International Journal of Multidisciplinary Research and Publications
ISSN (Online): 2581-6187

The Relationship between Grinding Time of Mill Scale and Physicochemical Properties of the Produced Pellets and Its Reduction Kinetics in a Static Bed via Hydrogen

H. H. Abdul-wahab[1], El-Hussiny N.A[2], M. M. Ali[1], A. A. Omar[3], Shalabi M.E.H.[2*], M. R. Moharam[3]
[1]Al-Azhar University, Faculty of Engineering, Qena, Egypt
[2]Central Metallurgical Research and Development Institute, CMRDI, Cairo, Egypt
[3]Al-Azhar University, Faculty of Engineering, Cairo, Egypt
Email address: mehshalabi @ hotmail.com

Abstract**—***The obtained mill scale sample from the Egyptian Iron and Steel Company was screened on 4.75mm sieve from which the passed material was subjected to sieve analysis to determine the particle mean size. Furthermore, the passed material was subjected to grinding for specific periods of time (1 hour and its multiples up to 4 hours). Mill scale passing through the 4.75mm sieve and all grinding products were agglomerated on cold by pelletizing method by adding 2% molasses as a binder material. Then the agglomerated products were tested by drop damage resistance and compressive strength tests in both green and dry states to identify the quality of each. Some parameters were studied exclusively for the reduction process; grinding time, hydrogen flow rate, and reduction temperature. The agglomerated products were subjected to reduction by Hydrogen with different flow rates at different temperatures (600 - 1000ºC). All reduced pellets at 1000ºC were characterized chemically by using XRF, mineralogically by using XRD, microscopically by optical microscope and, finally by performing SEM-EDS analysis. The obtained results arose from this study showed that the maximum reduction percentage was 99.98% for pellets made from 3 hours grinding time series, at 2 L/min. H_2 gas flow rate, 1000ºC reduction temperature, and 45 minutes reduction time. Kinetic study showed that the rate controlling step of all reduction reactions is that of diffusion with activation energy (E_a) of 8.27 kJ/mole.*

Keywords**—** *Grinding time, pelletizing, Reduction kinetics.*

I. INTRODUCTION

Rolling mill scale is a solid by-product of the steelmaking industry that contains metallic iron (Fe) and three types of iron oxides: (α-Fe_2O_3), (Fe_3O_4), and (FeO). It also contains traces of non-ferrous metals, alkaline compounds and oils from the rolling process. The iron content is normally around 70 %, also the chemical composition of mill scale varies according to the type of steel produced and the process used [1].

In the whole world, the production of hot rolled product in year 2016 was about 1.597 billion tons [2]. Depending on the process and the nature of the product, the weight of mill scale can vary between 20 and 50 kg/ton of hot rolled product. The average specific production of this by-product is around 35–40 kg/ton of hot rolled product [3]. Therefore, the minimum amount of the resultant mill scale per whole world production of hot rolled product in year 2016, would not be less than 31.94 million tons at the least estimation, which requires the maximum utilization of this huge amount. The recycling and utilization of iron-bearing by-products have long been promoted in iron and steel-making industry due to their various benefits which include: (i) To reduce the depletion of the earth's limited natural resources;(ii) To reduce pollution produced by discharging untreated waste; and (iii) To save energy indirectly [4]. Generally, these by-products were recycled by the metallurgical processes such as the blast furnace or the direct reduction reactors that uses coal as reducing agent to produce pre-reduced briquettes or pellets intended for the re-melt in electric steel plant. Besides the steelmaking, recycling, part of these by-products was already supported by the powder metallurgy where the economic recovery was more favorable [5].

II. MATERIALS AND METHODS

The materials used in the present study are; Mill scale, Hydrogen gas, Nitrogen gas, and Molasses (binder material). Mill scale was provided by the Egyptian Iron and Steel Company.

2.1 Assessment of Raw Materials and Reduced Product

All materials used in experiments were specified by one or more of the following: sieve analysis, chemical analysis, and X-Ray diffraction analysis to know what are their sizes, elements, and phases.

Also, the reduced Mill scale pellets at optimum conditions (maximum obtained reduction percentage, max. R %) were examined by the following methods:- Chemical analysis to estimate the weight %, of each ingredient present in the reduced products, Mineralogical examination in order to identify the phases of iron in the reduced pellets, and therefore know the extent to which the reduction process reached and its compliance for calculations, Optical microscope examination where, the microstructure data of the reduced pellets can be

H. H. Abdul-wahab, El-Hussiny N.A, M. M. Ali, A. A. Omar, Shalabi M.E.H., and M. R. Moharam, "The relationship between grinding time of mill scale and physicochemical properties of the produced pellets and its reduction kinetics in a static bed via hydrogen," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 1, Issue 4, pp. 1-8, 2018.

used to understand the characteristics of products and as a reference for the possible future products, and Scanning electron microscope (SEM) with Energy dispersive x-ray spectrometer (EDS) examination for metallographic examinations or morphology characteristics of the reduced pellets.

2.2 Experimental Procedures

The proposed flow sheet for producing sponge iron from the Egyptian mill scale is shown in Figure 1.

