



# Reduction of Low Grade Egyptian Manganese Ore via Hydrogen at 800°C - 950°C

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## Abstract

Low grade manganese ore fine was briquetted with different amounts of molasses under different pressure was studied in this investigation. In this study, the characterizations of raw materials were studied by different methods of analyses such as X-ray and chemical analyses. The results of briquetting show that as the pressing pressure load increased both the drop damage resistance and crushing strength increased and the optimum amount of molasses added was 2% and the pressing pressure was 216.7745 MPa. The produced briquettes were reduced by different flow rate of hydrogen at different temperatures, and the reduction kinetics was determined. The results indicated that: 1) The reduction rates by hydrogen increased with increasing temperature of the reduction; 2) Increase hydrogen flow rate at constant temperature of reduction leads to increase rate of reduction; 3) The zero order is control step at time 0 - 5 min and from 5 to 20 min the gaseous diffusion in case of cylindrical products and from 20 to 60 min the reaction controlled by nucleation and growth.

## Keywords

Low Grade Manganese Ore, Briquetting, Reduction Kinetic by Hydrogen

**Subject Areas:** Chemical Engineering & Technology, Mineral Engineering

## 1. Introduction

Manganese plays an important role in several industrial applications, such as steel production, preparation of di-

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etary additives, fertilizers, cells and fine chemicals, as well as colorants for bricks, dyes and medicines [1]-[3].

Manganese metal is readily available at a low price and is mostly used in the form of ferromanganese in steelmaking. The major use of manganese is as an alloying addition to steel, where it acts as a desulphuriser and a deoxidizer which is a very important function in steelmaking. Manganese also provides improved rolling and forging characteristics, improved strength, toughness, harden ability and wear resistance by suppressing the hardening transformation of steel on quenching. It is also added to Al, Ag, Mg, Ni, Ti and Zn alloys as an alloying element. Manganese is added in the form of its ore during iron making or as ferromanganese alloy at the steelmaking stage.

The normal classification of manganese ore is as follows [4]:

1) Manganese ores, containing more than 35% Mn suitable for the manufacture of high or low-grade ferromanganese;

2) Ferruginous manganese ores containing 5% - 35% Mn suitable for the manufacture of spiegeleisen;

3) Manganiferous iron ores with 5% - 10% Mn used for the manufacture of manganiferous pig iron.

In practice, manganese ores and concentrates have a wide and complex range of chemical and physical specifications most often employing a specific end-use prefix [5].

Metallurgical-grade used in the iron and steel industry requires 35% - 55% Mn, generally with a Mn/Fe ratio larger than 5. Battery-grade requires 70% - 85% MnO<sub>2</sub> that is equivalent to 44% - 54% Mn, and should contain less than 0.05% of metals more electronegative than zinc, such as copper, nickel, cobalt, and arsenic.

Chemical-grade has various specifications depending on the specific end use such as feedstock for electrolytic manganese and manganese dioxide, manganese chemicals, colorants, and uranium processing.

Fertilizer and feed grade requires 30% - 60% Mn; ferrites need particularly low levels of CaO, K<sub>2</sub>O, Na<sub>2</sub>O, BaO, and SiO<sub>2</sub>.

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 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 [6].

Swamy *et al.* [7] studied this phenomenon with TGA tests. They found that the optimum pre-reducing temperature for increasing the Mn/Fe ratio of the ore non-magnetic part would be 850°C, and they also observed that a finer particle size (-0.15 mm) gave a better Mn/Fe ratio compared to the coarser ore (-6 to +3 mm). Rudramuniyappa *et al.* [8] reported that reduction roasting followed by magnetic separation is considered to be the best method for upgrading the Chikkanayakanahalli manganese ores. They also showed that tabling studies carried out were not encouraging, probably due to the similar behavior of Mn and Fe. Rao *et al.* [9] reported, that in reduction roasting of low grade manganese ore followed by magnetic separation, 60% of phosphorus can also be removed [10].

