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Kinetic Reduction of Mill Scale via Hydrogen

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Abstract:

Mill scale is very attractive industrial waste since it is rich in iron (about = 72 % Fe) and it is suiTab. for direct recycling to the blast furnace via sintering plant. In this paper the characterizations of raw materials were studied by different methods of analyses. The produced briquettes were reduced with different amounts of hydrogen at varying temperatures, and the reduction kinetics was determined. Two models were applied and the energy of activation was calculated.
Key words: Mill scale, Reduction by hydrogen.

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1. Introduction

In several iron and steel making processes, about 500 kg/ton of solid wastes of different nature are generated. One of this wastes is the mill scale which represents about 2% of steel produced [1]). Mill scale is very attractive industrial waste due to very rich in iron (about = 72 % Fe) [2]).

In the whole world 13.5 million tons of mill scales are generated annually [3]. Mill scale is suiTab. for direct recycling to the blast furnace via sintering plant [4]. Approximately 90% of mill scale is directly recycled within steelmaking industry and small amounts are used for ferroalloys, in cement plants and in the petrochemicals industry [5-8]. Some authors [9] studied the replacement of some amount of Baharia high barite iron ore concentrate by mill scale waste and they indicated that replacement of some iron ore by mill scale increased the amount of ready made sinter, sinter strength and productivity of the sintering machine and productivity of blast furnace yard.

The reduction of iron oxides via gaseous and solid reductants has been already extensively studied [1].

Some investigator [1] studied the kinetics of scale reduction by carbon monoxide in the temperature range 800-1200 ˚C and the results indicated that un-reacted shrinking core model with one interface under chemical reaction control fits well with the experimental data at the initial stage of reduction and the activation energy about 80 kJ/mol. Some authors [2] found that the best reduction of mill scale was obtained at 1050 ˚C at 180 min in pure carbon monoxide gas.

It was indicated that with increase the temperature, the percentage reduction increases with increase in time and the activation energy of reduction depend upon the type of binder

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Some author [11] found that varying the total pressure of the reduction system by hydrogen and carbon monoxide had no effect on the rate of reduction. Commercial iron powders are classified in three types, reduced iron powder, atomized iron powder, and electrolytic iron powder, depending on the production method, and are used in various applications, taking advantage of their respective properties. Iron powders are used in many different industries for many different applications. Following are some examples of the iron powder uses: Brazing, Sintered Products, Friction Products, Soft Magnetic Products, Chemicals, Metallurgy, Filtration, Printing, Surface Coating, Welding, Iron Fortification. Iron powder cores are commonly used to produce high Q inductors and transformers for selective circuits. Iron powder cores used in RF applications are composed of extremely small particles of highly pure carbonyl iron.

This study aims at investigating the reduction kinetic of Egyptian mill scale briquette via hydrogen to produce iron powder.

2. Experimental work
2.1. Material

The rolling mill scale used in this work was provided by mill of Egyptian iron and steel Co. The sample was submitted to chemical and x- ray analysis.

The chemical analyses of mill scale are illustrated in Tab.I.

Tab. I The chemical analyses of mill scale.

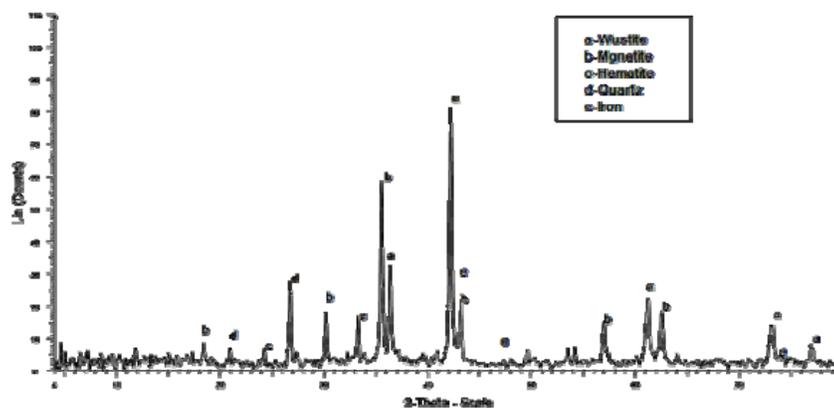| Weight %	Element
69.33	Fe
49	Fe^{+2}
12.5	Fe^{+3}
7.83	FeO
0.33	S
0.22	P
0.51	Mn
0.9	Si

Fig. 1. X-Ray analysis of mill scale sample.