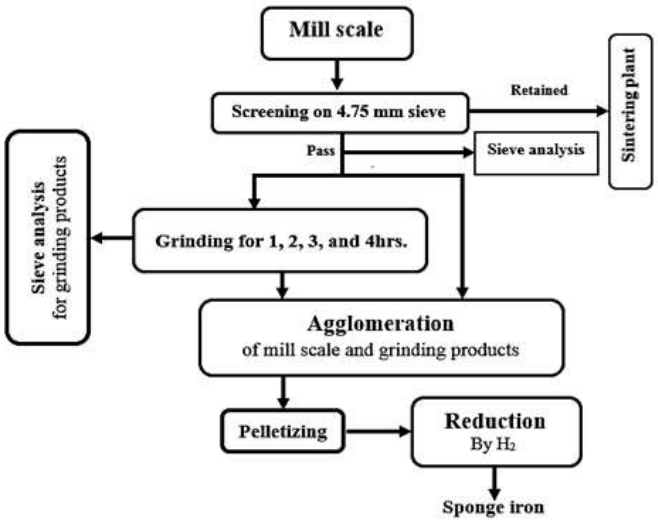

Fig. 1. The proposed flow sheet for producing sponge iron from the Egyptian mill scale

2.3 Preparation of Materials and Accompanied Equipment

The materials used are prepared to match the subsequent processes and necessary specifications as follows:

Mill scale was subjected to screening by Tyler standard screen 4.75 mm with electric shaker and the passed was taken. The passed mill scale (- 4.75 mm) was subjected to grinding for specific periods of time (1hr. and its multiples up to 4 hrs.). Grinding of mill scale was carried out in a laboratory ball mill of model (I L E - Cat. No. I L-207). It has 3 kg capacity, 15 Cm diameter, 40 Cm length, L/D ratio = 2.66, 100 rpm speed with balls to load weight ratio of 2:1. The operation cycle of this mill is 3 hours from which 2 hours milling and 1 hour rest. The used stainless steel in each test are mixture of 10, 15, and 20 mm diameter balls. A sample of about 200 gm from each mill scale series was placed on a stack of sieves arranged from the largest to the smallest opening in order to determine the particle mean diameter of each mill scale series. The selection of sieves series was based on the range of particles in the sample. Each mill scale series; passed through 4.75 mm. sieve, and the ground products for 1, 2, 3, and 4 hours were agglomerated individually by the pelletizing method in the form of pellets (sphere shape) to be tested by mechanical tests in both green and dry states, and reduced at different temperatures by hydrogen gas.

2.4 Preparation and Production of Mill Scale Pellets

The pellets were prepared in a disc pelletizer (Figure 2) with a diameter of 400 mm, collar height 100 mm, angle of inclination 52^o, disc rotating speed 17 rpm., and 10 minutes residence time. Mill scale fines (200 gm) were fed to the pelletizer. The predetermined amount of water (10%) with or without molasses (2%) was then sprayed onto the rolling bed of material in the disc pelletizer. At the end of the experiment, a pellet sample was collected and screened to collect the (- 7 +3 mm diameter) fraction which was taken as a measure of the productivity of pellets through the disc pelletizer machine according to the following Equation (1) [6].

Fig. 2. Disc pelletizer machine

$$P_p = (W_1/W_2) * 100 \quad (1)$$

Where: P_p is the productivity of the pellets (-7+3 mm size),%.
W_1 is the weight of the pellets (-7 +3 mm size), gm.
W_2 is the weight of the charge fed to disc pelletizer, gm.

2.5 Mechanical Tests

The produced briquettes and pellets were dried in air atmosphere for three hours for carrying out the mechanical tests in green state. For carrying out the mechanical tests in dry state the produced briquettes and pellets were dried by the same manner but for three days to ensure the evaporation of the water which was used during the agglomeration process. Taking into consideration, that the produced briquettes and pellets go through a number of handling and transportation operations until it reach the metallurgical furnaces, so the briquettes should have a sufficient strength to withstand all such external forces [7]. The produced briquettes and pellets were subjected to mechanical tests; such as drop damage resistance test and compressive strength test in both green and dry states.

2.5.1 Drop damage resistance test of agglomerates

The produced briquettes and pellets were subjected to drop damage resistance test. The drop damage resistance indicates how often green and dry briquettes and pellets can be dropped from a height of 46 Cm before they show perceptible cracks or crumble. Ten of briquettes and pellets in both cases were individually dropped on to a steel plate under gravity acceleration. The number of drops is registered for each briquette and pellet. The arithmetical average values of the crumbing behavior of ten briquettes and pellets yield the drop damage resistance for them [8, 9].

H. H. Abdul-wahab, El-Hussiny N.A, M. M. Ali, A. A. Omar, Shalabi M.E.H., and M. R. Moharam, "The relationship between grinding time of mill scale and physicochemical properties of the produced pellets and its reduction kinetics in a static bed via hydrogen," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 1, Issue 4, pp. 1-8, 2018.

2.5.2 Compressive strength of agglomerates

The average value of compressive strength of briquettes was done by compressing 10 briquettes of equal size between two parallel steel plates up to their breaking. The average compressive strength of pellets is controlled by compressing at least 10 pellets (5 pellets of - 7 +5 mm in diameter, and 5 pellets of -5 +3 mm in diameter) between parallel steel plates up to their breakage [8-10].

2.6 Reduction Procedure

The agglomerated mill scale particles; briquettes and pellets were dried in muffle furnace maintained at 100 ± 5˚C for half an hour to remove any moisture content present in samples which will be reduced. The reduction of mill scale agglomerates with hydrogen or coke breeze were performed in thermo gravimetric apparatus as shown in Figure 3. This apparatus is 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 - 1000 ˚C) and maintained constant to ±5 ˚C. At initial time air should be removed before each experiment as well as after the end of reduction; so all reduction experiments were done in nitrogen atmosphere (0.5 L/min).

