The relationship between theoretical substitution ratio of CaO and BOF process parameters based on thermal equilibrium

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Abstract. In consideration of material balance, relationship between the surplus heat and the parameters including compositions and temperature of molten iron, amount of scrap steel and tapping temperature were established by heat balance calculation in converter. Meanwhile theoretical substitution ratio of CaO $\eta$ with limestone instead of active lime in steelmaking was defined, and the function relation between theoretical substitution ratio of CaO and surplus heat was established for exploring the effects of parameters on theoretical substitution ratio of CaO. The results indicated: theoretical substitution ratio of CaO can be significantly improved by increasing temperature and carbon content of molten iron. When temperature of hot metal $< 1300^\circ$C, theoretical substitution ratio of CaO increased with the increasing of silicon content; while temperature of hot metal $> 1300^\circ$C, theoretical substitution ratio of CaO decreased with the increasing of silicon content. When the basicity of slag and the tapping temperature were constant, theoretical substitution ratio of CaO can be significantly increased by reducing the amount of scrap steel.

1. Introduction

Active lime is one of high quality and light burned lime with good chemical properties, powerful chemical reaction ability, and less S, P and other harmful elements. It has the characteristics of small volume density, large porosity, large specific surface area, tiny grain size, high activity (generally greater than 300mL) and so on. Because of high activity, it is easier to react with harmful elements in molten steel and beneficial to remove impurities in converter steel, so it has been widely used in the field of converter steelmaking. But the calcination process needs to be done in rotary kiln or vertical kiln and complex. It is usually fully preheated at 700–900$^\circ$C, then heated to 1100–1200$^\circ$C rapid burnt a few hours\cite{1~3}. Produced lime is unstable in the air so it must be stored and transported in a dry and airproof environment and used as soon as possible. This mode of production wastes a lot of manpower and material resources, at the same time it runs counter to the spirit of energy saving, emission reduction and low-carbon metallurgy. The above steps can be omitted, and the special environment is not needed for storage and use by direct use of limestone in steelmaking. Moreover the surplus heat in converter can be directly utilized by limestone decomposition endothermic. The CO$_2$ produced by decomposition can also be applied to the oxidation of molten iron. In view of the above advantages, researchers began to consider using part of limestone instead of active lime in converter under the...
condition of guaranteeing the quality of steel products, remarkable cost reduction and energy-saving have been achieved [4–11].

Due to the initial exploration stage, there is only the factory test data without the theoretical basis on limestone ratio. The equation between the theoretical substitution ratio of CaO and compositions of molten iron, temperature of molten iron, amount of scrap steel and tapping temperature were established by the material balance and heat balance were calculation while assuming limestone to decomposition and absorption heat were supplied by the surplus heat. And the relationship between the parameters and the theoretical substitution ratio of CaO were derived. This will provide a theoretical guidance for limestone instead of active lime in steelmaking.

2. Model Building

2.1. Material balance calculation.
Considering the heat balance, the material balance of converter must be calculated first. And suppose single slag process with Non residual slag operation were used. Taking 100kg molten iron as an example in steelmaking process, the process parameters are supposed in Table 1.

| Name                     | Parameter                  | Name                     | Parameter                  |
|--------------------------|----------------------------|--------------------------|----------------------------|
| Smoke and Dust           | 1.5% molten iron           | Splash loss              | 1% molten iron             |
| Iron of smoke and dust   | 75% FeO, 20% Fe₂O₃         | Oxycarbide in molten iron| 90%CO, 10%CO₂              |
| Slag temperature         | molten steel temperature   | Dephosphorization rate   | 90%                        |
| Gas average temperature  | 1450 ℃                    | desulfurization rate     | 35%(10% Gasification)      |
| Free oxygen of gas       | 0.5% (volume ratio)        | Iron loss in slag        | 4% slag                    |
| Iron ore                 | 1 kg                       | Iron of Final slag       | 10% FeO, 5%Fe₂O₃           |
| Dolomite                 | 3% molten iron             | Oxygen component         | 99% O₂, 1% N₂              |
| Lining erosion           | 0.5% molten iron           | Oxidation of manganese   | 70%                        |

Setting carbon content and silicon content in hot metal as w(C) and w(Si), and the content of C, Si, Mn, S and P in molten iron and molten steel were shown in Table 2. The chemical composition of lime, iron ore, dolomite and lining were shown in Table 3.

