

## An Investigation on the Reduction of Iron Ore Pellets in Fixed Bed of Domestic Non-Coking Coals

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### Abstract

In this study, the isothermal reduction of iron oxide pellets, made of Iranian Chadormalo, Gole-gohar, and Sangan iron ores, was investigated in the temperature range of 900-1100°C. Tabas, Pabdana, Babnizoo, Karmozd, and Shahrood domestic coals were used as reductants. Parametric studies were performed and the effects of such factors as temperature, average particle size of iron ore and coal fines, pellet size, and BaCO<sub>3</sub> additive on reduction process were investigated.

It was found that both the rate of reduction in the early stages of the process and overall reduction increased for all the iron ores used with increasing temperature. Overall reduction, however, decreased when the size of Sangan iron ore pellet increased. It was also observed that the rate of reduction decreased when the particle size of Sangan iron ore fines increased at the early stages of the process but increased thereafter during the process. The rate of reduction and the overall reduction in Sangan iron ore also increased considerably when BaCO<sub>3</sub> was added to Tabas coal at 1100 °C. Finally, a kinetic study was performed for reduction of Sangan iron ore using Tabas coal to determine the activation energy of the reduction reaction. It was found that the activation energy decreased from 159 to 133 kJ/mol by increasing the BaCO<sub>3</sub> content from 0% to 5%.

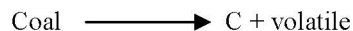
*Keywords:* Iron ore, Pellet, Direct reduction, Coal.

### 1- Introduction:

The direct reduction/electric arc furnace method has nowadays become the conventional route for steel making <sup>1,2</sup>. Lower capital and operation costs are some of the major factors favoring this route when compared to the traditional blast furnace and converter methods. In addition, coking operations are costly and environmentally problematic. Moreover, during mining of coal for use in the coke making process, considerable amounts of coal are wasted as non-coking coal. The abundance of non-coking coals and the relative cost of natural gas used as the reducing agent have stimulated interest in the potential use of less expensive coal or coal mining by-products to produce directly reduced iron <sup>3-6</sup>.

In the direct reduction process, oxygen is removed from the iron ore by reducing agents at temperatures

below the melting points of the constituents. In coal-based direct reduction processes, iron oxides are reduced by solid carbon, volatile matter, and reducing gas produced by gasification of the carbon in coal. Direct reduction of iron ore by solid carbon plays only a small role in reduction <sup>7</sup>. Volatile matter in the coal evolves and hydrocarbons in the volatile are cracked <sup>8</sup>:



The amount and the composition of volatile matter depend on the type and size of coal and the conditions prevailing in the reaction environment <sup>9</sup>.

It has now been accepted that direct reduction in the Fe-O-C system is mainly carried out via gaseous intermediates and the overall rate is controlled by the gasification of carbon. Many researchers have tried to study the true direct reduction reaction under the conditions of direct contact of iron oxide with carbon. They have reported about the significant role of H<sub>2</sub> in the reduction of pellets, which is produced through cracking of higher to lower hydrocarbons.

The work of Otsuka and Kunii <sup>10</sup> motivated a series of studies on iron oxide direct reduction with carbon. They showed that the reaction proceeded in two stages: 1) the reduction of an oxide to a sub-oxide or to a metal; and 2) the regeneration of carbon monoxide according to the Boudouard reaction. Specifically, hematite was reduced to magnetite, then

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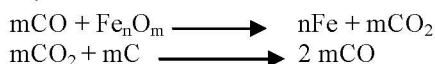
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to Wustite, and finally to metallic iron. Carbon dioxide produced by the reactions subsequently reacts with solid carbon to produce more carbon monoxide. This regeneration reaction was found to control the overall reaction rate. The final reduction stage could be represented by the following equations (11):



The literature on the so-called isothermal reduction studies confirms that a significant fraction of reduction actually takes place while the sample temperature is rising<sup>12,13</sup>. The direct reduction takes place by direct contact of iron ore fines with coal fines.

There are many coal deposits containing considerable amounts of non-coking coal fines. Moreover, many iron mines exist across a wide distribution of places. It is believed that the coal-based direct reduction of iron ore could be a suitable method of iron making. Therefore, direct reduction of Iranian iron ores by domestic coals and the effects of such factors as temperature, average particle size of iron ore and coal fines, pellet size, and BaCO<sub>3</sub> additive on the reduction process needed to be investigated; hence, the motivation for the present study.