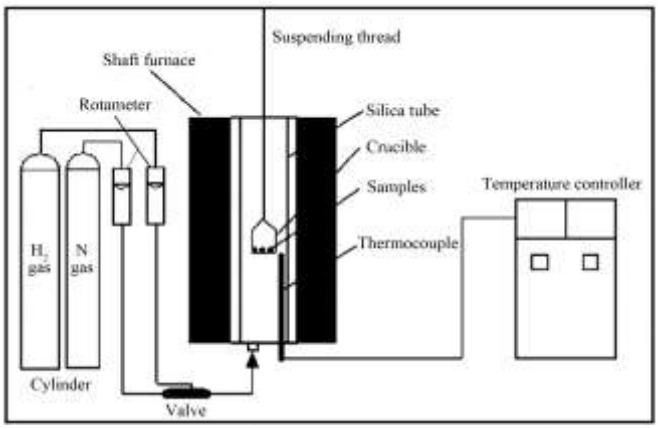

Fig. 3. Schematic diagram of the thermo gravimetric apparatus for mill scale pellets reduction

The weight of the sample was continuously recorded every 5 minutes to the end of the run. All reduced products were cooled from selected reaction temperature to room temperature in the desiccators. The reduction percentage was calculated according to Equation (2):-

$$\text{Percent of reduction (R \%)} = \left[\frac{w_o - w_t}{\text{Oxygen mass}}\right] \times 100 \qquad (2)$$

Where:

Wo: The initial mass of mill scale sample after removal of moisture, gm.

Wt: mass of sample after each time interval, gm.

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

III. Results and Discussions

3.1 Characterization of Individual Raw Materials

All materials used in the present study were specified to know what are their phases, elements or sizes.

3.1.1 Mill scale

Mill scale was characterized by chemical analysis, X-ray diffraction and sieve analysis as follows:

3.1.1.1 Chemical composition

The chemical analysis of mill scale is illustrated in Table 1. From this table it is clear that iron is the major element (Fe total 69.33%) in the form of (Fe_2O_3 =70 % by weight, Fe_3O_4 =17.26 % by weight, and FeO =7.83% by weight), while the other ingredients are present in trace amounts.

TABLE 1. Chemical analysis of mill scale sample

Contents	Fe_{total}					S	P	MnO	SiO_2	C
	Wt. %	69.33				0.33	0.22	0.66	1.92	0.04
	Phase	Fe	Fe_2O_3	Fe_3O_4	FeO					
Wt. %		1.74	70	17.26	7.83					

3.1.1.2 X-ray diffraction analysis

X-ray diffraction analysis was performed in order to identify the phases present in raw material. The X-ray diffraction analysis of mill scale is illustrated in Figure 4. It is clear from this figure that mill scale mainly consists of Fe_2O_3, Fe_3O_4, FeO, SiO_2 and Fe.

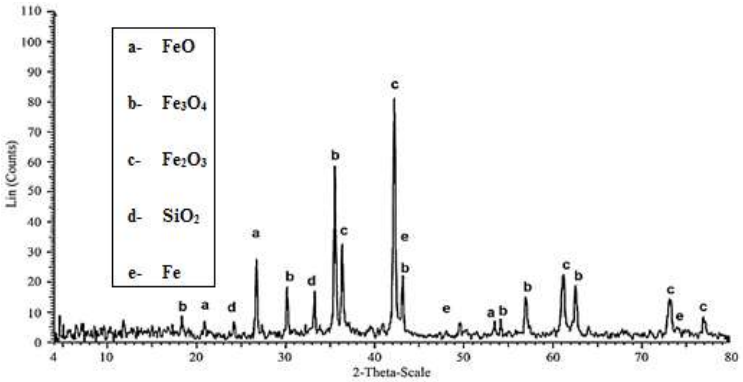

Fig. 4. X-ray diffraction analysis of mill scale sample

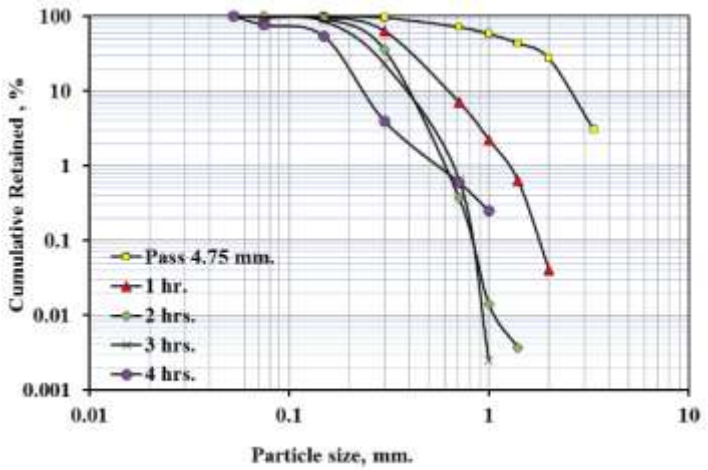

Fig. 5. Sieve analysis of mill scale passed through 4.75 mm and its ground products in a ball mill for different milling times

H. H. Abdul-wahab, El-Hussiny N.A, M. M. Ali, A. A. Omar, Shalabi M.E.H., and M. R. Moharam, "The relationship between grinding time of mill scale and physicochemical properties of the produced pellets and its reduction kinetics in a static bed via hydrogen," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 1, Issue 4, pp. 1-8, 2018.

