Sintering and Reduction of pellets of El-Baharia iron ore with Dolomite by Hydrogen

N.A. El-Hussiny (1), I.A. Nafeea (2), M.G. Khalifa (3), S.S. Abdel-Rahim (2), M.E.H. Shalabi (1)*

Abstract—This paper studied the effect of dolomite addition to iron oxide raw material on the physicochemical properties of its green and indurate pellets form. Also the effect of this addition on the degree of reduction was studied. The results indicated that the addition of dolomite decrease the mechanical strength of the green and indurate pellets. Also the reduction of these pellets by hydrogen was studied and the model of reduction was put in this paper.

Index Terms—Dolomite addition to iron ore, Indurate pellets, models of reduction.

1 INTRODUCTION

El Kassabgy and Lu [1], indicated that the presence of MgO and CaO in the reduction of iron oxide promote the metallization of wustite.

Sarat [2] was studied the influence of MgO addition on sinter mineralogy on sinter produced with a wide range of MgO/ CaO ratios at several basicity between 0.7 to 1.9. The results indicated that MgO favors the formation of glass and suppresses the precipitation of dicalcium silicates in favor of Ca-Fe-Mg olivines and pyroxenes.

Khwdr and Abdel-Khalek [3] contributed that the replacement of CaO by MgO leads to a decrease of the cold strength of the produce iron ore sinter. At 1113 K, they found that the rate of reduction was gradually increased with the increase of reduction temperature. At 1073 K and 1173 K the reduction rate of sinter containing lime stone is higher than that dolomite.

Min et al [4] illustrated that the six additives, limestone, lime, magnesite, magnesia, dolomite and light-burned-dolomite to iron ore for investigating their influences on the pellet quality. For green balls, adding lime and light-burned-dolomite makes the wet drop strength decrease firstly, and then increase with further increase of additive dosage. Ca(OH)2 affects the bentonite properties at the beginning, but the binding property of Ca(OH)2 will be main when the dosage is higher. The other four additives decrease the drop strength for their disadvanta geous physical properties. For preheated pellets, no matter what kind of additive is added, the compressive strength will be decreased because of unmineralized additives. For roasted pellets, calcium additives can form binding phase of calcium-ferrite, and suitable liquid phase will improve recrystallization of hematite, but excessive liquid will destroy the structure of pellets, so the compressive strength of pellet increases firstly and then drops. When adding magnesium additives, the strength will be decreased because of the oxidation of magnetite retarded by MgO.

Bin et al [5] demonstrated that 1) With the increase of dolomite dosage from 0 to 10.5%, the porosity of pellets increases from 35% to 40%. Moreover, magnesium ferrite is generated and the incorporation of magnesium into calcium silicate happens during the pellets roasting with the addition of dolomite. 2) The pores not only absorb part of the volume expansion during crystal transformation but also reduce the gas diffusion resistance during the process of reduction. Magnesium ferrite stabilizes the crystal of hematite and reduces the volume expansion when Fe2O3 is transformed into Fe3O4. The incorporation of magnesium into calcium silicate suppresses the phase transition of 2CaO-SiO2. Thus, the reduction swelling property of roasted pellets is improved.

Gao et al [6] investigated The effect of MgO on reduction metallurgical properties of pellets, such as low-temperature reduction degradation index(RDI), reduction index(RI)and reduction swelling index(RSI). The results show that, with the addition of MgO-bearing additive from 0 to 2.0% in pelletizing, the RDI and RSI decrease gradually, and the value of RDI and RSI decrease by 6.46% and 6.21% respectively, which means that the reduction degradation phenomenon and reduction swelling phenomenon are inhibited. The RI of pellets increased by 4.66% with the addition of MgO bearing additive from 0 to 2.0% in pellets, and therefore the addition of MgO is favorable to improve the reduction metallurgical properties of pellets. Based on the pore space analysis and mineral composition analysis of different MgO-bearing pellets.