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

2.2 Preparation of the briquetting and its physical properties

The mill scale was grinding in vibrating mill to powder with size less than 75 μm. The mill scale powder (10 g) are mixed with 2% molasses and then pressed under different pressure. The briquette subjected to drop number test and crushing strength tests. The drop number indicates how often green briquette 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 number.

The average crushing strength is done by compressed 10 briquettes between parallel steel plates up to their breaking [12].

2.3. Reduction process

The reduction of mill scale by hydrogen was done in a thermo balance apparatus. (A schematic diagram of thermo balance apparatus is shown in Fig. 2 [13]. 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 ± 5 ˚C. Then samples were placed in hot zone.

The nitrogen flow rate was 0.5 l/min in all the experiments (at 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:-

$$\text{Percent of reduction} = \frac{(W_0 - W_t) * 100}{\text{Oxygen (mass)}}$$

where:

W_0: the initial mass of mill scale sample after removal of moisture.

W_t: mass of sample after each time, t.

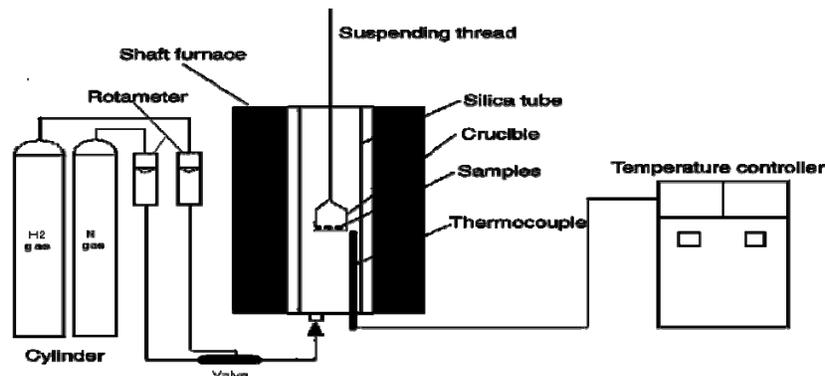Oxygen (mass): indicates the mass of oxygen percent in mill scale in form FeO & Fe_2O_3.

Fig. 2. A schematic diagram of thermo balance apparatus [13].

3. Results and Discussion
3. 1. Effect of the pressure load with constant amount of binding material on the quality of the briquette

Fig. 3 and 4 shows the relation between the change of pressure load at constant amount of molasses (2%) on the drop number (drop damage resistance) and cold crushing strength of the briquette It is clear that as the pressing pressure load increased both the drop damage resistance and crushing strength increased.This may be due to the fact that increase pressure load increases the compaction of briquette and subsequently the Vander Waals forces increased [14-15], also the increase of briquetting pressure leads to progressive crushing of the macro pores [16].
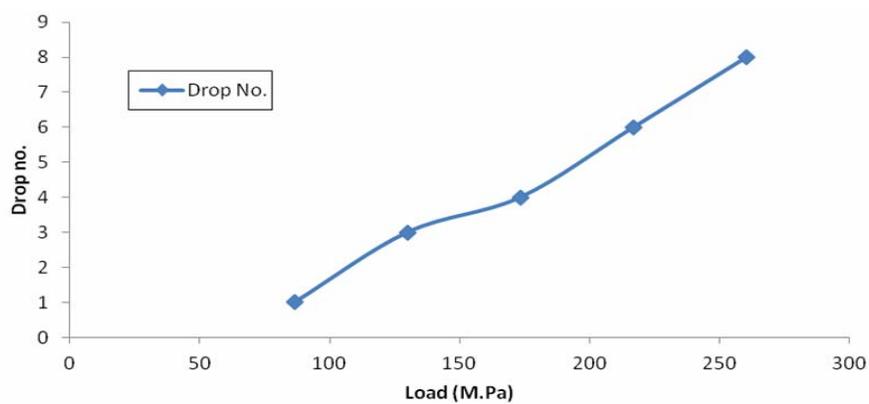