Main purpose of this study was to find the reduction rate of low grade manganese ore briquette by hydrogen.

## 2. Materials and Experimental

### Material

The low grade of manganese ore used in this work was provided by Sinai ferromanganese Co. The sample was submitted to chemical and X-ray analysis. The chemical analysis of low grade manganese ore is illustrated in **Table 1**.

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

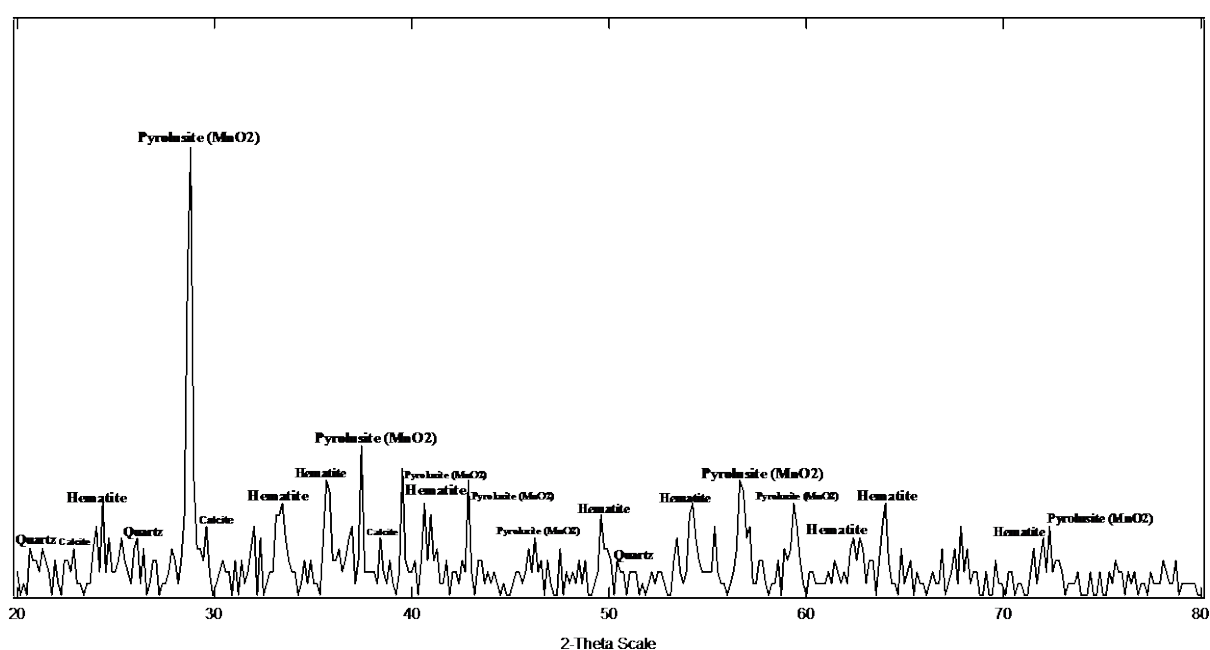
## 3. Experimental Procedures

### 3.1. Preparation of Samples

The low grade of manganese ore was grinding in vibrating mill to powder with size less than 75 micrometers. The low grade of manganese ore powder (10 g) 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. Under different pressure (the pressure

**Table 1.** Chemical analysis of Egyptian low grade of manganese ore.

Constituent	Weight (%)
Fe total	23.2
K <sub>2</sub> O	0.25
Al <sub>2</sub> O <sub>3</sub>	2.3
MgO	0.95
CaO	2.4
P	0.2
Mn	28.6
SiO <sub>2</sub>	15.3
Na <sub>2</sub> O	0.2

