Development of Fluxed Iron Oxide Pellets Strengthened by CO₂ Treatment for Use in Basic Oxygen Steel Making

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Lump lime is presently being used as a fluxed material in basic oxygen steel making process. However, problems are often encountered in operation due to its high melting point, poor dissolution property, fines generation and hygroscopic nature. Binary CaO–Fe₂O₃ has a eutectic point (1 200°C) with 22% CaO. An agglomerate of lime and iron oxide under BOF condition would thus generate low melting oxidizing slag at the beginning of blow and would facilitate refining process. In this study, lime fluxed iron oxide pellet has been prepared using waste iron oxides and its strength was developed by CO₂/CO₂ containing gas treatment at room temperature, while no separate binders has been used. Industrial waste gases, say, blast furnace gas (BFG) may suitably be used as CO₂ source. The pellet making process parameters such as composition of pellets, grain size of iron ore fines, treatment conditions etc. have been optimized through physical characterization like cold compressive strength, drop strength, abrasive resistance etc. Up to around 30 kg/pellet cold compressive strength, around 150 drop strength and excellent abrasive property have been achieved.

KEY WORDS: fluxed pellets; CO₂ treatment; characterization; CCS; drop strength; abrasive property; porosity.

1. Introduction

The basic ingredients for the oxygen steelmaking process include hot metal from the blast furnace, steel scrap and/or any other metallic iron sources (such as DRI), ore (Fe₂O₃), and fluxes such as burnt lime, dolomitic lime (CaO–MgO), lime stone (CaCO₃) and fluorspar (CaF₂).

Use of burnt lime as flux involves some operational problems due to its high melting point, poor dissolution property, fines generation and hygroscopic property. Binary CaO–Fe₂O₃ has a eutectic point (1 200°C) with 22% CaO. An agglomerate of lime and iron oxide under BOF condition would thus generate low melting oxidizing slag at the beginning of blow and would facilitate refining process. In this study, lime fluxed iron oxide pellet has been prepared using waste iron oxides and its strength was developed by CO₂/CO₂ containing gas treatment at room temperature, while no separate binders has been used. Industrial waste gases, say, blast furnace gas (BFG) may suitably be used as CO₂ source. The pellet making process parameters such as composition of pellets, grain size of iron ore fines, treatment conditions etc. have been optimized through physical characterization like cold compressive strength, drop strength, abrasive resistance etc. Up to around 30 kg/pellet cold compressive strength, around 150 drop strength and excellent abrasive property have been achieved.

KEY WORDS: fluxed pellets; CO₂ treatment; characterization; CCS; drop strength; abrasive property; porosity.
ported by the investigators. Irmler et al. \cite{10} also observed no significant foaming on use of fluxed sinter, in addition, better flux dissolution, earlier slag formation, greater removal of both sulfur and phosphorous and increase in metallic yield has been reported.

Investigators \cite{8,12,13} have used iron oxide fines in form of pellets made with cement as binder and cured for 28 d. \cite{31} However, such a long curing for strength development is not suitable for industrial application. Choi and Kim \cite{14} used lime pellets coated with iron oxides (a mixture of mill scale, yellow soil and silica) to enhance slag formation in the BOF. A low-melting slag was formed by iron oxides and a part of burnt lime at the initial stage of blowing. This low melting point slag acted as a seed for further slaggling of the lime, which improved the refining efficiency and decreased the frequency of slopping. A plant trial with this quoted pellets at Pohang Works in a 100-ton converter showed improvement in lime consumption, enhancement of metallic yield, increase in slag basicity and improvement in dephosphorisation compared to the conventional process. However, the difficulties encountered in coating of lime pellets restrict its commercialization.

The reported literature indicate that charging of iron oxide wastes in form of pellets, briquettes or sinter may be advantageous for process improvement and waste utilization. Although, burnt lime is essential to maintain the basicity of slag, it poses problems in dissolution as well as in handling. The binary phase diagram shows (Fig. 1) \cite{15} an eutectic melting point at around 1200°C with approximately 22% CaO. Accordingly, a FeO–CaO combination, containing 20–30% lime is expected to be compatible with BOF conditions in view of low softening point, faster dissolution and early formation of FeO rich slag would accelerate refining of the bath. Guangqing Zuo \cite{16} has reported that BOF slag with high FeO and FeO, content (16.4% and 8.08% respectively) shows very low softening point (1400°C), but, when its FeO and FeO3 content reduced to a low level (5.3% and 1.5% respectively) shows high softening point (1520°C). Therefore, development of lime fluxed iron oxide in suitable agglomerated form viz. sinter, briquette or pellet should be an important step towards gainful utilization of steel plant oxide wastes. But the practiced agglomeration techniques involve certain limitations towards such an endeavor. For example, the requirement of high temperature and the restriction on the lower limit of the particle size, not only make the production of the fluxed sinter a relatively expensive process but also limit the scope of utilization of iron ore fines. Similarly, use of organic binders for making briquettes/pellets renders the product costly; inorganic binders, on the other hand, increase the slag volume in the BOF. The making of fired pellets is also involved with high energy consumption and high cost. Considering cold handling strength along with chemistry be the primary requirements, this study, aims at developing a novel pellet making technique which apparently is free from all the above limitations.

