

The Layered Reduction of Hematite (Iron Oxide) Ore by Non-Coking Coal: The Effect of Calcium Carbonate on Reduction

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Abstract

Due to the abundance of the non-coking coal and limitations as well as the high costs of the natural gas, the present study examined the direct reduction of hematite (iron oxide) ore in the temperature range of 800-1000 °C by the non-coking coal volatiles. Approximately, 74.9% of the total amounts of volatiles and gases exit the coal up to 800°C. The onset temperature to exit volatiles from the non-coking coal was approximately 525°C. The SEM micrographs and XRD results indicated the non-uniform layered reduction of the hematite layer. As temperature was increased, the reduction of hematite ore was increased. At a constant temperature of 1000°C, the reduction rate of the hematite layer reached a maximum after 30 min and then it was decreased. Adding various amounts of calcium carbonate to the non-coking coal in optimal reduction conditions increased the reduction rate of the hematite ore. The optimal concentration of this catalyst was 5 wt% (relative to the coal).

Keywords: Direct reduction, Iron ore, Non-coking coal, Calcium Carbonate.

1. Introduction

The direct reduction by electric furnace is more economically affordable than the traditional method used for iron production (blast furnace-converter) due to less costs and easier application. Given the abundance of the non-coking coal, the high costs and restrictions on the use of natural gas as well as the production of significant amounts of the non-coking coal in coking operations, this kind of coal has been extensively used as a reduction agent¹⁻⁴. In the direct reduction process, the oxygen is removed from the iron ore at temperatures below the melting point using the reduction agents⁵. The volatiles resulting from burning coal are converted to hydrocarbons⁶.

Coal → Carbon + Volatiles (1)

Many researchers have studied the direct conversion of iron oxides to carbon and volatiles resulting from the thermal decomposition of coal. The results have shown the important role of H₂ resulting from the cracking of heavier hydrocarbons to the lighter ones in the direct reduction process^{7,8}. Rao et al.⁹ studied

the direct reduction of iron oxide by reduction agents resulting from the thermal decomposition of coal. Their results indicated that the main kinetic-controlled reactions occurred in two stages. The rate of reduction reactions can be increased by controlling temperature, the use of catalyst, etc.

The reduction of an oxide to another oxide with lower oxygen content is⁹:



The reproduction of Co according to Boudouard reaction is⁹:



The present study examined the direct layered reduction of hematite ore by volatiles and emissions resulting from the thermal decomposition of the non-coking coal to prevent the contamination of the reduction as well as the solid products resulting from the thermal decomposition of coal. In addition, the effect of various factors including temperature, time and addition of calcium carbonate catalyst to the non-coking coal was studied.

2. Materials and Methods

2.1. Raw Materials

The laboratory grade hematite powder and bituminous coal with high volatiles content

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were used in experiments. Tables 1 and 2 show the chemical composition of iron oxide and the non-coking coal used in this study.

Table 1. The chemical composition of the hematite powder:

Compound	SiO ₂	Al ₂ O ₃	Na ₂ O	TiO ₂	MnO	CaO	P ₂ O ₅	Fe ₂ O ₃	Size (µm)
wt%	0.010	0.03	0.01	0.02	0.21	0.05	0.05	98.8	50-100

Table 2. The composition of the non-coking coal.

Compound	Humidity	Ash	Volatiles	Carbon
wt%	0.010	0.03	0.01	0.02

Hematite powder, the non-coking coal and aluminum oxide with a particle size less than 53 µm were used. Laboratory grade calcium carbonate powders with the particle size of 44 µm and the purity of more than 98% were used as the catalyst.