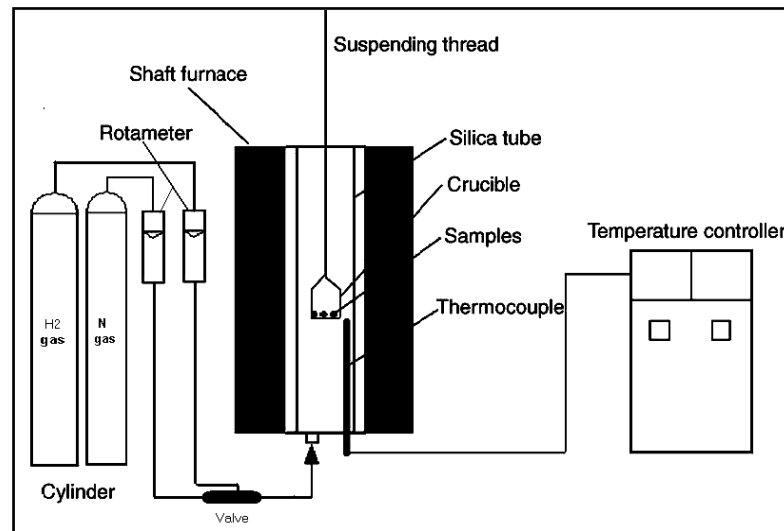
**Figure 1.** X-ray of low grade of manganese ore.

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 [11]-[14].

### 3.2. Reduction Procedures

The reduction of low grade manganese ore with hydrogen was performed in thermogravimetric apparatus. This scheme is similar to that present elsewhere [14] [15] (Figure 2). 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  $\pm 5^\circ\text{C}$ . 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 air should be removed before each experiment and also after the end of reduction. The weight of the sample was continuously



**Figure 2.** Schematic diagram of the reduction apparatus.

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:

$$\text{Percent of reduction} = \left[ \frac{(W_o - W_t) \times 100}{\text{Oxygen mass}} \right]$$

where:

W<sub>o</sub>: the initial mass of mill scale sample after removal of moisture.

W<sub>t</sub>: mass of sample after each time, t.

Oxygen mass: indicates the mass of oxygen percent in low grade of manganese ore in form FeO, Fe<sub>2</sub>O<sub>3</sub> and manganese oxide.

## 4. Results and Discussions

### 4.1. Effect of Adding Molasses as Binding Materials on the Quality of Produced Briquettes

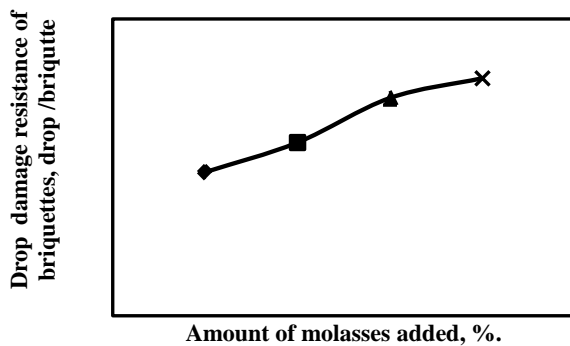
**Figure 3** and **Figure 4** illustrate the effect of percentage of molasses added on the drop number (drop damage resistance) and cold crushing strength of the briquette (the pressing load is constant = 216.7745 MPa.). It is clear that as the percentage of binding materials increased both the drop damage resistance and crushing strength increased; this may be due to the effect of binding material.

### 4.2. Effect of the Pressure Load with Constant Amount of Molasses on the Quality of the Briquettes

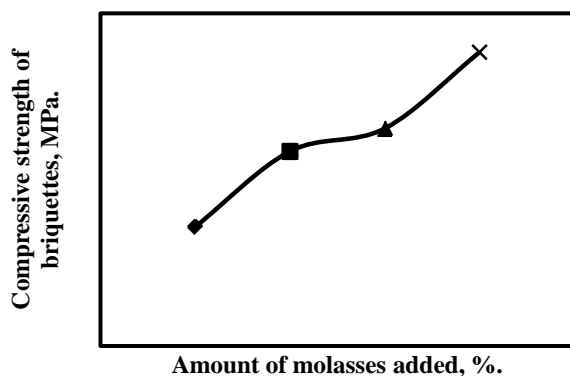
**Figure 5** and **Figure 6** show the relation between the change of pressure load at constant amount of molasses (2%) on the drop number (drop damage resistance) and cold crushing strength of the briquette. It is evident that as the pressing pressure load increased both the drop damage resistance and crushing strength increased. This may be due to the fact that increase pressure load increase the compaction of briquette and subsequently the Vander Waals forces increased [16] [17], also this may be due to the increase of briquetting pressure leads to progressive crushing of the macropores [18].

