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Abstract
In this research, the effects of oxygen injection during the induration process were studied in order to improve the quality specifications and increase the rate of production of the iron oxide pellets. Several experiments were carried out in palletizing pilot plant in different conditions of oxygen injection. The results suggested that if only the extra oxygen was injected into the furnace in a specific range of time and temperature, shortening of the time of heating process and increasing the rate of production in the induration machine could be achievable. Furthermore, the optimal condition for oxygen injection into the combustion gas was determined for the pellets containing the coke powder. The microstructures of a cross section of the pellets were investigated via scanning electron microscopy. The results showed that oxygen injection into the furnace provided the condition for the production of a uniform homogenous structure without cracks and microstructure defects in iron ore pellet.

Keywords: Magnetite, Oxygen injection, Iron ore pellet, Coke powder.

1. Introduction
To compete with foreign suppliers, Mobarakeh Steel Co. (located in Middle East, Iran) needs developing innovative technologies for producing superior iron ore pellets at lower costs. This is achieved partly by regulating oxygen concentration in the process gas and the time available before the peak induration temperature is reached.

In the pelletizing process, different types of iron ore concentrates such as hematite, hematite-magnetite and magnetite iron ores are used. In magnetite concentrates, the oxidation reaction is highly exothermic and it actually provides more than two-thirds of the total sintering energy in pelletizing. Therefore, it is more appropriate to use magnetite concentrate for saving more energy. Coke breeze and other solid fuels are successfully used in the production of pellets from hematite and hematite-magnetite concentrates. Part of hematite concentrates will be reduced and converted to magnetite with adding solid fuels to raw materials mixture by burning coke powders in the induration furnace.

At first, the bed of wet green pellets is transported through the drying zones such as updraft and/or downdraft drying. After drying, the bed is transported through the temperate preheat zone. In this zone, the main part of magnetite oxidation takes place. The temperature of the incoming gas at the preheat zone is around 1150–1250 °C and the oxygen content of the gas is 16 to 18%. The traveling time through the preheat zone is 6 to 7 min. During this time, the upper part of the pellet bed is heated up to the gas temperature, while the bottom of the pellet bed barely reaches 1000 °C. After the preheat zone, the pellets are transferred to the firing zone and sintered at around 1280 °C.

The oxidation of magnetite particles takes place in two main steps. The first oxidation step runs at low temperatures, below 350 °C. The second step starts soon after the low temperature oxidation is finished and completed between 900 and 1100 °C in magnetite concentrates of typical pelletizing fineness. The oxidation and thermal history of pellets also influence the final pellet quality. The purpose of commercial pelletizing furnaces is to complete the conversion of most magnetite to hematite during the preheat period or at least early in the firing process to aid in the heating of the pellets. In a straight-grate, less than half of the magnetite to hematite conversion occurs during the preheat period and most of the oxidation takes place during the induration period.

Pape et al. reported that the reason why sufficient oxidation is not attained in the preheat portion of the firing operation is the residence time. Increasing the oxygen concentration during this short time should increase the percentage of magnetite oxidation, thereby permitting higher production rates.

Oxidation of magnetite was best accomplished when sufficient oxygen and time were available before the peak induration temperature was reached. The rate
of magnetite oxidation was increased directly with the gas oxygen content during the preheat period at 700 °C and above. With 30% (or more) oxygen in process gas and a preheat rate of 200 °C/min, most magnetite was oxidized during the preheat period \(^3\). At lower oxygen levels and/or higher preheat rates, a duplex structure will be formed. In this situation, more coalescing (sintering) of the magnetite particles occurs in the pellet core. This coalescing action results in the shrinking and cracking of the magnetite in the pellet core that is often pulled away from the hematite shell. This is because the outer shell of pellets is oxidized before the sintering temperature is reached \(^7,8\).