2.2. The Crucible and Layered System

Fig. 1 shows the schematic design of the stainless steel crucible used in this study. As shown in Fig. 1(a), a hole was embedded on the crucible lid to exit emissions and prevent the increased pressure during the process. The raw materials were placed on each other as layers without applying any external pressure. As shown in Fig.1, the first, second, third and fourth layers were composed of the non-coking coal, aluminum oxide, iron oxide and aluminum oxide, respectively. The non-coking coal and hematite layers were separated by the inert aluminum oxide layer. The second inert Al₂O₃ layer prevented the mixing and contamination of coal and hematite layers. It also reduced the outflow of volatiles. The fourth Al₂O₃ layer prevented the outflow of volatiles from the reaction chamber while preventing the oxidation of the hematite layer by the oxygen entering the crucible from the lid hole.

The control crucible was composed of the non-coking coal and aluminum oxide layers. The coal content in the control crucible was equal to the amount of coal in the test crucible. To provide same conditions for both crucibles, the total heights of materials in the test and control crucibles were equal. Fig.1b shows the control crucible. The design of the control crucible was of great importance, because the volatiles and reduction rate were calculated based on the weight loss in the control crucible.

2.3. The Reduction Rate of Hematite

The following equations were used to calculate the reduction rate of the hematite layer:

A) the control crucible

The weight loss of the non-coking coal layer is:

$$\Delta w_{(c)} = w_1 - w_2 - \Delta w_{(m)} \quad (4)$$

$$\text{The outflow of volatiles is: } \% \Delta w_{(c)} = \frac{\Delta w_{(c)}}{w_c} \times 100 \quad (5)$$

B) The test crucible

The weight loss of the test crucible is:

$$\Delta w_{(Fe_2O_3+C)} = w_3 - w_4 \quad (6)$$

The weight loss of the hematite layer is:

$$\Delta w_{(Fe_2O_3)} = \Delta w_{(Fe_2O_3+C)} - \Delta w_{(c)} - \Delta w_{(m)} \quad (7)$$

The total oxygen content in the hematite layer is:

$$w_{(O_2)} = \frac{48}{160} \times \left(\frac{98.86}{100} \times (gr \text{ consumed hematite}) \right) \quad (8)$$

The reduction rate of the hematite layer is:

$$\%R = \frac{\Delta w_{(Fe_2O_3)}}{w_{(O_2)}} \times 100 \quad (9)$$

where w_1 is the weight of the control crucible before the test, w_2 is the weight of the control crucible after the test, $w_{(c)}$ is the weight of the test crucible before the test, w_4 is the weight of the test crucible after the test and $\Delta w_{(m)}$ is the weight difference of the crucible because of oxidation. All weights are in grams.

2.4. Sample Preparation

2.4.1. The height and appropriate amounts of materials in the layers

The layer height should not be too much so that the internal pressure of the crucible can be increased, thereby leading to material outpour because of high temperature and gas production. Moreover, the layer height should not be too low as the materials cannot be optimally used for the reduction process in this condition. According to the previous studies¹⁰, a higher stoichiometric ratio of "carbon to hematite" can result in a higher reduction rate (Eq. 8) was used to calculate the stoichiometric ratio of "carbon to hematite". Accordingly, 22.5 g carbon and 43.27 g non-coking coal (with 52% carbon fixed) were required to reduce 100 g hematite¹⁰.



To reduce the total height of materials in the crucibles, a "carbon to hematite ratio" of 1/1.2, 3.9 g coal and 7.5 g hematite were used. The optimal content of aluminum oxide in the control crucible was 14 g. A higher Al₂O₃ content resulted in material outpour. The Al₂O₃

content in the second layer of the test crucible was more important than the fourth layer. Accordingly, the total heights of the materials in the test and control crucibles were equalized with the optimal choice of 4 and 1 g Al_2O_3 for the second and fourth layers, respectively.

2.5. Chain Reactions

Given the ultimate goal of this study, the following chain reactions occurred to achieve the optimal conditions and maximum reduction rate by adding the metal catalysts to the system.