Fig. 3. Relationship between the change of pressure load and drop no. of mill scale briquette.
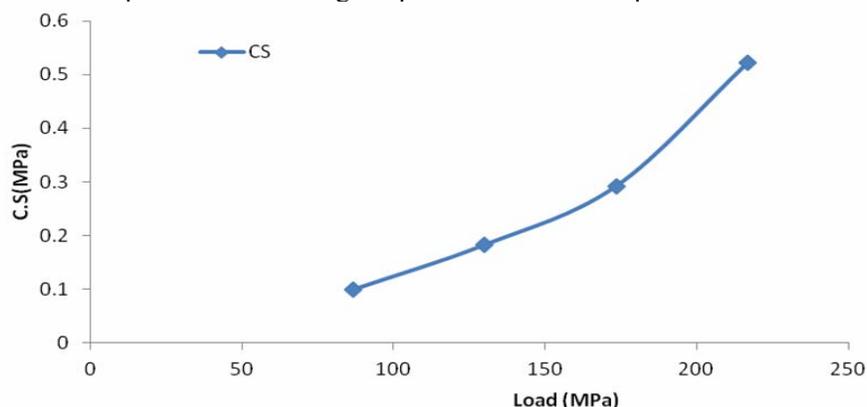

Fig. 4. Relationship between the change of pressure load and cold crushing strength (C.S) of mill scale briquette.

3.2. Effect of flow rate on the degree of reduction

Fig. 5 illustrated the effect of change hydrogen flow rate on the degree of reduction of mill scale briquette at 900 ˚C (pressure load 216.85 M.Pa). From this Figure it is clear that the degree of reduction increased as the hydrogen flow rate increased. This may be attributed that 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 subsequently the rate of reaction increased [17] or the increase of flow rate increased the gas diffusion across the boundary layer subsequently the reduction ion increased [18]. Also may be the higher flow rate

prevailing in the reaction zone which enhances the rate of hydrogen absorption and subsequently the rate of chemical reaction steps increased [19]. .
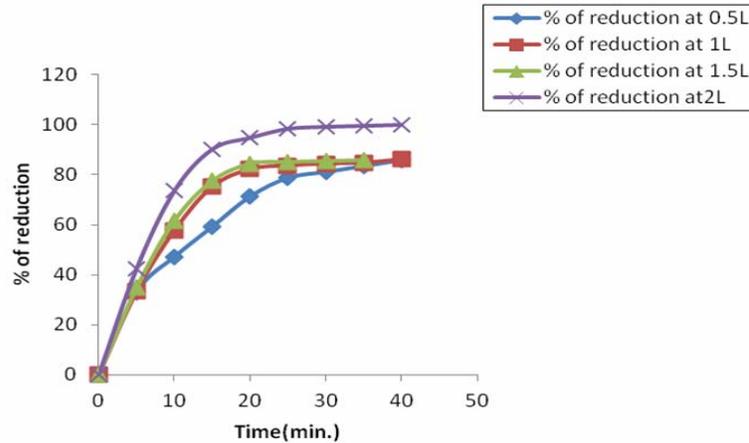

Fig. 5. Effect of change hydrogen flow rate on the degree of reduction of mill scale briquette. (Pressure load 216.85 M.Pa, and temperature of reduction 900˚C).