### 4.3. Effect of Hydrogen Flow Rate on the Reduction Degree

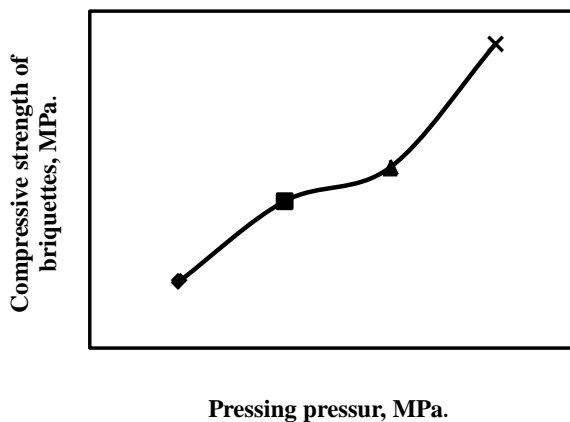
**Figure 7** illustrates the relation between the reduction degree and hydrogen flow rate when the reduction was done at constant temperature (900°C) and constant weight of the sample. It is clear that as the flow rate of hydrogen increased the reduction percentage increased. This may be the increase 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 [19] or the increase of flow rate increased the gas diffusion across the



**Figure 3.** Effect of molasses addition on the drop damage resistance of produced briquettes compressed at 216.8845 MPa.



**Figure 4.** Effect of molasses addition on the compressive strength of produced briquettes compressed at 216.8845 MPa.

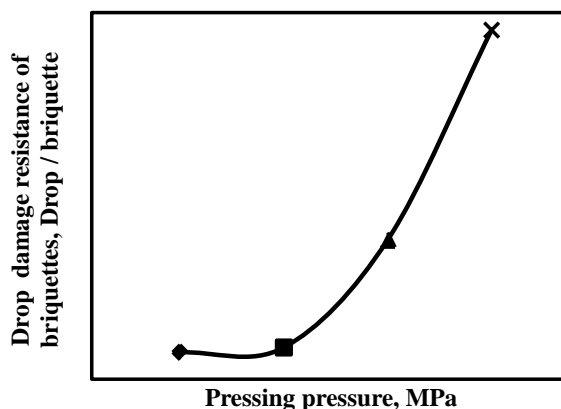


**Figure 5.** Effect of pressing pressure on the compressive strength of produced briquettes at 2% molasses added.

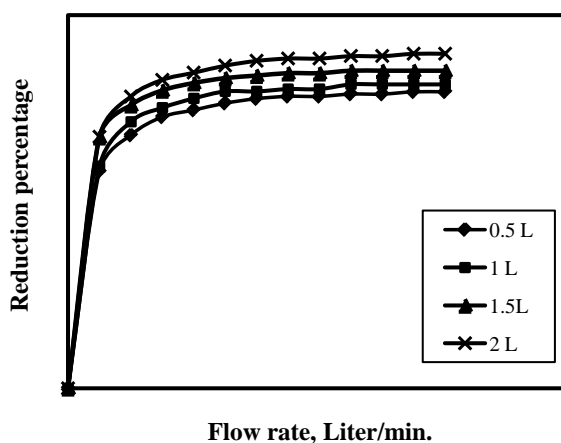
boundary layer subsequently the reduced ion increased [20]. Also may be the higher flow rate prevailing in the reaction zone which enhances the rate of hydrogen absorption and subsequently the rate of chemical reaction steps increased [21].

