Effects of calcium ferrite slag on dephosphorization of hot metal during pretreatment in the BOF converter

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\textbf{A B S T R A C T}

A study was carried out to examine effects of calcium ferrite slag on dephosphorization of hot metal in the steelmaking BOF, with aims to pick up the speed of slag-forming, increase the slag dumping rate. Laboratory tests using a resistance furnace were performed to examine melting characteristics of calcium ferrite pellets, designed with the optimum ratio of iron oxides (total Fe 55\%) to CaO of 3:1. The pellets were put in crucibles with furnace temperature held in the range of 1250–1350 °C for 10 min. The results showed that the melting of pellets was nearly completed at 1250 °C and main mineral phases, detected by XRD, in the melted samples were CaO\textsubscript{3}Fe\textsubscript{2}O\textsubscript{5} and 2CaO\textsubscript{3}Fe\textsubscript{2}O\textsubscript{5}. Based on results of the laboratory tests, experiments of full scale were performed using a converter of 120t, charging the hot metal with C 3.46–6.81\%, Si 0.1–1.16\%, Mn 0.12–0.30\%, P 0.10–0.18\%, S 0.017–0.13\% and temperature of 1234–1430 °C. For the 13 test heats with 6 min of oxygen blowing, the rate of dephosphorization and phosphorus distribution ratio reached to 50–60\% and 55.9\%, respectively, when the calcium ferrite pellets were charged. Averaged slag basicity 1.5–2.0, slag melting point 1280–1310 °C, slag viscosity 0.5 Pa.s were obtained for the BOF heats adding the calcium ferrite pellet, which ensured the slag foaming height controlled at 2.5–3.0 m during the early stages of the blow. Using above smelting process has increased the rate of slag dumping controlled at 50–70\% and enhanced the rate of hot metal dephosphorization over 90%.

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The pretreatment of hot metal dephosphorization technology has wide utilization in steelmaking fields and gets better effects [1–3]. However many factors make hot metal dephosphorization rate unstable and it is very difficult to product low phosphorus steel. These factors include that high basicity slag is not formed and the dephosphorization slag formed is hard to dump.

The technical difficulties in hot metal dephosphorization are the dephosphorization slag with higher phosphorus content hard to dump, which is shown as Fig. 1. If the dephosphorization slag has bad liquidity, it is very difficult to dump the dephosphorization slag and remove the phosphorus con-

tent of molten steel in smelting end-point. The research results of ITO K [4,5] and JIANG R [6] showed that the foaming of a steelmaking slag is caused by the dispersion of carbon monoxide inside the slag when this compound is released from the liquid steel. The main factor of influencing slag foaming is physical property of slag, such as slag viscosity, density and surface tension. Among the physical property the slag viscosity and melting point has most influence on slag foaming height. 

SANTHY K [7] and REHACKO A L [8] have measured slag viscosity for CaO-SiO$_2$-Al$_2$O$_3$ slag at 1200-1500°C. SELIVANOV E N [9] studied the viscosity variety of FeO$_2$-CaO slag. WANG Z J [10,11] measured slag viscosity of CaO-SiO$_2$-MgO-Al$_2$O$_3$-Fe$_2$O$_3$. SEOK S H [12] and JI F Z [13] analyzed high basicity slag viscosity for CaO-SiO$_2$-MgO-FeO$_2$ slag at 1600°C. Above research results reveal slag viscosity variety under conditions of high temperature (1400-1600°C), high basicity (>2.3). However there are few research on converter dephosphorization slag viscosity for CaO-SiO$_2$-FeO-MnO$_2$ slag at 1300-1350°C.

It is imperative for the iron-steel industry to develop new types of fluxing agents, in order to decrease the consumption of slag forming materials for dephosphorization and to eliminate fluorite for slag forming. Early research showed that an enhanced lime melting can effectively improve the dephosphorization of hot metal and increase the partition of phosphorus in the steelmaking slag. Some researchers have used laterite and bauxite as fluxing agents instead of fluorite [14,15]. These materials were beneficial for slag forming and for desulfurization of molten steel, but less effective for the dephosphorization of hot metal.