## 2- Experimental:

### 2- 1- Raw materials

Different types of iron ores and coals from various Iranian mines were collected. Chemical analysis of the iron ores and coals used are presented in Tables 1 and 2, respectively.

### 2- 2- Sample preparation

Chadormaloo, Gole-gohar, and Sangan iron ores with an average size smaller than 74 μm were collected. In order to study the effect of particle size of iron ore fines on reduction, Sangan iron ore fines of different sizes between 105-149 μm and 149-177 μm were used, to which 2%wt of bentonite, as a

binder, and about 11%wt of water were added and mixed for 5 minutes. Pellets were made by hand with average diameters of 10, 12, and 15 mm. The pellets were kept in the air for 7 hours and, finally, dried at 110 °C for 2 hours. The dried pellets were then fired at 1200°C for about 2.5 hours. They were then kept in the desiccator before using in reduction experiments. In each series of experiments, six alumina crucibles of 30 ml capacity, containing a weighted oxide pellet embedded in coal bed, were used. Coal fines had an average size smaller than 420 μm. The crucibles were placed in the furnace at desired temperatures and reduction experiments were performed isothermally. Every 15 minutes, one of the crucibles was taken out of the furnace and cooled in the desiccator. Reduction degree was calculated based on the weight loss of pellets according to:

$$\text{Reduction degree} = (w_1 - w_2) / w_0 * 100$$

Where:

W<sub>1</sub> = weight of oxide pellet before reduction

W<sub>2</sub> = weight of oxide pellet after reduction

W<sub>0</sub> = total weight of oxygen combined with iron in pellet

## 3- Results and discussion:

### 3- 1- Effects of temperature, iron ore, and coal types on reduction:

Figures 1-9 show variations of reduction degree versus time at different reduction temperatures of 900°C, 1000°C, and 1100°C for different iron ores and coals studied. It is evident from Figures 1 to 9 that the maximum reduction degree obtained when Babnizoo and Pabdana coals were used. This behavior could be related to the higher carbon content of these two types of coal (more than 48%) compared with other types of coal used. They also showed lower ash contents. In all the samples and for all studied temperatures, reduction rate, obtained from the slopes of the curves, increased with increasing temperature in the early stages of the reduction process.

Table 1. Chemical composition of iron ores used (in wt%).

Source of Iron ore	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MnO	S	P	Fe <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>t</sub>
Sangan	0.5	1.05	0.01	2.11	0.071	0.001	0.012	71.52	23.55	68.37
Chador maloo	0.28	0.73	0.29	1.37	0.05	-	0.053	-	13.1	67.45
Gole-gohar	0.86	0.35	0.15	1.3	-	0.04	-	-	17.3	67.6

Table 2. Composition of domestic coals used.

Source of coal	Ash (wt%)	Volatile matter (wt%)	Fixed carbon (wt%)
Tabas	15.5	37	47.5
Babnizoo	12.1	28.2	48.8
Karmozd	11.7	30.7	45.24
Pabdana	12.2	28.9	48.08
Shahrood	13.7	25.3	47.16

At the initial stages of reduction process, when the samples reach the appropriate temperature, volatile materials are released intensively that take part in the reduction reaction. So, for most of the samples, the rate of reduction was considerably high in the first stage as a result of the volatile matter evolving from coal and the higher flux of heat due to the higher temperature gradient<sup>14</sup>.

Using this explanation and considering the highest content of volatile matter observed in Tabas coal (Table 2), the maximum reduction rate at the initial stages of reduction reaction was related to the reduction of Sangam iron ore in the bed of Tabas coal (Figure 2).

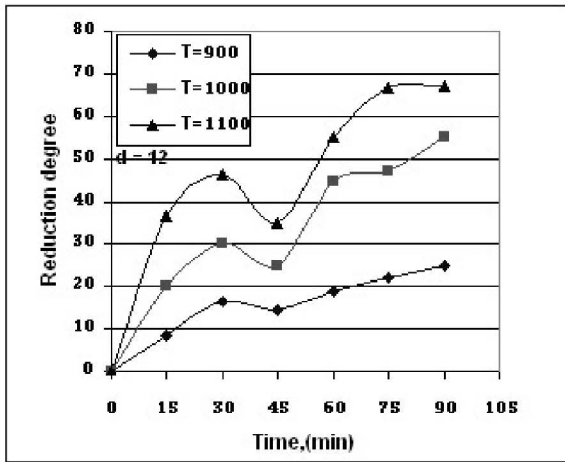


Fig. 1. Variations in reduction degree vs. time for different temperatures in Sangam iron ore pellet reduced by Tabas coal.

