The Effect of Lime Coating of Hematite Pellets on Soot Formation and Reduction Rate with CH_4/H_2

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In some of the Direct Reduction (DR) methods, the iron oxides would be reduced with reformed natural gas. Due to the reduction conditions, temperature, gas flow, pressure, and the component of the reducer gas, the decomposition of CH_4 , and CO to C_{sol} /soot formation on the surface of the pellets is possible. Consequently, the rate of reduction, and the consumption of the reducer gas could be changed. In this research, the effect of coated hematite pellets with lime on the reduction rate of iron oxides, and also C_{sol} /soot formation, is reported. By increasing of 3–8 % lime on the surface of the pellets with a diameter of 10 mm, 15–40 % H_2 in H_2/CH_4 mixture, and 1 050 to 1 250°C reaction temperature, the rate of C_{sol} /soot formation is decreased, and the rate of reduction is increased.

KEY WORDS: double-layer pellet; direct reduction; lime coating of pellet; CH_4 and CO decomposition; C_{sol} /soot formation; effect of temperature; reducer gas component on the reduction rate.

1. Introduction

In the recent decades, the technology of sponge iron production, by direct reduction (DR) methods have been improved. In some of the DR methods, the natural gas, and in some others, coal or coke is used as reducing agent.^{1–3)} The most important factors, which affect the rate of reduction, are the size, reducibility, porosity of the pellets, and also the reduction temperature.⁴⁾ Due to need of a higher production rate, the reduction would be carried out at high temperature as much as possible. By injection of limited oxygen in the reducer gas, its temperature and consequently, the reduction rate increase.⁵⁾ The sintering and cluster formation of the pellets by the reduction and their reducibility by the production of DRI, and also the resistance of DRI to oxidation are the most important factors.^{6–8)} Lime coating of pellets exhibits sintering of the DRI, and could decrease the reduction rate. This depends on physical and chemical properties of the pellets, the reducer gas composition, and the conditions of reduction. C_{sol} /Soot formation over reduction, could affect the rate of reduction. Lime coating of pellets could also change their reducibility.^{6,9,10)}

The reducer gas, which includes H_2 , CO, CH_4 are used for reduction of iron oxide according to the following reactions:

By Midrex DR, reforming of the natural gas with exhaust gas, including CO_2 and H_2O , could be carried out in a gas reformer by a catalyst at 950°C. In modified H.Y.L 3, Midrex, and Ghaem, the reducer gas is produced by partial oxidation of the natural gas in a reactor with O_2 .^{11–14)} Because of the higher temperature of the reducer gas almost at 1 050°C, and its transition to the furnace, a part of CH_4 decomposed according to the reaction (4):

C_{sol} /Soot formation could decelerate the transition of CO and H_2 into the hematite pellets, and decrease the rate of sponge iron production. Based on CH_4 cracking, which is an endothermic reaction, the temperature of the reducer gas, decreases. Decreasing of temperature in Boudouard reaction (reaction (5)), produces more C_{sol} /Soot:

2. Materials and Methods

The iron ore, used in Khuzestan steel company (**Table 1**), was mixed with 2% bentonite, and 8% water for produc-

Table 1. The chemical composition of the used iron dry ore for production of the pellets at Khoozestan steel company.

Component of the pellet	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	P	S
Weight %	10.01	85.67	2.09	0.35	0.48	0.38	0.051	0.034

Table 2. The chemical composition of bentonite, which was used in this experiment.

Chemical Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	TiO ₂	CaO	MgO	P ₂ O ₅	Na ₂ O	K ₂ O
Weight %	64.75	19.8	4.22	0.56	2.55	2.06	2.95	0.19	0.9	1.94

tion of the pellets. The pellets are produced in a pelletizing disc with 11 mm in diameter. The rotation of disc was 10 rpm within a period of 10 to 15 min. The pellets were then soaked in a mixture of 40 mL water, containing CaO (3 to 8%, equals to 0.15 to 0.4 g), and bentonite (1%, equals to 0.05 g). **Table 2** shows the chemical composition of bentonite, which was used in this experiment. A mechanical shaker with a speed of 2300 rpm was used to avoid the precipitation of the CaO in water. The coated pellets were dehydrated for 4 h at 130°C, and sintered for 2 h at 800°C, respectively.

The effects of temperature, coating CaO, and H₂ in H₂/CH₄ mixture on the final rate of reduction, and the produced C_{Sol}/Soot over reduction were measured by TGA with accuracy of ±0.0001 g. To wash the reactor before running any experiment, N₂ was flown in the reactor of furnace (**Fig. 1**) and then temperature was set.¹⁵⁾ The pressure of the N₂, H₂, and the CH₄ mixture was one atmosphere. The gas flow was controlled constantly, and set with a flow-meter. The flow of N₂ and CH₄ was 50 NL/h and 20 NL/h, respectively. The primary weight of the pellets, and their changes over reduction were measured. The experiments were run under isothermal conditions as shown in the **Table 3**.