| Materials       | C    | Mn   | S   | Si   | P    |
|-----------------|------|------|-----|------|------|
| Molten iron     | w(C) | 0.60 | 0.032 | 0.200 |
| Molten steel    | 0.10 | 0.18 | 0.021 | 0.020 |

| composition     | CaO  | FeO  | Fe₂O₃ | Igloss | S    | H₂O  | C    | SiO₂ | MgO  | Al₂O₃ |
|-----------------|------|------|-------|--------|------|------|------|------|------|-------|
| Lime            | 90.00| -    | 0.50  | 2.14   | 0.06 | 0.20 | -    | 3.00 | 2.60 | 1.50  |
| Iron ore        | 1.00 | 29.4 | 61.8  | -      | 0.07 | 0.50 | -    | 5.61 | 0.52 | 1.10  |
| Dolomite        | 55.00| -    | 1.00  | 5.00   | -    | -    | -    | 3.00 | 33.0 | 3.00  |
| Lining erosion  | 1.20 | -    | 1.60  | -      | -    | 14.00| 3.00 | 78.80| 1.40 |
Material incomes in converter steelmaking include lime, scrap (W kg), oxygen, dolomite, iron ore, molten iron (100 kg) and Lining erosion. Material expenditures include molten steel, slag, gas, iron loss, splash loss and dust in slag. Table 4 presented the material balance in 100 kg molten iron.

### Table 4. Sheet of material balance of BOF process

| Item                        | Income item Mass(kg) | Expenditure item Mass(kg) |
|-----------------------------|----------------------|---------------------------|
| Lime                        | 9.435w(Si)-1.367     | 97.557-3.035w(Si)-w(C)+ W  |
| Scrap                       | w                    | 13.315w(Si)+3.505         |
| Oxygen                      | 1.494w(C)+1.650w(Si)+0.520 | 2.494w(C)+0.236w(Si)+0.056 |
| Dolomite                    | 3                    | 0.533w(Si)+0.140          |
| Iron ore                    | 1                    |                           |
| Molten iron                 | 100                  |                           |
| Lining erosion              | 0.5                  |                           |
| Total                       | 1.49w(C)+11.08w(Si)+W+103.65 |                 |

2.2. *Heat balance calculation.*
First, we supposed that all of the materials in converter were 25°C (except molten iron).

2.3. *Heat incomes.*
Heat incomes \(Q_i\) mainly included physical heat of molten iron, chemical heat of element oxidation, oxidation heat release of smoke and dust, oxidation heat release of carbon in lining (ignoring the physical heat brought by scrap, lime, dolomite, ore, and oxygen). The average specific heat capacity of various materials used in calculating exothermic and endothermic were listed in Table 5. The thermal effect of chemical reaction at steelmaking temperature which can calculate oxidation heat of element and slag forming heat were listed in Table 6.

### Table 5. Specific heat capacity of materials

| item                  | average specific heat capacity of solid materials (kJ·kg\(^{-1}\)·K\(^{-1}\)) | latent heat of fusion (kJ·kg\(^{-1}\)) | average specific heat capacity of liquid or gaseous material (kJ·kg\(^{-1}\)·K\(^{-1}\)) |
|-----------------------|-------------------------------------------------|----------------------------------------|-----------------------------------------------|
| Pig iron              | 0.745                                           | 217.568                                | 0.8368                                        |
| steel                 | 0.699                                           | 271.96                                 | 0.8368                                        |
| gas                   | —                                               | —                                      | 1.136                                         |
| slag                  | —                                               | 209.20                                 | 1.247                                         |
| Smoke and dust        | 1.000                                           | 209.20                                 | —                                              |
| ore                   | 1.046                                           | 209.20                                 | —                                              |
Table 6. Chemical reaction heat effect at steelmaking temperature

| element | Chemical reaction | ΔH(kJ·kg⁻¹) |
|---------|-------------------|-------------|
| C       | [C]+1/2O₂=CO      | 11639       |
| C       | [C]+1/2O₂=CO₂     | 34834       |
| Si      | [Si]+O₂=SiO₂      | 29202       |
| P       | 2[P]+5/2O₂=P₂O₅   | 18980       |
| Mn      | [Mn]+1/2O₂=MnO    | 6594        |
| Fe      | [Fe]+1/2O₂=FeO    | 4250        |
| Fe      | 2[Fe]+3/2O₂=Fe₂O₃ | 6460        |
| SiO₂    | 2CaO+SiO₂=2CaO₂SiO₂ | 1620    |
| P₂O₅    | 4CaO·P₂O₅=4CaO·P₂O₅ | 4880 |

Assuming the initial temperature of molten iron was T₁. Heat income were calculated.

