

Wei Yan\*, Weiqing Chen, Xiaobo Zhao, Yindong Yang and Alex McLean

# Effect of $\text{Cr}_2\text{O}_3$ Pickup on Dissolution of Lime in Converter Slag

DOI 10.1515/htmp-2016-0067

Received March 29, 2016; accepted August 2, 2016

**Abstract:** Application of low-nickel laterite ore containing chromium as charging material for ironmaking can reduce raw material costs, but result in an increase of chromium content in the hot metal and hence,  $\text{Cr}_2\text{O}_3$  content in the steelmaking slag, which subsequently causes many problems related to lime dissolution for the steelmaking operation. In this work, a rotating cylinder method was employed to study the effect of  $\text{Cr}_2\text{O}_3$  on lime dissolution in steelmaking slag. The lime dissolution mechanism, rate control step and affecting factors, including slag basicity,  $\text{FeO}_x$  and  $\text{B}_2\text{O}_3$  content, and the formation of phases at reacted layer, were discussed. It was found that mass transfer was the rate control step in slag phase, increase of  $\text{Cr}_2\text{O}_3$  and slag basicity delayed lime dissolution due to the formation of high-melting temperature phases of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel and  $2\text{CaO} \cdot \text{SiO}_2$  at the slag/lime reacted interface. Addition of  $\text{B}_2\text{O}_3$  promoted lime dissolution and suppressed formation of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel.

**Keywords:**  $\text{Cr}_2\text{O}_3$ , Lime dissolution, converter slag, low-nickel laterite ore

## Introduction

Slagmaking is a key operation in steelmaking, which plays a critical role in dephosphorization reactions during the basic oxygen furnace (BOF) steelmaking. A rapid generation of molten slag during steelmaking can shorten refining time, increase productivity, improve steel

quality, reduce production cost and eliminate splashing and sticking lance. High basicity slag containing  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{Fe}_x\text{O}$  and  $\text{SiO}_2$  is often used in steelmaking process, lime will be added continuously to maintain high slag basicity. An effective steelmaking practice requires rapid dissolution of lime in the early blowing-stage within approximate 4 min to form molten slag for dephosphorization. Therefore, it is important to accelerate lime dissolution during steelmaking. A number of researchers [1–9] have reported their study results on lime dissolution, rate control factors and dissolution mechanism. Typically, Deng et al. [1–3] studied the dissolution of  $\text{CaO}$  cube in molten converter slags and found that lime dissolution in the slags was very fast in the  $\text{FeO}$ - $\text{SiO}_2$  slag, and it became slow in the case of  $\text{FeO}$ - $\text{SiO}_2$ - $\text{CaO}$  slag. The formation of a dense  $2\text{CaO} \cdot \text{SiO}_2$  layer on the surface of lime particles was the reason to slow down lime dissolution. Hamano et al. [4, 5] studied lime dissolution mechanism and mass transfers between solid lime and molten slag, intermediate phase formation and the rate control step were reported. In addition to these, other researchers [6–9] also reported similar studies.

Similarly, most investigations besides the above only concentrated on lime dissolution in conventional slags without  $\text{Cr}_2\text{O}_3$ . In order to reduce cost of raw materials, a kind of low-nickel laterite ore containing chromium from Indonesia was used as charging material in the blast furnaces in some steel plans in China, and then the hot metal containing chromium was produced for BOF steelmaking. During steelmaking, a significant increase of  $\text{Cr}_2\text{O}_3$  from zero to almost 8 % as shown in Table 1 was found in the converter slag within 4 min of oxygen blowing according to the sampling analysis, and it caused a series of unexpected problems, such as low lime dissolution rate, low basicity slag, sticky converter slags, high melting temperature, severe lance sticking with the slag, low dephosphorization rate and refining performance. The primary compositions of the ore powders, hot metal and converter slags are listed in Table 1. To the best of our knowledge, very few study on dissolution behavior of lime in  $\text{Cr}_2\text{O}_3$ -containing primary converter slag was reported. Based on the problems found during steelmaking of Cr-containing hot metal, the present study was aimed at covering this gap through investigating the

\*Corresponding author: Wei Yan, State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China; Department of Materials Science and Engineering, University of Toronto, Ontario M5S 3E4, Canada, E-mail: yanweimetal@gmail.com

Weiqing Chen, Xiaobo Zhao, State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China

Yindong Yang, Alex McLean, Department of Materials Science and Engineering, University of Toronto, Ontario M5S 3E4, Canada