#### 4.4. Effect of the Reduction Temperature on the Reduction Degree

The reduction was carried out at different temperatures ranging from 800°C to 950°C, where the weight of the



**Figure 6.** Effect of pressing pressure on the drop damage resistance of produced briquettes at 2% molasses added.



**Figure 7.** Effect of hydrogen flow rates (L/min.) on the reduction percentage of produced briquettes compressed at 216.88 MPa. at 900°C.

briquette were constant and the hydrogen flow rate = 1.5 liter /min. The results of the investigation are shown in **Figure 8** for the briquette binding by 2% molasses. It is clear that the increase of temperature favors the reduction rate and degree. The analyses of the curve relating the reduction percentage and time of reduction, shows that each curve has 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 rate [19] [22]. Also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rate of desorption [20]-[23].

#### 4.5. Kinetics Reduction of Low Grade Manganese Briquette

It is clear that from **Figure 8** there are three rates; therefore we try applied three models First model from time 0 to 5 min.

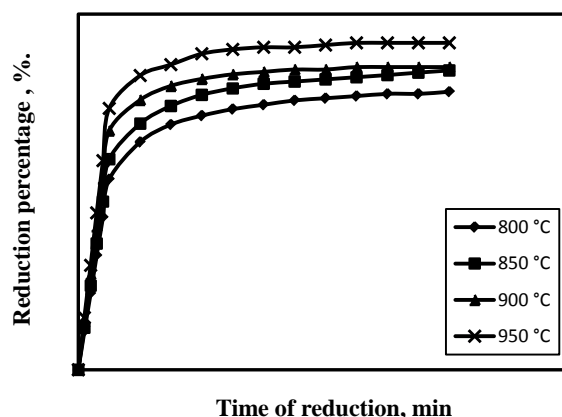
Zero order  $R = k_1 t$

Second model from 5 to 20 min for gaseous diffusion in case of cylindrical products can be written as [24]:

$$R + (1 - R) \ln(1 - R) = k_2 t$$

Third model from 20 to 60 min  $\ln[\ln(1 - R)] = k_3 t$  (Avrami equation, this mean the reaction controlled by nucleation and growth [25]-[27]).

Where R is fractional reduction, t is time of reduction,  $k_{1,2,3}$  is the rate constant for each model.



**Figure 8.** Effect of reduction temperatures on the reduction percentage of produced briquettes compressed at 216.88 MPa. at 1.5 flow rate of hydrogen gas/min.

**Figure 9** illustrates the relation between  $R$  against time of reduction for different reduction temperature (at time range 0 to 5 min.). 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 **Figure 10** from which it is clear that the activation energy = 23.4 kJ/mole.

**Figure 11** illustrates the relation between  $R + (1-R)\ln(1-R)$  against time of reduction for different reduction temperature (at time range 5 to 20 min.). From which it is clear that, the straight line was observed and this mean the reaction controlled by gaseous diffusion in case of cylindrical products in this range [24].

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrate in **Figure 12** from which it is clear that the activation energy = 23.05 kJ/mole.

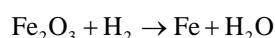
**Figure 13** illustrates the relation between  $\ln[\ln(1-R)]$  against  $\ln t$ , time of reduction for different reduction temperature (at time range 20 to 60 min.). From which it is clear that the straight line was observed this mean the reaction controlled by nucleation and growth [25]-[27].

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrate in **Figure 14** from which it is clear that the activation energy = 55.5 kJ/mole.

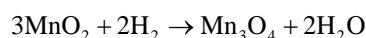
#### 4.6. X-Ray Analyses of the Reduced Sample

It is clear that the phases of the sample after reduction at 950°C (time of reduction 60 min.) (**Figure 15**) are metallic iron, MnO, Mn<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub>.

