Reduction of Low Grade Egyptian Manganese Ore by Carbon of Coke Breeze in the Briquette Form

N. A. El-Hussiny[1], Hala H. Abd El-Gawad[2], Marwa. M. Ahmed[3]., M. E. H. Shalabi[1]*
1-Centeral Metallurgical Research and Development Institute (CMRDI)Egypt
2-Faculty of Science and Arts, Mohail Asser, King khalid University, Mahil, Saudi Arabia
3-Faculty of Engineering (Mataria), Helwan University, Helwan, Egypt
Email: *Corresponds :- shalabimeh@hotmail.com

***Abstract*—Because of intensive mining of high-grade manganese ores for a long time while leaving behind the low-grade ores, the utilization of the latter has become necessary. There are several physicochemical differences among the components in manganese ores, which can be used for the enrichment of manganese. In particular, the abundant low-grade manganese ores, which contain iron oxide, may be upgraded by pre-reduction and magnetic separation.**

In this study, ferruginous low-grade manganese ore was pre-reduced by coke breeze as source of carbon which converted iron oxide to Fe_3O_4, while manganese ore was reduced to Jacobsite and Iron manganese oxide compounds which can be separated later. The reduction in the temperature up to 950 ºC was controlled either by chemical controlling mechanism with energy of activation = 10 kJ/mole or solid diffusion process with energy of activation = 29.26 KJ/mole.

***Key words*—Low grade manganese ore, reduction by coke breeze, Energy of activation, sowas reduced to Jacobsite and Iron manganese oxide compounds which can be separated later. The reduction in the temperature up to 950 ºC was controlled either by chemical controlling mechanism with energy of activation = 10 kJ/mole or solid diffusion process with energy of activation = 29.26 KJ/molewas reduced to Jacobsite and Iron manganese oxide compounds which can be separated later. The reduction in the temperature up to 950 ºC was controlled either by chemical controlling mechanism with energy of activation = 10 kJ/mole or solid diffusion process with energy of activation = 29.26 KJ/molelid diffusion mechanism**

1. Introduction

Manganese plays an important role in several industrial applications, such as steel production, preparation of dietary additives, carbon–zinc batteries production, fertilizers, cells and fine chemicals, as well as colorants for bricks, dyes and medicines (1-4). The world annual consumption of manganese is above 1,300,000 annual tons and it is destined to increase. Low grade ores are gaining increasing attention due to developments in exploitation technologies (2)

The utilization of the low grade manganese ore has become necessary. There are several physicochemical differences among the components of manganese ores, which can be used for the enrichment of manganese. In particular, the abundant low-grade manganese ores, which contain iron oxide, may be upgraded by pre reduction and magnetic separation (5).

Manganese plays a crucial role in the iron and steel industry. As an alloying element, it improves the strength, toughness; harden ability, and workability and abrasion resistance of the ferrous products, especially steel. About 90 – 95 of all the manganese produced in the world is used in iron and steel production in the form of alloys such as ferromanganese and silicomanganese.

Manganese has two important properties in steelmaking as: its ability to combine with sulphur to form MnS and its deoxidation capacity. Today about 30% of the manganese used in steel industry is used for its properties as a sulphide former and deoxidant. The other 70% of the manganese is used purely as an alloying element (6)

Bo Zhang et al. (7), used high temperature carbon tube furnace for reduction of manganese ore pellets containing carbon . The experimental results showed that, the reaction rate in the earlier stage was controlled by the chemical reactions between FeO, MnO and carbon as a reductant, and the activation energy was 28.85 KJ/mol. In the later stage, as the carbon reductant replaced by CO, the reaction rate was controlled by CO-diffusing in solid products, and the corresponding activation energy was 86.56 KJ/mol. Reaction rate of the later stage was less than the earlier one.

The aim of this paper was to establish the reduction rate, mechanisms and conditions for solid state reduction of low grade manganese ore by solid carbon in the temperature range from 600 up to 950 ºC.