Melting points of calcium ferrite phases are rather low, which can lead to a full melting of lime to promote the transfer of phosphorus to the slag. WRIGHT S [16] and SUKENAGA S [17] studied slag viscosity variety through adding calcium ferrite. JEON J W [18], KONGOLI F [19] and PAANANEN T [20] have made the fundamental research on effects of calcium ferrite for the phosphorus transfer to the steel slag. HIROMI S [21] studied the mechanism and effect of calcium ferrite fluxes on the lime melting. TAKASHI S [22] conducted experiments on the hot metal dephosphorization by using calcium ferrite material during the production of high carbon steel. GUO M I [23] used synthetized calcium ferrite for hot metal dephosphorization, achieving satisfactory results.

These early studies have demonstrated the potential of using calcium ferrite fluxes to replace fluorite for slag forming and hot metal dephosphorization. However, most of calcium ferrite products commercial available are made by pre-fusing of mixtures of lime powder and iron oxide, resulting in relative high costs for the products. The high costs have limited the application of calcium ferrite materials for hot metal dephosphorization. Solid by-products from steel plants, lime powder and mill scales, were used in the present work as raw material to develop calcium ferrite pellets for hot metal dephosphorization in the steelmaking converter. Both laboratory and plant scale experiments were conducted. Results of the studies are reported and discussed.

1. Experimental methods

1.1. Design and preparation of the calcium ferrite pellets

According to CaO-Fe$_2$O$_3$ phase diagram [24] the calcium ferrite formed by CaO and Fe$_2$O$_3$ can have three compounds, namely C2F (2CaO·Fe$_2$O$_3$), CF (CaO·Fe$_2$O$_3$) and CF2 (CaO·2Fe$_2$O$_3$), with melting point of 1438°C, 1218°C and 1205°C, respectively. The relatively low melting temperature for the compounds and their contents of CaO and Fe$_2$O$_3$ have made the calcium ferrite the best alternative to replace fluorite and a suitable and important material for hot metal dephosphorization in the steelmaking BOF.

The commercial calcium ferrite products are made by pre-fusing of mixtures of lime powder and iron oxide with CaO and Fe$_2$O$_3$ content ranges of 10-40% and 50-75%, respectively. There are also SiO$_2$ (<4.0%) and MgO (<6.0%) in the products, as well as traces of F, P and S. By referring to the specification for the commercial products, 4 types of calcium ferrite pellets were designed for heating and melting tests. The pellets were coded as A, B, C and D with the ratio of iron oxides (total Fe 55%) to CaO of 1:3.1, 2:1, 3:1 and 4:1, respectively. These designed pellets were made of solid by-products obtained in steel plants, including lime powder and mill scales from continuous casting and rolling operations.

1.2. Equipment and procedures for heating and melting tests of the calcium ferrite pellets, lime and other slag forming materials

The experimental method used first determined the melting point of four ferrite calcium samples by using a melting point instrument to determine the sample with the lowest melting point.

A resistance furnace was used to carry out the tests. In general, the furnace was power on for 10-15 min to heat crucibles or refractory blocks to the desired test temperature.
ranging 1250–1350 °C. While reaching the desired temperature, the crucibles or blocks were removed from the furnace for charging the test materials in the crucibles or on the surface of the blocks and then quickly returned back in the furnace for the heating tests. The test time was 10–15 min, after which the crucible/block was taken out of the furnace to examine melting characters of the test materials after cooling.

1.3. On experiments of hot metal dephosphorization in a BOF converter

The experiments were performed using a 120 t converter, with refining time and average tapping weight of molten steel, respectively, of 37 min and 116 t. The supply intensity for the top oxygen lance and for the bottom stirring system was 3.3 Nm3/t•min and 0.03–0.08 Nm3/t•min, respectively. The hot metal charged was 115 t with temperature of 1234–1430 °C and C, Si, Mn, P and S of, respectively, 3.46–6.81%, 0.1–1.16%, 0.12–30.3%, 0.10–0.18% and 0.017–0.13%. The scrap charged for the steelmaking was 8 t. The slag forming materials were lime, light-burned dolomite, sintered ore and the calcium ferrite pellets.

For the experimental heats, lime and the light-burned dolomite needed for the first slag were added in the beginning of oxygen blowing. Afterwards, the sintered ore and calcium ferrite pellets were charged according to the progress of the slag forming in the period of 3 min. The constant pressure and variable lance height were adopted for oxygen supply. After 6 min for the oxygen blowing, the converter was tilted to tap, as much as possible, the first, phosphorus-enriched slag.

