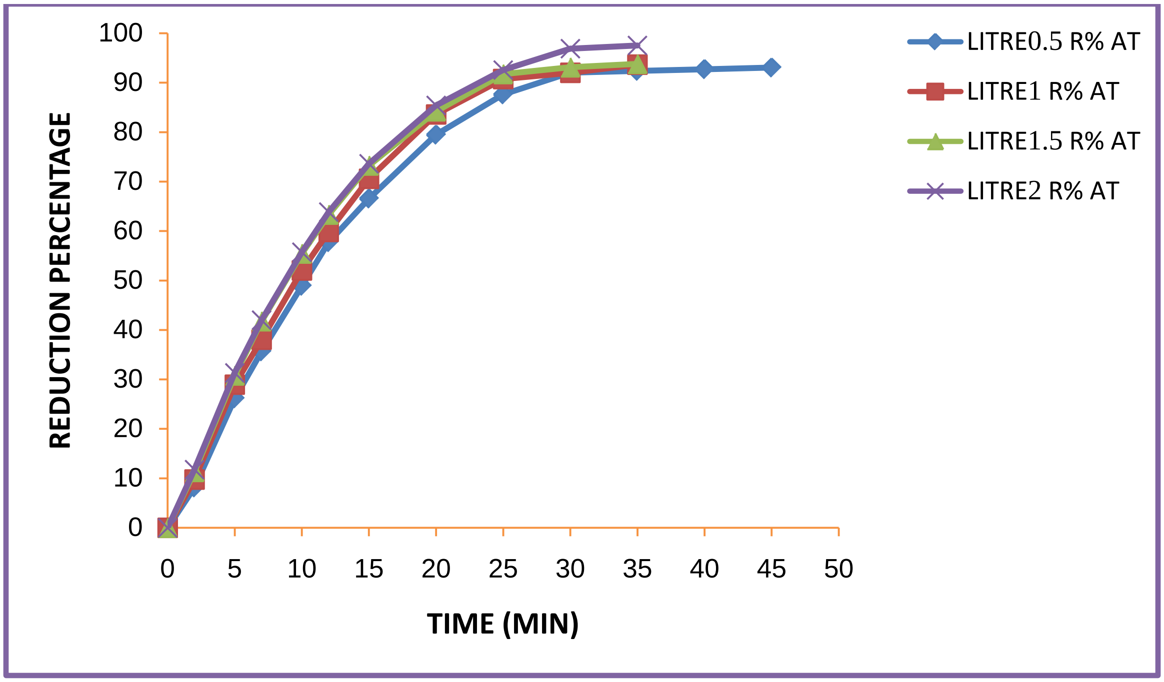


Fig. 8.Schematic diagram ofreduction percentage at 0.5, 1, 1.5, 2 litre hydrogen

3.6.Reduction percentage at 700, 800, 900, 1000 °C

The reduction was carried out at different temperatures ranging from 700˚C to 1000˚C, where the briquettes weight are constant and the hydrogen flow rate was 2 liter/min. The results of the investigation are shown on Figure 9 , from which it is clear that the increase of temperature favors the reduction rate this is may be due to oxygen removal increase with increasing temperature. Also the increase of reduction percentage with temperature could be due to increase of number of reacting moles having excess energy which leads to the increase rate of reaction . Also increasing temperature leads to increase the rate of mass transfer of the diffusion and rate of chemical reaction [19-20].