2. Experimental Work

2.1. Characteristics of samples

The low grade of manganese ore used in this work was provided by Sinai ferromanganese Co. and the coke breeze which delivered from Iron and Steel Company, Helwan, Egypt. The samples of low manganese ore and coke breeze were submitted to chemical and X- ray analysis. The chemical analysis of low grade manganese is illustrated in Table 1 (4) and the analysis of coke breeze is illustrated in Table 2

Table1. Chemical analysis of Egyptian low grade manganese ore

Constituent	Weight %
Fe total	23.2
K_2O	0.25
Al_2O_3	2.3
MgO	0.95
CaO	2.4
P	0.2
Mn	28.6
SiO_2	15.3
Na_2O	0.2

Table2. Chemical analysis of coke breeze

Constituent	Weight %
Ash	10.26%
V.M	1.08%
S	1.04%
Fixed Carbon	86.992

The X- Ray analysis of low grade manganese ore is illustrated in Fig.1. From which it is clear that low grade manganese ore mainly consists of pyrolusite, hematite and quartz.

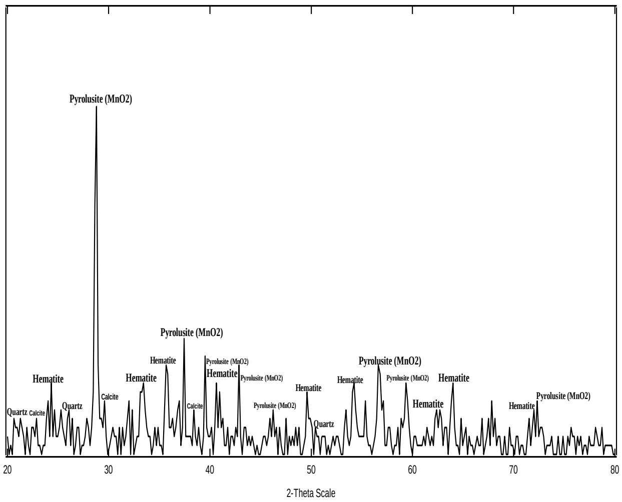

Fig.1. X-ray analysis of low grade manganese ore

While the X- ray analysis of coke breeze is illustrated in Fig.2. From which it is clear that it is mainly consists of graphite and quartz (SiO_2).

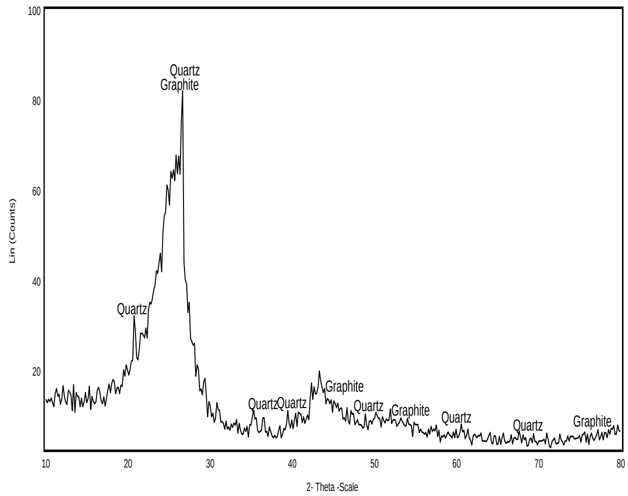

Fig.2. X-ray analysis of coke breeze

2. 2. Experimental Procedures

2.2.1. Preparation of Samples

The low grade of manganese ore and coke breeze were grinding in vibrating mill to powder with size less than 75 micrometers. The low grade of manganese ore powder and powder coke breeze were mixed with 2% molasses and then *pressed* in the mould (12 mm diameter and a height 22 mm using MEGA.KSC-10 hydraulic press. Under different pressure (the pressure ranges from 75 MPa up to 250 MPa). *The* produced briquettes were subjected to drop damage resistance tests (drop number tests) and compressive strength tests (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 (8-9)

2.2.2. Reduction Procedures

The reduction of the briquettes low grade manganese ore with coke breeze was performed in thermogravimetric apparatus. This scheme is similar to that present elsewhere (8 , 10) (Figure 3). It consisted of a vertical furnace, electronic balance for monitoring the weight change of reacting sample and temperature controller. The briquettes 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. . 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:

Percent of reduction = [(Wo–Wt)*16*100/ 28 Oxygen mass] (1)

where:

Wo: the initial weight of the briquettes sample g.

Wt: weight of sample after each time t. g.

Oxygen mass: indicates the mass of oxygen percent in low grade of manganese ore in form FeO, Fe_2O_3 and manganese oxide.