In this research, the effect of enriching the oxidizing gas in the preheat zone and the firing zone was studied to improve the quality properties of the oxide pellets. Furthermore, in order to shorten the time of induration process, the best conditions for oxygen injection into the process gas were obtained for pellets containing the solid fuel.

2. Materials and Methods

Experimental measurements were carried out by hematite-magnetite concentrate for making iron ore pellets. The chemical composition of this concentrate is given in Table 1.

<table>
<thead>
<tr>
<th>Component content in the concentrate (%)</th>
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<tbody>
<tr>
<td>Fe(_{\text{tot}})</td>
</tr>
<tr>
<td>67.65</td>
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</table>

The additive to the fine iron ore (85% of particle number with the size being less than 45 µm), their amount, as well as chemical compositions to make green pellets are presented in Table 2. According to this Table, two types of green pellets- one containing coke breeze and the other without coke breeze- were prepared for the tests.

To study the effects of oxygen injection on the quality and metallurgical properties of pellets in distinct layers of green pellets beds, some tests were performed using pilot pellet indurative plant. This plant had a cylindrical crucible (35 cm diameter and 50 cm height) which could handle about 100 kg of green pellets. To record the pellets temperature differences in distinct layers of the bed, four thermocouples in 10 cm intervals of each other were inserted through the pellet bed. All thermocouples were located in the center of the cylindrical crucible. The first thermocouple, that was located at top of the bed, was considered as the reference point for the temperature control in the induration furnace. The heat profile, imposed on the reference thermocouple (T1) as set points temperature, is shown in Figure 1.

![Fig. 1. Temperature profile of reference thermocouple (T1) during the firing regime.](image)

In tests using the coke powder as the solid fuel in the composition of raw materials, the maximum induration temperature was 20 °C less than the ones without coke. In tests that did not use injected extra oxygen, oxygen enough only for combustion reactions was included in the pipe of air transfer. But in pellet induration tests, the required oxygen entered the combustion chamber through a separated nozzle using enriched oxygen gas (Figure 2). Finally, after performing each test in the pilot plant, pellets around each thermocouple were sampled and compression strengths of them were analyzed. In each sampling, 30 pellets were chosen in random, and their strength was measured through compression strength measuring test. The processed microstructure pellets were then assessed by Scanning Electron Microscopy (SEM). To prepare microscopic samples, the pellets underwent the cold mantle treatment by resin epoxy; after that,

<table>
<thead>
<tr>
<th>Type</th>
<th>Raw materials compound of green pellets</th>
<th>Chemical analysis of iron ore concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iron ore powder (wt%)</td>
<td>Bentonite (wt%)</td>
</tr>
<tr>
<td>1</td>
<td>90.8</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>90.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>
the surface preparation of samples was done by silicon carbide sandpapers with different grits (80, 150, 320, 600 and 1000). After surface washing treatment by alcohol, the samples were placed in an oven to dry completely.

3. Results and Discussion

In all induration tests and in pilot plant, the chemical composition and physical properties of the green pellet used were considered constant. Therefore, just by controlling the thermal profile and using oxygen in pilot furnace, we could reach an optimized condition for producing the fired pellets with the desired physical and metallurgical properties. In Table 3, the lists of pilot induration tests, as well as the test results on fired pellets in distinct layers of the bed are presented.

Comparing the results of tests 1 and 2 in Table 3 suggests that in an induration process, without using the extra oxygen (test 1), the compression strength average in the upper layers is reduced and the number of pellets with the strength less than 200 kg/pellet is increased. But in the test 2, where extra oxygen was used, the result was quite the opposite. In testing the lower layers, the strength was reduced and the number of pellets with the strength less than 200 kg was increased. Measured temperatures for different layers of the bed are shown in Figures 3 and 4.