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Qiang-jian et al. [7] studied the compressive strength of MgO-fluxed pellets was investigated and compared with traditional acidic pellets in this paper. Based on the piston flow concept and experimental data, a kinetic model fitting for the gas-solid phase reduction of pellets in tubular reactors (blast furnace, BF) was built up, and the equations of reduction reaction rate were given for pellets. A series of reduction experiments of pellets were carried out to verify the model. As a result, the experimental data and calculated result were fitted well. Therefore, this model can well describe the gas-solid phase reduction process and calculate the reduction reaction rate of pellets. Besides, it can give a better explanation that the reduction reaction rate (reducibility) of MgO-fluxed pellets is better than that of traditional acidic pellets in BF.

Feng-man [8], studied the compressive strength of MgO-fluxed pellets was investigated before and after they were reduced. The porosity and pore size of green pellets, product pellets, and reduced pellets were analyzed to clarify how MgO affects the strength of the pellets. Experimental results show that when the MgO-bearing flux content in the pellets increases from 0.0wt% to 2.0wt%, the compressive strength of the pellets at ambient temperature decreases, but the compressive strength of the pellets after reduction increases. Therefore, the compressive strength of the pellets after reduction exhibits no certain positive correlation with that before reduction. The porosity and pore size of all the pellets (with different MgO contents) increase when the pellets are reduced. However, the increase in porosity of the MgO-fluxed pellets is relatively smaller than that of the traditional non-MgO-fluxed pellets, and the pore size range of the MgO-fluxed pellets is relatively narrower. The reduction swelling index (RSI) is a key factor for governing the compressive strength of the reduced pellets. An approximately reversed linear relation can be concluded that the lower the RSI, the greater the compressive strength of the reduced pellets is. El-Hussiny et al. [9], concluded that:-

1) The reduction of iron ore with dolomite briquette by hydrogen depend on the temperature of the reduction, as the temperature increased the reduction increased.
2) As the percentage of dolomite in the briquette increased the reduction rate decreased.
3) The reduction of the iron ore with dolomite briquette control by one of the following models.
   A) Diffusion models, Ginstling-Brounshtein equation
   \[1-2/3R-(1-R)1/3 = kt\]
   B) Geometrical contraction models (contracting volume) or diffusion model
   \[1-(1-R)1/3 = kt\]

In this paper, the effect of addition of dolomite as a fluxing material on both physical and reduction properties of the pellets produced from Egyptian iron ores with using molasses as binding materials will discuss.

2 Experimental Work

2.1. Raw material

El-Baharia iron ore samples was supplied by the Egyptian Iron and Steel Company, and the Dolomite ore from gebel Ataaq Suez, . The chemical composition of iron ore [9] and Dolomite ore are shown in Table 1 from which it is clear that the mean compounds of iron ore is \( \text{Fe}_2\text{O}_3 \) total = 52.35%, MnO= 2.92%, \( \text{SiO}_2 \) = 10.84%. While the dolomite ore mainly consists of CaO 29.4%, MgO 21.6%.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Iron ore Weight %</th>
<th>Dolomite Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>74.79</td>
<td>0.27</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>10.84</td>
<td>0.31</td>
</tr>
<tr>
<td>MnO</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.39</td>
<td>29.40</td>
</tr>
<tr>
<td>MgO</td>
<td>0.18</td>
<td>21.60</td>
</tr>
<tr>
<td>( \text{P}_2\text{O}_5 )</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>1.44</td>
<td>0.10</td>
</tr>
<tr>
<td>( \text{TiO}_2 )</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>BaO</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>L.O.I.</td>
<td>5.18</td>
<td>46.9</td>
</tr>
</tbody>
</table>

The X- Ray analysis of El-Baharia iron ore and dolomite are illustrated in figures 1 and 2. From which it is clear that El-Baharia iron ore mainly consists of hematite and quartz. While the X-ray analysis of dolomite mainly consists of CaMg(CO₃).
clination 60 oC, disc rotating speed 17 rpm and residence time 30 min. After the materials were fed to the pelletizer the predetermined moisture amount (8.5% water + 2.5% of molasses) was then sprayed onto the rolling bed of material in the pelletizer. The green pellets in the size range 5-7 mm diameter were screened out to dry and then indurate in the computerize furnace.