3.1.1.3 Sieve analysis

The mill scale passed through the standard screen 4.75 mm and the grounded mill scale for different times (1 hr. and its multiples up to 4 hrs.) were subjected to sieve analysis by Tyler standard sieve set with electric shaker. The results are represented in Figure 5 and the particles mean diameter of mill scale products is presented in Table 2.

The results show that as the time of grinding increases, the particles mean diameter decreases.

TABLE 2. The particles mean diameter for both of mill scale head sample passed through standard screen 4.75 mm and grinding products after different grinding times

Mill scale/grinding products	Pass 4.75 mm	1hr.	2 hrs.	3 hrs.	4 hrs.
Particles mean diameter, mm	0.88	0.341	0.295	0.213	0.125

3.1.2 Chemical composition of Molasses

The components of molasses include major components (water, sugars, and nonsugars) and minor components such as trace elements, vitamins and growth substances. The average composition of cane molasses are presented in Table 3.

TABLE 3. Average composition of cane molasses

Constituents	**Water**	**Sugars**			**Nonsugars**	**Ash**
		Saccharose	**Fructose**	**Glucose**	**Nitrogenous material & gummy substances**	
Molasses, wt%	20	32	16	14	10	8

3.2 Physicochemical Properties of Mill Scale Pellets

Physicochemical properties of mill scale pellets with 2% molasses (as a binder material) are discussed in detail as follows:

3.2.1 Productivity of pellets

Productivity of pellets for mill scale material passed through 4.75 mm sieve and its all grinding products was calculated according to Eq. (1). The productivity results for each series is tabulated below in Table 4.

TABLE 4. Productivity of pellets for different mean particle sizes of mill scale

Series	**Particle Mean size, mm**	**Experimental conditions**	**Pellets product size**	**Productivity, %**
Pass 4.75 mm. (Head sample)	0.88	Sample weight of 200 gm & Disk pelletizer speed of 17 rpm. & 2 % molasses & 10 % water & Run time of about 10 min.	(-7 mm. + 3 mm.)	0
1 hr. grinding	0.341			**53**
2 hrs. grinding	0.295			64.3
3 hrs. grinding	0.213			100
4 hrs. grinding	0.125			**100**

From the presented results in Table 4; it is clear that as the mean size of the particle decreases (increase of grinding time), the productivity of pellets in size range (-7 mm + 3 mm) increases. This is may be due to that the capillary pressure of the liquid between finer particles is higher than that of coarser particles which causes binding of them, or related to that inter particle forces decrease with increasing the particle size [11].

3.2.2 Mechanical properties of produced pellets

The produced pellets were subjected to drop damage resistance and compressive strength tests, and their results will be discussed as follows:

3.2.2.1 Drop damage resistance of mill scale pellets

The relationship between grinding time and drop damage resistance of pellets in both green and dry states is graphically represented in Figure 6.

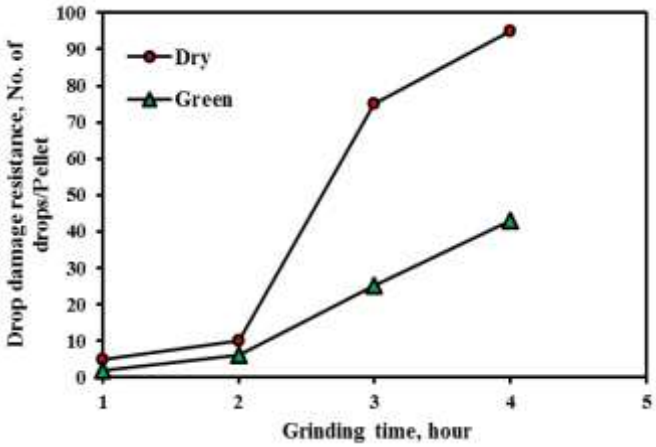

Fig. 6. Effect of grinding time on the drop damage resistance of mill scale pellets in both green and dry states

The max. results in dry state are 75 and 95 drops for pellets made from 3 and 4 hrs. grinding time series respectively with an increase ranging between 66.6 and 54.7 % over green state. The corresponding results in green state are 25 and 43 drops. But the drop damage resistance of pellets made from 1 and 2 hrs. grinding time series shows poor results. This is because of its larger particle sizes which in turn, increase the porosity of pellets, and consequently decrease the mechanical properties of pellets.

The drop damage resistance of pellets in dry state is more than green state. This is may be due to vaporization of moisture content which lead to more hardening.

3.2.2.2 Compressive strength of mill scale pellets

The relationship between the change in grinding time and the compressive strength of pellets in both green and dry states is graphically represented in Figure 7.

It has been observed that, there is a gap between the results of 1, 2 hrs. grinding time series and 3, 4 hrs. grinding time series. This is may be due to the same reason as mentioned before (particle size decrease). The max. results in dry state are 0.48 and 0.55 MPa for pellets made from 3 and 4 hrs. grinding time series respectively and the corresponding results in green state are 0.14 and 0.21 MPa. The compressive strength of pellets made from 1, 2 hrs. grinding time series

H. H. Abdul-wahab, El-Hussiny N.A, M. M. Ali, A. A. Omar, Shalabi M.E.H., and M. R. Moharam, "The relationship between grinding time of mill scale and physicochemical properties of the produced pellets and its reduction kinetics in a static bed via hydrogen," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 1, Issue 4, pp. 1-8, 2018.

shows very poor values due to weak bonding between mill scale particles because of high porosity ratios.

It is clear that as the grinding time increases (decrease of particle size); the compressive strength increases. Generally, the finer the grind, the higher the strength and durability.