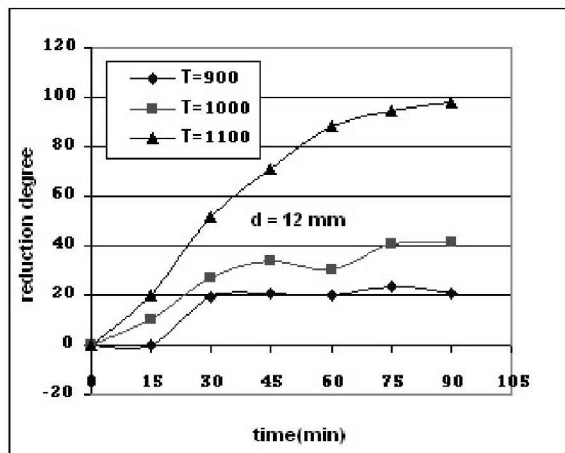


Fig. 2. Variations in reduction degree vs. time for different temperatures in Chadormaloo iron ore pellet reduced by Karmozd coal.

As the reduction process continues, the Boudouard reaction (carbon gasification) intensifies and the pressure of the reducing gas in the reduction atmosphere increases. When carbon monoxide forms and diffuses through the pellet, favorable conditions

for the reduction of iron oxide inside the pellet obtains.

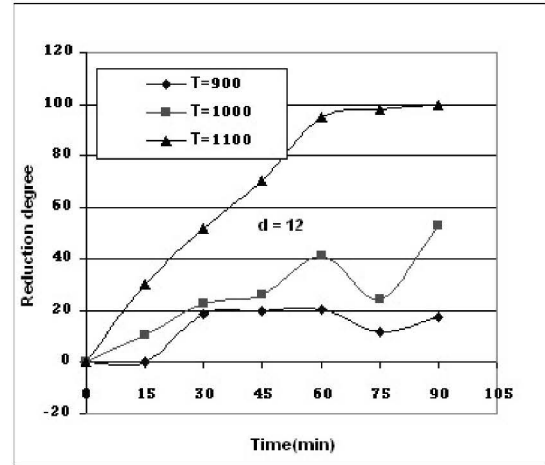


Fig. 3. Variations in reduction degree vs. time for different temperatures in Chadormaloo iron ore pellet reduced by Pabdana coal.

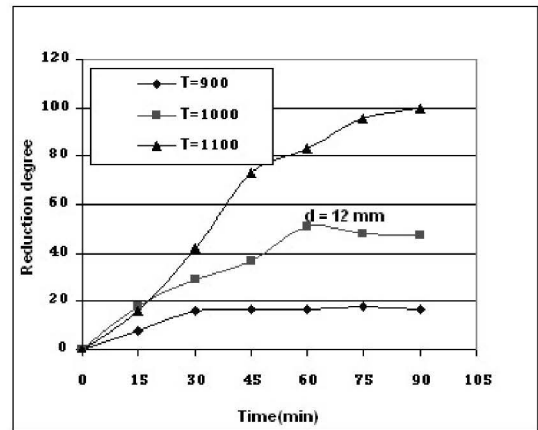


Fig. 4. Variations in reduction degree vs. time for different temperatures in Chadormaloo iron ore pellet reduced by Babnizoo coal.

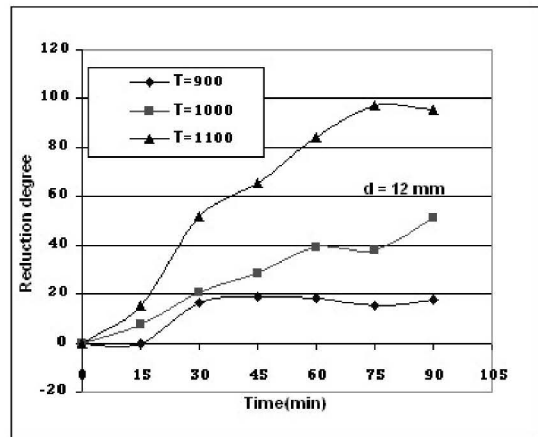


Fig. 5. Variations in reduction degree vs. time for different temperatures in Chadormaloo iron ore pellet reduced by Shahrood coal.