First Step: the materials were dried and dehumidified in an oven at 120°C for 1 h. Then the test and control crucibles were prepared and weighed as shown in Fig. 1. The crucibles were placed in an oven with ambient temperature. The temperature was raised to 800°C with a heating rate of $2.5 \frac{^\circ\text{C}}{\text{Min}}$. The heated crucibles were removed and cooled in a desiccator by placing a ceramic lid on the crucibles lids. The crucibles were again weighed to calculate the reduction rate and the outflow of volatiles at this temperature. The process was repeated at $850, 900, 950$ and 1000°C .

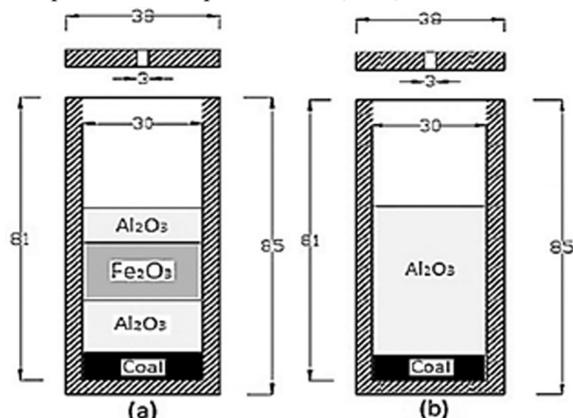


Fig.1. A view of (a) the test crucible, and (b) the control crucible.

Second Step: the maximum reduction rate at 1000°C was first determined. The samples underwent further reduction in optimal conditions at the constant temperature. To investigate the effect of time on the reduction rate, some samples were prepared by the previous procedure. The samples were kept at 1000°C for 0, 5, 15, 30, 45 and 60 minutes. The results were calculated as obtained for the previous samples. A temperature of 1000°C and a duration of 30 minutes were selected as the optimal conditions for the next steps.

Third Step: in this step, 0, 0.5, 1, 2, 3, 4, 5 and 6 wt% calcium carbonate was uniformly added to the non-coking coal. The samples were kept at 1000°C for 30 min. Then, the crucibles were removed and the reduction rate and the outflow of volatiles were calculated for both test and control crucibles.

An optimal concentration of 5 wt% (relative to the coal) was obtained. The effect of adding 5wt% calcium carbonate to the non-coking coal on the reduction rate and the outflow of volatiles as well as other coal products was investigated in the optimal conditions ($T=1000^\circ\text{C}$, $t=30$ min).

3. Results and Discussion

3.1. The effect of time and temperature on the maximum reduction rate (First and Second Steps)

Fig. 2 shows the results obtained from the first step. As temperature was increased, the reduction rate of the hematite layer and the outflow of volatiles were increased. According to the slope of the curve in Fig. 2(b), the outflow of volatiles at the early stage of reduction reaction was increased with increasing the temperature. The outflow of volatiles and the reduction rate were reduced at the higher temperatures. The onset temperature for the outflow of volatiles was 525°C . Up to this temperature, 11.44% of volatiles exit the coal. Approximately 74.9% of the coal volatiles were removed up to 800°C . At the lower temperatures, CH_4 and CO_2 contents were higher than the reduction agents, including CO and H_2 ⁽¹⁾. Accordingly, the reduction rate was insignificant up to 800°C . The outflow of volatiles was increased with increased temperature. Slope and reduction rate were increased with the further outflow of volatiles, including CO and H_2 , because of Boudouard reaction and increased reduction agents. The reduction rate was reduced at about 1000°C due to reduced volatiles and reduction agents in the reaction chamber.