At the time of slag tapping, the metal temperature and the slag basicity was controlled in the range of 1310–1330 °C and 1.5–1.8, respectively.

Samples of metal and slag were taken for chemical analyses and other studies.

2. Results

2.1. Test of melting point of calcium ferrite sample

The melting temperatures of the four samples A, B, C, and D were measured in a melting point apparatus. The specific measurement results are shown in Table 1 and as shown in Fig. 2. As can be seen from Table 1, Sample C has the lowest melting temperature, followed by Sample D, Sample B, and Sample A.

Fig. 2 shows the hemisphere temperatures of the four samples. As can be seen from the figure, sample C has the lowest hemisphere temperature of 1209 °C. Next is the hemispherical temperature of sample D, which is 1218 °C. The hemisphere temperatures of samples B and A were higher, at 1338 °C and 1361 °C, respectively.

Samples C and D were considered to have lower melting temperatures based on the determination of the melting temperatures of the four samples. In order to further verify the fluidity of the four samples, the measurement of the fluidity of the sample was carried out in an electric resistance furnace.

2.2. Characters of melting and liquefy of the designed calcium ferrite pellets

The melting characters for mixtures of calcium ferrite pellet coded as A, B, C and D with designed ratio of iron oxides to CaO of 1:3:1, 2:1, 3:1 and 4:1 were tested respectively, cooled after heating at 1350 °C for 10 min in crucibles. The results show that there are different degrees of partially melting on the surface for sample A, B and D. Under the surface of the samples some powder was found remaining in solid state. But, there is not solid powder found on and under the surface for sample C, indicating a totally melting of the sample in the crucible heated at 1350 °C for 10 min. A similar result is shown in Fig. 3.
Fig. 3 – Melting characters for mixtures of calcium ferrite pellet coded as A, B, C and D with designed ratio of iron oxides to CaO of 1.3:1, 2:1, 3:1 and 4:1, respectively, cooled after heating at 1350 °C for 10 min on the surface of refractory blocks.

Fig. 4 – Melting characters for samples of calcium ferrite pellet type C with designed ratio of iron oxides to CaO of 3:1 cooled after heating at 1250–1350 °C for 10 min in crucibles.

Fig. 5 – The x-ray diffraction analysis of samples of calcium ferrite pellet type C at 1250 °C and 1350 °C.

for the samples solidified on surface of refractory blocks. The results demonstrated a best character of melting and liquefy for sample C, which design with ratio of iron oxides to CaO of 3:1 was thus selected to make calcium ferrite pellets for the present study.

The calcium ferrite pellets made based on the design of sample C and dried at 110 °C for 2 h were heated in crucibles for 10 min at high, medium and low temperature or at 1350, 1300 and 1250 °C for each of the tests. The results in Fig. 4, a complete melting of the pellets at the high, medium and low temperature, demonstrate that the melting point of the calcium ferrite pellet is below 1250 °C.

Fig. 5 shows results of x-ray diffraction analysis and major mineral phases of the calcium ferrite pellets melted at 1250 °C and 1350 °C being CaO•Fe2O3 and 2CaO•Fe2O3. The average density measured for the calcium ferrite pellets is 3.02 g/cm³.

2.3. Effects of the calcium ferrite pellets on hot metal dephosphorization in BOF converter

The dephosphorization by double-slag process has been used to produce low phosphorus steel products. Because of shorter process time, the slag melting and tapping of the first slag were often incomplete, which led to problems for dephosphorization in the earlier stage and near the end-point of the converter heats. The calcium ferrite pellets developed in the present study were thus used in the earlier stage of converter process as the dephosphorizing agent to solve the problems.

For a better interpretation of the experimental results, the rate of dephosphorization, \( \eta_r \), and phosphorus distribution ratio between the slag and metal, \( L_p \), defined by Eqs. 1 and 2, respectively, are calculated using data of phosphorus contents.
in the metal and slag samples obtained from the converter experiments.

\[ \eta_p(\%) = \frac{[w_0([p]) - w([p])] }{w_0([p])} \times 100 \]  \hspace{1cm} (1)

\[ L_p = \frac{w([P])}{w([p])} \]  \hspace{1cm} (2)

where, \( w([P]) \) and \( w([p]) \) stands for the mass percent concentration of phosphorus in slag and metal, respectively, and the subscript 0 denotes initial stage, namely the starting point of the process step.