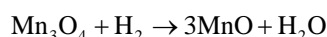
The metallic iron formed according the following reaction:



While Mn<sub>3</sub>O<sub>4</sub> and MnO formed according the following reactions:

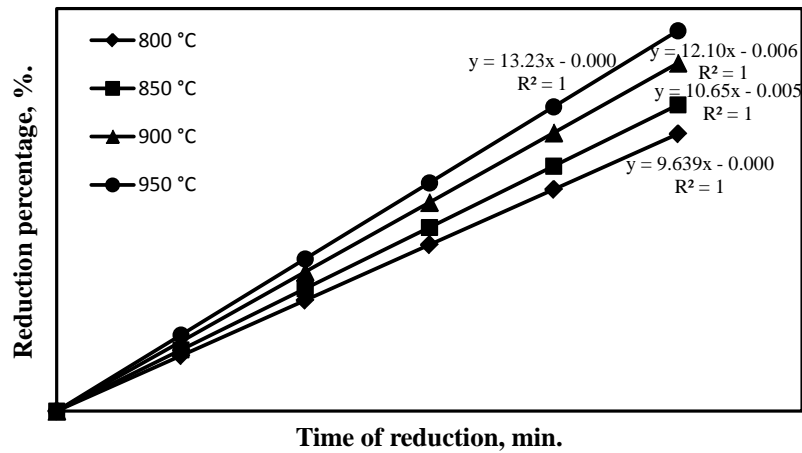


and

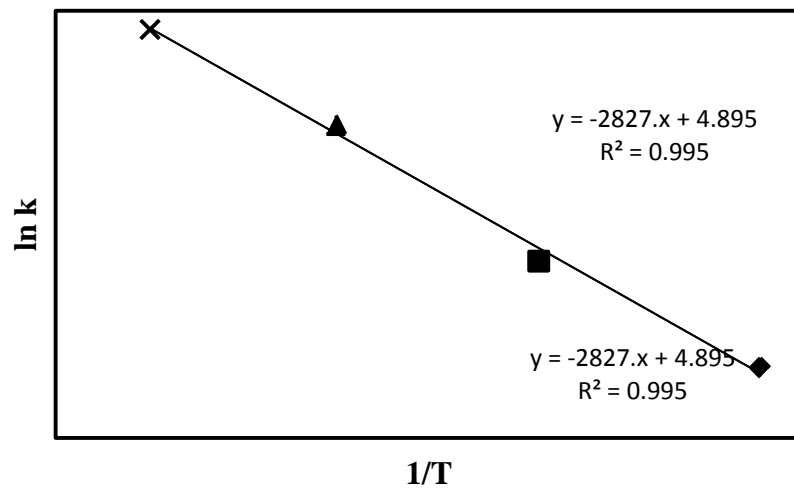


## 5. Conclusions

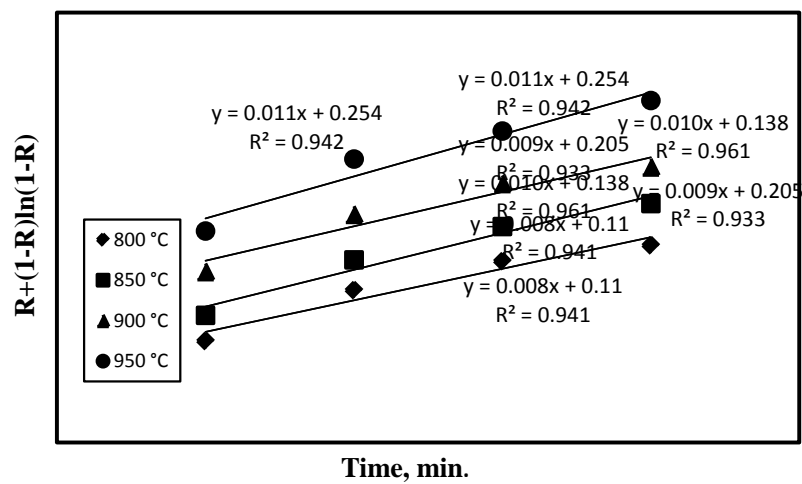
Manganese plays an important role in several industrial applications. The utilization of the low grade manganese ore has become necessary. There are several physicochemical differences among the components in manganese ores, which can be used for the enrichment of manganese. In particular, the abundant low-grade manganese ores, which contain iron oxide, may be upgraded by prerreduction and magnetic separation. The reduction of Egyptian



**Figure 9.** The relationship between time of reduction and R at different temperatures.



**Figure 10.** The relation between 1/T and ln K for reaction at time 0 - 5 min. (Arrhenius plot for reduction reaction).