2. Experimental

In this technique, the fluxed pellets were produced with waste iron oxide fines and lime without any costly binder and firing. They were subsequently treated with carbon dioxide in a reaction chamber at room temperature to transform the calcium hydroxide (Ca(OH)2) into hard calcium carbonate (CaCO3) for strength improvement.

2.1. Raw Materials Analysis

The raw materials for the preparation of fluxed iron oxide pellets were iron ore fines (which is considered to represent a number of waste iron oxides, namely, sludges, grits, and mill scale) and lime. The iron ore fines were collected from Barbil, Orissa, India while the lime used was of commercial-grade. The chemical analyses of iron ore (sampling standard IS 1405-1982) and commercial grade burnt lime are given in Table 1. As the first step toward the preparation of fluxed iron oxide pellets, the iron ore fines were dried and classified into two broad size ranges with ASTM mesh numbers of 30 + 72 mesh and 72 mesh. The details of each size distribution are given in Tables 2 and 3, respectively.

2.2. Making of Green Pellets

The sized iron ore fines were manually mixed with the burnt lime (30 mesh) fines (20 to 40%) and hydrated with spray of water (10–12% of total mix) to convert all the CaO in to Ca(OH)2. The hydrated mixture was then pelletized.

<table>
<thead>
<tr>
<th>Materials</th>
<th>FeO wt%</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron ore fines</td>
<td>66.46</td>
<td>3.05</td>
<td>1.34</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Lime</td>
<td>-</td>
<td>0.73</td>
<td>1.12</td>
<td>95.1</td>
<td>0.8</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 1. Chemical analysis of iron ore fines and lime, wt%.

<table>
<thead>
<tr>
<th>Size range, ASTM mesh</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>-200</td>
<td>80</td>
</tr>
<tr>
<td>-170 + 200</td>
<td>4.2</td>
</tr>
<tr>
<td>-150 + 170</td>
<td>1.6</td>
</tr>
<tr>
<td>-100 + 150</td>
<td>2.35</td>
</tr>
<tr>
<td>-72 + 100</td>
<td>11.85</td>
</tr>
</tbody>
</table>

Table 2. Size fraction of 30 + 72 mesh iron ore fines.

<table>
<thead>
<tr>
<th>Size range, ASTM mesh</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60 + 72</td>
<td>20.23</td>
</tr>
<tr>
<td>-52 + 60</td>
<td>52.35</td>
</tr>
<tr>
<td>-30 + 52</td>
<td>27.42</td>
</tr>
</tbody>
</table>

Table 3. Size fraction of 30 + 72 mesh iron ore fines.
with intermittent manual spray of water (total: 15–18%) for nucleation and growth of pellets in a 1.5-kg capacity pelletizer rotated at 30 rpm speed. The pellet size was maintained between \(\frac{3}{16}\) to \(\frac{1}{16}\) mm. After sufficient rolling the pellets were discharged and subjected to natural drying for 1–3 d. The kinds of the pellets with different composition are given in Table 4.

### Table 4. Composition of different kinds of pellets made.

<table>
<thead>
<tr>
<th>Kinds of pellets</th>
<th>Composition, w%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lime</td>
</tr>
<tr>
<td></td>
<td>-30+72 size</td>
</tr>
<tr>
<td>A</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>25</td>
</tr>
<tr>
<td>C</td>
<td>30</td>
</tr>
<tr>
<td>D</td>
<td>30</td>
</tr>
<tr>
<td>E</td>
<td>30</td>
</tr>
<tr>
<td>F</td>
<td>40</td>
</tr>
</tbody>
</table>

