Reduction low grade Egyptian manganese ore by carbon of coke breeze in the form pellets

N.A. El-Hussiny [1] ,Hala. H. Abd El-Gawad [2], F.M.Mohamed [1,3] , M.E.H. Shalabi[1*)]

Abstract -Egyptian low grade manganese ore pellets were reduced by coke breeze in this work in the temperature range 600 -950ºC. The results indicated that the reduction rate increased with temperature rise. And it was found that the reaction model is either : $-[1 - (1-R)^{1/3}]^2 = kt$ or $K t = 1 - (2/3)R - (1 - R)^{2/3}$ and the energy of activation is 53.37 or 56.43 kJ/ mole kJ/mole for both models respectively .
Key words - Low grade manganese ore, pelletization , . reduction by coke breeze , Energy of activation, solid diffusion mechanism

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1. INTRODUCTION

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: its ability to combine with sulphur to form MnS and it's deoxidation capacity. Today about 30% of the manganese used in steel industry for its properties as a sulphide former and deoxidant. The other 70% of the manganese is used purely as an alloying element [1,2]

Yubo Gao [3] illustrated that 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. It was pre-reduced, ferruginous low-grade manganese ore by CO, which converted iron oxide to Fe_3O_4, while manganese oxide was reduced to MnO. Then, the iron-rich component was collected by magnetic separation.

The aim of this work is studying the reduction of low grade manganese ore pellets by carbon of coke breeze.

2. EXPERIMENTAL Work

2.1. Preparation of samples

The low grade of manganese ore used in this work was delivered from Sinai ferromanganese Co. and the coke breeze was delivered from iron steel Co. Helwan Egypt.

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The chemical analysis of low grade manganese is illustrated in Table 1 [1 , 4] and coke breeze is illustrated in Table 2 [5,6]

Table 1. Chemical analysis of Egyptian low grade of 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

Table 2. 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.{1, 4} While figure 2 illustrate the x –ry of coke breeze from which it is clear that the main component of coke breeze are Graphite , Quartz SiO_2 and Calcite.[5.6]

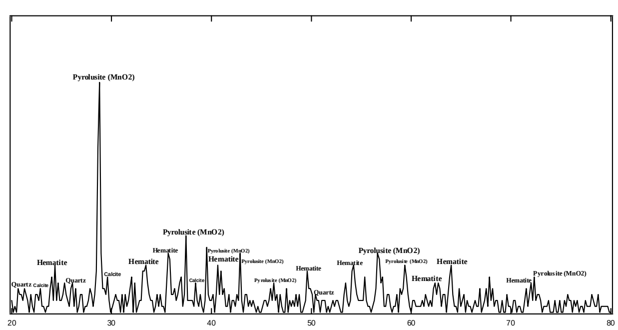

Fig.1. X-ray of low grade of manganese ore

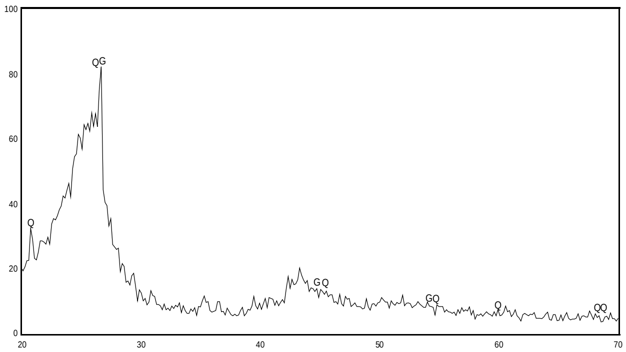

Fig.2. X-ray of coke breeze.[G: - Graphite , Q: - Quartz SiO_2, C: - Calcite]

2.2. Preparation of the pellets and Its Physical Properties

Low grade manganese ore and coke breeze were grinding separate in vibrating mill to powder with size less than 75 micrometers. After which the pellitization of low grade of manganese ore with the predetermine of coke breeze were done in a disc pelletizer of diameter 400 mm, collar height 100 mm Fig. 3 [1].