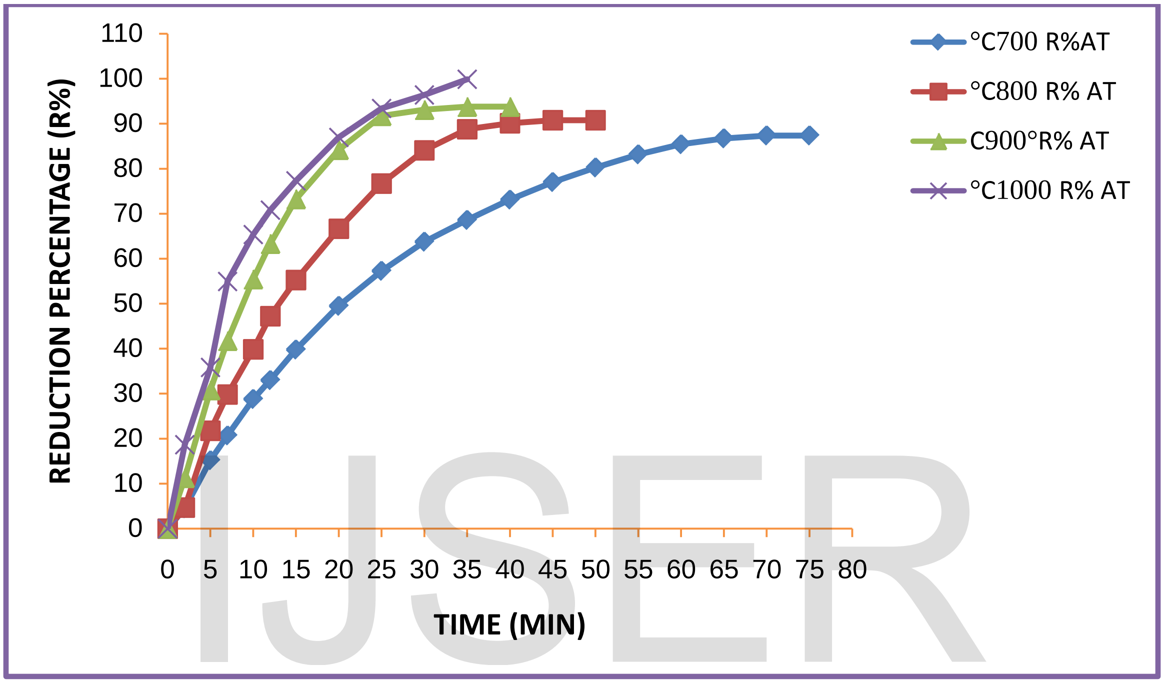


***Fig. 9.Schematic diagram of* reduction percentage at 700, 800, 900, 1000 °C**

3.7. Kinetic of reduction of mill scale briquette

Figure 10 illustrates the relation between $(1-(1-R)^{1/3}$ against time of reduction for different reduction temperature(700 -1000C^{O}). From which it is clear that the relationship is represented by straight line. The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results were illustrated on Figures 11 from which it is clear that briquette has activation energy = 30.96 kJ/ mole.