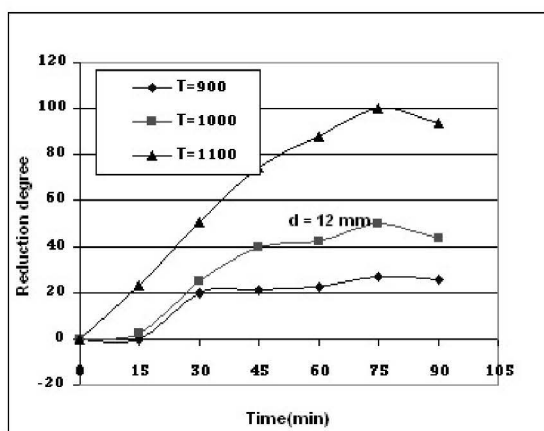


Fig. 6. Variations in reduction degree vs. time for different temperatures in Gole-gohar iron ore pellet reduced by Karmozd coal.

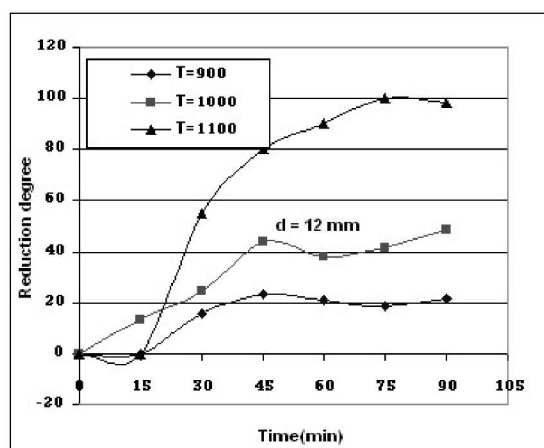


Fig. 7. Variations in reduction degree vs. time for different temperatures in Gole-gohar iron ore pellet reduced by Pabdana coal.

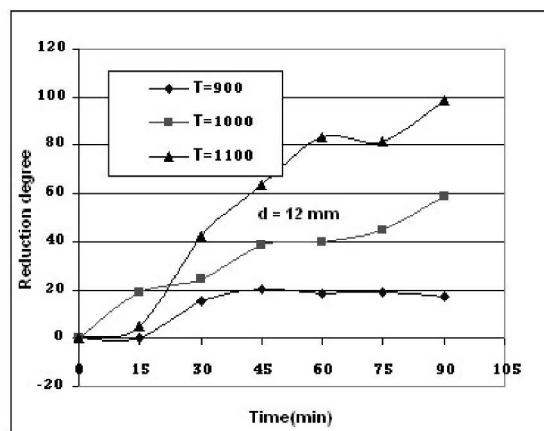


Fig. 8. Variations in reduction degree vs. time for different temperatures in Gole-gohar iron ore pellet reduced by Shahrood coal.

Ross et al. showed that the Boudouard reaction was the rate-controlling step of solid-state reaction<sup>15</sup>. The heat required for this highly endothermic reaction is easier to be supplied at higher temperatures. So, it leads to increased reduction rate

with increasing temperature. In most cases, the reduction proceeds at 900 °C up to about 20% as a result of the presence of the reducing gas formed by decomposition of volatile matter. But, the intensity of Boudouard reaction is very low at this temperature and causes a restriction on the reduction process.

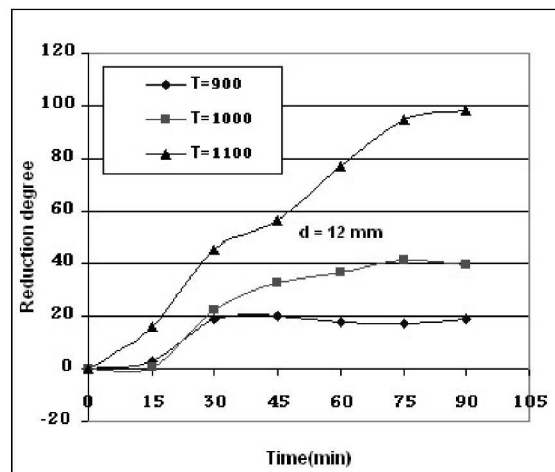


Fig. 9. Variations in reduction degree vs. time for different temperatures in Gole-gohar iron ore pellet reduced by Babnizoo coal.