The pellets were located in a metal basket, which was connected to thermo-balance by a chain at the reduction zone under constant temperature. The reduction zone was detected by a thermocouple. The changes of weight of the pellets were measured, and the reduction of the iron oxides (*R*) was calculated according to Eq. (6):

$$R = \frac{(m_{O,0} - m_O)}{m_{O,0}} \times 100 \quad \text{.....(6)}$$

In Eq. (6), *m*_{O,0} is the primary Oxygen of pellet, *m*_O is the Oxygen at the reduction time (*t*). The reduction of pellet over time, based on the 60% of the reduction, was determined, and the reduction rate constant (*k*) was calculated according to Eq. (7):

$$k = \frac{R_{60}}{t} \quad \text{.....(7)}$$

To measure *m*_{O,0}, the weights of MgO, CaO, P, S, Al₂O₃, and SiO₂ were subtracted from the primary weight of the pellets, and then the *R* is calculated. The experiment was stopped at the time, which the reduction rate was equal or

lower than the rate of C_{Sol}/Soot formation. The sample was then cooled down by N₂, taken out of furnace, and its weight was measured after removing the soot. The change of the weight can be observed according to:

- Decreasing the weight of the pellets due to reduction of iron oxides with N₂/H₂ mixture.
- Increasing the weight of the pellets due to C_{Sol}/Soot formation.

The weight change (Δm), was calculated according to Eq. (8):

$$\Delta m = \Delta m' + \Delta m'' \quad \text{.....(8)}$$

In Eq. (8), $\Delta m'$ is weight decrease of the pellets due to reduction, and $\Delta m''$ is weight increase of pellets due to C_{Sol}/Soot precipitation which is calculated at any 10-min interval. After 60% reduction, the precipitated C_{Sol}/Soot on the pellets was removed.

3. Results and Discussions

Figure 2 shows the reduction of pellets, coated with 8% CaO in H₂/CH₄ mixture with 40% H₂, over the time at different temperatures. The rate of reduction of hematite to magnetite (Fe₃O₄), and wustite (Fe_{1-x}O) is also shown in this figure. **Figures 3 to 6** show the precipitated C_{Sol}/Soot on the pellets over the time of reduction.

Figures 7 and 8 show the reduction rate constant (*k*) of pellets, coated with 3 to 8% CaO, at different temperatures. The reduction rate constant increased by increasing of temperature according to Arrhenius equation (Eq. (9)):

$$k = k_0 e^{-\frac{E_a}{RT}} \quad \text{.....(9)}$$

The reduction rate constant, was also increased by increasing of H₂ in the H₂/CH₄ gas mixture. The main purpose of the experiments was to study the effect of CaO on C_{Sol}/Soot formation on the surface of the pellets. **Figures 9 and 10** show the dependence of the reduction rate constant on CaO, coated on the pellets. **Figures 11 and 12** show the effect of the coating lime on the precipitated C_{Sol}/Soot over the pellets. The figures show that at a constant temperature, the reduction rate constant and consequently, the reduction rate were increased by increasing of coating lime. Also, by constant amount of CaO, the reduction rate constant was increased by increasing of the temperature. Increasing the coating lime on the pellets, decreased the amount of the precipitated C_{Sol}/Soot.

Fig. 1. A schematic figure of the reactor, used for the measurement of the weight alterations of the pellet during reduction.¹⁵⁾

Table 3. The isothermal conditions of the experiments.

Temperature (°C)	1050, 1100, 1150, 1200, 1250
Coating lime (%)	3, 5, 8
Hydrogen, mixed with CH ₄ (%)	15, 25, 40

Because of the coating lime, the following reactions also carried out under the experimental conditions:

On base of the exothermic reaction (10), CaO reacted with CH₄, and produced CaC₂, CO and H₂. Consequently,

Fig. 2. The reduction of pellets, coated with 8% CaO in H₂/CH₄ with 40% H₂.

Fig. 3. The precipitated soot on the surface of the pellets, coated with 3% CaO, reduced in the mixture of H_2/CH_4 with 15% H_2 .

Fig. 4. The precipitated soot on the surface of the pellets, coated with 3% CaO, reduced in the mixture of H_2/CH_4 with 40% H_2 .