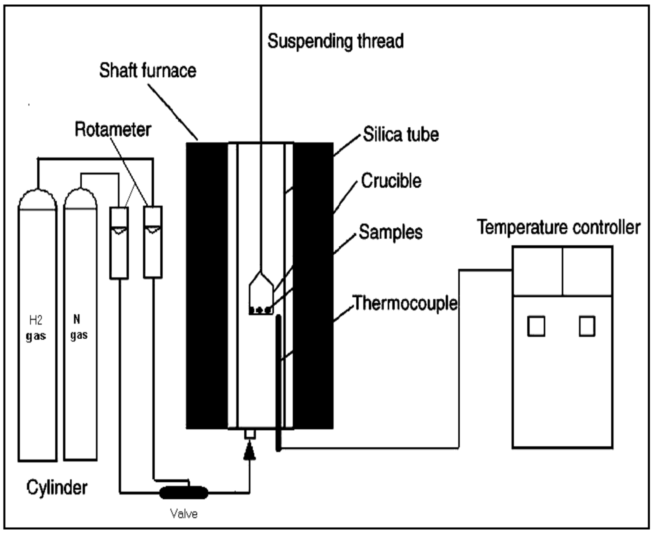

Figure 3. Schematic diagram of the reduction apparatus

3-Results and Discussions

3.1. Effect of adding coke breeze materials on the quality of produced briquettes

Figs. 4-5, illustrate the effect of percentage of coke breeze added on the drop damage resistance and compressive strength of the green briquette (the pressing load is constant = 216.8 MPa.). It is clear that as the percentage of coke breeze materials increased both the drop damage resistance and compressive strength decreased.

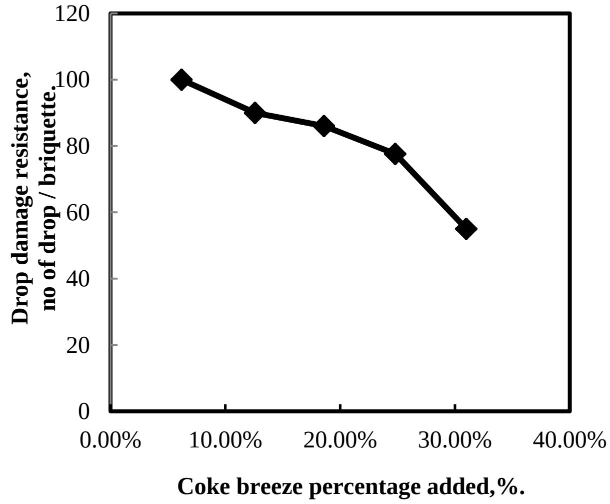

Fig. 4 Relation between coke breeze precentage added and drop damage resistance of the produced briquettes.

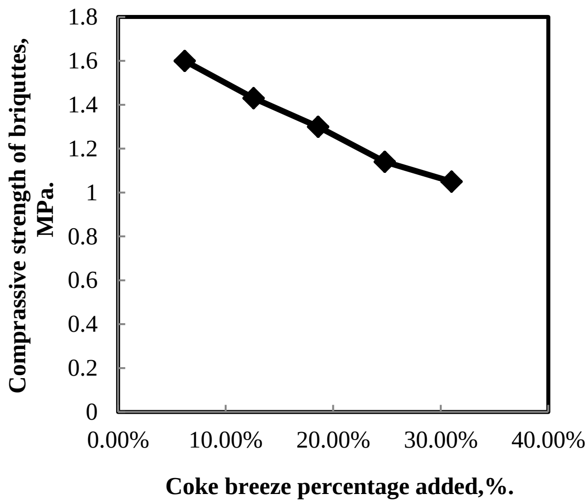

Fig. 5 Relation between coke breeze precentage added and compressive strength of the produced briquettes.

3.1. Effect of adding coke breeze materials on the degree of reduction of produced low manganese ore briquettes

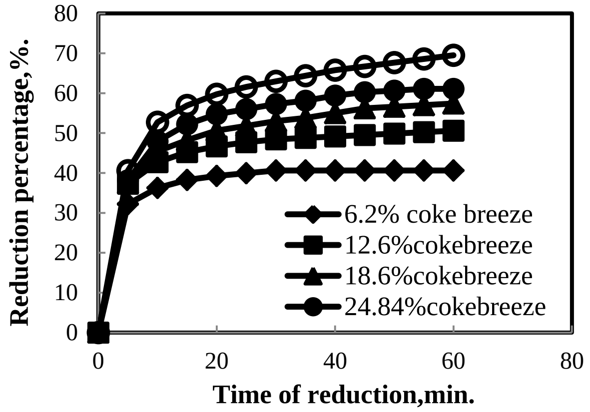

Fig. 6 *Relation between different* time of reduction and reduction percentage of the produced briquettes at different amount of coke breeze added at 900ºC.