2.3. CO₂ Treatment

The naturally dried pellets were then hardened in a chamber by passing CO₂ for a period of 5 to 22 min through a packed bed of pellets. Hardening was intended by the formation of hard CaCO₃ on the pellet. The schematic of the hardening unit is shown in Fig. 2. It is a mild steel chamber of 50 mm I.D, 250 mm length and could accommodate approximately 400 g of pellets per batch. Approximately, 180 g of dried pellets were fed inside the chamber and carbon dioxide gas (purity: 99.5%) at a flow rate of 5 lpm was admitted through the top inlet at ambient temperature. After passing through the bed, the reacted gas was withdrawn from the bottom outlet. The gauge pressure of the chamber was varied between 0 to 5 kgf/cm². The pressure inside the chamber could be controlled by regulating the outlet valve at the bottom. The pellets were treated under different hardening conditions, such as, treatment time, gas pressure, gas composition and moisture content of the untreated pellets. In order to assess the influence of gas composition, two gas mixtures namely CO₂:N₂ equals to 13 : 87, and CO₂:CO:N₂ equals to 13 : 25 : 62, were also used during hardening experiments. The moisture content of the air dried pellet was measured by the weight loss suffered by a representative sample (20–25 g) on heating at 110°C. Four hours of heating was found to be sufficient to ensure constancy in weight.

2.4. Tests of Pellet Strength

After discharging the pellets from the hardening unit, the samples were kept in open ambient for one day for natural drying and then preserved in sealed plastic envelopes. The preserved pellets were subjected to various tests like cold compressive strength (CCS), drop strength, abrasive resistance and porosity for physical characterization.

2.4.1. Compressive Strength

The breaking compressive load of pellets in terms of ‘kg per pellet’ was measured in a universal testing machine (Honsfield’s Materials Testing Machine, Model: H 10K-S) in the range of 0–2.5 kN load.

2.4.2. Drop Strength

The drop strength was conventionally measured by repeatedly dropping an individual pellet upon a mild steel plate from a height of 450 mm. The number of drops required to break the pellet is a measure of its drop strength, the DSN. Actually, in an LD converter, flux materials are generally discharged from a greater height of about 1000 mm at different stages of material transportation. Therefore, the pellets which yielded good CCS (＞15 kg/pellet) were further subjected to the drop tests from a height of 1000 mm and the corresponding number of drops is termed as the DSM (Drop Strength from a Meter height).

2.4.3. Abrasive Resistance

The abrasive resistance property, expressed as Degradation Index (DI) was measured by rotating a representative batch of the CO₂-treated pellets (500 g) at 30 rpm for 7 min in a mild steel drum, of 130 mm internal diameter and 200 mm length. The percentage of the \(\frac{3}{16}\) mm fraction thus produced has been reported as DI of the pellets.

2.5. Porosity and Bulk Density

Both apparent porosity (standard IS: 1528, part-VIII-1974) and bulk density (standard IS: 1528, part-XII-1974) of the CO₂-treated and untreated pellets were measured in kerosene medium.

2.6. XRD Study

Quantitative phase analysis of both untreated and CO₂ treated pellets were carried out using a Siemens D500 X-ray diffractometer with Cu-Kα radiation at a scanning speed of 2°/min. In order to identify the different phases in core and surface in CO₂ treated pellets, the samples were collected manually from the surface (up to 2 mm depth) and inner core (rest 6 mm diameter) and ground into fine powder (＜10 mesh) for phase analysis. Fe₂O₃, CaCO₃,
Ca(OH)$_2$ and CaO peaks were identified by JCPDS file Nos.: 85-0987, 85-1108, 84-1276 and 82-1691, respectively.

### 2.7 Measurement of CaCO$_3$ and Ca(OH)$_2$ Content

The percentage of CaCO$_3$ and Ca(OH)$_2$ in CO$_2$ treated pellets was estimated by weight loss measurement on heating and soaking at respective dissociation temperatures. Ca(OH)$_2$ dissociates below 500°C and CaCO$_3$ dissociates at the temperature 894°C at 1 atm pressure. Therefore the weight loss of the samples due to soaking at 500°C and 975°C (3 h at each temperature) was measured. Percentage of CaCO$_3$ was calculated from the difference in weight loss at these two respective temperatures and remaining lime was considered in form of unreacted Ca(OH)$_2$.

In brief the pellets having different composition and grain size of iron ore fines was treated under CO$_2$ upon a number of process variables viz. moisture content of the air-dried green pellet, treatment time, gas pressure and treatment gas composition etc. The obtained pellets has been characterized through measurements of a number of physical properties of pellets, such as cold compressive strength, drop strength, shear strength and porosity. Apparent best combination of these independent variables was worked out.