3.3. Effect of temperature on the reduction degree of mill scale briquettes

Experiments were performed for briquette which pressed   at load 216. 85 M.Pa. , in the temperature range of 650 to 950ºC in hydrogen atmosphere (2 L/min. Plots of the reduction percentage as a function of time are shown in Fig. 6. From this Fig., it is clear that the reduction rates increased with increasing temperature. At high reduction temperatures (more than 900 and up to 950˚C), with increasing temperature, the oxygen removal favorable increased.
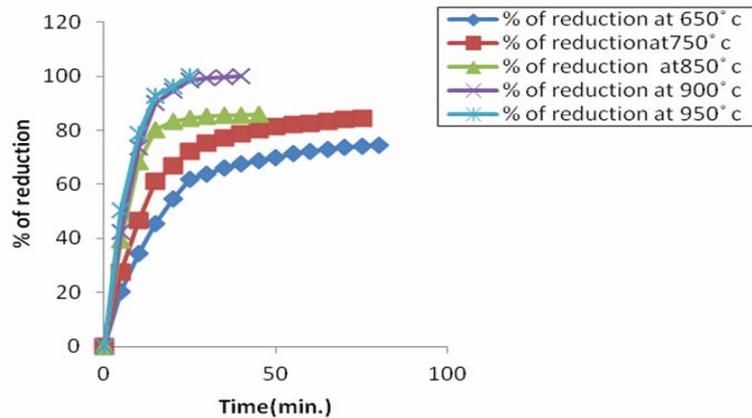

Fig. 6. Effect of change temperature on the reduction degree of mill scale briquettes.

The analyses of the curves relating the reduction percentage and time of reduction, shows that each curve has 3 different slopes indicating 3 different values of reduction rates. The first value is high, while the second is somewhat slower and the third is slowest one. 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 the increase of reduction

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rate [17,20]. Also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rat of desorption [18-21].

3.4. Kinetics reduction of mill scale briquette

Using two models:
1- Diffusion process controls equation Ginsling-Brounshtein (22-23)
$1-(2/3) R (1-R)^{2/3} = kt$
2- Diffusion process controls equation (24).
$1- (1- R)^{0.5} = kt$

   Where R is fractional reduction, t is time of reduction, k is the rate constant. Fig.7. illustrate the relation between $1- (2/3) R- (1-R)^{2/3}$ against time of reduction for different reduction temperature. From which it is clear that the straight line was observed.
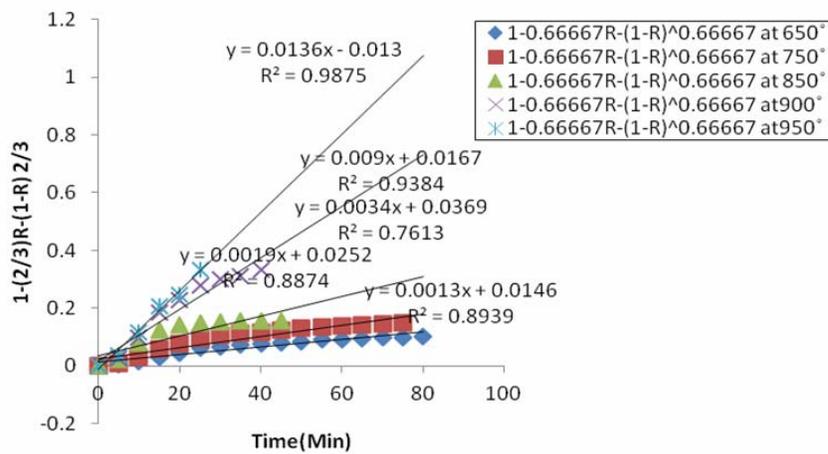

Fig. 7. the relationship between time of reduction and $1-(2/3) R- (1-R)^{2/3}$ at different temperature.