Table 7. Heat income item in converter steelmaking

| heat income item | Unit kJ |
|-----------------|---------|
| Physical heat of molten iron | 83.7T₁+920w(C)+73.6w(Si)+5853.26 |
| Chemical heat of molten iron | 13958.5w(C)+40545.48w(Si)+5318.476 |
| Oxidative heat release of smoke and dust | 5075.35 |
| Oxidative heat release of carbon in lining | 977.10 |
| Total heat incomes | 83.7T₁+14878.5w(C)+40619.08w(Si)+17224.186 |

2.4. Heat expenditure.
Heat expenditures Qₑ included physical heat of molten steel (formed by smelting molten iron and scrap), physical heat of slag, physical heat carried away by gas, physical heat of smoke and dust, heat absorption of ore in temperature rise and decomposition, physical heat of shot iron in slag, physical heat of spattered metal and heat loss. Assuming that the tapping temperature was T₂(℃) and the temperature of slag equals to molten steel in converter. The temperature of gas and dust was 1450℃. Heat loss was 5% of heat income, and heat expenditure items were calculated.

2.5. Surplus heat.
The surplus heat in converter Qₛ (kJ) was the difference between heat income and heat expenditure. The surplus heat can be used to balance the extra heat absorption when we employ limestone instead of lime in slagging.

\[
Qₛ=Qᵢ-Qₑ=79.515T₁+10138.763w(C)+35948.031w(Si)+4802.106-W*0.8368T₂+45.029-
(88.007+14.510w(Si)-0.8368w(C))T₂
\]  

(1)

From formula (1) we can see when using active lime (100%) in slagging, the surplus heat Qₛ related to molten iron composition and temperature, amount of scrap and tapping temperature.
Table 8. Heat expenditure item in converter steelmaking

| heat expenditure item                                | value kJ                                                                 |
|------------------------------------------------------|--------------------------------------------------------------------------|
| Physical heat of molten iron                         | [97.557-3.035w(Si)-w(C)](0.8368T \(_2\)+45.029)                         |
| Physical heat of molten scrap                         | (0.8368T \(_2\)+45.029)-W                                               |
| Physical heat of slag                                 | [16.604w(Si)+4.371]T \(_2\)+2370.403w(Si)+625.66                         |
| Physical heat carried away by gas                      | 4040.841w(C)+382.373w(Si)+90.733                                        |
| Physical heat carried away by dust                     | 2451.3                                                                  |
| Heat absorption of ore                                | 4040.841w(C)+382.373w(Si)+90.733                                        |
| Physical heat of iron shot in slag                    | [0.446w(Si)+0.117]T \(_2\)+23.982w(Si)+6.313                             |
| Physical heat of spattered metal                      | 0.8368T \(_2\)+45.029                                                  |
| Heat loss                                             | 4.185T \(_1\)+743.925w(C)+2030.954w(Si)+861.209                        |
| Total heat expenditures                               | 0.83w(C)T \(_2\)+4671.05w(Si)+4739.73w(C)+12422.08                     |

2.6. CaO substitution ratio η.

When limestone instead of active lime in slagging, the extra heat absorption included the heat of temperature rising, decomposition, and minus the heat consumption of active lime in temperature rising. The temperature rising heat of limestone referred to the energy absorption from 25°C to 900°C. The decomposition heat of limestone referred to the energy absorption when CaCO\(_3\) decomposed. So the unit temperature rising heat of limestone \(Q_a\) (kJ/kg) as follow:

\[
Q_a = \int_{298}^{1173} (104.516 + 21.924 \times 10^3T - 25.941 \times 10^5T^{-2})dT
\]  

\(Q_a = 99.07\text{kJ/mol}=990.70\text{kJ/kg}\)

Enthalpy change of CaCO\(_3\) decomposition

\[
\text{CaCO3}=\text{CaO+CO2} -1777.6\text{J/kg}
\]  

The unit temperature rising heat of active lime \(Q_b\) (kJ/kg) as follow:

\[
Q_b = \int_{298}^{1173} (49.622 + 4.519 \times 10^3T - 6.945 \times 10^5T^{-2})dT
\]  

\(Q_b=44.59\text{kJ/mol}=796.25\text{kJ/kg}\)