Increasing temperature to 1000°C causes maximum reduction degree to reach 40-60%. In most samples, the reduction degree increases with time up to 45-60 minutes and remains almost constant after that. It is also observed in most samples that when the reduction degree reaches 30-40%, the reduction rate decreases and then increases again after a short while. The reasons for the decreasing reduction rate could be:

- 1) Formation of a sponge iron layer at the surface of the pellet which prevents the inward diffusion of the reducing gas.
  - 2) Lack of adequate reduction potential to reduce Wustite to metallic iron. The increase in reduction rate could be the formation of metallic iron which acts as a catalyst in the Boudouard reaction.
- At 1100 °C, the maximum reduction degree of the samples was between 95% and 100%, except for Sangan Iron ore reduced in Tabas coal. This is caused by the increasing of reduction potential (CO/CO<sub>2</sub> ratio), resulting from temperature increase. In the primary stage of reduction, a poor reduction potential is enough to transform hematite and magnetite to Wustite. But reduction of Wustite to metallic iron requires more strong reduction potential. The same explanation can be used for Sangan iron ore. Since Wustite percentage (23.55%) in Sangan iron is higher compared with other iron ores, a less reduction degree is obtained.

### 3- 2- Effect of iron ore particle size

Figure 10 shows variations of reduction degree versus time for different particle sizes of

Sangan iron ore fines. The temperature of the reduction process and the diameter of the pellet were 1100°C and 12mm, respectively.

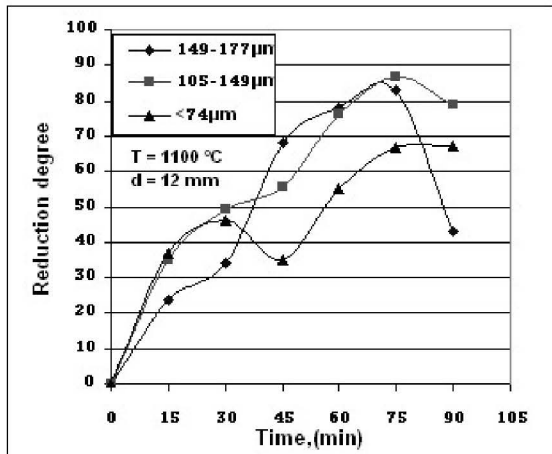


Fig. 10. Variations in reduction degree vs. time for different particle sizes of iron ore.

The results show that at the beginning of the reduction process, the reduction degree decreases with increasing particle size of Sangan iron ore fines. This may be due to poor contact between particles of coal and iron ore when the particle size increases. It should be mentioned that direct reduction with solid carbon is the main reaction in the first step. In the next stage of the reduction process, as shown in Figure 10, reduction degree increases with increasing particle size of iron ore fines. This behavior could be related to the increasing pore size due to coarsening of iron ore fines and the decreasing of resistance to gas flow through the pellet.

### 3-3- Effect of size of pellet

Variation of reduction degree vs. time at different sizes of pellets made of Sangan iron ore is shown in Figure 11. In this series of experiments, reduction temperature was 1100 °C and particle sizes of Tabas coal and iron ore were about 420 and 74 μm, respectively. The results show that the reduction degree decreases with increasing pellet size. This may be due to the fact that the surface to volume ratio decreases with increasing pellet diameter which leads to the decreasing of contact surface area between iron oxides and reducing agents.

### 3-4- Effect of BaCO<sub>3</sub> addition

Reduction degree–time plots for different percentages of BaCO<sub>3</sub> containing coals and Sangan iron ore are shown in Figure 12. It can be seen that addition of BaCO<sub>3</sub> to the coal considerably increases reduction degree. The effect of adding BaCO<sub>3</sub> to the coal at the first stages of reduction was negligible. This is due to the fact that, in the first stages, the

reduction reaction is mainly accomplished by the volatile matter from coal.