   The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrate in Fig.8. From which it is clear that the activation energy= 72.25 kJ / mole.
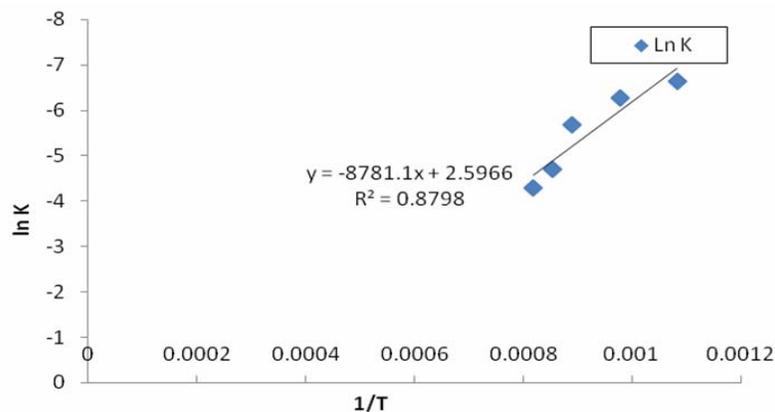

Fig. 8. The relation between 1/T and ln K for first model (Arrhenius plot for reduction reaction.

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Fig. 9. illustrate the relation between 1-(1-R) $^{0.5}$ against time of reduction for different reduction temperature. From which it is clear that the nearly straight line was observed.
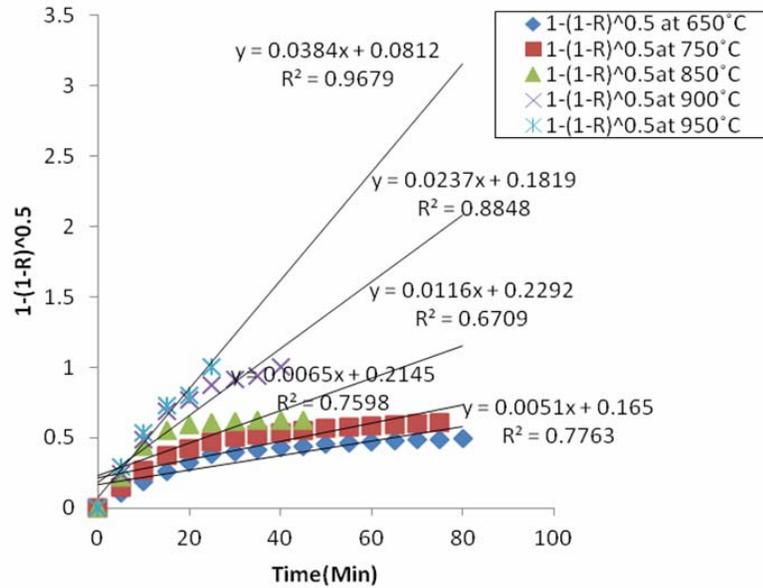

Fig. 9. The relationship between time of reduction and 1-(1-R) $^{0.5}$ at different temperature.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrate in Fig.10 from which it is clear that the activation energy= 61.5 kJ / mole.
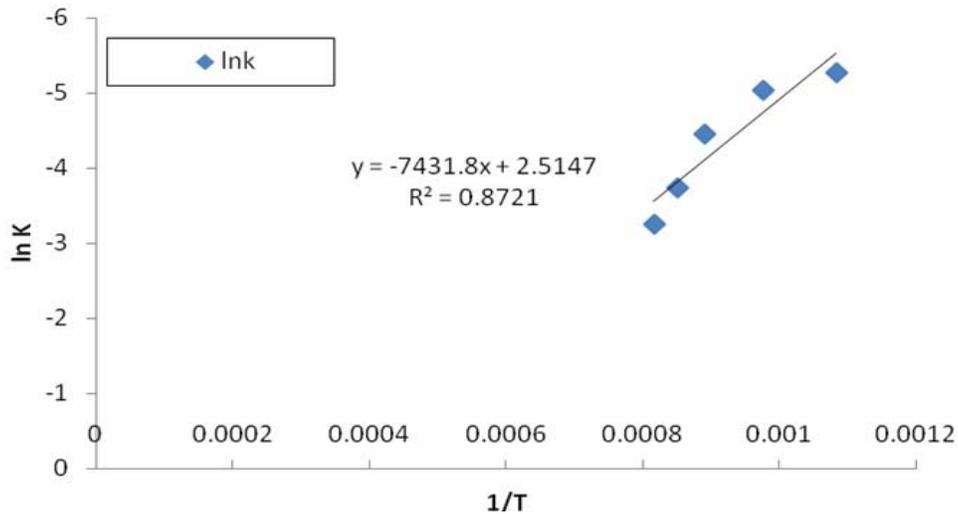