CaO substitution ratio η means the ratio of CaO in limestone instead of CaO in active lime:

\[
\eta = \frac{\text{The amount of CaO in limestone}}{\text{The amount of CaO in active lime}} \times 100\%
\]  

Suppose the CaO content in limestone was 56%, and per 100kg molten iron added X kg limestone. If the CaO content in lime was 90%, the amount of active lime in slagging process is \(w_1\). The quality of CaO in slag must be the same at two kinds of slagging system, when using part of limestone instead of active lime in steelmaking, so

\[
56\% \times X = 90\% \times w_1 \times \eta
\]  

\(w_1=9.435w(\text{Si}) \times 1.367\)
Obtained from the upper equations (6) and (7):

\[ X = \eta \left[ 8.492w(\text{Si}) - 1.230 \right] / 0.56 \]  

(8)

The necessary condition for limestone replaced active lime is that the surplus heat \( Q_S \) can meet the extra heat consumption of limestone.

\[ Q_S = (990.7 + 1777.6)X - (8.492w(\text{Si}) - 1.23) \times \eta \times 796.25 = [35215.464w(\text{Si}) - 5102.23] \times \eta \]  

(9)

\[ \eta = \frac{Q_S}{35215.464w(\text{Si}) - 5102.23} \times 100\% \]  

(10)

3. Results and Discussions

3.1. Effect of the temperature of molten iron.

Combined equations (1) and (9), given \( w(C) = 3.6\% - 4.4\% \), \( w(\text{Si}) = 0.30\% \), adding amount of per 100kg molten iron \( W = 10kg \), Tapping temperature \( T_2 = 1650^\circ\text{C} \), theoretical substitution ratio of CaO \( \eta \) was a linear function of the molten iron temperature \( T_1 \):

\[ \eta = 8.851 \times 10^{-3} T_1 - 11.3 \]  

(11)

As shown in Fig. 1, theoretical substitution ratio of CaO was proportional to temperature of molten iron. If temperature of molten iron increased, the amount of lime which was substituted by limestone also increased gradually. While \( w(C) = 4.4\% \), theoretical substitution ratio of CaO was 1.82\% when molten iron temperature \( T_1 \) was 1264\(^\circ\text{C} \). But theoretical substitution ratio of CaO changed as high as 54.23\% when molten iron temperature \( T_1 \) was 1300\(^\circ\text{C} \).

Fig. 1 Relationship between theoretical substitution ratio of CaO and temperature of molten iron

The theoretical substitution ratio of CaO depended on the surplus heat of the converter. The molten iron temperature was the basic characterization of the physical heat of the molten iron which is one of the main sources of converter heat. Obviously the molten iron temperature increased and the physical heat of converter increased. Showing from fig. 1, theoretical substitution ratio of CaO affected with the change of \( w(C) \). If \( w(C) \) increased, theoretical substitution ratio of CaO got larger.

3.2. Effect of the C, Si content of molten iron.

Set initial temperature of molten iron \( T_1 \) as 1300\(^\circ\text{C} \) and 1350\(^\circ\text{C} \), scrap amount \( W \) was 10\% of molten iron, Tapping temperature \( T_2 = 1650^\circ\text{C} \), according to equation 9 effect of C, Si content of molten iron on theoretical substitution ratio of CaO were shown in Figure 2. Under the premise of constant heat expenditure, theoretical substitution ratio of CaO depended on the heat income. The chemistry heat of
carbon in molten iron was one of the most important heat sources in converter. When \( w(C) \) increased, theoretical substitution ratio of CaO raised gradually in figure 2. As Temperature of molten iron was 1350 ℃, \( w(Si)=0.40\% \), if \( w(C) \) changed from 3.7% to 4.2%, theoretical substitution ratio of CaO also raised from 0.37% to 64.84%. Therefore, \( w(C) \) increased in molten iron will promote theoretical substitution ratio of CaO raised. In addition, as the molten iron temperature dropped, the straight line moved to the right as a whole, the theoretical substitution ratio of CaO declined.