**Table 1:** Main compositions of ore powders, hot metal and converter slags (in mass percent).

Ore powders	Cr	Ni	P	S	TFe	
	1.725	0.116	0.083	0.072	52.67	
Hot metal	Cr	Si	P	S	Mn	Ti
	0.35	0.46	0.154	0.019	0.59	0.057
Converter slags	CaO/SiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	MgO	Al <sub>2</sub> O <sub>3</sub>	TFe
4 min slag	0.36	6.81	12.95	1.44	1.53	28.55
Final slag	2.1	2.69	7.32	6.93	2.36	15.57

effect of Cr<sub>2</sub>O<sub>3</sub> on the dissolution behavior of lime in primary converter slags by associating the laboratory and industrial studies. Moreover, lime dissolution mechanism, rate control step and affecting factors on lime dissolution in Cr<sub>2</sub>O<sub>3</sub>-containing primary converter slag were discussed.

## Experimental

### Experimental materials and slags preparation

Limestone from industrial source was crushed into powder with the size of 200 meshes or less. The powder was mixed with a small amount of water and pressed into cylinders (25 × 25 mm) using a steel model under the pressure of 50 KN. Subsequently, the limestone cylinders were heated in muffle furnace at 1,373 K (1,100 °C) for 3 h to convert limestone to lime. The lime cylinders obtained were placed in a drying box for future lime dissolution tests.

Chemical compositions of experimental slags used to simulate the initial slags of BOF steelmaking were shown in Table 2, which were designed with varying basicity (CaO/SiO<sub>2</sub>), Cr<sub>2</sub>O<sub>3</sub>, and FeO<sub>x</sub> and fixed MgO, MnO, Al<sub>2</sub>O<sub>3</sub>

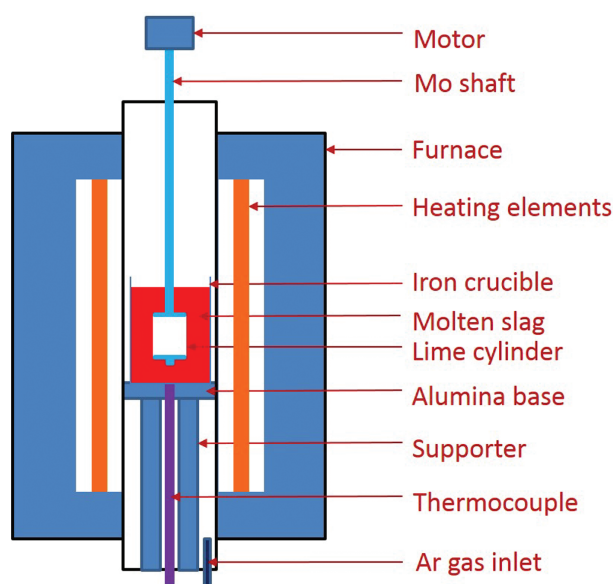
**Table 2:** Chemical compositions of experimental slags (in mass percent).

Slag	CaO/SiO <sub>2</sub>	CaO	SiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO <sub>x</sub>	MgO	MnO	Al <sub>2</sub> O <sub>3</sub>
L1	0.4	16.0	40.0	0	30	7	6	1
L2	0.4	14.9	37.1	4	30	7	6	1
L3	0.4	13.7	34.3	8	30	7	6	1
L4	0.4	16.6	41.4	8	20	7	6	1
L5	0.4	10.9	27.1	8	40	7	6	1
L6	0.8	21.3	26.7	8	30	7	6	1
L7	1.2	26.2	21.8	8	30	7	6	1

contents. The slags with the designed compositions were prepared by mixing the reagent grade CaO, SiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, MgO, MnO, and Al<sub>2</sub>O<sub>3</sub>. Before mixture all reagents were dried in advance at 473 K (200 °C) for 3 h to remove moisture. Iron oxide FeO<sub>x</sub> powder made from the iron oxide scales of carbon steel rolling were used in the synthetic slags.

### Experimental procedure

Lime dissolution tests were conducted in a high temperature vertical furnace with the rotating cylinder apparatus. The experimental setup is schematically shown in Figure 1. During the experiment, a pure iron crucible (I.D. 46 mm, O.D. 56 mm, height 70 mm) was placed on the alumina base, the position of which was initially adjusted in the constant temperature zone of the furnace. A hole was made in the right of the alumina base for the installation of the thermocouple with the tip in thermal contact with the bottom of the crucible. The diameter, height, and mass of the lime cylinder were measured separately three times, using a digital caliper and balance prior to performing the experiments. The lime cylinder was placed between two thin molybdenum caps, connected using a vertical, rotatable molybdenum shaft of variable speeds, and fixed by a Mo stopper.