Fig. 10. The relation between 1/T and Ln K For second model (Arrhenius plot for reduction reaction.

X-ray analysis of some reduced samples

        Figs. 11 and 12 illustrate x-ray analyses of a reduced mill scale at different temperature (650-950˚C) in hydrogen atmosphere. From which it is clear that the reduction at high temperature more iron is produced and reached to about 100%.
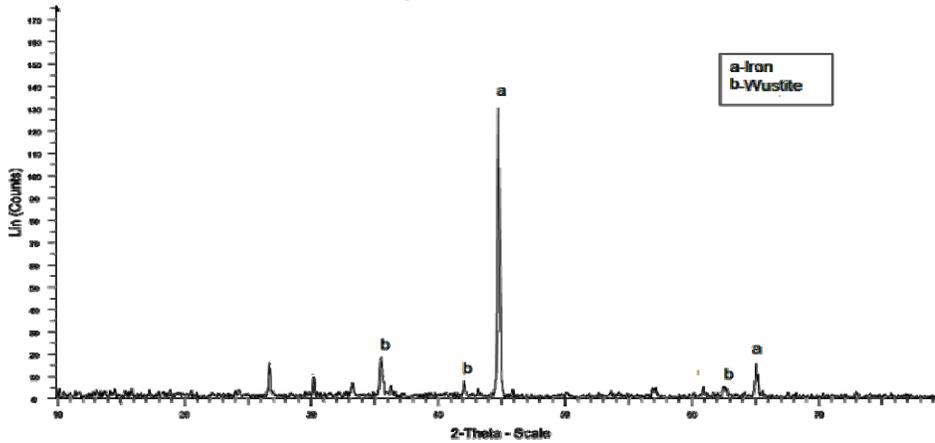

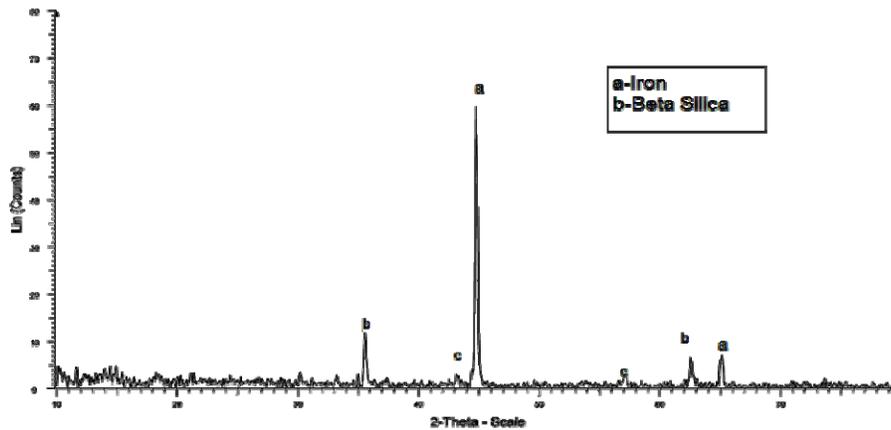**Fig.11.** X-ray analysis of sample produced at 650˚C.