Fig. 6 illustrates the relation between the reduction degree of low grade of manganese ore and amount of coke breeze used when the reduction was done at constant temperature (900^{o}C) and constant weight of the sample; it is clear that as the percentage of coke breeze increased the reduction percentage increased. From the same figure it is also clear that the reduction not reach to 100% (this mean that the reduction was not reached to metallic iron).This is due to the temperature of reaction not sufficient to reach the metallic iron.

3.2. Effect of temperature change on the reduction degree of low grade manganese ore briquette

The results of the investigation of change temperature are shown in figure 7. It is clear that the increase of temperature favors the reduction rate and degree. The analyses of the investigated curves relating the reduction percentage and time of reduction within the investigated work shows that each curve has 2 different values of reduction rates. The first value is high, while the second is somewhat slower. 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 rate (11- 12) . Also the rise of temperature leads to an increase of the rate of mass transfer of the diffusion and rat of desorption (8,12 – 15) .

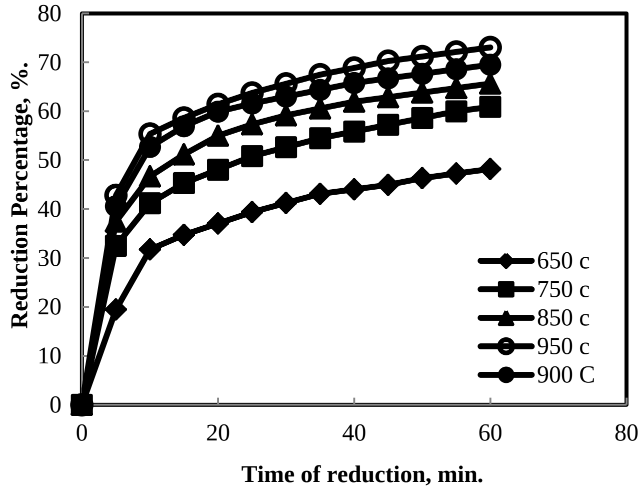

Fig. 7 Relation between different time of reduction and reduction percentage of the briquettes contained 31 % of carbon at different reduction temperature .

3.3. Kinetics reduction of low grade manganese briquette

From figure 7 It is clear that there are three rates; therefore we try applied two models:-

a. contracting volume model (16)

1-(1-R) ^{⅓}=kt ----------------- (2)

b. Solid state reaction model (16)

R+ (1-R) Ln (1-R) =kt ------ (3)

Where; k is constant of reduction rate.

R is the fraction of reduction.

t is the time of reaction , min.

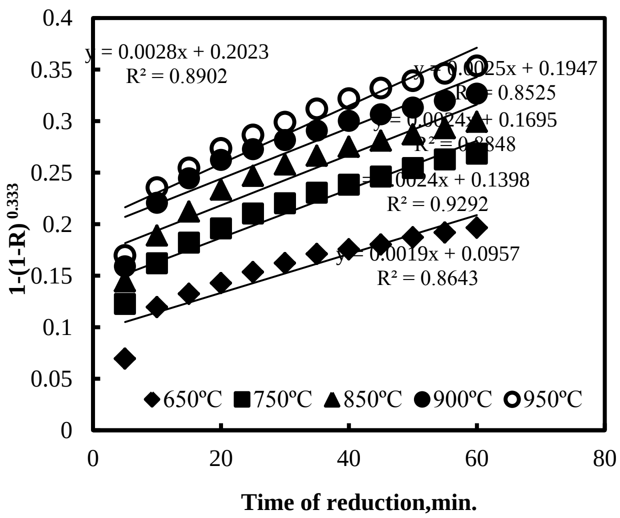

Fig. 8 Relation between different time of reduction and 1-(1-R)$^{0.333}$ of the briquettes contained 31% of carbon at different reduction temperature .

Figure 8, illustrates the relation between 1-(1-R) ^{⅓} and time of reduction in the time range 5-60 min. from this figure it is clear that the relation is approximately straight line.

While figure 9, illustrates the relation between the second model R+ (1-R) Ln (1-R) with time of reduction in the same range 5-60 min. the results is straight line more perfect than the previous one and R^2 is very high value.

