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$_{soot}$/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$_{soot}$/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$_{soot}$/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$_{soot}$/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 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$_{soot}$/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:

\[
3\text{Fe}_2\text{O}_3 + \text{H}_2(\text{CO}) = 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}(\text{CO}_2)................................(1)
\]

\[
\text{Fe}_3\text{O}_4 + \frac{1-4X}{1-X}\text{H}_2(\text{CO}) = \frac{3}{1-X} \text{Fe}_{1-x}\text{O} + \frac{1-4X}{1-X}\text{H}_2\text{O}(\text{CO}_2)........................(2)
\]

\[
\text{Fe}_{1-x}\text{O} + \text{H}_2(\text{CO}) = (1-x)\text{Fe} + \text{H}_2\text{O}(\text{CO}_2)........................(3)
\]

By Midrex DR, reforming of the natural gas with exhaust gas, including CO$_2$ and H$_2$O, 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$_2$. By increasing of 3–8% lime on the surface of the pellets, due to 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):

\[
\text{CH}_4 = \text{C} + 2\text{H}_2, \quad \Delta H^\circ > 0..........................(4)
\]

C$_{soot}$/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 Boudward reaction (reaction (5)), produces more C$_{soot}$/Soot:

\[
2\text{CO} = \text{CO}_2 + \text{C}, \quad \Delta H^\circ < 0..........................(5)
\]

2. Materials and Methods

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

\[ R = \frac{(m_{0,0} - m_O)}{m_{0,0}} \times 100 \] ......................(6)

In Eq. (6), \( m_{0,0} \) 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):

\[ k = \frac{R_{60}}{t} \] ......................(7)

To measure \( m_{0,0} \), 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 \( \Delta m \), was calculated according to Eq. (8):

\[ \Delta m = \Delta m' + \Delta m'' \]...........................(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 (Fe₁₋ₓO) 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)):

\[ k = k_0 e^{-\frac{E_a}{RT}} \] ......................(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.

| Component of the pellet | FeO   | Fe₂O₃ | SiO₂ | Al₂O₃ | CaO   | MgO   | P     | S     |
|-------------------------|-------|-------|------|-------|-------|-------|-------|-------|
| Weight %                | 10.01 | 85.67 | 2.09 | 0.35  | 0.48  | 0.38  | 0.051 | 0.034 |

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

| Chemical Composition | SiO₂ | Al₂O₃ | Fe₂O₃ | FeO  | TiO₂ | CaO   | MgO   | P₂O₅ | Na₂O | K₂O |
|----------------------|------|-------|-------|------|------|-------|-------|------|------|-----|
| Weight %             | 64.75| 19.8  | 4.22  | 0.56 | 2.55 | 2.06  | 2.95  | 0.19 | 0.9  | 1.94|

Table 2. The chemical composition of bentonite, which was used in this experiment.
Because of the coating lime, the following reactions also carried out under the experimental conditions:

\[
3\text{CH}_4 + \text{CaO} = \text{CaC}_2 + \text{CO} + 6\text{H}_2, \quad \Delta H^F < 0 \quad \text{(10)}
\]

\[
\text{CaC}_2 + 9\text{Fe}_2\text{O}_3 = 6\text{Fe}_3\text{O}_4 + \text{CaO} + 2\text{C}, \quad \Delta H^F < 0 \quad \text{(11)}
\]

\[
\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2, \quad \Delta H^F > 0 \quad \text{(12)}
\]

\[
3\text{Fe} + \text{C} = \text{Fe}_3\text{C}, \quad \Delta H^F < 0 \quad \text{(13)}
\]

On base of the exothermic reaction (10), CaO reacted with \text{CH}_4, and produced \text{CaC}_2, \text{CO} and \text{H}_2. Consequently,
on base of the exothermic reaction (11), CaC₂ reduced hematite to magnetite, and CaO produced, and the reduction process continued. By increasing of CaO, CH₄, and production of CaC₂, on base of reaction (10), less CH₄ would be available to be decomposed for C₆₀/Soot formation (reaction (4)).

At higher temperature, the decomposition of CH₄ in the reducer gas, produce C₆₀/Soot on the pellets (reaction (4)), which reduces the reduction rate, and is also used for carbide production (reaction (13)). Under the constant conditions of reduction, increasing of hydrogen in the reducer gas, increase the reduction rate.

It is to consider that by increasing the temperature, the C₆₀/Soot formation increases due to the decomposition of CH₄ (reaction (4)), but less amount of C₆₀/Soot precipitated on the pellets at higher temperature because the reac-
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 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 Boudward reaction, CO is produced due to the reaction (5). The iron carbide (Fe$_3$C) 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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