Table 3. Specifications of pilot tests according to the results of pellet properties for distinct bed layers

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Volume of Injected extra oxygen (Nm³)</th>
<th>Maximum temperature through the firing zones (°C)</th>
<th>Average of bed layers compression strength (kg/pellet)</th>
<th>Average of remaining FeO at the bed layers (wt%)</th>
<th>Average of compression strength less than 200 (kg)</th>
<th>Maximum temperature of pellets at t=37 minutes (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>---</td>
<td>1280°</td>
<td>BL₁: 286, BL₂: 356, BL₃: 395, BL₄: 327</td>
<td>BL₁: 0.46, BL₂: 0.61, BL₃: 0.46, BL₄: 0.55</td>
<td>BL₁: 16.7, BL₂: 10.0, ---, ---</td>
<td>507</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>1280°</td>
<td>BL₁: 380, BL₂: 344, BL₃: 380, BL₄: 410</td>
<td>BL₁: 0.55, BL₂: 0.44, BL₃: 0.22, BL₄: 0.61</td>
<td>BL₁: 10.3, BL₂: 13.3, 3.3, 3.3</td>
<td>586</td>
</tr>
<tr>
<td>3</td>
<td>---</td>
<td>1260°</td>
<td>BL₁: 297, BL₂: 273, BL₃: 316, BL₄: 315</td>
<td>BL₁: 0.72, BL₂: 0.84, BL₃: 0.85, BL₄: 1.93</td>
<td>BL₁: 10, BL₂: 13.3, 3.3, 3.3</td>
<td>543</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>1260°</td>
<td>BL₁: 253, BL₂: 291, BL₃: 344, BL₄: 374</td>
<td>BL₁: 0.33, BL₂: 0.27, BL₃: 0.22, BL₄: 0.44</td>
<td>BL₁: 13.3, BL₂: 16.7, 10, 6.7</td>
<td>572</td>
</tr>
<tr>
<td>5</td>
<td>---</td>
<td>1260°</td>
<td>BL₁: 236, BL₂: 281, BL₃: 245, BL₄: 308</td>
<td>BL₁: 2.15, BL₂: 1.81, BL₃: 2.93, BL₄: 3.47</td>
<td>BL₁: 23, BL₂: 10, 23.3, 6.7</td>
<td>207</td>
</tr>
<tr>
<td>6</td>
<td>22</td>
<td>1260°</td>
<td>BL₁: 296, BL₂: 310, BL₃: 333, BL₄: 370</td>
<td>BL₁: 0.40, BL₂: 0.39, BL₃: 0.89, BL₄: 1.41</td>
<td>BL₁: 13.3, BL₂: 6.7, 6.7, 3.3</td>
<td>220</td>
</tr>
<tr>
<td>7</td>
<td>27</td>
<td>1260°</td>
<td>BL₁: 268, BL₂: 271, BL₃: 298, BL₄: 367</td>
<td>BL₁: 0.39, BL₂: 0.41, BL₃: 0.96, BL₄: 3.96</td>
<td>BL₁: 6.7, BL₂: 6.7, 6.7, 3.3</td>
<td>195</td>
</tr>
</tbody>
</table>

*Pellets Without solid fuel, BL₁-the first layer against to bed surface (distance from the surface =0-10 cm), BL₂-the second layer (distance from the surface=10-20 cm) BL₃-the third layer (distance from the surface =20-30 cm), BL₄-the fourth layer (distance from the surface =30-40 cm)
Comparing the temperatures suggests that despite the high temperature of layer T1 and T2 in test 1, in comparison to test 2, compression strength was lower. It should be considered that the percentage of the remaining FeO in distinct layers in test 1 was at the desired level. Therefore, dropping the compression strength in pellets was not due to either the unfired pellets or the low temperature. However, the result should be related to the absence of extra oxygen in the process gas. In fact, since the heating rate of pellets in the upper layers is larger than in the lower ones, in the upper layers, a shorter time is needed for magnetite oxidation completion than in the lower layers. Therefore, in test 1, the essential oxygen value for performing the oxidation was not reached in the pellets core of the upper layers. However, in the lower layers, due to the smaller slope of pellets heating, there was enough time to diffuse the oxygen into the pellets core. In test 2, the better conditions for values of compression strength in pellets without solid fuel were prepared by injecting oxygen in the process gas. Then, the conditions of oxygen injection for firing the pellets with solid fuel in pilot plant were going to be analyzed.