**Figure 1:** Schematic of experimental apparatus.

Lime dissolution test was carried out when the furnace was heated up to 1,673 K (1,400 °C) and kept constant

under Ar gas atmosphere with a flow rate of 3 L/min. About 180 g slags were added into the crucible through quartz tube. The slags were melted and kept at a constant temperature for 30 min for homogenization. Thereafter, the preheated lime cylinder rotating at a speed of 100 rpm was immersed into molten slag at a position of 15 mm to the bottom of crucible. After a certain immersion time, the lime cylinder was lifted out quickly from the molten slags for air cooling. After removing the slags adhered to the lime cylinder, the diameter and height of the lime cylinder were measured three times to get a mean value of diameter and height. The white part (unreacted lime) in the core of lime was separated carefully from the black parts (which are reacted lime and penetrated into by the molten slag) with dissecting needle. The mass of the white parts of unreacted lime was weighed. Several black parts in the interfacial region of reacted and unreacted lime were mounted with denture acrylic and polished with alcohol for Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis.

## Results

### Lime dissolution behavior in the liquid primary converter slags

According to the experimental process, the lime cylinders after cooling are easy to break into small pieces including outside reacted lime (black parts) and inside unreacted lime (inside white parts). Based on this behavior, the lime cylinder after dissolution can be divided into slagging layer (consisting of dissolution layer and reacted layer adhered to the unreacted lime) and unreacted layer from

outside to inside along the radius, which are shown schematically in Figure 2. Inevitably, the dissolution and slagging ratios of lime cylinder should be taken into account for quantitative analysis to understand the dissolution process. In this study, lime dissolution is defined as slow and gradual removal or diffusion of  $\text{CaO}$  from lime into slags. Slagging is defined as penetration degree of slags into lime, which consists of dissolved lime and reacted lime that is still adhering on the surface of lime cylinder.

Lime dissolution rate,  $R_d$  (mm/min), defined as decrease in the radius of lime cylinder per unit time, can be calculated using eq. (1).

$$R_d = -\frac{dr}{dt} = -\frac{r - r_0}{t} \quad (1)$$

where  $r$  is radius after immersion time  $t$  (min),  $r_0$  is original radius of lime cylinder.

The slagging rate of lime,  $R_s$  (mm/min), is defined as slagging depth along radius of lime cylinder per unit time, which reveals penetration ability of slag into lime, and can be calculated using eq. (2).

$$R_s = -\frac{dr}{dt} = -\frac{r_u - r_0}{t} \quad (2)$$

The radius  $r_u$  of unreacted lime is difficult to measure, which can be calculated indirectly by combining the eqs (3)–(5).

$$V_u = \pi h(r_u^2 - r_i^2) = \frac{W_u}{\rho_{\text{CaO}}} \quad (3)$$

$$\rho_{\text{CaO}} = \frac{W_0}{V_0} \quad (4)$$

$$r_u = \sqrt{\frac{W_u V_0}{\pi h W_0} + r_i^2} \quad (5)$$

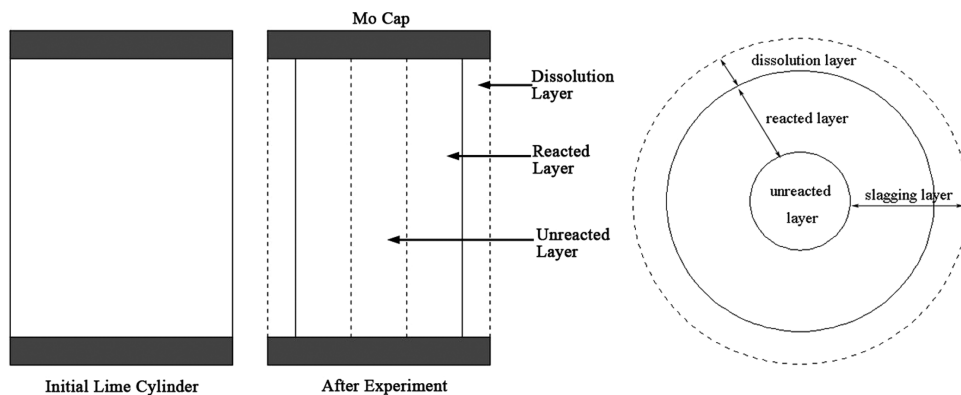


Figure 2: Schematic structure of lime cylinder before and after dissolution.

where  $r_u$  is radius of unreacted lime cylinder,  $V_u$  and  $W_u$  are volume and mass of unreacted lime cylinder.  $h$  is height of original lime cylinder, which is considered to be constant.  $r_i$  is the radius of inside hole of lime cylinder (3.00 mm) which is designed to fix molybdenum bar of the rotation facility.  $\rho_{\text{CaO}}$  is density of lime cylinder.  $W_0$  and  $V_0$  are original mass and volume of lime cylinder.