The green produced pellets subjected to drop number test from 46 cm height and crushing strength tests. The crushing strength test used MEGA.KSC-10 hydraulic press (Fig.4). The drop number indicates how often green or dried pellets can be dropped from a height 46 cm before they show perceptible cracks or crumble [10]. Ten green pellets are individually dropped on to a steel plate. The number of drops is determined for each pellet and the arithmetical average values of the crumbling behavior of the ten pellets yield the drop number. The average crushing strength is done by compressed 10 pellets by MEGA.KSC-10 hydraulic press up to their breaking [11-17].

2.3. Reduction Procedures

The reduction of the produced pellets by hydrogen were done on thermo gravimetric apparatus (A schematic diagram of thermo gravimetric apparatus is shown in Fig.5) [18-20]. It consisted of a vertical furnace, electronic balance for monitoring the weight change of reacting sample and temperature controller. The sample was placed in an Ni-Cr basket which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the required temperature (700-950 oC) and maintained constant to ±5 oC. Then samples were placed in hot zone. The nitrogen flow rate was 0.5l/min on all the experiments. at initial time and after the end of reduction only. The weight of the sample was continuously recorded. At the end of the run, the samples were withdrawn from the furnace and putted in the desiccators. The amount of removable oxygen was determined by the weight loss in the sample (Wo-W) during the experiment of reduction with H2 in the furnace. The percentage of reduction was calculated according to the following equations [21-23]

\[
\text{Percentage of reduction} = \left(\frac{\text{Wo} - \text{Wt}}{\text{Wo}}\right) \times 100\%
\]

Where Wo the initial mass of sample after removal of moisture, g.

Wt mass of sample after each time, t.

Oxygen (mass) indicates the mass of oxygen percent in the pellets in form Fe₂O₃, g.
3. RESULTS AND DISCUSSION

3.1 Quality of the produced green pellets

The drop damage resistance and compressive strength of the produced green pellets are shown in Figs.6 and 7. From this figure it was found that the drop damage resistance and the compressive strength for green pellets decreased as the percentage of dolomite added increased.

![Fig.6 The relation between drop number of the green iron ore pellets and the amount of dolomite added](image)

Fig.7 The relation between cold crushing strength of the green iron ore pellets and the amount of dolomite added

3.2 Effect of firing temperature on strength of pellets of iron ore contain different amount of dolomite

The compressive strength of the produced pellet after firing at different temperature is shown in Fig. 8. From this figure it was found that the compressive strength of the fired pellets decreased as the percentage of dolomite added increased, while as the temperature of firing increased the strength of firing pellets increased.

![Fig.8 Effect of the firing temperature on the crushing strength of iron ore with different amount of dolomite briquette](image)

3.3 Effect of the amount of dolomite added to iron ore on the reduction by constant hydrogen flow rate at 900°C

Figure 9 shows the effect of different dolomite added to iron ore on the percentage of reduction of the pellets of El-Baharia iron ore with dolomite when the reduction were done at constant temperature (900°C) and the weight of the sample was constant. It is clear that as the amount of dolomite increased the reduction percentage decreased.

3.4 Effect of change of temperature on the reduction percentage

In order to examine the effect of temperature on the reduction of pellets of El-Baharia iron ore with 4% and 8% dolomite respectively (pellets (5-7 mm), 2 L/min hydrogen flow rate), experiments were carried out at 700 - 950°C. Plots of the reduction percentage as function of time are shown in Figs. 10 and 11. From this figure it is clear that the increase in temperature causes an increase in the extent of reduction as observed previously [9.24-25]. The increase of reduction percentage with temperature could be due to increase number of reacting moles having excess energy which leads to the increase of adsorption rate. Also increasing temperature leads to increase the rate of mass transfer of the diffusion and rate of chemical reaction (9.16,26.-28).

3.4. Kinetics reduction of reduction of pellets of indurate El-Baharia iron ore with dolomite

Kinetic studies for estimation of apparent activation energies were carried out for the pellets at different temperatures range from 700°C up to 950°C for different time intervals in the range of 0-60 min.

1- Using diffusion models, Ginstling-Brounshtein equation

\[ 1-2/3R-(1-R)2/3 = kt \]  

(1)

Where: (R) is fractional reduction,
(t) is time of reduction, (k) is the rate constant of the reduction.