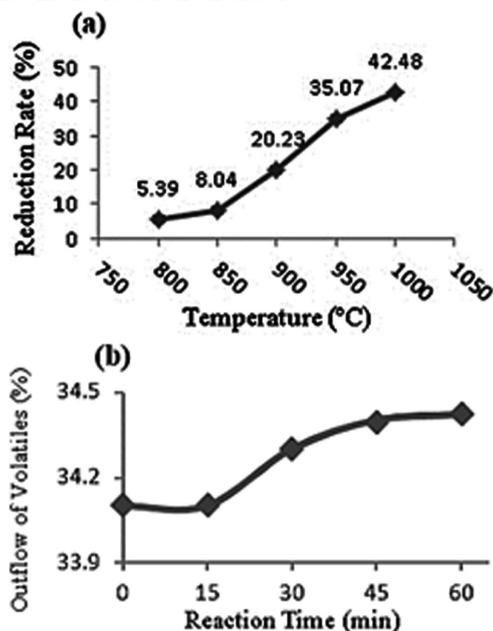
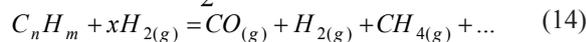
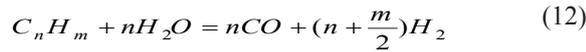
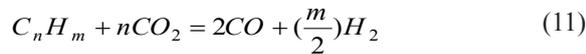


Fig.3. The effect of reaction time at the optimal temperature on (a) the reduction rate of the hematite layer in the test crucible, and (b) the outflow of volatiles and pyrolysis products from the coal layer.

With increasing the reaction time, the reduction rate of the hematite layer was increased due to the optimal kinetic conditions at 1000°C (due to the high temperature) and the higher reduction rate of iron oxides by products resulting from reforming and cracking of the heavier hydrocarbons (*called tar*) in the hematite and the second Al₂O₃ layers. The tar reforming and cracking reactions are as follows ¹²:



The reduction rate reached its maximum value after 30 minutes and then it was decreased because of the reduced outflow of volatiles and consequently, the diffusion of oxygen from the atmosphere to the hematite layer and the re-oxidation of iron and wustite.

The reduction rate of samples (a), (b), (c) and (d) at 850, 900, 950 and 1000°C was 8.04, 20.23, 35.07 and 42.48%, respectively. The X-ray diffraction analysis was used to investigate the crystalline phases formed during the reduction process. Fig. 4 shows the XRD pattern of the middle part of the hematite layer. In the case of sample (a), the formation of the new magnetite phase in the initial hematite mixture was observed. Accordingly, the first reduction step of the hematite layer occurred at a temperature lower than 850°C. The primary iron oxide (hematite) was not observed in the XRD pattern of sample (b). In addition, the new wustite phase was formed in sample (b). Given the peak intensity of the wustite phase, the new phase was formed in the early stages. According to the XRD pattern of the sample (c), the third reduction stage of the hematite ore occurred at a temperature less than 950°C and therefore, the metallic iron emerged in the sample. The increased intensities of iron peaks in the sample (d) indicated the reduction of the wustite phase to the metallic iron.

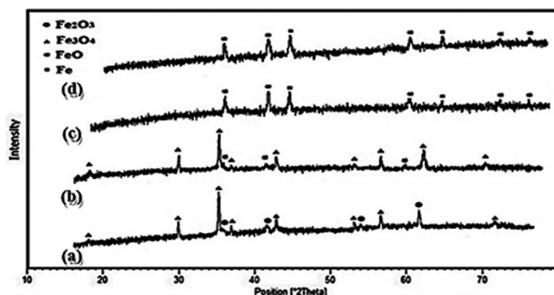


Fig.4. The XRD patterns of the partially reduced iron oxide samples.

The reduced samples showed an evident color difference (Fig. 5(a)) and higher ferromagnetic properties in the lower parts of the hematite layer (the areas closer to the coal layer) as compared with those in the upper parts. The differences in color and magnetic properties indicated the different reduction rates and thus, different phases in the lower and upper parts of the reduced sample. The SEM micrographs (Fig. 5) and energy dispersive X-ray (EDX) results (Fig. 6) confirmed the above observations.