## Effect of slag compositions on dissolution rate

Study on dissolution rate of lime in  $\text{Cr}_2\text{O}_3$  containing converter slags was conducted at a fixed temperature 1,673 K and a revolution speed of 100 rpm. During oxygen blowing for the refining of Cr containing hot metal in converter, the  $\text{Cr}_2\text{O}_3$  content in the primary slag increased from zero to about 8 % within 4 min according to our field sampling as shown in Table 1. Therefore, study on the influence of  $\text{Cr}_2\text{O}_3$  on lime dissolution in the converter slag is necessary. Figure 3 illustrates the change of dissolution rate and slagging rate as a function of  $\text{Cr}_2\text{O}_3$  content in slag with basicity of 0.4 and 30 %  $\text{FeO}_x$ . It can be seen that dissolution and slagging rate of lime decrease obviously with increasing  $\text{Cr}_2\text{O}_3$  content. The slagging rate (including dissolution and slag penetration) is far more than dissolution rate, which indicates the slag penetration is typically faster than dissolution. But slagging rate decreases obviously which indicates  $\text{Cr}_2\text{O}_3$  inhibits the penetration of slag into lime. Very few study on effect mechanism of  $\text{Cr}_2\text{O}_3$  on lime dissolution and slag penetration has been reported in publications, which will be discussed below.

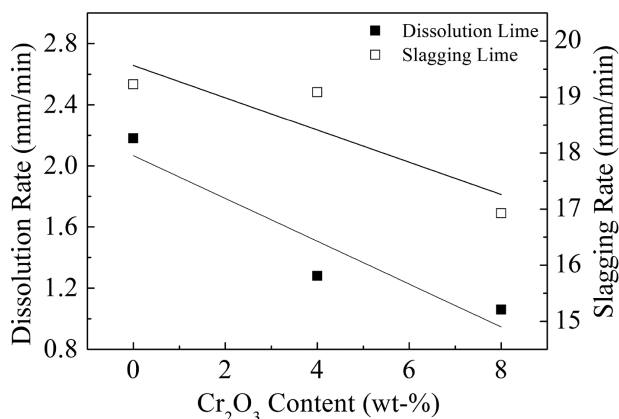


Figure 3: Effect of  $\text{Cr}_2\text{O}_3$  on lime dissolution and slagging rate.

The influence of basicity ( $\text{CaO}/\text{SiO}_2$  mass ratio) of primary slags on the dissolution and slagging rate of lime cylinder in the converter slag with 8 %  $\text{Cr}_2\text{O}_3$  were examined, the

results obtained are presented in Figure 4. It can be observed that lime dissolution and slagging rate decrease with increasing basicity. Figure 5 shows the effect of  $\text{FeO}_x$  on dissolution and slagging rate of lime in converter slag with basicity of 0.4 and 8 %  $\text{Cr}_2\text{O}_3$ . It was seen that the addition of  $\text{FeO}_x$  significantly increases the dissolution and slagging rate.

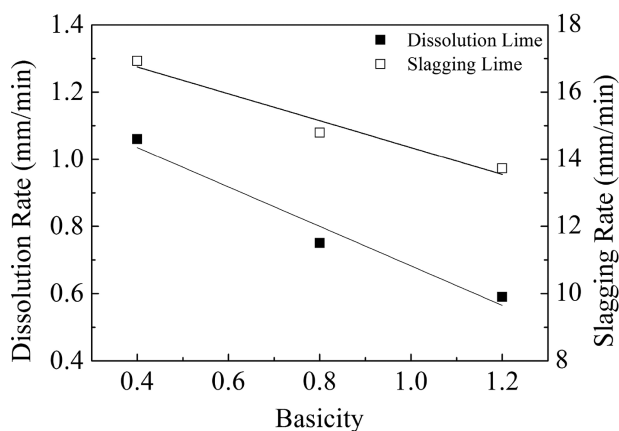


Figure 4: Effect of basicity on lime dissolution and slagging rates.