Some data related to the earlier stage dephosphorization with blowing time of 6 min for the converter experiments are shown in Fig. 5. It is seen from the left figure of Fig. 6 that the rate of dephosphorization, \( \eta_p \), and the averaged phosphorus distribution ratio, \( L_p \), are 50–60% and 55.9, respectively, while the calcium ferrite pellets were used for the slag formation, which are higher than the \( \eta_p \) and averaged \( L_p \) values of 33.9–53.9% and 31.35, respectively, obtained from the experiments without using the calcium ferrite pellets. The results show that the slag with additions of the calcium ferrite pellets was more effective for hot metal dephosphorization than the slag not adding the pellets.

It is seen from the right figure of Fig. 5 that the slag basicity and total iron content, \( TFe \), in slag are more stable and less fluctuate with the calcium ferrite pellets for the slag formation than those without the pellets. The results indicate that the calcium ferrite pellets can contribute to the formation of an early slag with higher stability and fluidity than the slag formed without the pellets.
Table 2 – Slag forming materials consumed in different converter experiments, kg/t (averaged value).

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Lime</th>
<th>Light-burned dolomite</th>
<th>Sintered ore</th>
<th>Calcium ferrite pellets</th>
<th>Sum of the materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add calcium ferrite pellet</td>
<td>18.9</td>
<td>13.1</td>
<td>12.65</td>
<td>4.3</td>
<td>48.95</td>
</tr>
<tr>
<td>No calcium ferrite pellet</td>
<td>20.55</td>
<td>13.66</td>
<td>18.12</td>
<td>0</td>
<td>52.33</td>
</tr>
</tbody>
</table>

Optical microscopy results of a sample from the converter slag formed in the earlier stage, 5 min, without using the calcium ferrite pellets in Fig. 7 show high contents of C3S, C2S and free calcium oxide in the slag sample, which can increase viscosity and melting temperature for the slag and, hence, decrease its efficiency for dephosphorization. The composition of phase is: 1-C3S 10–15%; 2-C2S 40–45%; 3-RO phase 15–20%; 4-C4AF phase 15–20%; 5-fCaO 5–8%.

There is no C3S and free calcium oxide found in the sample for the slag in the earlier stage, 4.5 min, formed with using the calcium ferrite pellets, Fig. 7. The composition of phase is: 1-C2S 25–30%; 2-RO phase 20–25%; 3-Glass phase 35–40%. The C2S content has decreased to 25–30% and contents of low melting point phases, such as RO and glass phase, are also quite high. With the phase compositions, the slag can have higher efficiency for heat and mass transfer and higher ability to adsorb phosphorus than the slag formed without using the pellets.

Averaged weight of slag forming materials consumed in converter experiments adding the calcium ferrite pellets is 3 kg/t less than this for the experiments without the pellets as indicated in Table 2. Using waste materials to make the calcium ferrite pellets has resulted in decreased consumptions for lime and sintered ore, as well as the enhanced rate for hot metal dephosphorization, which is considered economic and environmentally beneficial for the steelmaking industry.

3. Results analysis and discussions

3.1. The petrographic composition and viscosity of the calcium ferrite slag

The dephosphorization slag was taken in hot metal pretreatment, which chemical composition is CaO 37.88%, SiO₂
Table 3 – The comparison between two kinds of process.

<table>
<thead>
<tr>
<th>Original process</th>
<th>New process</th>
<th>Achieve effects by new process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slagging material includes lime, light burn</td>
<td>Slagging material includes lime, light</td>
<td>The slag basicity is changed</td>
</tr>
<tr>
<td>dolomite, sintere ore</td>
<td>burn dolomite, sintere ore and calcium</td>
<td>from 1.2 to 1.4 to 1.8–2.0 by</td>
</tr>
<tr>
<td>The supplied oxygen flow rate is 26000–27000</td>
<td>ferite</td>
<td>the same lime consumption</td>
</tr>
<tr>
<td>Nm³/h</td>
<td></td>
<td>The blowing time is from 3–4</td>
</tr>
<tr>
<td>The bath temperature is 1350–1400</td>
<td>The bath temperature is 1330–1350</td>
<td>min to 4–5 min</td>
</tr>
<tr>
<td>The bottom blowing and stirring strength is</td>
<td>The bottom blowing and stirring</td>
<td>To keep good slag melting and</td>
</tr>
<tr>
<td>0.03–0.04 Nm³/t.min</td>
<td>strength is 0.06–0.08 Nm³/t.min</td>
<td>suitable viscosity at 1320–1350</td>
</tr>
</tbody>
</table>