### 3. Results and Discussion

The CO$_2$ treatment in pellet shows a considerable improvement in strength depending upon treatment conditions. Before discussing the effect of treatment conditions, it is imperative to discuss about the mechanism of strengthening which is as follows:

When the lime (CaO), present in the base mixture, comes in contact with water, added before pelletization, reacts to form calcium hydroxide:

$$\text{CaO (s)} + \text{H}_2\text{O (l)} = \text{Ca(OH)2}$$

On pelletization, this calcium hydroxide provides primary bonding amongst the particles and imparts strength to the green pellet. During subsequent treatment of the air-dried green pellets by the stream of flowing CO$_2$, the Ca(OH)$_2$ undergoes the following reaction:

$$\text{Ca(OH)2 (s)} + \text{CO}_2(\text{g}) = \text{CaCO3 (s)} + \text{H}_2\text{O (l/g)}$$

Due to the above reaction, a hard CaCO$_3$ phase is formed in the pellet. The observations on this phase transformation, studied through X-ray diffraction has been presented in the subsequent section. In this context it may be mentioned that Min Chen et al. has produced coating of CaCO$_3$ having low porosity by CO$_2$ treatment on Ca(OH)$_2$ pellet to prevent hydration.

A part of the free moisture gets removed during natural curing of the green pellet in open atmosphere for 1–3 d, prior to the CO$_2$-treatment. The voids thus produced facilitates penetration of CO$_2$ into the pellet during the treatment. The formation of calcium carbonate is primarily responsible for imparting good strength to the pellet. The molar volumes of CaCO$_3$ and Ca(OH)$_2$ are 34.10 cm$^3$/mol and 33.59 cm$^3$/mol respectively. In Reaction (2), one mole of CaCO$_3$ is produced from one mole Ca(OH)$_2$, therefore, the transformation results in 1.52% volume expansion of lime. This volume expansion is likely to be accommodated by the internal pores of the pellet leading to decrease in porosity and increase in compactness of the pellet. Hence, the volume expansion associated with the transformation of Ca(OH)$_2$ to CaCO$_3$ is likely to play a predominant role for strength development.

The equilibrium constant for the Reaction (2) may be expressed as

$$K = a_{\text{CaCO3}} \cdot a_{\text{H2O}} / a_{\text{Ca(OH)2}} \cdot p_{\text{CO2}}$$

As both Ca(OH)$_2$ and CaCO$_3$ are solids and considering H$_2$O as condensed phase, the above expression for equilibrium constant transform to

$$K = 1 / p_{\text{CO2}}$$

It is apparent from the above expression that in order to maintain constancy of $K$ at a particular temperature, the rate of forward reaction will increase with increase in applied $p_{\text{CO2}}$.

Again, in reality, all the moisture produced though the Reaction (2) may not be present as a condensed phase. Instead of subjecting to CO$_2$ treatment, if the green pellet was kept in open atmosphere ($p_{\text{CO2}} = 0.015$ atm), Reaction (2) would still occur, but only at a slow rate. In order to verify this assessment, a few pellet samples of each category were left in open atmosphere and the strength of the pellets were examined periodically. It was found that a 15-min treatment of the pellets with pure CO$_2$ gas is equivalent to a prohibitively long 6–8 month exposure in natural weathering from the point of view of pellet strength development.

In view of optimization of hardening process through CO$_2$ treatment, the effects of different variables like pellets composition and treatment conditions on physical properties of obtained pellets are plotted and discussed subsequently. Repeat test for compressive strength, drop strength, abrasion and porosity confirmed that data could be reproduced within ±5% deviation. In few of the figures, the error limit is also presented graphically and intentionally removed for other figures to avoid overlapping. Considering the non-uniformity in shapes of the pellets and manual handling, these levels of uncertainties are accepted to be within the limits of experimental error. Since the strength and related properties of a pellet depend upon its diameter, a pellet diameter of 10 mm was typically chosen for optimization of the remaining process variables.