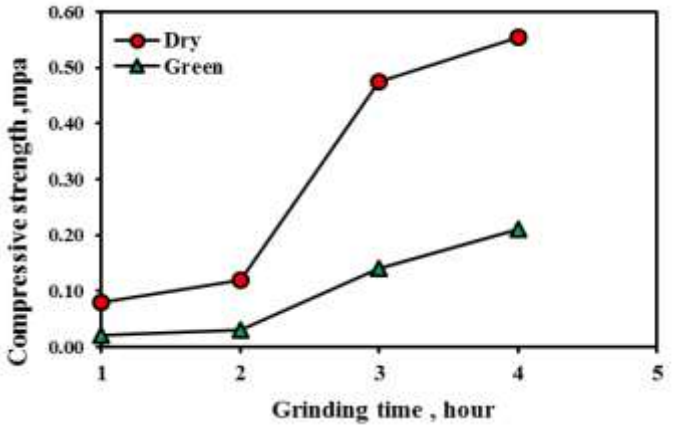

Fig. 7. Effect of grinding time on the compressive strength of mill scale pellets in both green and dry states

3.2.3 Factors affecting reduction of mill scale pellets

There are many important factors affecting the reduction percentage of mill scale pellets such as reduction time, grinding time, flow rate of reducing agent and reduction temperature. The results of these factors will be discussed as follows:-

3.2.3.1 Effect of reduction time on the reduction percentage at different grinding times

The pellets quality that made from some mill scale products such as: raw material passing through 4.75 mm sieve and 1&2 hours grinding products have not sufficient mechanical properties to be handled through metallurgical plants because of their coarse particle size, which make them weak in durability[12]. Hence, the current investigation will be focused on grinding series of 3 and 4 hours.

The effect of varying grinding time on the degree of reduction of mill scale pellets at constant conditions of (1000˚C reduction temperature and 0.5 L/min. Hydrogen flow rate) for different reduction times was investigated and shown in Figure 8.

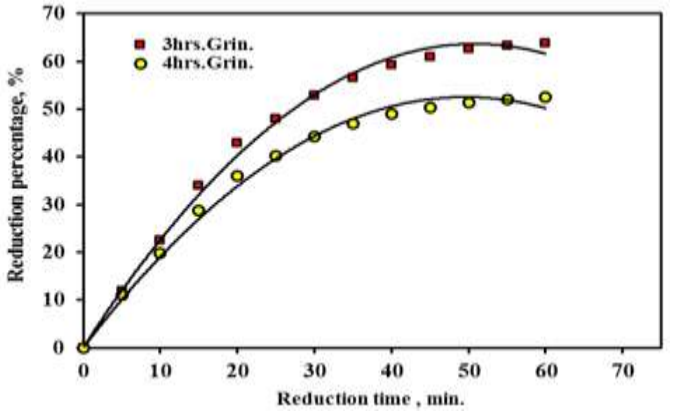

Fig. 8. Effect of reduction time on the reduction percentage of mill scale pellets at different grinding times (600 ºC and 0.5 L/Min. H_2 gas flow rate)

Results of this investigation under the given conditions show that the maximum reduction percentages of mill scale pellets at 60 minutes for series of 3 and 4 hrs. are 63.86, and 52.51 % respectively with a difference equal to 11.35 % for pellets that made from 3 hrs. over that of 4 hrs. grinding time. This is may be due to that the small particle sizes may fill the micropores during pelletizing process, thereby decreasing the chances of reduction.

3.2.3.2 Effect of reduction time on the reduction percentage at different hydrogen flow rates

Four mill scale pellets reduced at 600 ºC with different flow rates were tested to check flow rate influence on the reduction percentage. Each pellet consists of mill scale with a mean size of 0.213 mm resulting from grinding mill scale for 3 hours. The reducing gas (hydrogen) flow rates totally were 0.5, 1, 1.5, and 2 L/min. The effect of varying hydrogen flow rate on the reduction of mill scale pellets are shown in Figure 9.

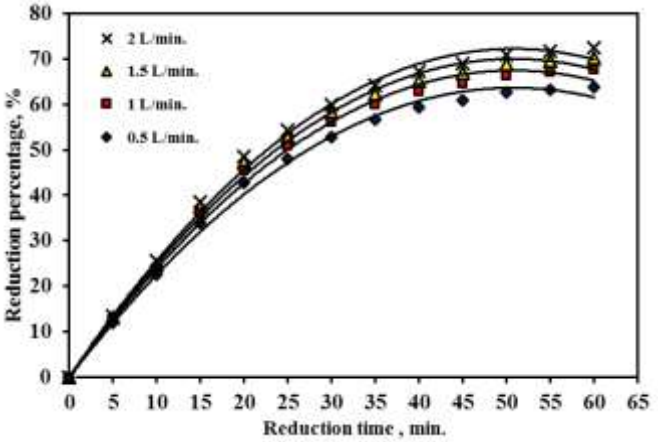

Fig. 9. Effect of reduction time on the reduction percentage of mill scale pellets at different hydrogen flow rates (Mill scale ground for 3 hours and 600ºC reduction temp.)

Results of this investigation under the given conditions show that the maximum reduction percentages occurs at 60 minutes for all flow rate series (0.5, 1, 1.5, and 2 L/min.). They are 63.86 & 67.69 & 70.25, and 72.48 % respectively. It is clear that as the flow rate of hydrogen increases, the reduction percentage increases. This may be due to that the increase of flow rate leads to an increase of number of hydrogen moles in the bulk phase, which in turn leads to the raise of hydrogen adsorption and subsequently increase the rate of reaction [13]. Alternatively, the increase of flow rate, increases the gas diffusion across the boundary layer which subsequently increases the reduced ions [14].