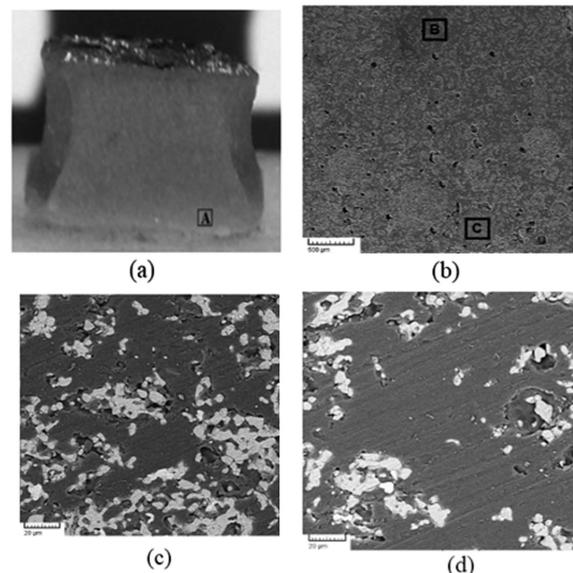


Fig.5. (a) The cross section of the sample (c), (b) the SEM micrograph of the sample (c) from area A (scale bar: 500 μm), (c) the SEM micrograph of the sample (c) from area B (scale bar: 20 μm), and (d) the SEM micrograph of the sample (c) from area C (scale bar: 20 μm).

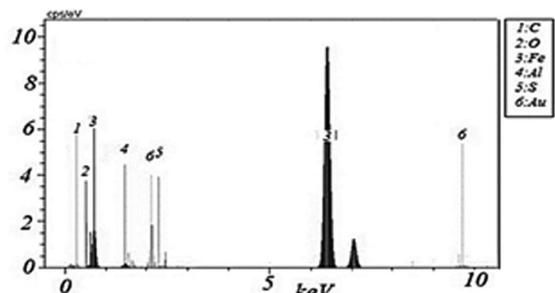


Fig. 6. The semi-qualitative energy dispersive X-ray (EDX) analysis of the lighter areas in the SEM micrographs (scale: 20 μm).

Due to porosity as well as the limitations for the preparation of highly reduced samples, among the samples reduced at T=950°C and t=0 min, sample (c) was examined by the scanning electron microscope. A vertical cross section of the sample was cut to prepare the SEM sample. Fig. 5(a) shows the cross section of sample (c). Fig. 5(b) shows the SEM micrograph of the vertical section in the vicinity of area A (scale: 500μm).

As can be seen, the number of voids in the lower portion was higher, while the sponge iron texture was denser in the upper portion with lower voids. Since the coal produced the reduction agents, the lower portions of the hematite layer were more exposed to reducing emissions as compared to the upper portions. Consequently, the lower layer was more porous because of the rapid sponge iron formation. According to Fig. 5 (c) and (d), the lighter areas in the upper portion were decreased. According to the semi-qualitative EDX analysis (Fig.6), the lighter areas were rich in iron.

Accordingly, the reduction of the hematite layer involved a non-uniform system from the lower parts to the upper portions. In addition, the carbon peaks that appeared in the semi-qualitative EDX patterns confirmed the reform of the precipitated tar (heavy hydrocarbons) by metallic iron particles resulting from the reduction of the hematite layer. As a result, with increasing the holding time at 1000°C, the reduction rate was increased because of suitable thermodynamic and kinetic reduction conditions as well as the production of significant volumes of H₂ and CO. The reduction rate reached its maximum value after 30 minutes.

3.2. The optimal concentration of calcium carbonate in the optimal temperature and time (Third Step)

Fig. 7 depicts the effect of adding calcium carbonate to coal on the reduction percentage of hematite layer in the main crucible, and on the escape percentage of volatile compounds in the control crucible after 30 min incubation at 1000 °C. According to Fig. 7-a, by adding different values (wt%) of calcium carbonate to coal, the reduction percentage reached to its highest level when adding 5 wt% carbonate calcium. As can be seen in Fig. 7-b, adding carbonate calcium up to 3 wt% did not have any significant effect on the escape of volatile compounds. Calcium carbonate was decomposed to CaO and CO₂ during the reaction (Eq.15) at 820 °C¹³. Given the presence of sulfur in coal (1.46%), CaO reacted with SO₂ and H₂S produced from thermal decomposition and gasification of coal and yields of CaS and CaSO₄^{14, 15}. Therefore, its catalytic effect on tar correction reactions was reduced.