Fig. 3. Disc pelletizer equipment

Angle of inclination 60 ^oC, disc rotating speed 17 rpm and residence time 30 min. The materials were feed to the pelletizer. The predetermined moisture amount (8.5% water) and 2.5 % of the charge molasses added) was then sprayed onto the rolling bed of material in the disc pelletizer. The green pellets in the size range 5-7 mm diameter were screened out to dry its in the air for 3 days, to ensure the evaporation of all water used during the granulation process.

The green and dry pellets subjected to drop number test and crushing strength tests. The crushing strength test used MEGA.KSC-10 hydraulic press) Fig.4.

Fig.4. MEGA.KSC-10 hydraulic press

The drop number indicates how often green and dry pellets can be dropped from a height 46 cm before they show perceptible cracks or crumble. Ten green and dry pellets are individually dropped on to a steel plate. The number of drops is determined for each pellets . The arithmetical average values of the crumbing behavior of the ten pellets yield the drop number[7-13] .The average compressive strength tests of at least 10 pellets; between parallel steel plates of MEGA.KSC up their breaking. The mean value of the tested pellets gives their compressive strength. [7-13].

The device used in the reduction process of the produced pellets shown in Fig.5.

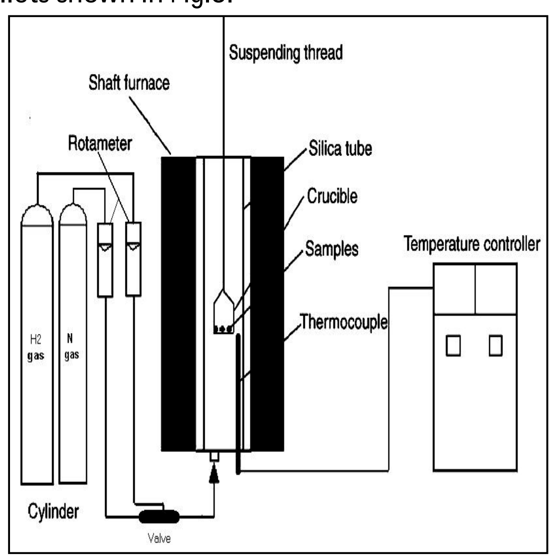

Fig. 5. Schematic diagram of the reduction apparatus

3. RESULTS AND DISSECTIONS

3.1. Effect of Adding Coke Breez Materials on The Quality of Produced Pellets

Figs. 6-9. Illustrate the effect of percentage of coke breeze added on the drop number (drop damage resistance) and cold crushing strength of the green and dried pellets . It is clear that as the stociometric amount of coke breeze added to pellets increased both the drop damage resistance and crushing strength decreased for both green and dried pellets. .

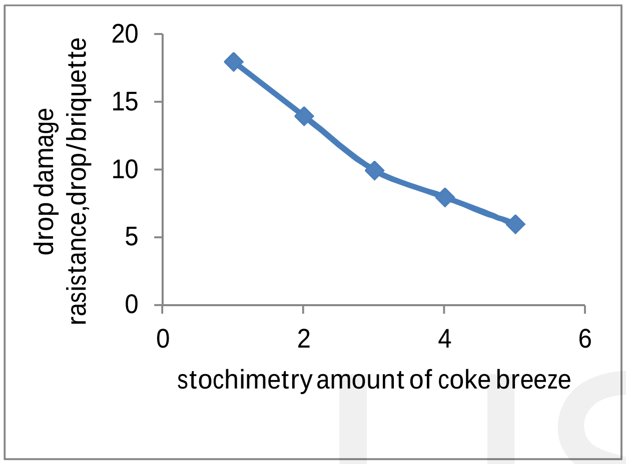

Fig. 6. Relation between amount of coke breeze present in the pellets and the drop number of green pellets..