3.2.3.3 Effect of reduction time on the reduction percentage at different temperatures

To determine the effect of temperature; mill scale pellets were reduced by hydrogen gas under different temperatures of 600, 700, 800, 900, and 1000˚C at conditions of 3 hrs. grinding series and 2 L/min. hydrogen flow rate. The results are shown in Figure 10.

Results of this investigation under the given conditions show that, the max. reduction percentages after 60 minutes

H. H. Abdul-wahab, El-Hussiny N.A, M. M. Ali, A. A. Omar, Shalabi M.E.H., and M. R. Moharam, "The relationship between grinding time of mill scale and physicochemical properties of the produced pellets and its reduction kinetics in a static bed via hydrogen," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 1, Issue 4, pp. 1-8, 2018.

reduction time at 600, 700, 800 and 900 ˚C are 72.48 & 81.45 & 89.88 and 98.84 % respectively. The max. reduction percentage obtained in this run is about 99.98% which was achieved at a shorter time reaction (45 min.) and temperature of 1000 ºC. For max. reduction percentage, it is observed that the time is reduced by 25 % at 1000 ºC if it compared to the time taken at 900 ºC. These results confirm that, high temperature leads to higher diffusion rate of reducing gases that gave higher reduction degree.

It is clear that increase of temperature favors the reduction rate and consequently reduction percentage. The increase of reduction percentage with rise of temperature may be related to the increase of number of reacting moles having excess of energy which leads to the increase of reduction rate[13, 15].

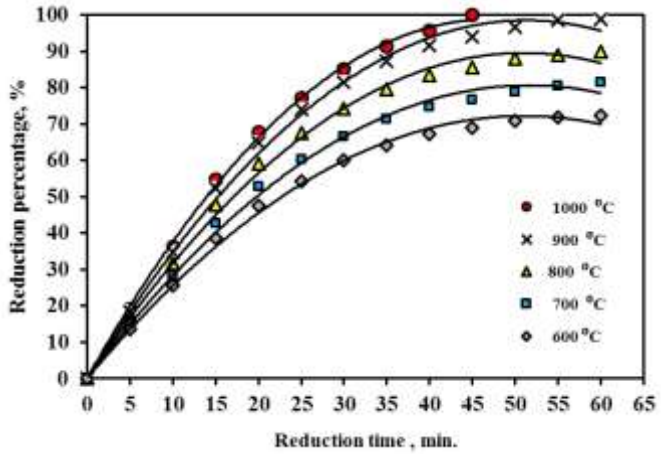

Fig. 10. Effect of reduction time on the reduction percentage of mill scale pellets at different temperatures (Mill scale ground for 3 hours, and 2 L/min. hydrogen flow rate)

Finally, it is clear that as the temperature increases, the reduction percentage increases and this is may be due to the initially formed product of iron of porous layer which leading to the highest degree of reduction (99.95%).

3.3 Kinetics of Reduction Process

Kinetic study of the reduction process of these reactions will be discussed in the following sections:

3.3.1 Application of solid state reduction models

Figure 11 shows the relationship between 1- (2/3) R - (1-R) $^{(2/3)}$ against time of reduction at different reduction temperature for pellets from which it is clear that the straight lines are observed. The mathematical modeling of experimental data suggests that Ginstling - Brounshtein equation 1- ((2/3) R) - (1-R) $^{(2/3)}$ is the most applicable model for all reduction isotherms. Hence, one may conclude that the reaction mechanism is diffusion controlled.

3.3.2 Calculation of the reaction activation energy

The natural logarithmic values of these reaction rate constants (k) were plotted against the reciprocal of the absolute reduction temperatures (T) according to Arrhenius equation as shown in Figure 12. The activation energy of the reaction is calculated from the slope of the straight line and found to be 8.27 kJ. mol.$^{-1}$ (1.98 kCal/mol.).

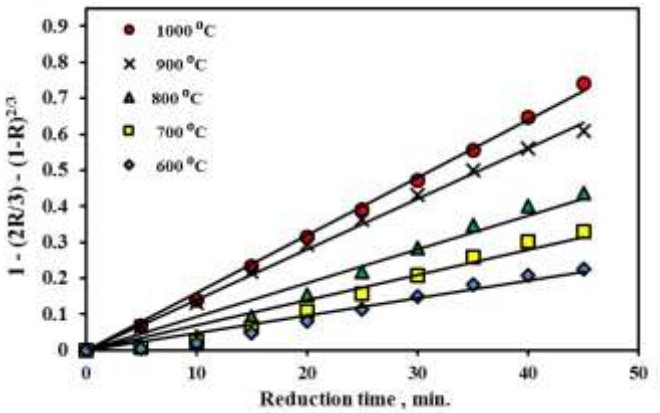

Fig. 11. Plot of 1- (2 R / 3) - (1-R) $^{(2/3)}$ Vs. time of reduction at different reduction temperatures

The results of activation energy indicated that, the reaction which carried between hydrogen gas and iron oxides from mill scale pellets is diffusion controlled.