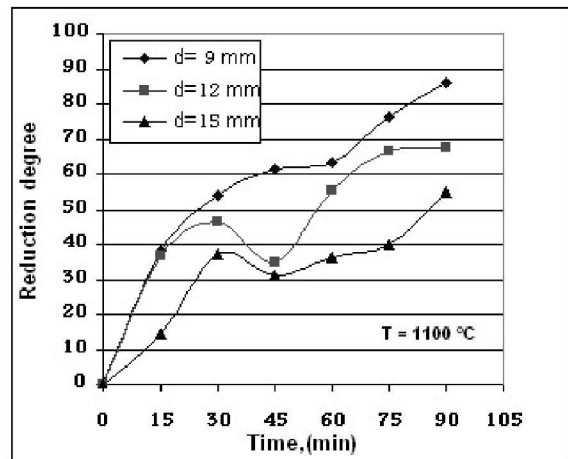


Fig. 11. Variations in reduction degree vs. time for different sizes of oxide pellets.

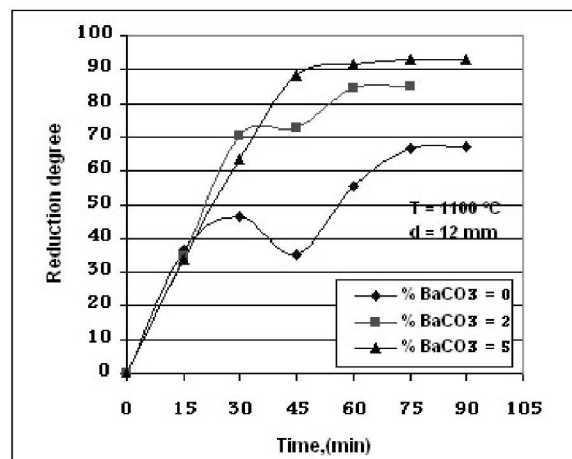


Fig. 12. Variations in reduction degree vs. time for different quantities of BaCO<sub>3</sub>.

Meanwhile, because of the low temperature during the initial stages of the reduction process, the conditions are not suitable for BaCO<sub>3</sub> decomposition and CO<sub>2</sub> generation. Subsequently, reduction degree increases in the next step of the reduction process as a result of BaCO<sub>3</sub> decomposition and increasing amounts of CO<sub>2</sub>, which reacts with solid carbon to produce CO. Moreover, researchers have pointed out the catalytic effect of BaCO<sub>3</sub> on the reduction process.

### 3-5- Evaluation of activation energy

The kinetics of the direct reduction process is complex and many models have been developed in this regard. To ensure that an appropriate kinetic model is developed, the functional values of G(R) are first calculated. Different kinetic models were examined by using experimental data obtained in the present study. It was found that the experimental data

would fit in the Ginstling–Brounshtein equation (1)

$$G(R) = 1 - 2/3R - (1-R)^{2/3} = kt \quad (1)$$

The experimental data obtained for Sangan iron ore reduced by 5% BaCO<sub>3</sub> contained Tabas coal were used for model evaluation. The results are shown in Figure 13.

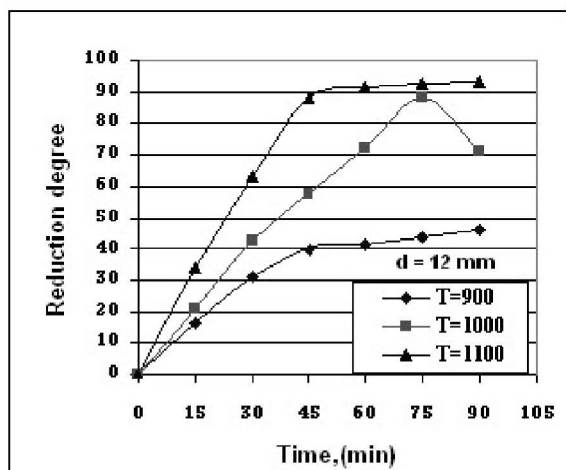


Fig. 13. Variations in reduction degree using Tabas Coal and 5% BaCO<sub>3</sub> versus time.

Figures 14 and 15 show the plot of experimental results according to the Ginstling–Brounshtein equation. The model shows that the reduction process is controlled by diffusion.