To study the effect of oxygen enrichment in process gas on the properties of pellets containing coke powder, a comparison was drawn between the pilot tests 3 and 4. Based on the chemical composition of fired pellets in Table 3, the remaining FeO in the pellets of distinct layers, especially in the lower layers, was remarkably reduced by adding oxygen to the pilot furnace process gas at test 4. However, due to the absence of preheating the oxygen gas in the pilot plant and the low temperature of inlet oxygen gas, the upper layers strength was lightly reduced. In the following tests, the qualities of the pellet were improved by controlling the temperature range for oxygen blowing and changing the starting time of it (Figure 5).

As shown in the figure, in addition to the increase of the pellets heating rate in the preheat zone, to shorten the time of the induration process, the residence time of pellets in maximum temperature was also slightly reduced. Table 3 shows the results of Test 5 with the new heating set in the absence of oxygen injection, indicating that physical and chemical properties in all layers of the pellet bed were dropped dramatically in the absence of oxygen. As comparison with the results of tests 3 and 5, both done in the absence of extra oxygen blowing, shows that it has a remarkable impact on dropping the pellets qualities by reducing 4 minutes of the time during the induration process. However, the results of tests 6 and 7 confirmed that the compression strength of pellets was improved evidently by using the extra oxygen injection for the new heating set. Furthermore, reduction of the FeO residues in pellets was certainly related to the oxygen injection treatment. In test 7, the FeO residues were more reduced and optimized conditions were achieved especially for the last layers of the pellet bed and it was accomplished with widening the temperature range of oxygen injection and increasing the time of oxygen blowing (Figure 7).
A cross section of a pellet of test 5 is shown in Figure 8. By considering the pellet induration conditions and lowering the compression strength of upper layers (Table 3), the surface of the pellet was oxidized (hematite) first and then sintered, but the core of it was sintered first and then oxidized. This difference in the order of structure transfer between the surface and the core of pellet resulted in the formation of an inhomogeneous structure. This inhomogeneous structure caused the structure stresses, forming some cracks and discontinuities in the pellet core. In the presence of these cracks and deep gaps, there was a drop in the pellet compression strength values in the compression test. However, the pellet could have been fired and indurated in high temperatures; as a result, the pellets microstructure which was fired by using oxygen injection in furnace was investigated. An image of the central region of a sample pellet related to test 7 is shown in Figure 9.

Fig. 8. The presence of cracks and discontinuities in the central region of pellet of test no. 5.

Fig. 9. Microstructure of a pellet fired by oxygen injection in the process gas (test no. 7).

The evident point here - despite Figure 8 - is the absence of cracks and discontinuities in the central region of pellet. Therefore, not forming the defects and discontinuities in the central region of pellet was the major factor in improving the compression strength values in test 7. This was due to uniform, continuous and simultaneous oxidation in different regions of pellet during the induration process. As a result, the availability of oxygen for the oxidation of magnetite particles in the preheat zone and the beginning of the firing zone had this positive effect.

4. Conclusions

1. Due to the more efficiency of increasing the oxygen concentration than increasing the temperature in the magnetite oxidation of pellets containing solid fuel, oxygen enrichment of the gas process can play an effective role in speeding up the oxidation reactions.
2. To avoid delaying the released heat of magnetite oxidation during the induration process, the reaction should be performed in lower temperatures and high oxygen concentration.
3. The results of pilot tests suggested that if only the extra oxygen was injected into the furnace in a specific range of time and temperature, the pellet qualities could be improved. As a result, shortening the time of pellet heating process may be possible.
4. Oxygen injection into the furnace in the preheat zone and the beginning of the firing zone resulted in a uniform homogenous structure without cracks and microstructure defects in iron ore pellet.

References