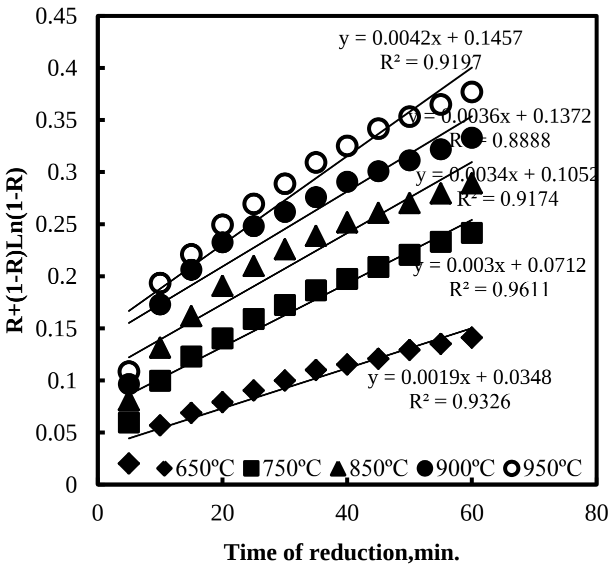

Fig. 9 Relation between different time of reduction and R+(1-R)Ln(1-R) of the briquettes contained 31% of carbon at different reduction temperature .

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

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (4)$$

$$\ln k = \ln k_0 - \frac{E}{RT} \quad (5)$$

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 low manganese ore with coke breeze briquettes is shown in figures 10-11, from which it is clear that briquette has activation energy for modeling one = 10.31 kJ/mole , while for second models the activation energy =22.96 kJ/mole

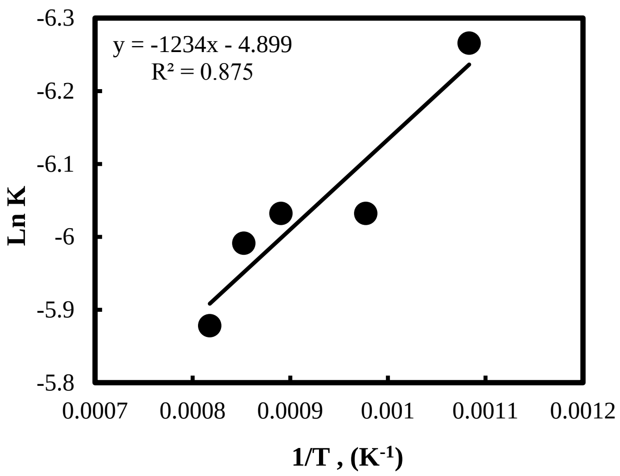

Fig.10. The relation between the reciprocal of absolute temperature 1/T and lnK (Arrhenius plot for reduction reaction) for model equation $1-(1-R)^{0.333}$

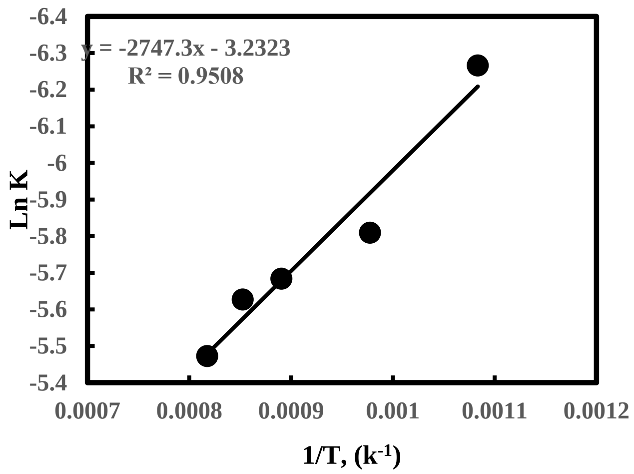

Fig. 11. The relation between the reciprocal of absolute temperature 1/T and lnK (Arrhenius plot for reduction reaction) for model equation R+(1-R)Ln(1-R)

3.5. X-ray analyses of the reduced briquette

Figure 12, shows the X-ray analyses of the sample reduced at 950˚C shows that the main phases formed magnetite, jacobsite syn. and iron manganese oxide, while no iron metal present this mean that the reduction to iron need more temperature more than 950ºC.