CaS and CaSO₄ were not stable at high temperatures (> 900 °C), thereby resulting in the reformation of CaO at high temperatures and the significant release of corrosive sulfur gases in the reaction chamber¹³. These gases reduced the reduction potential of volatiles at high temperatures.

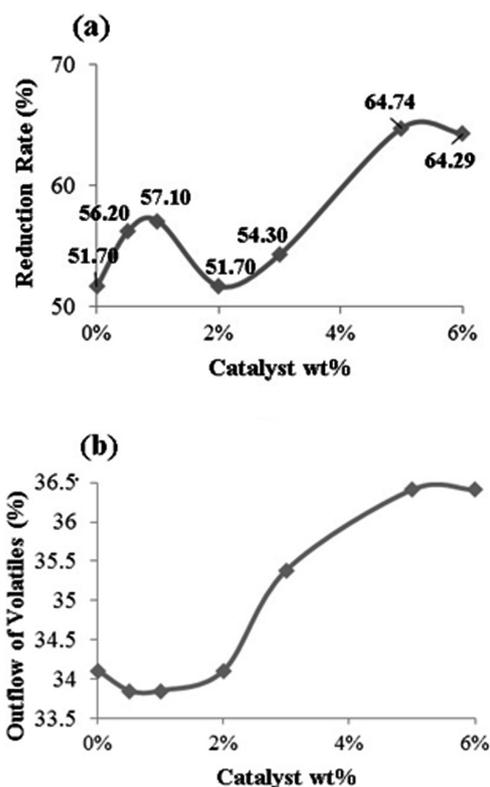


Fig.7. The effect of adding calcium carbonate to the coal layer on (a) the reduction rate of the hematite layer in the test crucible, (b) the outflow of volatiles from the coal layer.

As can be seen in Fig. 8, the corrosion of the inner walls of the control and the main crucibles containing 2 wt% calcium carbonate confirmed the significant escape of oxidizing agents in those gases evaporated from coal, as well as the decrease of the reduction potential in the reaction chamber. Therefore, the reduction percentage of hematite layer was not significantly increased after adding levels less than 3 wt% calcium carbonate (Fig. 7-a).

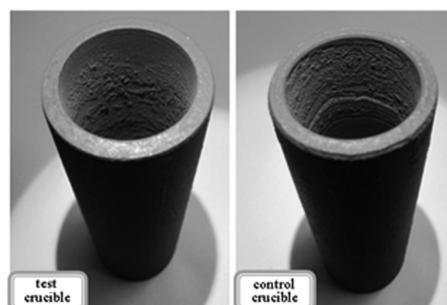


Fig.8. Corrosion of the inner walls of the control and original crucibles after the process of reduction under optimum conditions in the sample containing 2wt% calcium carbonate in the coal layer.

Fig. 7-b shows that the addition of 5wt% calcium carbonate to coal improved the catalytic activity of this catalyst as an accelerating agent of coal cleavage and reforming reactions (Eqs. (11) to (14)) and increased the escape percentage of volatiles and reducing agents in the reaction chamber. Thus, adding 5 wt% calcium carbonate in the optimum conditions of reduction (incubation at 1000 °C for 30 min) resulted in the maximum increase from 51.70% to 64.74%.

3.3. The effect of adding 5wt% calcium carbonate to the coal layer on the reduction process in the optimal conditions (fourth Step)

The effects of adding the optimum percentage of calcium carbonate on the escape of volatiles and the reduction percentage of hematite layer are demonstrated as non-isothermic until reaching the optimum temperature (1000 °C), as shown in Fig. 9, and as isothermic until reaching to the optimum time (30 min), as shown in Fig. 10.