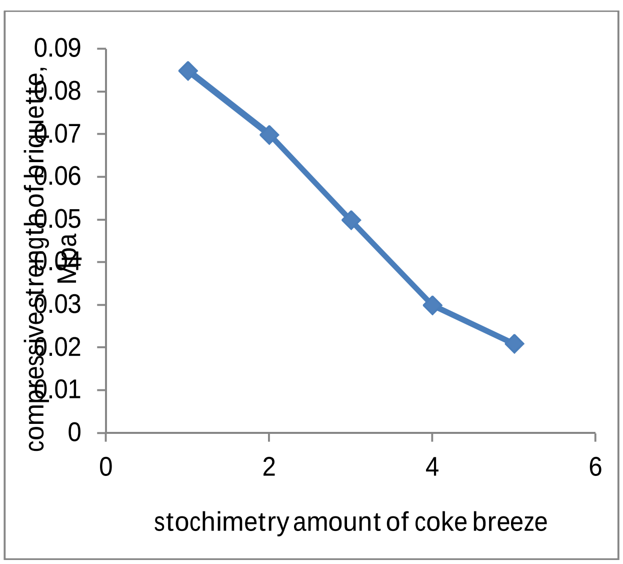

Fig. 7. Relation between amount of coke breeze present in the pellets and the strength of the green pellets.

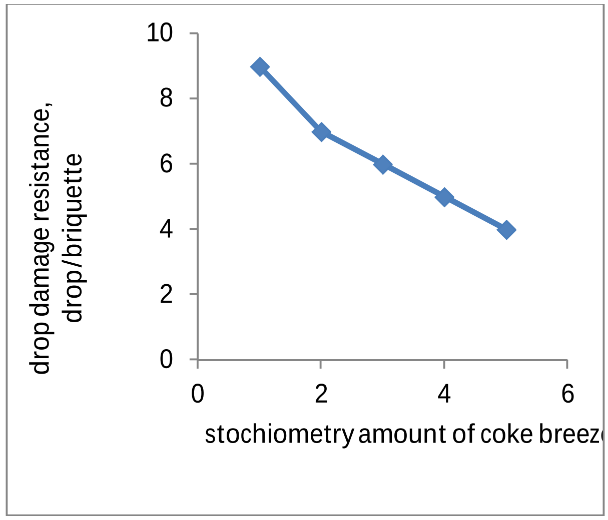

Fig. 8. Relation between amount of coke breeze present in the pellets and the drop number of dried pellets.

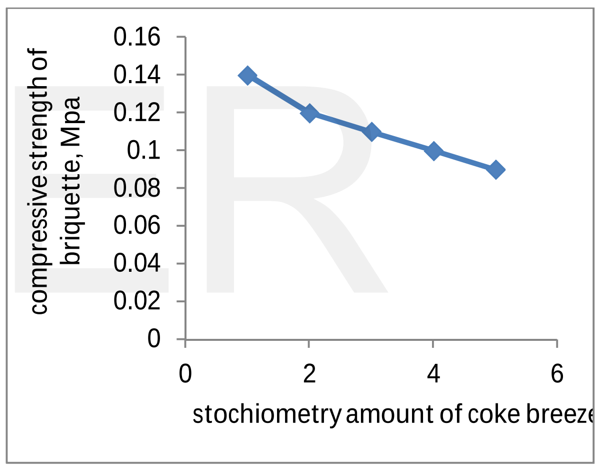

Fig. 9. Relation between amount of coke breeze present in the pellets and the strength of the dried pellets.

3.2. Effect of Stociometric of Coke Breez on The Degree of Reduction of Low Grade Manganese Ore

The reaction done at constant temperature 900^{o}C and ½ L nitrogen flow rate and constant weight of sample . Fig. 10 illustrates the relation between the reduction degree of low grade of manganese ore and different stochiometric amount of coke breeze used . It is clear that as the stochiometric amount of coke breeze increase the reduction percentage of low grade of manganese ore increased.