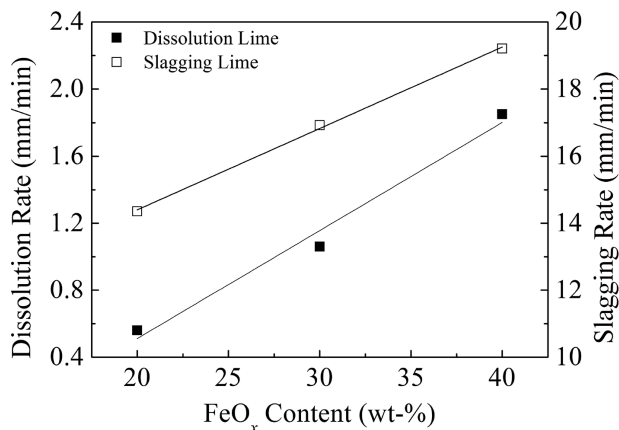


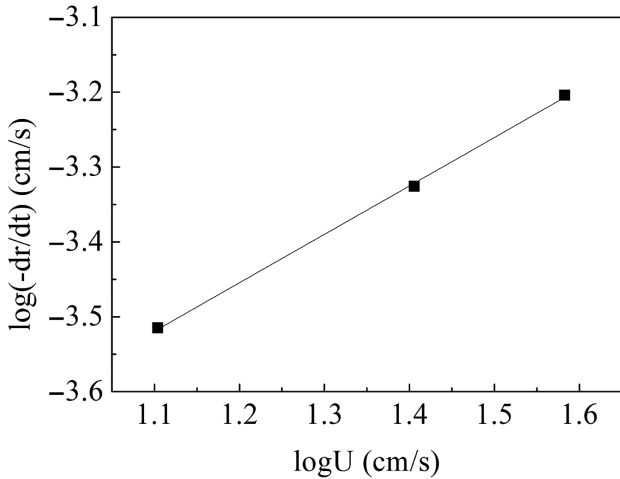
Figure 5: Effect of  $\text{FeO}_x$  content on lime dissolution and slagging rate.

## Discussion

### Rate control step of lime dissolution

The effect of revolution speed on lime dissolution in  $\text{Cr}_2\text{O}_3$  containing slags was examined using slag L3 with basicity of 0.4 and 8 %  $\text{Cr}_2\text{O}_3$ . The revolution speed during the test was in the range of 100–300 rpm. Figure 6 illustrates the





**Figure 6:** Relationship between lime dissolution rate and revolution speed.

relationship between logarithms of lime dissolution rate,  $R_d$  (cm/s), and logarithms of periphery velocity  $U$  (cm/s) of rotating lime cylinder, which can be calculated according to the eq. (6) [10].

$$R_d = -\frac{dr}{dt} = A \cdot U^b \quad (6)$$

Periphery velocity  $U$  can be calculated using eq. (7).

$$U = \frac{\pi \bar{d} m}{60} \quad (7)$$

where  $A$  is constant,  $U$  is periphery velocity (cm/s),  $\bar{d}$  is mean diameter (mm) of lime cylinder,  $m$  is revolution speed of lime cylinder (rpm),  $b$  can be obtained by regression using the experimental data. Previous studies reported that  $b$  value was 0.48, 0.57, or 0.69, for dissolution of lime [10–12], and 0.88 or 0.81 for dolomite and alumina [13, 14], respectively.

It can be seen from Figure 6 that  $\log R_d$  (cm/s) increases linearly with increasing  $\log U$  (cm/s), which means that increasing revolution speed can accelerate dissolution of lime in  $\text{Cr}_2\text{O}_3$  containing converter slags. As shown in Figure 6, the  $b$  value of 0.7 can be obtained by calculating the slope of the line presented in Figure 6, which is close to the values reported in references [10–12]. From the aforementioned result it can be reasonably concluded that the lime dissolution rate in  $\text{Cr}_2\text{O}_3$  containing converter slag mainly depends on the rotation speed, and hence mass transfer across the boundary layer can be the rate control step of lime dissolution under the present experimental conditions.

The mass transfer flux  $J$  ( $\text{g}/\text{cm}^2 \cdot \text{min}$ ) of lime can be expressed as eq. (8).

$$J = k(n_i - n_b) \quad (8)$$

where  $k$  is mass transfer coefficient of lime in the converter slag, (cm/min).  $n_i$  and  $n_b$  are mass densities of lime at the lime/slag interface and in the liquid bulk slag, respectively, ( $\text{g}/\text{cm}^3$ ).

The relationship between mass transfer flux  $J$  and dissolution rate  $-dr/dt$  can be obtained by the mass balance equation expressed as eq. (9).

$$\rho_{\text{CaO}} \cdot A \cdot \left( -\frac{dr}{dt} \right) = A \cdot J \quad (9)$$

where  $\rho_{\text{CaO}}$  is the density of lime cylinder ( $\text{g}/\text{cm}^3$ ).  $A$  is interfacial area between lime cylinder and liquid converter slag ( $\text{cm}^2$ ).