#### 3.1. Pellet Composition

Cold crushing strength (CCS) and drop strengths (DSN) of CO$_2$-treated pellets at 5 kgf/cm$^2$ gas pressure for varying lime contents are shown in Figs. 3 and 4, respectively. The reason for fixing the CO$_2$ gas pressure at 5 kgf/cm$^2$ for studying the effect of the variables on the pellet properties will be discussed in the subsequent section. It may be noted from the figures that both CCS and DSN attain maximum values (CCS: 29 kg/pellet and DSN: 150) corresponding to the 25% lime content and decrease with further increase of lime in the pellet. In Fig. 5, the plot of degradation index (DI) against lime content of pellets shows that the percentage of $\sim 3.15$ mm fraction is in the range of 1–3% only, indicating excellent abrasive resistance of the treated pellets.
High abrasive resistance is helpful to minimize generation of fines during cold handling of pellets. It may further be noted that maxima of CCS and DSN curves coincide with the minima of DI plot with 25% lime in the pellet. When the CCS and DSN values decrease from 28.7 kg/pellet and 150 with 25% lime to 11.5 kg/pellet and 25 with 40% lime respectively, the DI values undergo a marginal increase from 1.16 to 2.81% only. Apparently insignificant influence of lime content on DI is possibly due to the fact that the abrasive resistance of the pellet is largely controlled by the characteristics of the surface only. Harder the surface of a pellet, better would be its resistance to degradation. As the pellet surface is always rich with CaCO₃ under all compositional and treatment conditions, the DI values are very low.

**Figure 6** shows that the apparent porosity increases (and the bulk density decreases) with increasing lime content for both the treated and untreated pellets. The treated pellets have lower porosity in all the cases than the untreated ones. This is possibly due to the volume expansion associated with the transformation of Ca(OH)₂ grains to CaCO₃ by the CO₂ treatment (Reaction (2)), as explained previously. An increase in the bulk density is observed after treatment owing to net weight gain of pellet after CO₂ treatment. Notably, the pellet with high lime content (treated/untreated) has lower bulk density. Hence, higher lime containing pellets are likely to dip less in the hot metal bath when used for refining purpose.

Porosity in the fluxed green pellet is essential for the progress of the hardening reaction. However, the result presented in Figs. 3 and 6 indicate that excessive porosity may be one of the reason for strength deterioration of pellets as has been observed with 40% lime. Excessive amount of carbonate and residual hydroxide in pellet may be the other reason too as shown in **Fig. 7**. This figure shows the percentage of transformed CaCO₃ after 15 min of CO₂ treatment against lime percentage of pellets which was estimated adopting procedure mentioned earlier.

It may further be noted from the Figs. 3, 4 and 6 that CCS, DSN and bulk density do not decrease much when the lime content is increased from 25 to 30%. In the current study, it has been intended to maximize the replacement of free lime in the BOF charge through fluxed iron oxide pellet. Hence, pellet with 30% lime has been considered to be most suitable composition and was used for studying effects of other parameters.

In view of the dependence of pellet strength on the lime content, an attempt was made to analyze the untreated as well as CO₂ treated pellets using optical microscopy. A few typical microphotographs of cold mounted polished samples are presented in **Fig. 8**. It has been observed that except progressive increase in fraction of lime containing...
phase with increased lime in the base mixture, no definite distribution of CaCO$_3$ could be established, since the two lime containing phases (CaCO$_3$ and Ca(OH)$_2$) were not individually distinguishable.

### 3.2. CO$_2$-treatment Time

Variation of compressive strength of pellets, containing 20, 25, 30, and 40% lime, with CO$_2$-treatment time is shown in Fig. 9. It may be noted from the figure that the compressive strength of a pellet increases with the treatment time up to 15 min, beyond which it becomes practically constant. Drop impact strengths also exhibit similar trend, as is evident from Fig. 10. From Fig. 9 it is revealed that CO$_2$ treatment in pellet B and C for 10 min or beyond CCS is quite satisfactory (>15 kg/pellet). In view of its application in BOF, drop strength from a meter height (DSM) was measured and found to be very encouraging as reported in Table 5.

From Figs. 9 and 10 it appears that Reaction (2) gets kinetically hindered after exposing the pellets for 15-min to CO$_2$, irrespective of the lime content. This is due to the restricted diffusion of CO$_2$ through the formed CaCO$_3$ layer. Further, a scrutiny of the results presented in Figs. 3 and 9 reveals that a combination of 25% lime and 15 min CO$_2$ treatment time has apparently yielded pellets with maximum CCS as well as DSN (Fig. 4). It is worth-noting that the projected pellet with 30% lime (pellet C) also exhibit CCS and DSN, very close to those of the pellet with 25% lime under identical treatment condition.

XRD pattern of the pellet C before and after treatment is presented in Fig. 11. It is significant to note that there is no peak for CaO even in pellet before treatment (untreated).