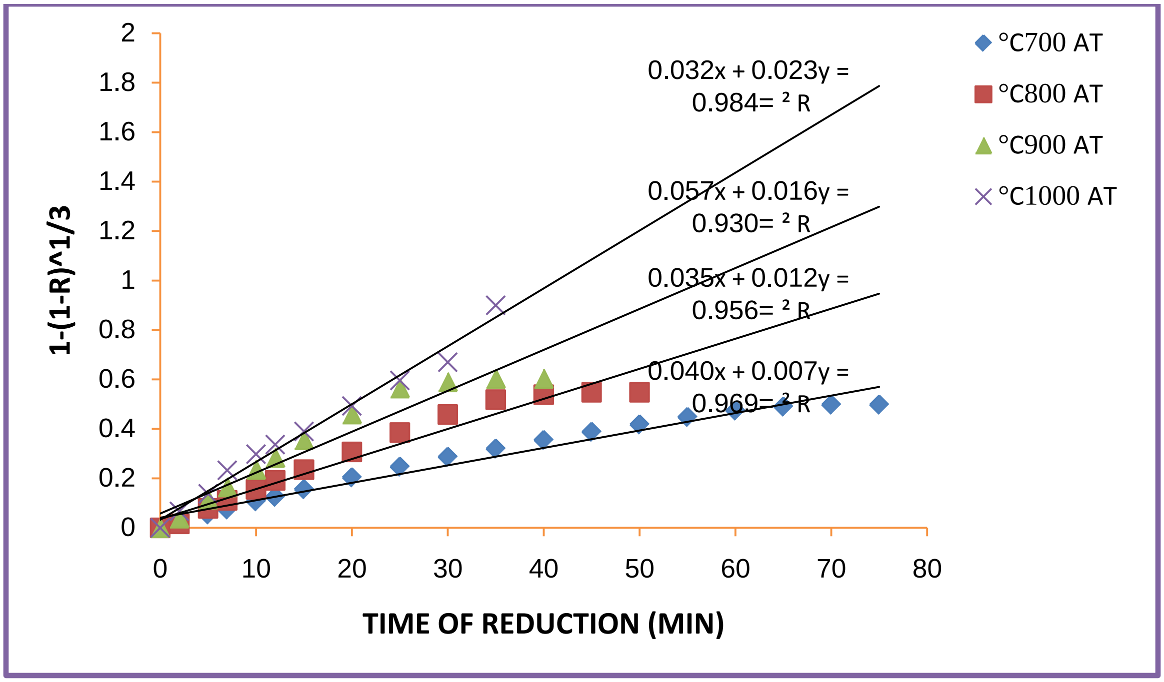


Fig. 10.Schematic diagram of the relationship between 1-(1-R)^1/3

Versus reduction time (min.) at 700, 800, 900, 1000 °C

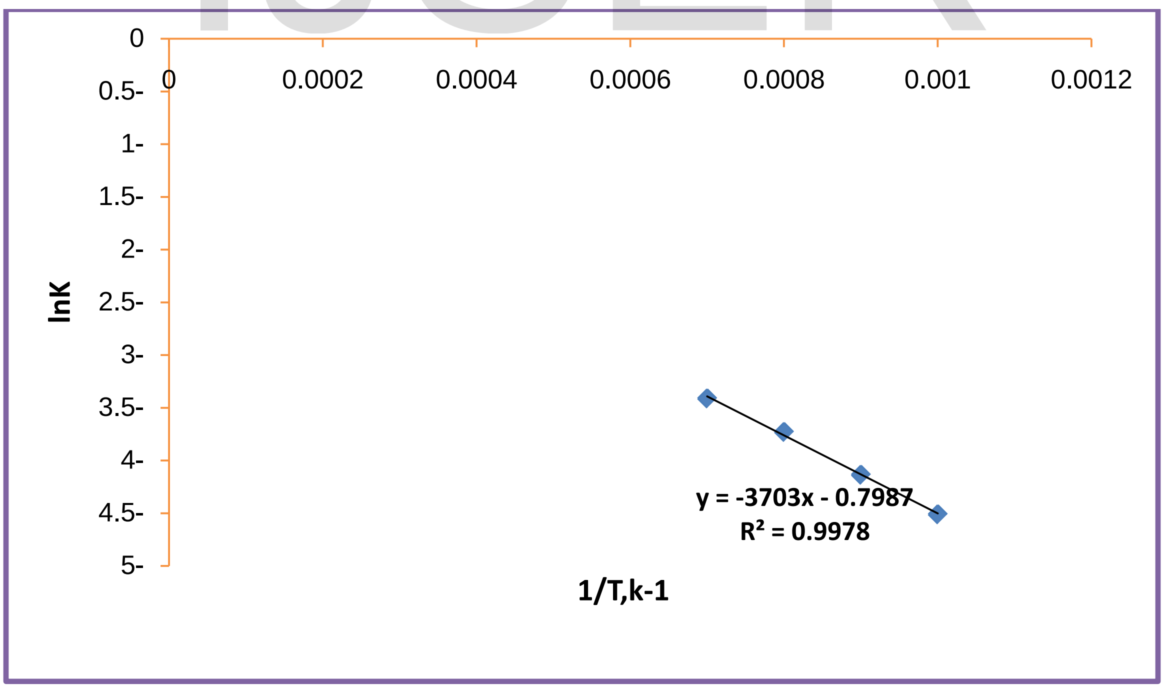


Fig. 11. Schematic diagram of the Arrhenius plot for the reduction process of briquettes

3.8-Conclusions:

From the obtained results, the following can be concluded:

1. Increase the pressing pressure leads to an increase both the drop number and compression strength of the green, dried and fired briquette.
2. Reduction of the briquettes formed increased applying a higher hydrogen flow rate.
3. The activation energies calculated for this process for the briquettes formed using equation **kt=1-(1-R)**$^{1/3}$ was = 30.96kJ/ mole

3.9.Referances

[1] M. C. Bagatini, V. Zymla, E. Osório and A. C. F. Vilela, “Characterization and Reduction Behavior of Mill Scale,” Isij International, 51, 7, 2011, .1072-1079.

[2 [O. Benchiheub, S. Mechachti, S. Serrai and M. G. Khalifa, “Elaboration of Iron Powder from Mill Scale,” Journal of Materials and Environmental Science, V 1, 4, 2010, . 267-276.

[3[Cho and J. Lee, “Metal Recovery from Stainless Steel Mill Scale by Microwave Heating,” Metals and Materials International, 14, . 2, 2008, 193-196,

[4] A. M. Fleischanderl, “Managing Steel Wastes and By- Products: Crisis and Opportunity,” Gorham/Intertech’s 13th International Iron and Steel Development Forum, Antwerp, 11-14 May 1998, .45-50.