The effect of \( w(Si) \) in molten iron on the theoretical substitution ratio of CaO was shown in figure 3. When the initial molten iron temperature \( T_1 \) was certain, with the change of \( w(C) \) in molten iron, the influence of \( w(Si) \) on the substitution ratio of CaO was different. When \( w(C) \) was a certain value, the substitution ratio of CaO was constant with different \( w(Si) \); When \( w(C) \) was great than this certain value, the substitution ratio of CaO dropped with the increase of \( w(Si) \) and tended to gentle; When \( w(C) \) was lower than this certain value, the substitution ratio of CaO raised with the increase of \( w(Si) \) and also tended to gentle at last. This certain value of \( w(C) \) was relevant with the molten iron temperature. The lower the molten iron temperature was, the higher certain carbon content was. \( w(C) \) is generally 2%~4.3%. So if molten iron temperature was lower than 1300 ℃, the substitution ratio of CaO raised with increase of \( w(Si) \) and molten iron temperature was higher than 1300 ℃, substitution ratio of CaO declined with increase of \( w(Si) \) in figure 3.

\[
(Si) + O_2 = (SiO_2) + Q
\] (12)
\[(\text{SiO}_2) + (\text{CaO}) = (2\text{CaO} \cdot \text{SiO}_2)\]  

(13)

Equation (11) and (12) showed that, on the one hand, the oxidation of silicon element in molten iron was exothermic reaction. The increase of w(Si) will promote rising of heat in converter. So more surplus heat will be provided. On the other hand, the Si oxidized to SiO\(_2\) in the molten iron gets into slag. When the slag basicity (CaO/SiO\(_2\)) is certain, the demand of CaO will rise up and heat absorption will also increase. This would lead to the decrease of surplus heat. Thus there is the contradiction between releasing heat of Si oxidation and consuming more heat of CaO increasing, which may serve to explain the complex influence of w (Si) on the theoretical substitution ratio of CaO in converter.

3.3. Effect of the tapping temperature.

Setting molten iron temperature were 1300°C and 1350 individually. C and Si content in molten iron were 4.2% and 0.4%. Scrap amount was 10% of molten iron. The effect of tapping temperature on theoretical substitution ratio of CaO was shown in Fig. 4. Obviously, Fig. 4 reflected tapping temperature rise caused the drop of theoretical substitution ratio of CaO. The influence of tapping temperature can be explained by surplus heat. So molten iron temperature increased, theoretical substitution ratio of CaO will be compensate as tapping temperature rising.

![Fig. 4](image)

**Fig. 4** Effect of tapping temperature on the theoretical substitution ratio of CaO

3.4. Effect of scrap amount.

Setting molten iron temperature were 1250°C, 1300°C and 1350°C individually. C and Si content in molten iron were 4.2% and 0.4%. Tapping temperature was 1650°C. The effect of scrap amount on theoretical substitution ratio of CaO was shown in Fig. 5.

![Fig. 5](image)

**Fig. 5** Scrap addition effect on the theoretical substitution ratio of CaO
From Fig. 5 we can obviously see when molten iron temperature was rising from 1250℃ to 1350℃, scrap amount and theoretical substitution ratio of CaO were all significantly increasing. With the increase of scrap amount rate, theoretical substitution ratio of CaO linearly dropped. This was mainly caused by limestone heating and decomposition heat absorption and scrap melting heat absorption. While molten iron temperature was certain, theoretical substitution ratio of CaO can obviously rise up with scrap amount decreasing. Only considering the heat balance of converter, even if the molten iron temperature was 1250℃, using limestone instead of active lime still can be achieved with the condition of fewer amount of scrap in steelmaking.

4. Conclusion

The relationship between surplus heat and molten iron temperature, molten iron content, scrap amount and converter tapping temperature were established through converter heat balance calculation. The functional relationship between theoretical substitution ratio of CaO and the surplus heat of converter was also established by defining theoretical substitution ratio of CaO which active lime was instead by limestone in steelmaking.

Heat income were mainly rooted in physical heat of molten iron and exothermic oxidation of elements. So theoretical substitution ratio of CaO gained a significant increase when rising temperature of molten iron and C content.

The effect of Si content of molten iron on theoretical substitution ratio of CaO had a relationship with C content and temperature of molten iron. When the temperature of molten iron was lower than 1300℃, increasing the Si content of molten iron can rise up the theoretical substitution ratio of CaO. Yet when the temperature of molten iron was higher than 1300℃, increasing the Si content of molten iron can reduce the theoretical substitution ratio of CaO.

When finishing slag basicity and tapping temperature were constant, Scrap melting heat was the most heat expense item. Therefore, reducing scrap addition amount can greatly improve the theoretical substitution ratio of CaO. Even if the molten iron temperature was 1250℃, we still can satisfy the thermodynamic condition of limestone 100% instead of active lime in steelmaking.

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