**Figure 11.** The relationship between time of reduction from 5 to 20 min. and  $R + (1 - R) \ln(1 - R)$  at different temperature.



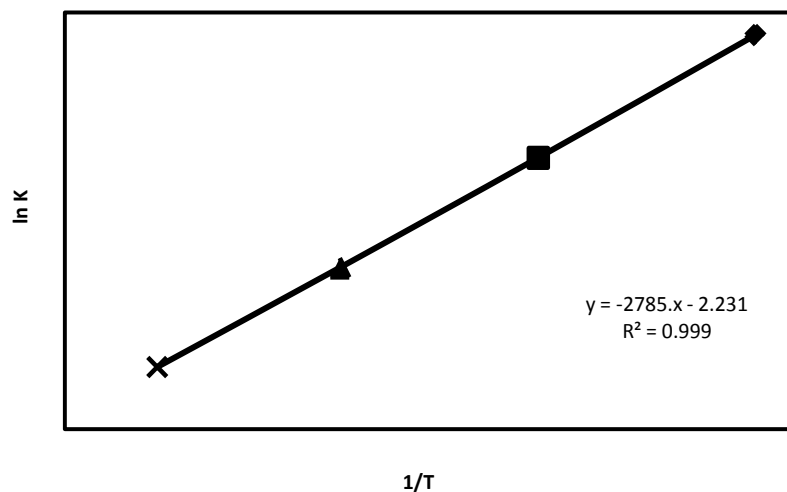


Figure 12. The relation between  $1/T$  and  $\ln K$  for reaction at time 5 to 20 min. (Arrhenius plot for reduction reaction).

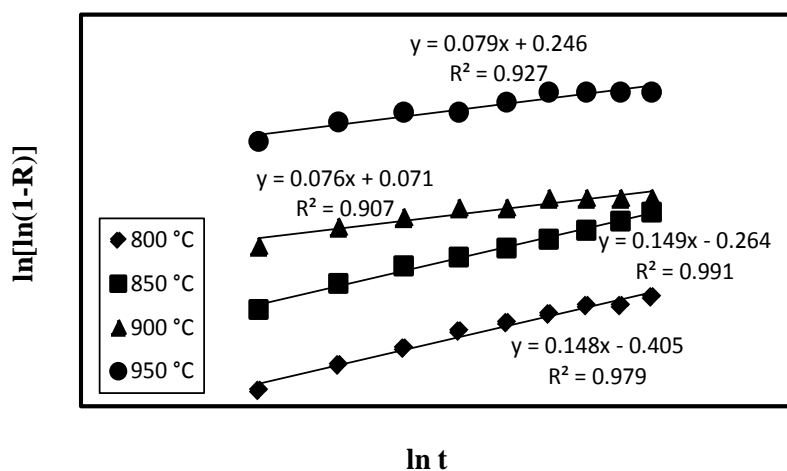


Figure 13. The relation between  $\ln[\ln(1-R)]$  against  $\ln t$  at different reduction temperatures (at time range 20 to 60 min.).