Fig. 5. The precipitated soot on the surface of the pellets, coated with 8% CaO, reduced in the mixture of H_2/CH_4 with 15% H_2 .

on base of the exothermic reaction (11), CaC_2 reduced hematite to magnetite, and CaO produced, and the reduction process continued. By increasing of CaO, CH_4 , and production of CaC_2 , on base of reaction (10), less CH_4 would be available to be decomposed for $C_{Sol}/Soot$ formation (reaction (4)).

At higher temperature, the decomposition of CH_4 in the reducer gas, produce $C_{Sol}/Soot$ on the pellets (reaction (4)), which reduces the reduction rate, and is also used for carbide production (reaction (13)). Under the constant condi-

Fig. 6. The precipitated soot on the surface of the pellets, coated with 8% CaO, reduced in the mixture of H_2/CH_4 with 40% H_2 .

Fig. 7. The dependence of the reduction rate constant on temperature for the pellets, coated with 3% CaO, reduced in mixture of H_2/CH_4 with 15, 25, and 40% H_2 .

Fig. 8. The dependence of the reduction rate constant on temperature for the pellets, coated with 8% CaO, reduced in the mixture of H_2/CH_4 with 15, 25, and 40% H_2 .

tions of reduction, increasing of hydrogen in the reducer gas, increase the reduction rate.

It is to consider that by increasing the temperature, the $C_{Sol}/Soot$ formation increases due to the decomposition of CH_4 (reaction (4)), but less amount of $C_{Sol}/Soot$ precipitated on the pellets at higher temperature because the reac-

Fig. 9. The dependence of reduction rate constant to coating CaO of the pellets, reduced in the mixture of H_2/CH_4 with 15% H_2 .

Fig. 10. The dependence of reduction rate constant to coating CaO of the pellets, reduced in the mixture of H_2/CH_4 with 40% H_2 .

Fig. 11. The dependence of soot formation with coating CaO on the pellets, reduced in the mixture of H_2/CH_4 with 15% H_2 .

tion (10) is exothermic. On the other hand, the production of CaC_2 and consequently, the consumption of CH_4 and CaO increase.

The activation energy (E_a) was about 31.62 and 26.60 kJ per mole by 3 and 8 wt% of lime (Figs. 6 and 7). It shows that a chemical reaction could control the rate of reduction.

Under the constant conditions of reduction, the reduction rate was increased by increasing the coating lime concentration over the pellets. Because the reaction of CaO with CH_4 inhibits the soot formation, which retards the reduction

Fig. 12. The dependence of soot formation with coating CaO of the pellets, reduced in the mixture of H_2/CH_4 with 40% H_2 .

rate (Figs. 8 and 9).

According to the reaction (12), and under the experimental conditions, CO is produced due to the combination of steam with $C_{Sol}/Soot$, which is formed during the decomposition of CH_4 (reaction (4)). CO_2 is produced due to the reduction of iron oxides by CO over the reactions (1) to (3). According to Boudouard reaction, CO is produced due to the reaction (5). The iron carbide (Fe_3C) could be produced in the reaction (13), and sponge iron, produced over the reduction.

CaC_2 , produced by the reaction (10), reduces iron oxide, and also forms CO (reaction (11)). Decreasing the amount of soot slows down the reaction (13) which causes the production of less amount of iron carbide.

The produced CaC_2 in the reaction (10), is used for the reaction (11) to reduce the iron oxides. Therefore it is anticipated that this phase (CaC_2) can not be found at the metallographic inspections at the end of the reduction process. CaO is used in the reaction (10) to produce CaC_2 , and then produced by the reduction of hematite with CaC_2 during the reaction (11). Considering the reactions, carried out by the coating lime over the hematite pellets, it speeds up the reduction process, and slows down the production of obstructive elements. In fact, lime plays as a catalyst.¹⁶⁾

4. Conclusions

(1) Increasing the time of reduction increases the reduction degree of iron oxide. The rate of reduction reaches the maximum at the beginning, then it gradually slows down, and finally reaches to the constant value. At the beginning of the reduction process, the chemical reaction, but at the end, the diffusion through the produced layers of iron oxides, spongy iron, or $C_{Sol}/Soot$, are the controlling mechanisms of the reduction rate.

(2) By increasing the time of reduction, and almost in a linear regression, the amount of $C_{Sol}/Soot$ formation on the surface of the pellets increases.

(3) Under the constant composition of the reducer gas, and the amount of the coating lime, increasing the temperature has negative effect on the soot formation over the pellets.

(4) Under the constant temperature, increasing the percentage of hydrogen in the reducer gas, and also coating

lime over the pellets, has negative effect on the soot formation but positive effect on the reduction rate.

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