In Fig. 9-a, adding 5wt% calcium carbonate at the thermal range of 800-950 °C increased the rate of reduction percentage in comparison with the samples free of additives. However, as shown in Fig. 9-b, adding 5wt% calcium carbonate to coal resulted in a uniform escape of volatiles and products of coal thermal decomposition in comparison with the original samples free of additives.

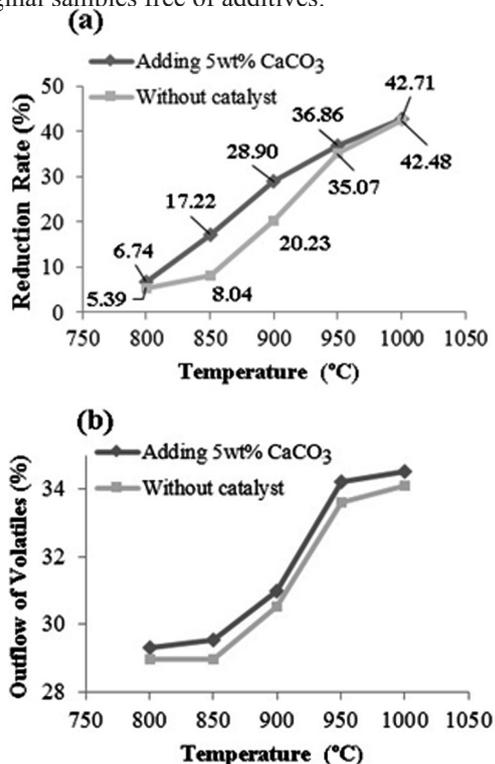


Fig. 9. The effect of adding 5wt% calcium carbonate to the coal layer on (a) the reduction rate of the hematite layer in the test crucible, and (b) the outflow of volatiles and pyrolysis products from the coal layer at different temperatures.

A reason for the increase in the reduction percentage of these samples can be the decrease in sulfur-containing oxidizing gases and the increase in H₂ and CO reducing agents in the escaped gases from coal. At temperatures higher than 820 °C, calcium carbonate was decomposed into CaO and CO₂^{13, 14}. It is known that at this temperature, the interaction between CaO and sulfur-containing compounds (generally H₂S and SO₂) is thermodynamically possible¹³. Therefore, the levels of oxidizing agents (sulfur-containing gases) were decreased at this thermal range in the reaction chamber and compounds with alkaline earth metals (such as calcium) acted as a catalyst to accelerate tar cleavage and reforming reactions and helped reducing hematite layer at the thermal range of 800-950 °C through increasing the percentage of reducing agents escaping from coal^{16, 17}. Meanwhile, the thermal decomposition of calcium carbonate at 820 °C and the release of CO₂, as well as the proper thermodynamic and kinetic conditions for Boudouard endothermic reaction (Eq. (3)), resulted in an increase in the percentage of reducing gases in the reaction chamber at the thermal range of 800-950 °C.

At temperatures higher than 900 °C, CaS and CaSO₄ were not stable and they were converted into CaO. Also, sulfur-containing reducing gases were found in gases escaping from coal at high temperatures¹⁸. On the other hand, the increased temperature resulted in the loss of the catalytic effect of calcium-containing particles; most importantly, this was due to the unfavorable reactions of these compounds with the organic materials in tar, as well as the toxicity of catalytic particles with the product of coal thermal dissociation¹². Therefore, because of the decrease in the reducing agents percentage and the reduction potential of gases escaping from coal and also, the slope of the reduction percentage curve in Fig. 9-a, the reducing rate of hematite layer was decreased at temperatures higher than 900 °C. Thus, according to the reported results in Fig. 9-a, the reducing rate of hematite layer was increased in samples containing calcium carbonate compared to the original samples (free of additives) at temperatures higher than 800 °C and lower than 950 °C.