Figs. (12) and (13), illustrate the relation between 1-2/3R-(1-R)2/3 against time of reduction for different reduction temperatures for 4% and 8% dolomite added to iron ore respectively. From these figures it is clear that the straight line was observed.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction for 4% and 8% dolomite added to iron ore. The results illustrate in Figs. 14 and 15 respectively, from which it is clear that the activation energy = 50 kJ/mole and 60.59 kJ/mole for the reduction of iron ore pellets contains 4% and 8% respectively.

2- Using geometrical contraction models (contracting volume) [29], or diffusion model [14&30]:-

\[ 1 - (1-R)^{1/3} = kt \] \hspace{1cm} (2)

Where R is fractional reduction, t is time of reduction and k is the rate constant.

Figures 16-17 illustrated the relation between 1- (1-R)^{1/3} against time of reduction for different reduction temperature for iron ore pellets contain 4% and 8% dolomite respectively, from which it is clear that the straight line was observed.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction for 4% and 8% dolomite added to iron ore. The results illustrate in Figs. 18 and 19 respectively, from which it is clear that the activation energy = 39.51 kJ/more and 46.2 kJ/mole for the reduction of iron ore pellets contains 4% and 8% respectively.

3- Using diffusion process control equation (Jander and Anorg Equation) [17,21,31-32]

\[ [1 - (1-R)]^{1/3} = kt \]

Figs. 20 and 21 illustrate the relation between [1 - (1-R) ^ {1/3}] against time of reduction for different reduction temperature for iron ore pellets contain 4% and 8% dolomite respectively, from which it is clear that the straight line was observed.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction for 4% and 8% dolomite added to iron ore. The results illustrate in Figs. 22 and 23 respectively, from which it is clear that the activation energy = 45.73 kJ/mole and 58.73 kJ/mole for the reduction of iron ore pellets contains 4% and 8% respectively.
Fig. 12: The relation between $1-2/3R-(1-R)^{2/3}$ against time of reduction for different reduction temperatures for 4% dolomite added to iron ore.

Fig. 13: The relation between $1-2/3R-(1-R)^{2/3}$ against time of reduction for different reduction temperatures for 8% dolomite added to iron ore.

Fig. 14: The natural logarithms of $k$ against $1/T$, $k-1$ for 4% dolomite added to iron ore.

Fig. 15: The natural logarithms of $k$ against $1/T$ for 8% dolomite added to iron ore.

Fig. 16: The relation between $1-(1-R)^{1/3}$ and time of reduction for different reduction temperatures for iron ore pellets contain 4% dolomite.

Fig. 17: The relation between $1-(1-R)^{1/3}$ and time of reduction for different reduction temperatures for iron ore pellets contain 8% dolomite.
Fig. 18: The natural logarithms of k against 1/T, k-1 for 4% dolomite added to iron ore.

Fig. 19: The natural logarithms of k against 1/T, k-1 for 8% dolomite added to iron ore.

Fig. 20: The relation between \([1 - (1-R)^{1/3}]^2\) and time of reduction for different reduction temperature for iron ore pellets contain 4% dolomite.

Fig. 21: The relation between \([1 - (1-R)^{1/3}]^2\) and time of reduction for different reduction temperature for iron ore pellets contain 8% dolomite.

Fig. 22: The natural logarithms of k against 1/T, k-1 for 4% dolomite added to iron ore.

Fig. 23: The natural logarithms of k against 1/T, k-1 for 8% dolomite added to iron ore.
3.4 X-ray differentation of the reduced iron ore with dolomite pellets

Figs.(24) and ( 25 ) illustrated the x-ray of the reduced pellets of iron ore with 4% or 8% dolomite by hydrogen at 950°C respectively from these figures, it is clear the Fe syncetic is mainly elements in both samples.

Fig.24 X-ray of the reduced pellets of iron ore with 4% dolomite by hydrogen at 950 oC

Fig.25 X-ray of the reduced pellets of iron ore with 8% dolomite by hydrogen at 950 oC

4 CONCLUSION

1- Addition of dolomite to iron ore and pelleted its decrease the drop number and crushing strength of the green and indurated pellets
2- The increase of amount of dolomite added to the iron ore leads to decrease the reduction degree of the indurated pellets.
3- The increase of reduction temperature causes an increase the extent of the reduction.

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