The slopes of the lines in Figures 14 and 15 give the values of k at a given temperature. In order to obtain the activation energy, variation of LnK versus T<sup>-1</sup> were plotted. According to the Arrhenius Equation (equation 2), activation energy was calculated. Figure (16) show the Arrhenius plots using Figures 14 and 15.

$$K = A \exp(-E/RT) \quad (2)$$

Activation energies were calculated and had values of 159 and 133 kJ/mol for 0 and 5% BaCO<sub>3</sub> contained Tabas coal, respectively.

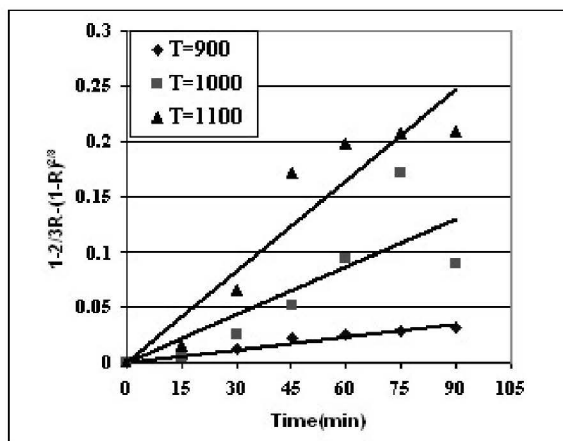


Fig. 14. Experimental data fitted in Ginstling–Brounshtein equation.

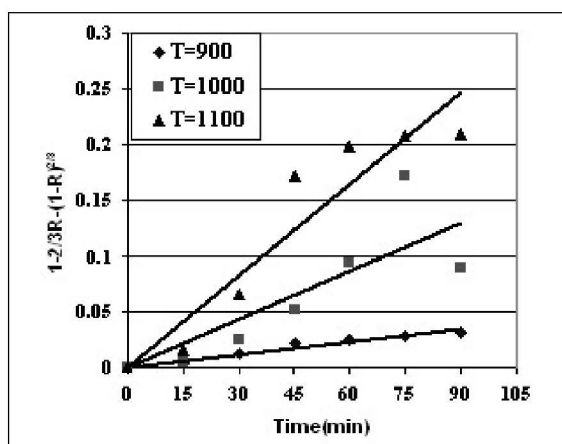


Fig. 15. Experimental data fitted in Ginstling–Brounshtein equation, in the reduction process using Tabas coal by adding 5% BaCO<sub>3</sub>.

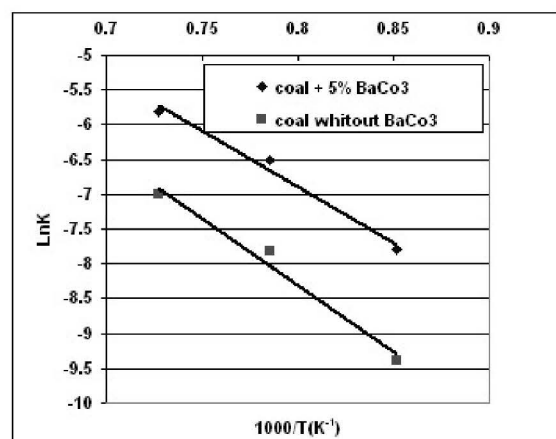


Fig. 16. Arrhenius plot resulting from Figures 14 and 15.

#### 4- Conclusions

- In all samples and for all studied temperatures, reduction rate increased with increasing temperature during the first stage of the reduction process.
- Maximum reduction degree was obtained with the higher carbon contents of Babnizoo and Pabdana coals (greater than 48%).
- A lower reduction degree was obtained with Sangan iron ore due to its higher Wustite content (23.55%) compared with other iron ores.
- In the initial stages of the reduction reaction and considering the highest content of volatile matter in Tabas coal, maximum reduction rate belonged to Sangan iron ore in the bed of Tabas coal.
- At the beginning of the reduction process, the reduction degree decreased with increasing particle size of Sangan iron ore fines; but in the next stage of the reduction process, reduction degree increased with increasing of particle size of iron ore fines.
- The reduction degree decreased with increasing Sangan pellet size, and vice versa.
- Addition of BaCO<sub>3</sub> to the Tabas coal considerably increased the reduction degree.

- By adding BaCO<sub>3</sub> from 0% by up to 5% to Tabas coal, activation energy decreased from 159 to 133 kJ/mole, so that the degree of reduction increased considerably.

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