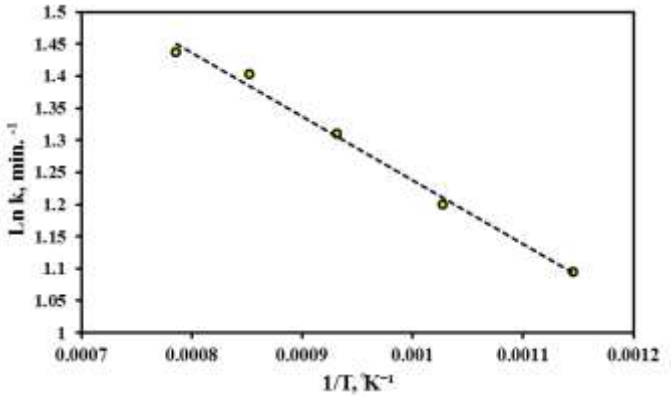

Fig. 12. Plot of Ln K against reciprocal of absolute temperature

3.4 Assessment of Reduced Product

Reduced pellets (mill scale pellet made from 3 hrs. grinding series) by 2 L/min. hydrogen flow rate at 1000˚C and 45 minutes were examined by XRF analysis, X-ray diffraction analysis, optical microscope, SEM with EDS analysis and apparent porosity test. The results of examination were as follows:

3.4.1 Chemical analysis of the reduced pellets

Chemical analysis of the reduced mill scale pellets made from 3 hrs. grinding series using XRF analysis revealed that the sample composed of five elements. Iron is the major element, while the remaining elements are present as traces as shown in Table 5.

TABLE 5. Chemical analysis of the reduced mill scale pellets by using XRF analysis at conditions, 3 hours grinding time, 1000 °C and 2 L/min. H_2 gas flow rat

Element	Fe	Mn	Si	S	P
Wt. %	98.80	0.69	0.12	0.10	0.29

3.4.2 X-ray diffraction analysis of the reduced pellets

XRD pattern of reduced mill scale pellets by hydrogen gas, has shown in Figure 13. There are variation in intensity of different peaks but metallic iron is the main phase.

H. H. Abdul-wahab, El-Hussiny N.A, M. M. Ali, A. A. Omar, Shalabi M.E.H., and M. R. Moharam, "The relationship between grinding time of mill scale and physicochemical properties of the produced pellets and its reduction kinetics in a static bed via hydrogen," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 1, Issue 4, pp. 1-8, 2018.

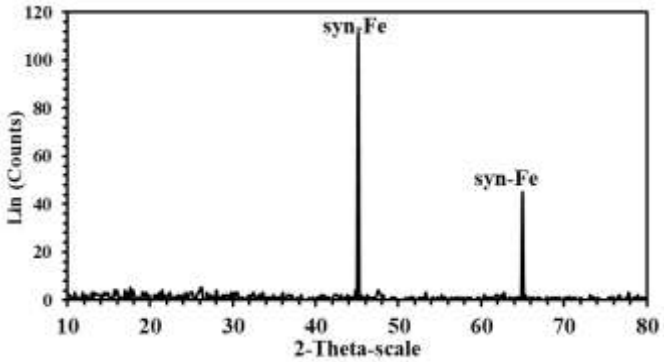

Fig. 13. X-ray diffraction pattern for the reduced mill scale pellets at 3 hrs. grinding series, 2 L/min. hydrogen flow rate, and 1000˚C

It can be seen from this figure that, no peaks of any iron oxides is present in the XRD pattern of the reduced mill scale pellets. Also, XRD pattern indicates that the reduction of mill scale pellets at the mentioned conditions is complete.

3.4.3 Optical microscopic examination

Figure 14 shows that the microscopic examination of the mill scale pellets which reduced by hydrogen gas (2L/min. flow rate) for 45 minutes at temperature of 1000 ˚C with two different magnifications (a) 100 X and (b) 200 X. From this figure it is clear that the microscopic examination illustrates the reduced pellet of iron (white) and pores (black). Also, it can be seen that pores have a good size and distribution which facilitates the completion of reduction.

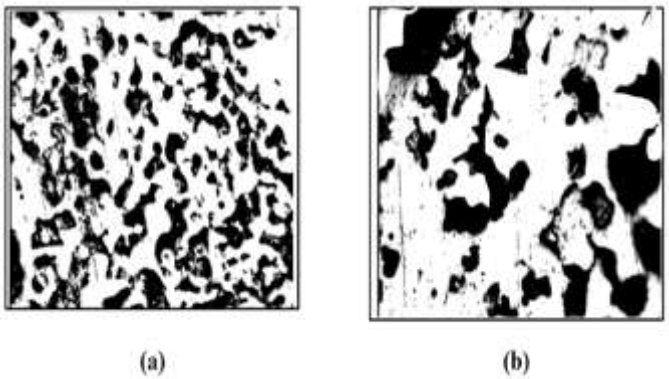

Fig. 14. Microstructure of reduced pellets by hydrogen gas (2 L/min.) at temperature of 1000ºC in two different magnifications (a) 100 X and (b) 200 X

3.4.4 Scanning electron microscope (SEM) with energy dispersive X-ray spectrometry (EDS) analysis

Figure 15 (a) shows SEM image of the obtained reduced pellets after reduction by using hydrogen gas with flow rate of 2 L/min. at temperature of 1000 ºC, and Figure 15 (b) the corresponding "EDS" analysis. Figure 15 (a) shows a reduced pellet with a spongy appearance, irregular but rounded, with a high specific surface area. "EDS" analysis confirms that the sample is comprised only of sponge metallic iron of great purity. The oxygen content in this sample equals to zero.