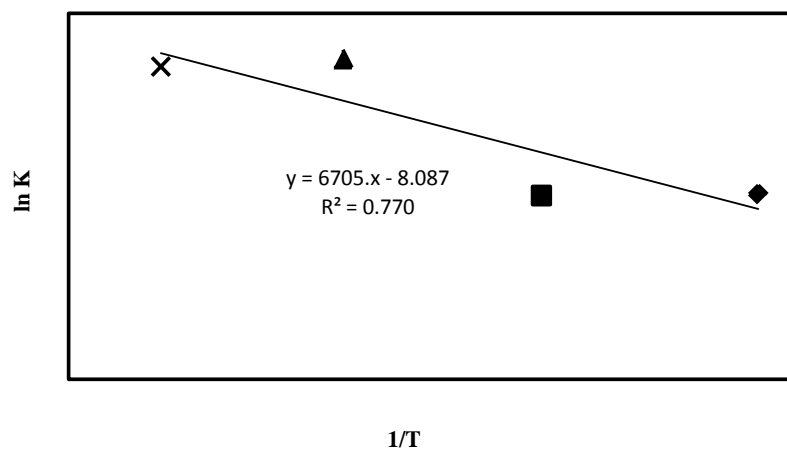
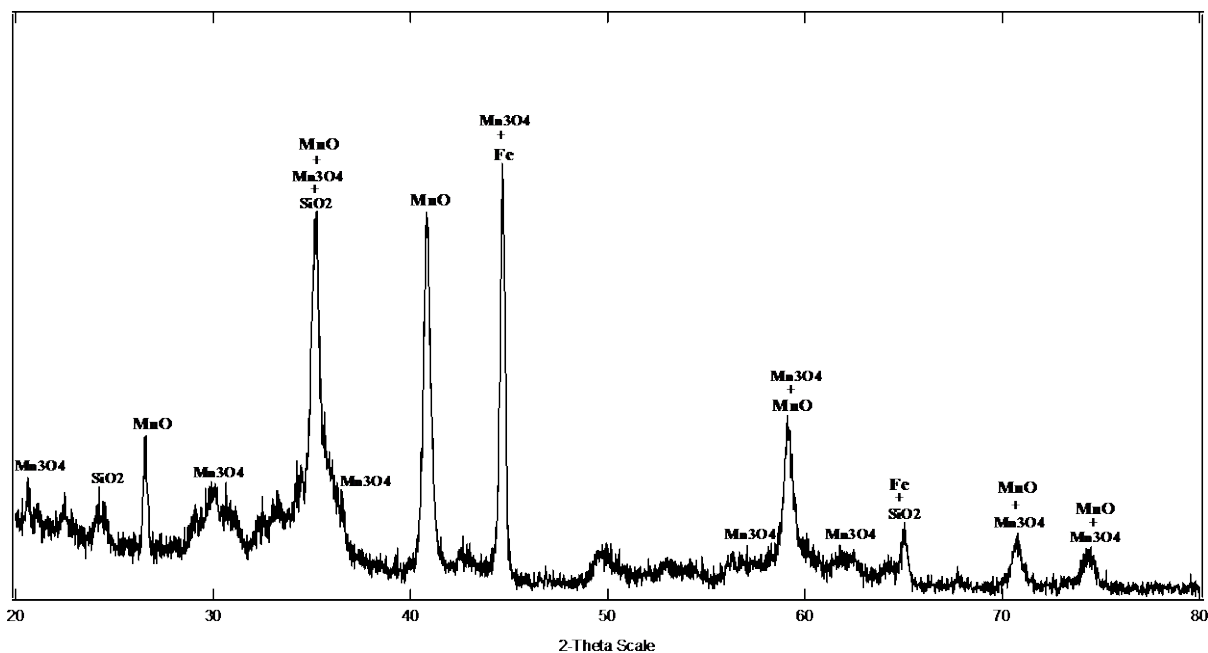


Figure 14. The relation between  $1/T$  and  $\ln K$  for reaction at time 20 to 60 min. (Arrhenius plot for reduction reaction).



**Figure 15.** X-ray of produced briquettes compressed at 216.88 MPa. under 1.5 flow rate of hydrogen gas/min at 950°C.

low grade of manganese ore by hydrogen in temperature indicated that:

- 1) The reduction rates increased with increasing temperature of the reduction.
- 2) Increase hydrogen flow rate at constant temperature of reduction leads to increase rate of reduction,
- 3) The zero order is control step at time 0 - 5 min and from 5 to 20 min the gaseous diffusion in case of cylindrical products and from 20 to 60 min the reaction controlled by nucleation and growth.

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