[5] Y.-K. Cho, “Making Method for Ferrite Used Mill Scales,” Patent Kr 9103783, June 1991.

[6] D. Osing, “Reuse of Metallurgical Fines,” Patent Wo 96/ 31630, 1996.

[7] A. Fleischanderl, J. Pesl and W. Gerbert, “Aspect of Re- cycling of Steelworks By-Products through the Bof,” Seaisi Quarterly, 28, . 2, 1999, 51-60.

[8] A. Poulalion, “Process of Recycling Mill Scale of Alloy- ed Steel in an Electric Furnace into a Ferro-Silicon Prod- uct,” Patent Ep 1122319, 2001.

[9] N. M. Gaballah, A. F. Zikry, M. G. Khalifa, A. B. Farag , N. A. El-Hussiny , M. E. H. Shalabi , Production of Iron from Mill Scale Industrial Waste via Hydrogen , Open Journal of Inorganic Non-Metallic Materials, 2013, 3, 23-28.

[10] L. Camci, S. Aydin, C. Arslan, “Reduction of iron oxides in solid wastes generated by steelworks”, Turkish J. Eng. Env. Sci., 26 ,(2002) 37-44.

[11] J.-W. Park, J.-C.Ahn, H. Song, K. Park, H. Shin, J.-S.Ahn, “Reduction characteristics of oily hot rolling mill sludge by direct reduced iron method” ,Resour. Conserv.Recy. 34(2) (2002) 129-140

[12] M.I. Martín, F.A. López, M.E. Rabanal1 and J.M. Torralba,” Production of Sponge Iron Powder by Reduction of a By-product of the Steelmaking Industry”, PM 20109World Congress – Water Atomized Powders, v.1.

[13] N.A.El-Hussiny ,H. H. Abdul-wahab , M. M. Ali , A. A. Omar , M.E.H. Shalabi , M. R. Moharam, Effect of grinding time of mill scale on the physicochemical properties of produced briquettes and its reduction via Hydrogen, International Journal of Scientific & Engineering Research, 6, I , 2015, 1642- 1658

[14] N.A. El-hussiny , N.M. Hashem , S.S.Abdel-Rahim , M.G. Khalifa , M.E.H. Shalabi Pelletization of El-Baharia iron ore (O) with different amount of mill scale (M) and reduction kinetics of these pellets via hydrogen, International Journal of Scientific & Engineering Research, 7, I 8, 2016, 109-116.

15. Forsmo S.P.E., Apelqvist A.J., Björkman B.M.T. and Samskog P.O., "Binding mechanisms in wet iron ore green pellets with a bentonite binder", Powder Technology 169,(2006), 147-158.

16. Forsmo S.P.E., Samskog P.O. , and Björkman B.M.T., "A study on plasticity and compression strength in wet iron ore green pellets related to real process variations in raw material fineness", Powder Technology 181,(2008).321-330.

17. Nafeaa I.A., Zekry A.F., Farag A.B., Khalifa M.G., El-Hussiny N.A. and Shalabi M.E.H., "Kinetic Study of Formation of Sodium Titanets by Roasting of Soda Ash and Ilmenite Ore Concentrate" , Indian Chemical Engineer , (2013) , 1–11.

18. N.A. El-Hussiny and M.E.H. Shalabi, "Studying the Pelletization of Rosetta Ilmenite Concentrate With Coke Breeze Using Molasses and Reduction Kinetics of Produced Pellets At 800-1150 °C", Science of Sintering, 44 (2012) 113-126.

19- Sayed, S.A., Khalifa, G.M., El-Faramawy, E.S.R. and Shalabi, M.E.H. (2002) Kinetic Reduction of Low Manganes Iron Ore by Hydrogen. *Egyptian Journal of Chemistry*, **45**,(2002) 47-66.

20 - El-Gawad, H.H.A., El-Hussiny, N.A., Wassf, M.A., Kalifa, M.G., Iskander, B.A. and Shalabi, M.E.H. Briquetting of Rosetta Ilmenite Ore with Different Organic Binder and Its Reduction in Hydrogen in the Temperature Range of 800-1200°C, *Górnictwo i Geoinżynieria*, **33**, (2009) 25-40.