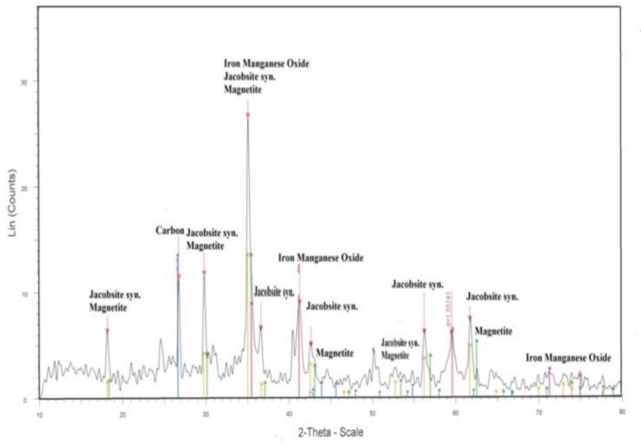

Fig. 12 X-ray of the sample reduced by coke breeze at 950ºC (time 60 min.).

4. Conclusions

1-The pressing pressure load in the briquetting process of low grade manganese ore with coke breeze powder increased both the drop damage resistance and compressive strength.

2- The degree of reduction of low grade manganese ore with coke breeze briquettes at constant temperature increased as the percentage of coke breeze increased.

3- The reduction rate of low grade manganese ore with coke breeze briquettes under a constant amount of coke breeze as reducing agent increased with increasing temperature.

4 The kinetic reduction of low grade manganese ore with coke breeze briquettes show that the reduction process is controlled either by contracting volume model mechanism with energy of activation = 10 kJ/mole or solid diffusion process with energy of activation = 29.26 KJ/mole.

5. References

1. R.N. Sahoo, , P.K. Naik, and S.C. Das, “Leaching of manganese ore using oxalic acid as reductant in sulphuric acid solution”, Hydrometallurgy 62, 157–163, (2001).

2. M.N. El Hazek, T.A. Lasheen and A.S. Helal, , “Reductive leaching of manganese from low grade Sinai ore in HCl using H_2O_2 as reductant”, Hydrometallurgy 84, 187–191, (2006).

3.Haifeng Su, Yanxuan Wen, Fan Wang, Yingyun Sun and Zhangfa Tong, “Reductive leaching of manganese from low-grade manganese ore in H_2SO_4 using cane molasses as reductant”, Hydrometallurgy 93,136–139, (2008).

4-Hala H. Abd El-Gawad, M. M. Ahmed, N. A. El-Hussiny and M. E. H. Shalabi, “Reduction of low grade Egyptian manganese ore via hydrogen at 800˚C - 950˚C”, Open Access Library Journal, I, 1: e427. July 2014

5- Yubo Gao, “Pre-reduction and magnetic separation of low grade manganese ore”, Master of Science Department of Metallurgical Engineering University of Utah , August 2011.

6- Ismail Seçkin Çardakli, M.Sc., “Production of high carbon ferromanganese from a manganese ore located in Erzincan. The Graduate School of Natural and Applied Sciences of Middle East Technical University, Septe, September 2010

7- Bo Zhang and Zheng-Liang Xue,“Kinetics analyzing of direction reduction on manganese ore pellets containing carbon”, International Journal of Nonferrous Metallurgy, 2, 116-120, 2013.

8- K. Mayer, Pelletization of iron ores ,Springer – Verlag Berlin Heidelberg, Berlin Heidelberg , 1980

9-N. M. Gaballah, A. F. Zikry, M. G. Khalifa, A. B. Farag, N. A. El-Hussiny and M. E. H. Shalabi , “Production of iron from mill scale industrial waste via hydrogen” , Open Journal of Inorganic Non-Metallic Materials, 3, 23-28, 2013.

10- N.A.El-Hussiny and M.E.H. Shalabi , A self reduced intermediate product from iron and steel plant waste material using a briquetting process , powder technology, 205,1-3. 2011, 217-223

11- 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.

12- 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, 45, 47-66, 2002.

13- S.A. Sayed, M.G. Khalifa, E.S R. El-Faramawy and M.E.H. Shalabi, “Reductions kinetic of El-Baharia iron ore in a static bed”, Gospodarka Surowcami Mineranymi, 17, 241-245, 2001.

14- 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, 21-26 September 1997, 362-376.

15- N.A. El-Hussiny, N.A. Abdel-Khalek, M.B. Morsi, O.A.Mohamed, M.E.H. Shalabi and , A.M. Baraka, “Influence of water amount added on the sintering process of Egyptian iron ore” , Gornictwo, 231, 93-115, 1996.

16- Ammar Khawam, and Douglas R. Flanagan , Solid-State Kinetic Models: Basics and Mathematical Fundamentals ,*J. Phys. Chem. B*, 2006, 110 (35), 17315-17328.