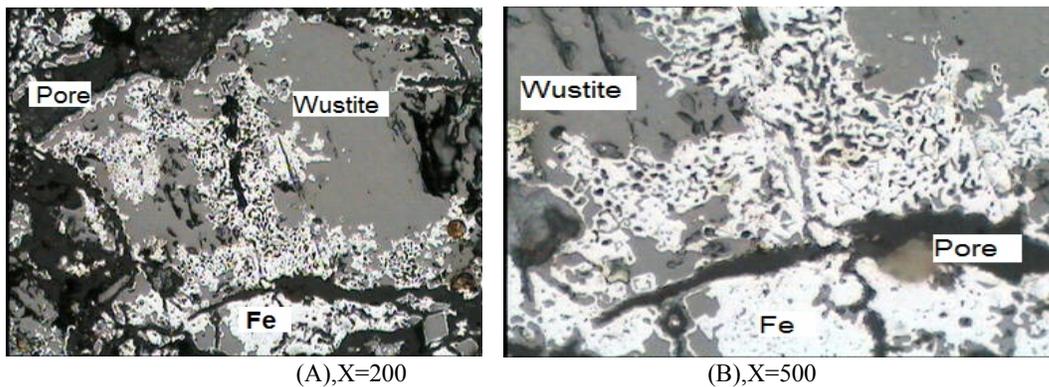**Fig.12**. X-ray analysis of sample produced at 950˚C.

(A),X=200   (B),X=500
Fig. 13. Microscopic structure of the reduced mill scale briquette at 650˚C.

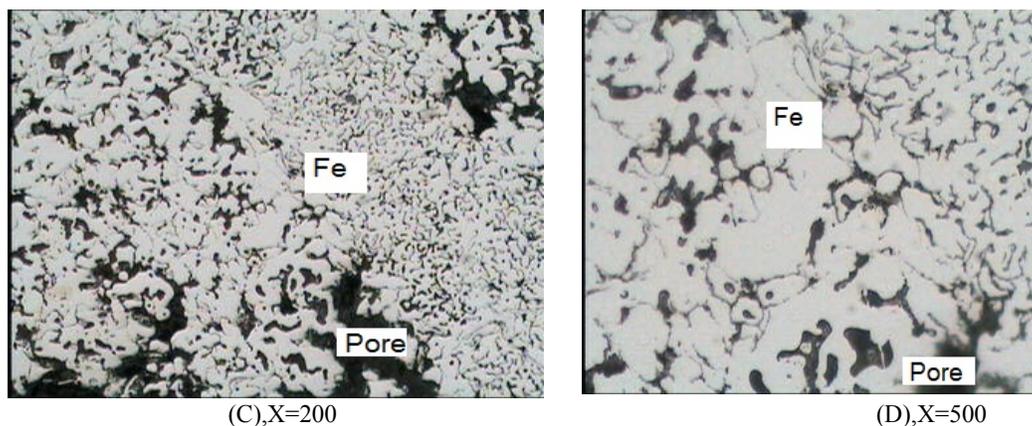(C),X=200   (D),X=500
Fig. 14. Microscopic structure of the reduced mill scale briquette at 950°C.

4. Conclusions

Mill scale is very attractive industrial waste due to very rich in iron (about = 72 % Fe).The pressing pressure load in the briquetting process of mill scale powder increased both the drop damage resistance and crushing strength increased.

The degree of reduction of mill scale briquettes at constant temperature increased as the hydrogen flow rate increased.

The reduction rate of mill scale briquettes under a constant flow rate of hydrogen (as reducing agent) increased with increasing temperature.

The kinetic reduction of mill scale briquettes show that the reduction process is controlled by diffusion process and the energy of activation is ranged between (61.5-72.25KJ/mol).

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Садржај: *Љуспице млина су веома атрактиван индустријски отпад обзиром да су богате гвожђем (садрже око 72 % Fe) и веома су погодне за директну рециклажу током процеса синтеровања. У овом раду проучавана је карактеризација сирових материјала различитим методама анализе. Добијени испресци су редуковани различитим количинама водоника на различитим температирама, и одређена је кинетика редукције. Примењена су два модела и израчуната је енергија активације.*
Кључне речи: *љуспице млина, редукција водоником.*