---

**Table 5.** DSM values of the pellets B and C for 10 min and 15 min treatment.

<table>
<thead>
<tr>
<th>Pellet code</th>
<th>Treatment time, min</th>
<th>CCS, kg/pellet</th>
<th>DSM</th>
<th>DSM</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>10</td>
<td>21.9</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>28.7</td>
<td>150</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>17.9</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>25.7</td>
<td>130</td>
<td>19</td>
</tr>
</tbody>
</table>

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Fig. 8. Photomicrographs of untreated and CO$_2$ treated (15 min) samples. (a) treated 20% lime, (b) treated 30% lime, (c) treated 40% lime, (d) untreated 30% lime.
This indicates that almost whole of the calcined lime got converted to calcium hydroxide during pelletization. Small peaks of CaCO₃ in untreated pellet may be attributed to the reaction of the pellet with the CO₂ in air during 1–3 d of natural drying. Figure 11 also indicates that after 22 min treatment whole Ca(OH)₂ transforms into CaCO₃.

Figures 12 and 13 present the XRD analysis of samples from surface and core of pellet C after 5 min and 15 min of CO₂ treatment respectively. It may be observed from Fig. 12 that for 5 min treated sample, both surface and core contain Ca(OH)₂ and the apparent amount of Ca(OH)₂ is higher at core than the surface. On the other hand, XRD pattern for 15 min treated sample as shown in Fig. 13 indicates that Ca(OH)₂ is practically absent at the surface and core contains lower amount of Ca(OH)₂ compared to 5 min treatment (Fig. 12). Thus it appears that the Reaction (2) proceeds from surface to core and gradient of CaCO₃ as well as Ca(OH)₂ are developed from surface to core with progress of reaction. It is also apparent that beyond 15 min of treatment, conversion of Ca(OH)₂ to CaCO₃ is sluggish as has been mentioned before.

The weight loss experiments were carried out towards quantitative assessment of CaCO₃ and Ca(OH)₂. The percentage of CaCO₃ thus estimated for pellet C is plotted against CO₂ treatment time in Fig. 14. It has been found that approximately 87% transformation of Ca(OH)₂ was complete within 15 min of treatment and no further observable change took place even with additional 7 min of treatment. The strength improvement of pellet C with treatment time is again reproduced in Fig. 14 as dotted line for the sake of clarity. The trend in increase of the pellet strength corresponds to the trend for increase in CaCO₃ formed and supports the postulate that formation of CaCO₃ is the primary reason for improvement in strength of pellet after CO₂ treatment.

Degradation indexes (DI) for abrasion of pellets were found to remain practically independent of the treatment time ranging between 5 to 22 min (Table 6). It has been discussed in the preceding section that abrasive resistance depends upon the hardness of the surface. From XRD study (Fig. 12) it is clear that a significant extent of reaction had...
occurred at surface of pellets even within 5 min of the treatment, resulting in formation of a hard CaCO$_3$ rich surface. This imparts excellent resistance to degradation during abrasion. However, formation of CaCO$_3$ in the interior of pellets during extended treatment time does not apparently improve the DI.

Since the CCS and DSN values are maximum with minimum DI at treatment time of 15 min and DSM is also satisfactory, this duration was considered to be the optimum.

### 3.3. Grain Size of Iron Ore Fines

Pellets made of iron ore fines of varying size exhibited different cold crushing strengths, as shown in Fig. 15. It was found that, for pellets with fine grain size (pellet E, −72 mesh), the compressive strength increases monotonously with increasing treatment time. For pellets with medium grain size (pellet C, −72 : −30 + 72 mesh=1 : 1), however, the compressive strength first increases with increasing treatment time up to 15 min and subsequently, it remains unchanged. Pellet C shows greater strength in a 15-min treatment time than what has been observed for pellet E even for 22-min treatment. For pellet with coarse grain size (pellet D, −30 + 72 mesh), maximum strength was achieved in just 5 min and further increase in treatment time did not improve the strength. Though the maxima for pellet D (at 5 min) was higher than the strength values of pellet C and E at the corresponding time, the observed maximum strength for pellet D was much lower than those of the other two category of pellets. The preceding observations may be explained as follows.

Table 7 presents the porosity values of the three categories of pellets, before and after CO$_2$ treatment. It may be noted from the table that untreated pellet containing coarse grained iron ore fines (pellets D) has higher porosity than that containing iron ore of finer size (pellets E). The porosity of all pellets decreases after treatment. It has also been found that porosity of treated pellets depend upon the size fraction of iron ore fines.