Combining eqs (8) and (9), lime dissolution rate can be derived and written as eq. (10).

$$R_d = -\frac{dr}{dt} = \frac{k \rho_b}{100 \rho_{\text{CaO}}} \cdot \Delta(\% \text{CaO}) \quad (10)$$

where  $\rho_b$  is the density of converter slag ( $\text{g}/\text{cm}^3$ ).  $\Delta(\% \text{CaO})$  (mass percent) is assumed to be equal to the concentration difference between saturation and initial concentration of CaO in the liquid bulk slag. Lime saturated concentration in the molten slag can be determined from the liquids line on the pseudo “CaO”- $\text{SiO}_2$ -“ $\text{FeO}_x$ ” ternary phase diagram using FactSage 6.2 software.

Since Mo caps were used to cover the top and bottom surfaces of lime cylinder, and only the cylinder side was in contact with converter slag, the dissolution of the side surface of the lime cylinder should represent dissolution pattern. Kosaka [15] derived the eq. (11) to describe the dependence of mass transfer coefficient  $k$  on Reynolds number  $Re$ , Schmidt number  $Sc$  and periphery velocity  $U$  (cm/s). Here  $Re = (\rho_b U d)/\eta$ ,  $Sc = \eta/(\rho_b D)$ ,  $U = \omega r$ . The diffusion coefficient  $D$  of lime is associated with the slag properties by Stokes-Einstein equation (12) [16]. Obviously, these parameters are related to physical properties of liquid converter slag (density  $\rho_b$ , dynamic viscosity of converter slags) and angular velocity of lime cylinder.

$$k = 0.065 \cdot Re^{-1/4} \cdot Sc^{-2/3} \cdot V \quad (11)$$

$$D = \frac{k_B T}{6\pi r \eta} \quad (12)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the Kelvin temperature,  $r$  is the effective molecules radius.

Combining eqs (10) through (12), lime dissolution rate,  $-dr/dt$  (cm/min), can be derived and written as eq. (13).

$$R_d = -\frac{dr}{dt} = \frac{\Delta(\% \text{CaO}) \rho_b}{100 \rho_{\text{CaO}}} \cdot 0.065 \cdot \text{Re}^{-1/4} \cdot \text{Sc}^{-2/3} \quad (13)$$

$$U = \frac{0.055}{100 \rho_{\text{CaO}}} \left( \frac{k_B T}{6\pi r} \right)^{2/3} \omega^{3/4} \rho_b^{17/12} \eta^{-13/12} \Delta(\% \text{CaO})$$

Assuming that  $\rho_{\text{CaO}}$  is constant, eq. (13) can be grouped into three parts: (1) A constant part  $\frac{0.055}{100 \rho_{\text{CaO}}} \left( \frac{k_B T}{6\pi r} \right)^{2/3}$  which is independent on slag composition; (2) second part is  $\omega^{3/4}$  which is related to experimental conditions; and (3) third part is  $\rho_b^{17/12} \eta^{-13/12} \Delta(\% \text{CaO})$  which depends on converter slag compositions. For the same converter slag,  $\frac{0.055}{100 \rho_{\text{CaO}}} \left( \frac{k_B T}{6\pi r} \right)^{2/3}$  and  $\rho_b^{17/12} \eta^{-13/12} \Delta(\% \text{CaO})$  can be viewed as constants due to minimal dissolution of lime into massive slag (180 g). Therefore, lime dissolution rate should be proportional exponentially to revolution speed of lime cylinder to the power of 0.75, which is very close to the power of 0.7 obtained in the present study and falls well in the range of 2/3 to 4/5 reported in the reference [17]. This implies that mass transfer across boundary layer is the rate control step for lime dissolution into Cr<sub>2</sub>O<sub>3</sub> containing slags with a fixed compositions.

### Effect of slag compositions

According to eq. (13), the effect of varying converter slags on lime dissolution rate in molten slags is mainly determined by the third part of the eq. (13), that is  $\rho_b^{17/12} \eta^{-13/12} \Delta(\% \text{CaO})$ . In the present study, Mills's density model [18] of slags is employed to estimate the density of Cr<sub>2</sub>O<sub>3</sub> containing converter slags. The calculated value of the slag density is about 3.3g/cm<sup>3</sup>, which can be assumed as a constant compared to other parameters because the change of the density value is very small.