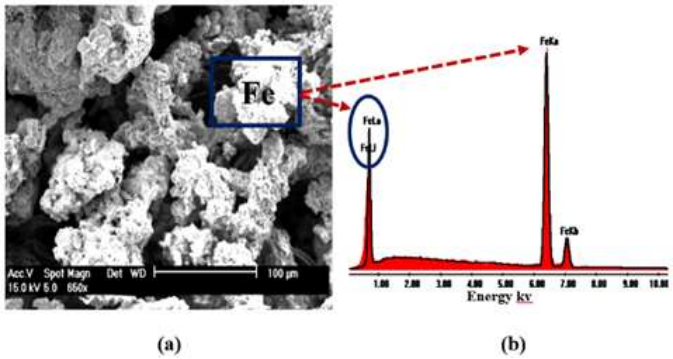

Fig. 15. (a) Secondary electron image of the reduced mill scale pellets by hydrogen at 1000ºC and (b) Corresponding "EDS" analysis

IV. Conclusion

There is a relative superiority in such reduction for a series of 3 hours grinding time, if compared with other series (4 hours) at the similar reduction conditions. In spite of this, the mill scale particles that ground for 3 hours and agglomerated by pelletizing method is the best ever since for many considerations:

1 - High reduction percentage (99.98),

2 - Low cost of grinding if it compared with 4 hours grinding series.

The conclusions can be summarized in the following points:-

1 - The maximum reduction percentage of mill scale pellets made from 3 hrs. grinding series by hydrogen was 98.98 % at 2 L/min. flow rate and 1000 ˚C after 45 minutes reduction time.

2 - The mechanical properties of mill scale pellets that made from 3 hrs. grinding series showed that, acceptable drop damage resistance (75 drops/pellet) and somewhat poor compressive strength value (0.48 MPa.)

3 - The reduced mill scale pellets that made from 3 hrs. grinding time series showed the least activation energy (8.27 kJ/mol.) over all types of the studied mill scale agglomerates.

4 - Morphology study of pellets shows that the reduced iron has a spongy appearance, irregular but rounded, with a high specific surface area, which make them suitable for powder metallurgy applications;

5 - EDS analysis confirms that, the sample is comprised only of metallic sponge iron of great purity. The oxygen content in this sample is zero percent.

6 - The obtained activation energy is 8.27 kJ/mole.

References

[1] M. Martín, F. López, M. Rabanal, and J. Torralba, "Production of Sponge Iron Powder by Reduction of a By-product of the Steelmaking Industry," *PM 2010 World Congress–Water Atomized Powders*, 2010.

[2] Anonymous, "Steel statistical yearbook 2014," Worldsteel Association, http://www.worldsteel.org/statistics/statistics-archive/yearbook - archive.html, (2017).

[3] Anonymous, "The management of steel plant ferruginous by-products," International Iron and Steel Institute, Committee on Environmental Affairs and Committee on Technology. Brussels, chapters 6 and 7, 1994.

[4] N. El-Hussiny, F. Mohamed, and M. Shalabi, "Recycling of mill scale in sintering process," *Science of Sintering*, vol. 43, pp. 21-31, 2011.

[5] O. Benchiheub, S. Mechachti, S. Serrai, and M. Khalifa, "Elaboration of iron powder from mill scale," *Journal of Materials and Environmental Science*, vol. 1, pp. 267-276, 2010.
[6] N. El-Hussiny and M. Shalabi, "Effect of recycling blast furnace flue dust as pellets on the sintering performance," *Science of Sintering*, vol. 42, pp. 269-281, 2010.
[7] N. El-Hussiny and M. Shalabi, "A self-reduced intermediate product from iron and steel plants waste materials using a briquetting process," *Powder Technology*, vol. 205, pp. 217-223, 2011.
[8] K. Meyer, *Pelletization of Iron Ores*, New York: Springer-Verlage Berlin Heidelberg, 1980.
[9] S. P. E. Forsmo, P. O. Samskog, and B. M. T. Björkman, "A study on plasticity and compression strength in wet iron ore green pellets related to real process variations in raw material fineness," *Powder Technology*, vol. 181, pp. 321-330, 2008.
[10] Annual Book of ASTM Standards, Standard test method for determination of crushing strength of iron ore pellets, ASTM E, 2012.
[11] W. Pietsch, *Agglomeration Processes, Phenomena, Technologies, Equipment*, Willy-VCH, chapters 5&6, pp. 29-138, 2002.
[12] N. Kaliyan and R. Vance Morey, "Factors affecting strength and durability of densified biomass products," *Biomass and Bioenergy*, vol. 33, pp: 337-359, 2009.
[13] M.E.H. Shalabi, "Kinetic reduction of El-Baharia iron ore and its sinter in static bed by hydrogen," *El-Tabbin Metallurgical Institute for Higher Studies*, Cairo, 1973.
[14] S. A. Sayed, G. M. Khalifa, E. S. R. El-Faramawy, and M. E. H. Shalabi, "Kinetic reduction of low manganes iron ore by hydrogen," *Egyptian Journal of Chemistry*, vol. 45, pp. 47-66, 2002.
[15] M. E. H. Shalabi, O. A. Mohamed, N. A. Abdel-Khalek, and N. A. El-Hussiny, "The influence of reduced sponge iron addition on the quality of produced iron ore sinter," *Proceeding of the XXIMPC, Aachen*, pp. 362-376, 21-26 September 1997.

H. H. Abdul-wahab, El-Hussiny N.A, M. M. Ali, A. A. Omar, Shalabi M.E.H., and M. R. Moharam, "The relationship between grinding time of mill scale and physicochemical properties of the produced pellets and its reduction kinetics in a static bed via hydrogen," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 1, Issue 4, pp. 1-8, 2018.