It is evident from the Fig. 15 that plots for all three pellets (pellets C, D and E) exhibit different nature. Out of these three pellets, pellet D had maximum initial porosity (43.3%). It appears that high green porosity favored the progress of CO$_2$ reaction in pellet D and majority of CaCO$_3$ was formed in the entire volume of pellet within as early as 5 min. Accordingly, the strength curve reaches a maximum at around 5 min and subsequent treatment for extended period did not show any significant influence on strength. On the other hand, the plot for the relatively dense pellet (pellets E) shows a gradual increase in strength for the entire period of treatment. At the initial stage, the strength rises owing to the formation of carbonate on the surface of the pellet. This is followed by interparticle pore diffusion of CO$_2$ from surface to core, continuing the reaction in the interior of the pellet. As a result, in the initial period, strength developed in pellets E was less than that of in pellets D, while, with longer treatment time, strength of the former much surpasses the latter. With pellets C, whose particle size is intermediate to those of pellets D and E, strength rises to the maximum value (25.7 kg) in some intermediate duration of treatment (15 min) and remains steady there after. Notably, this is also the highest strength obtained amongst all the pellets of C, D, and E types.

Beside porosity, the extent of CaCO$_3$ formation may have significant effect on the strength of a treated pellet. In pellets D, C and E the lime content is same while initial porosities are different. Figure 16 presents the amount of CaCO$_3$ formed and the residual Ca(OH)$_2$ in these three pellets after CO$_2$ treatment. Pellet E has lower porosity (30%) after 15 min of CO$_2$ treatment, but due to lower amount of CaCO$_3$ and higher amount of residual Ca(OH)$_2$ the strength is lower than pellet C after 15 min of CO$_2$ treatment. On contrary, after 15 min of CO$_2$ treatment, pellets C and D have apparently same porosity (~38%) while the transformed CaCO$_3$ content in pellet D is higher than C but the strength of C is much higher than D. It appears that for specific lime content, there is an optimum level of CaCO$_3$ where strength becomes maxima. Although, the variation in nature of the pores may be another reason for the observed difference in strength, no attempt has been made in the current study to characterize the pores. However, on the basis of the above results, gain size of pellet C was considered to be the most suitable for subsequent study.

### 3.4. Total Pressure of Gas

CO$_2$ treatment of pellet C was carried out at different...
total gauge pressures inside the packed bed chamber for varying durations. Cold crushing strength of the treated pellets versus chamber pressure is plotted in Fig. 17 for 5-min and 15-min treatment times. It has been found that the compressive strength of pellets increases with increasing total pressure for the 15-min treatment, while the effect of pressure beyond 1.0 kgf/cm² gauge pressure is almost insignificant in the 5-min treatment. Reaction (2) involves equal moles of reactant and product gases. Therefore, under equilibrium, the extent of formation of CaCO₃ from Ca(OH)₂ should be independent of total pressure. However, application of high pressure is likely to facilitate condensation of water and may increase the rate of forward reaction (Reaction (2)).

At the early stage of carbonate formation, when the surface reaction is predominant, pressure is likely to have insignificant influence on the conversion of hydroxide to carbonate and a gauge pressure of 1 kgf/cm² was found to be sufficient to convert all the surface hydroxide into carbonate. Thus, the improvement in the crushing strength of pellets in the 5-min treatment was found to be limited to the pressure range 0–1 kgf/cm². But during extended treatment time (15 min), pore diffusion of CO₂ to continue the reaction inside the pellet was enhanced by high pressures of CO₂. This resulted in continuous increase in the crushing strength of pellets with increasing total pressure, as shown in Fig. 17.

### 3.5. Moisture Content of Pellets

The moisture content of pellets plays an important role in strength development of the pellets by CO₂ treatment since both the Reactions (1) and (2) involve H₂O. Green pellets before normal air-drying had maximum moisture of about 16%. Subsequently, normal air-drying of pellets for varying lengths of time (1–3 d) reduced the moisture contents in the range of 1.2–12.0%. In order to obtain pellets, free of moisture, for comparison purpose, they were heated in oven at 110°C for 4 h. It may be noted here that moisture analyses for representative pellets of each batch was conducted as per the procedure discussed earlier. A batch of typically 200 g of pellet of each moisture content was subjected to the CO₂ treatment for 15 min at 5 kgf/cm² pressure and ambient temperature.

The variation of the strength with varied initial moisture content of pellets C is shown in Fig. 18. The maximum compressive strength (25.7 kg) was observed with the initial moisture content of about 1.7%. The possible reasons for lower strength with higher moisture content may be presented as follows:

With high moisture content, the interparticle pores of a pellet are likely to be partially/completely filled by water. This will cause hindrance for easy passage of CO₂ to the interior of the pellet. Further, with excess CO₂ and in presence of moisture, CaCO₃ tends to get converted into water soluble calcium bicarbonate, according to the following reaction

\[
\text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) = \text{Ca(HCO}_3)^-(l) \quad \text{(5)}
\]

If the pellets are treated by CO₂ immediately after pelletization, Reaction (5) is likely to take place simultaneously with Reaction (2), due to the presence of extra moisture in green pellets. Replacement of the carbonate with bicarbonate causes marked decrease in the cold crushing strength of pellets.