Models are not available for the calculation of the viscosity of Cr<sub>2</sub>O<sub>3</sub> containing slags. However the works reported by Tunezo [19, 20] showed that addition of Cr<sub>2</sub>O<sub>3</sub> could increase slag viscosity for CaO-SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> and CaO-SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub>-FeO systems; while increase of slag basicity and FeO<sub>x</sub> content would reduce slag viscosity. The relationship between viscosity and diffusion in molten slag were usually described in Eyring relation and Stokes-Einstein relation. Eyring's studies [16, 21] reported an inversely proportional relationship between lime diffusivity  $D$  in liquid slags and viscosity of liquid slags. The finding in this work agrees well with the relationship suggested by Eyring et al. that increasing viscosity inhibits CaO diffusion across boundary layer. That means

addition of Cr<sub>2</sub>O<sub>3</sub> inhibits lime diffusion but increases of basicity and FeO<sub>x</sub> promotes lime diffusion.

However, it was found that dissolution rate of lime decreased with increasing basicity. This could be due to the reason that an increase of basicity would result in an increase of lime concentration in the molten slag, and hence a decrease of driving force of lime diffusion as shown in Figure 7. Therefore, basicity influences lime dissolution mainly through decreasing driving force. Nevertheless, increases in Cr<sub>2</sub>O<sub>3</sub> and FeO<sub>x</sub> only introduce a negligible effect on driving force. So driving force is not the main influence aspect on dissolution in slag with varying Cr<sub>2</sub>O<sub>3</sub> and FeO<sub>x</sub> contents. Apart from this, slag compositions will affect lime dissolution by changing phases formed in the lime/slag reacted interface, which will be discussed in the following section.

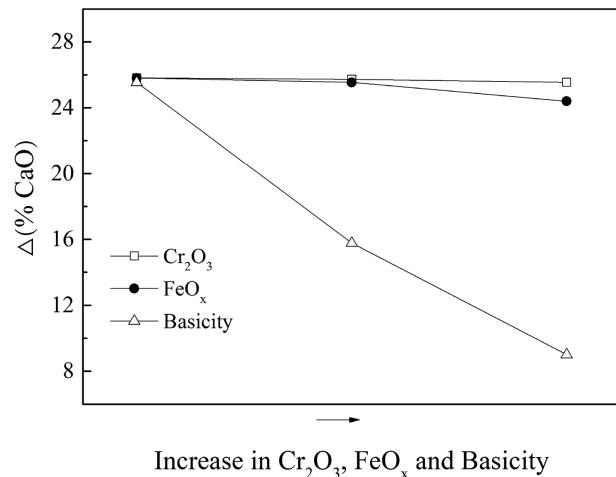
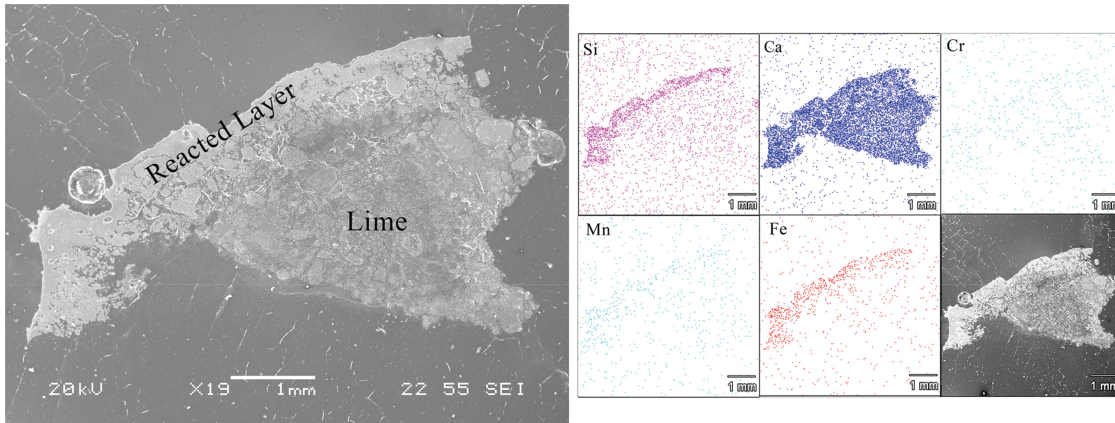