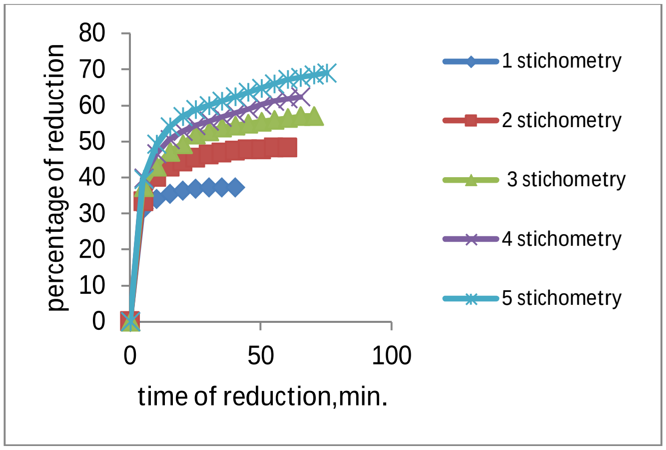

Fig. 10. The relation between the reduction degree of low grade of manganese ore and different stochiometric amount of coke breeze at 900 °C

3.3. The Effect of Change of Temperature on the reduction degree of the Low Grade Manganese Ore Pellets by Constant Amount of Coke Breeze (5 stochiometric).

The results of the investigation of change temperature from 600 °C to 950 °C are shown in Figure 11 . 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 whiten 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 [21] . Also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rat of desorption [22-23].

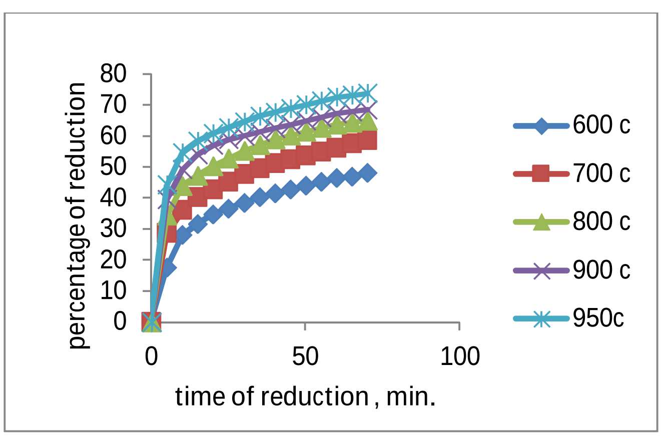

Fig.11. The Effect of change of temperature on the reduction degree of the low grade manganese ore pellets by constant amount of coke breeze(5 stochiometric)

3.4. Kinetics Reduction of Low Grade Manganese Ore by Coke Breeze in The Form Pellets

Kinetic studies for estimation of apparent activation energies were carried out for the pellets at different temperatures range from 600°C up to 950°C for different time intervals in the range of 10 to 70 min.

Using

1- diffusion process control equation (Jander and Anorg Equation)[24]

$$[1 - (1-R)^{1/3}]^2 = kt$$

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

Fig.12 illustrate the relation between $[1 - (1-R)^{1/3}]^2$ against time of reduction for different reduction temperature . From which it is clear that the straight line was observed.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrate in Fig.12 , from which it is clear that the activation energy= 53.37 kJ/ mole.

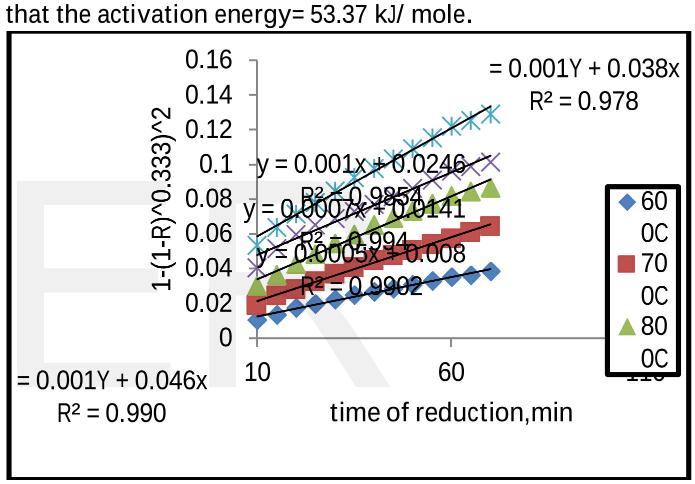

Fig.12. the relation between $[1 - (1-R)^{1/3}]^2$ and time of reduction for different reduction temperature.