The viscosity of the dephosphorization slag was measured by using RTW-10 melt viscometer. The slag amount is 140 g and the graphite crucible is used. The temperature drop is 5 °C/min. The test result shows that the viscosity value of dephosphorization slag at 1300–1400 °C is between 0.48 and 0.75 Pa·s.

3.2. The influence of converter process change on dephosphorization effects

In order to obtain better dephosphorization effects the operation process has been changed, which is seen as Table 3.

It is seen from Table 3 that the aim of process change is to promote the reaction between steel slag and drop converter slag as far as possible. The slag height is calculated according to previous research results [25–27].

The slag foaming height of converter:

$$H_f = \frac{Q_o \cdot \Sigma}{A} \quad (3)$$

The CO volume at the beginning of converter:

$$Q_o = G(C_1 - C_2) \times \frac{22.4}{12} \times \frac{60}{T} \times \frac{1.8}{3600} \quad (4)$$

The foaming index:

$$\Sigma = \frac{359 - \mu}{\sqrt{\rho g \rho}} \quad (5)$$

$$\rho = 2.46 + 0.018(\text{w%iron} - \text{oxides}) \quad (6)$$

Where $H_f$ is the slag height, m; $Q_o$ is CO volume at the beginning of converter, Nm³/s; $A$ is cross sectional area of converter bath; $\Sigma$ is the foaming index of slag; $G$ is the amount of hot metal charged, kg; $C_1$ is carbon content of hot metal, %; $C_2$ is carbon content of sample, %; 1.8 is empirical coefficient; $\mu$ is slag viscosity, Pa·s; $\rho$ is slag density, kg/m³; $g$ is the gravitational acceleration, m/s²; $\sigma$ is the surface tension of slag, kg/s².

The influence of slag change at initial stage on slag foaming height obtained by formula (3)–(6), which is shown as Fig. 9.

It is seen from Fig. 8 that the slag foaming height is 2.5–3.0 m obtained by new process. After the new process is adopted, the slag dumping rate is 50–70% and total dephosphorization rate is 90–94%.

4. Conclusions

The calcium ferrite pellets developed via laboratory experiments have been used as the dephosphorizing agent for the hot metal pretreatment during the earlier stage of BOF process, obtaining the following results:

1) The calcium ferrite pellets, made of solid by-products obtained in steel plants, including lime powder and mill scales, and with the ratio of iron oxides (total Fe 55%) to CaO of 3:1, possessed best melting characteristics as compared with the other slag forming materials.

2) The X-ray diffraction analyses of solidified samples melted at 1250 °C and 1350 °C have shown that CaO•FeO·SiO₂ and 2CaO•Fe₂O₃ were the main mineral phases in the calcium ferrite pellets at the temperature range.

3) The calcium ferrite pellets were used as the dephosphorizing agent in the hot metal pretreatment during the earlier blowing oxygen stage of a 120 t BOF converter. The achieved
rate of dephosphorization and the averaged phosphorus distribution ratio was 50–60% and 55.9, respectively, which are both higher than that for the heats without using the pellets.

4) With using the calcium ferrite pellets for slag formation, the slag basicity and total iron content in slag are more stable and have little fluctuation, as compared with the slag formed without using the pellets. Using the pellets also enhanced contents for phases with low melting points, which led to a better fluidity and higher ability to adsorb phosphorus for the slag than the slag formed without the pellets.

5) Averaged slag basicity 1.5–2.0, slag melting point 1280–1310°C, slag viscosity 0.5 pas were obtained for the BOF heats adding the calcium ferrite pellet, which ensured the slag foaming height controlled at 2.5–3.0 m during the early stages of the blow. Using above smelting process has increased the rate of slag dumping controlled at 50–70% and enhanced the the rate of hot metal dephosphorization over 90%.

Conflict of interest
The author declares no conflicts of interest.

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Appendix A. Supplementary data
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REFERENCES