Parkes¹⁷ has reported that dry slaked lime (Ca(OH)₂) does not absorb carbon dioxide unless a trace of moisture is present and thus, presence of low amount of moisture appears to catalyze the CO₂ absorption process. In the current study, when the moisture content is too low, the compressive strength is found to be significantly lower. This is possibly due to low absorption of CO₂, leading to decreased amount of CaCO₃. Therefore, the observation in the current study apparently supports the reported literature.

### 3.6. Gas Composition

In order to assess the effect of gas composition on strength, pellet C was treated with two different gas mixtures, namely 13%CO₂–25%CO–N₂ and 13%CO₂–N₂, at a pressure of 3.5 kgf/cm² for varying durations. The specific purpose of using the first gas mixture was to simulate industrial waste gas (say blast furnace off gas) composition for its possible utilization. In order to evaluate the effect of CO on hardening, the second gas mixture was freed from any CO and was supplemented with nitrogen.

The variation of cold crushing strength of pellet C, treated with the first gas composition at 3.5 kgf/cm² gauge pressures have been presented in Fig. 19 as a function of treatment time. The strength increases with increasing treatment time. Strength up to around 20 kg/pellet was achieved in 15 min treatment. Although, this value is slightly lower than that of the strength obtained by treating with pure CO₂ at 3 kgf/cm² gauge pressure (Fig. 16), the value is quiet encouraging. Similarly, DSN and DSM (98 and 10 respectively) are also exciting. Figure 19 also compares the effects of treatment time on crushing strength of pellets ob-
CO₂, 23–25% CO, and rest N₂ is easily available in blast furnace gas (BFG), which typically contains 13–20% CO₂ and is utilized for such pellet hardening treatments. For example, the absorption of CO₂ during the hardening treatment and this hardening purpose, it would get enriched with CO due to the transformation of Ca(OH)₂ to CaCO₃ with associated volume expansion.

Thus, waste gases containing CO₂ may be gainfully utilized for such pellet hardening treatments. For example, the blast furnace gas (BFG), which typically contains 13–20% CO₂, 23–25% CO, and rest N₂, is easily available in integrated and mini steel plants. Normally, in steel plant, the blast furnace gas is used for reheating and preheating furnaces owing to its high calorific value. If BFG is used for hardening purpose, it would get enriched with CO due to absorption of CO₂ during the hardening treatment and this would improve the calorific value of the gas further. Therefore, the use of the BFG in the hardening treatment is both feasible and advantageous.

A close scrutiny of the results presented so far would reveal that the best values in physical properties such as cold crushing strength, drop strength, abrasive strength and porosity/bulk density could be achieved for pellets prepared by mixing 25–30% lime with iron ore mixture (1 : 1) of (−72) and (−30 + 72) mesh and treated for 15 min in CO₂ at 5 kgf/cm² gauge pressure. As the intention is to incorporate maximum amount of lime without any marked deterioration of physical properties, 30% lime pellet prepared and treated under the above combination appears recommendable. Further study on the high temperature properties and assessment of performance of developed pellets in simulated laboratory scale basic oxygen process are under progress.

4. Conclusions

(1) The pellet making was possible with 20–40% lime in pelletizer.

(2) Strength in pellet was imparted in partially dry green pellet by CO₂ treatment at ambient temperature. This strength development was attributed to the transformation of Ca(OH)₂ to CaCO₃ with associated volume expansion.

(3) Strength of the treated pellet was sufficient (−30 kg/pellet) for cold handling. It varies on the mesh size of iron ore fines, composition of pellets, moisture content of green pellets, treatment time, pressure and composition of the reacting gas.

(4) The optimum conditions for pellet preparation may be −72 and +72 −30 mesh iron ore fines in 1 : 1 ratio, 30% lime content in the base mixture and optimum treatment condition may be 15 min of treatment at 5 kg/cm² gauge pressure and 1.5–2% moisture in green pellet.

(5) Significant strength could be developed with reacting gas containing 13% of CO₂. Therefore, the utilization of blast furnace off gas is also possible in this process.

(6) The proposed route successfully demonstrates the possibility of utilizing steel plant wastes both solid (iron oxides and lime fines) and gas (green house gas) for preparation of fluxed iron oxide pellets through a binderless process at ambient temperature.

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