According to Fig.10-b, the increased time at 1000 °C in the case of samples with 5wt% calcium carbonate significantly increased the escape percentage of volatiles and this increase caused an augmentation in the reducing rate in hematite layer, as shown in Fig. 10-a. At this temperature, no severe decline in the reduction percent was observed in comparison with other samples at 45 min. This difference was related to the level and the type of tar in the reaction chamber. The more the number and the larger the size of the hydrocarbon chains, the slower was the oxidation of reduced ferrous oxides in hematite layer. This was due to the performance of tar cleavage reactions because

of the high reduction potential of gases in the reaction chamber.

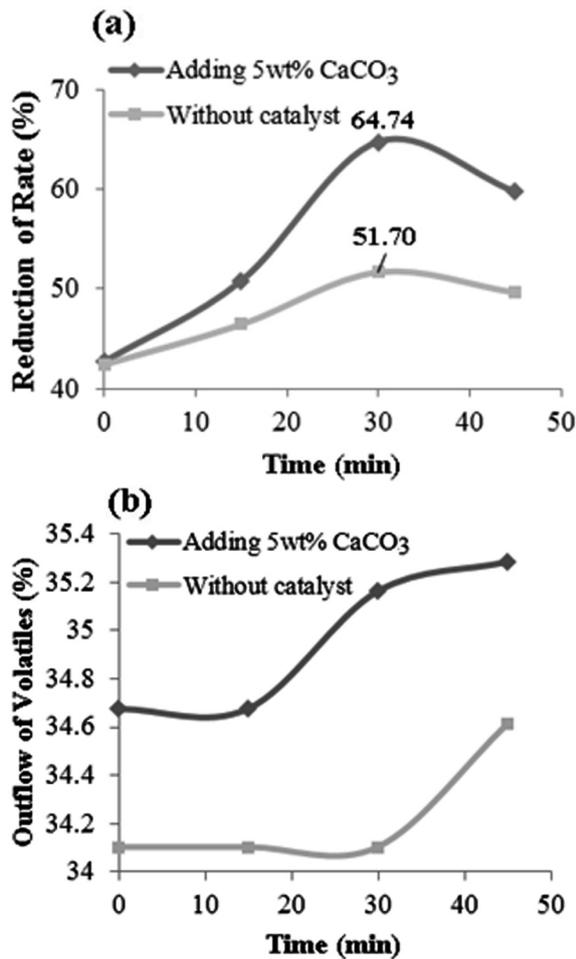


Fig.10. The effect of adding 5wt% calcium carbonate to the coal layer on (a) the reduction rate of the hematite layer in the test crucible, and (b) the outflow of volatiles and pyrolysis products from the coal layer at different holding times ($T=1000^{\circ}\text{C}$).

4. Conclusion

1. At lower temperatures, reduction rate was increased by increasing the temperature in the early stages and then it was decreased because of the reduced outflow of volatiles and the reducing agents.
2. The reduction process in the hematite layer was non-uniform in the vertical direction. However, the reduction reaction in the horizontal direction was uniform.
3. The maximum reduction rate was obtained to be at 1000°C within 30 minutes.
4. Adding 5wt% calcium carbonate (the optimal concentration) as the catalyst significantly increased the reduction rate of the non-coking coal.
5. The maximum reduction rate of 51.7-64.74% was

obtained by adding 5wt% calcium carbonate to the non-coking coal.

6. Approximately 74.90% of the volatiles exit the non-coking coal up to 800°C . At the higher temperatures, the reduction process was carried out by 25.10% of the volatiles and tar reforming and cracking reactions due to the favorable thermodynamic and kinetic conditions for reduction reactions. It should be noted that higher reduction rates were more dependent on increased temperature. Consequently, a maximum reduction rate of 64.74% could be achieved in the layered system using the volatiles and tar reforming and cracking at higher temperatures with some changes in the type and the duration of outflow through adding calcium carbonate catalyst to the non-coking coal.

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