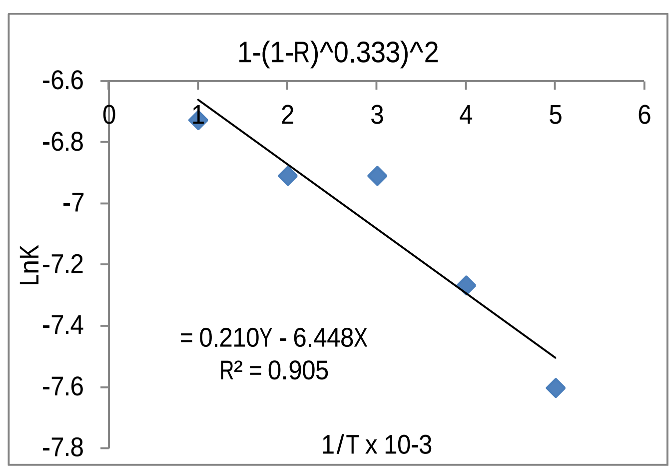

Fig.13. Relation between ln k and 1/T

2- using Ginstling-Brounshtein diffusion model [24]

$$K\,t = 1 - (2/3)R - (1 - R)^{2/3}$$

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

Fig.14. 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.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrate in Fig.15 , from which it is clear that the activation energy= 56.53 kJ/ mole.

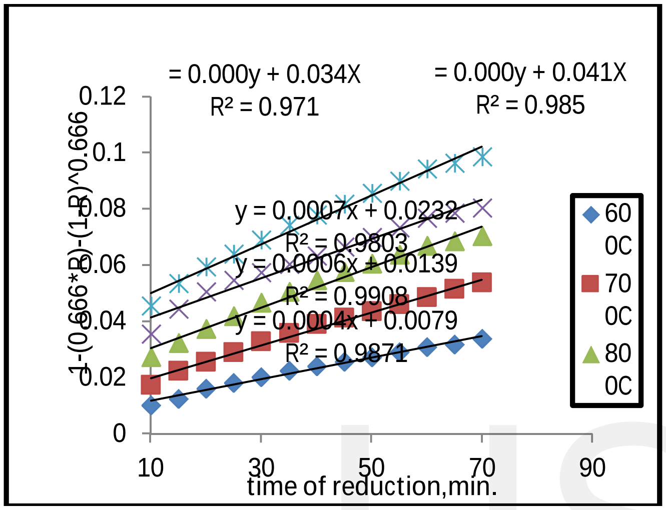

Fig.14. The relation between 1 - (2/3)R - (1 - R)$^{2/3}$against time of reduction for different reduction temperature .

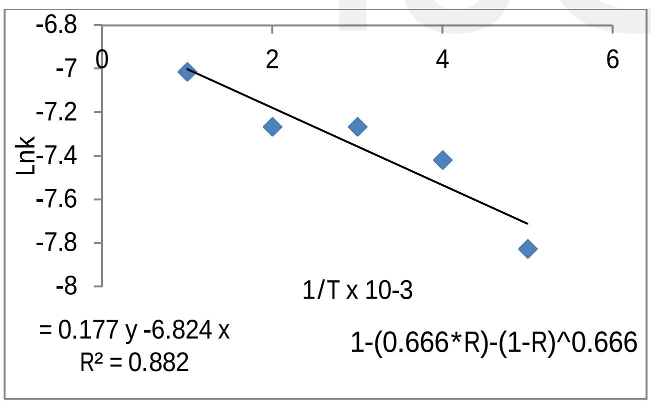

Fig.15. Relation between ln k and 1/T

4. CONCLUSIONS

1-The compressive strength and the drop damage resistances of wet and dry of the low grade manganese ore with coke breeze pellets decreased with increasing the amount of coke breeze

2- The reduction rates of low grade manganese ore with coke breeze increased with increasing temperature of the reduction from 600 up to 950°C.

3- The reduction rate increased with increased of amount of coke breeze at constant temperature.

4- The diffusion processes through the produced pellets is the reduction control step and the reduction have activation energy = 53.37 or 56.43 kJ/ mole.

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