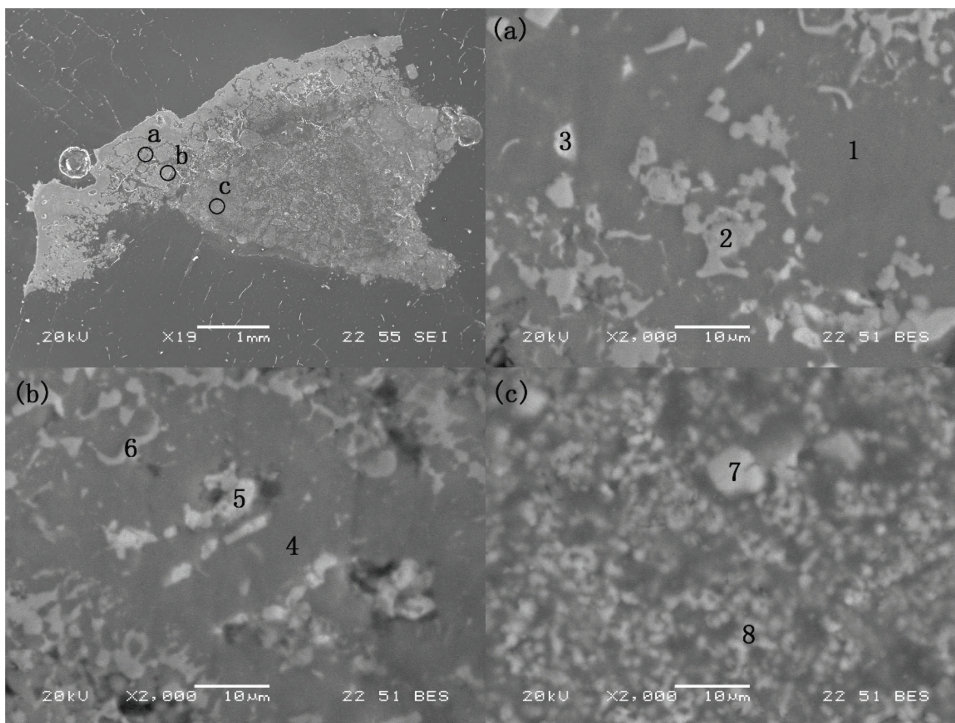
Figure 7: Effect of Cr<sub>2</sub>O<sub>3</sub>, FeO<sub>x</sub> and basicity on driving force.

### Effect mechanism of Cr<sub>2</sub>O<sub>3</sub> on lime dissolution

The above discussion focuses on the effect of liquid slag properties on diffusion of CaO across boundary layer. However, undissolvable solid layer or intermediate phases formed in the lime/slag interface can also lead to a significant effect on lime dissolution in CaO-FeO-SiO<sub>2</sub> slags [1–5, 14]. To the best of our knowledge, effect of Cr<sub>2</sub>O<sub>3</sub> in molten slag on the formation of intermediate phase in the boundary of the solid lime and molten slag has not been reported, and hence it is extremely necessary to make this mechanism clear. Figure 8 shows SEM image of slag sample taken from the lime dissolution in molten slag L2 (CaO/SiO<sub>2</sub> = 0.4, 4 %Cr<sub>2</sub>O<sub>3</sub>). A high concentration for Si, Ca,



**Figure 8:** SEM and element distributions in slag/lime interface after lime dissolution in slag L2 (4 %  $\text{Cr}_2\text{O}_3$ ).



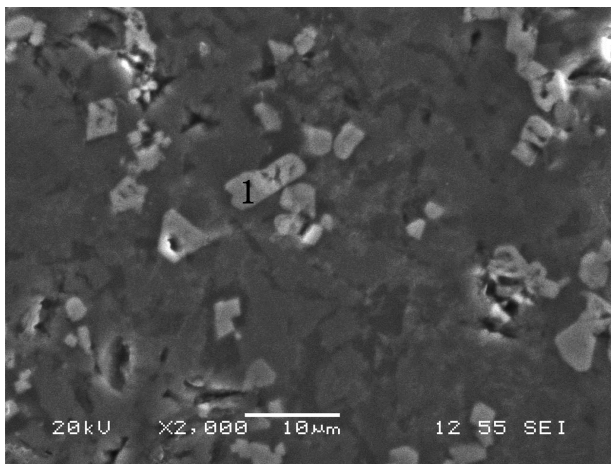
**Figure 9:** Phase morphology and compositions from reacted layer after lime dissolution in slag L2 (4 %  $\text{Cr}_2\text{O}_3$ ), (a) outer layer, (b) middle layer and (c) inner layer, phases 1–8 are listed in Table 3.

Cr or Fe can be found in the surface region of lime cylinder contacted with molten slag. Figure 9 presents the SEM images obtained in the slag/lime interface including: (a) outer layer near the slag, (b) middle layer and (c) inner layer near the unreacted lime. In the out layer of the slag, more  $2\text{CaO} \cdot \text{SiO}_2$  and  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  phases can be found (see Figure 9(a)). In the middle layer,  $2\text{CaO} \cdot \text{SiO}_2$  seems to decrease and some  $3\text{CaO} \cdot \text{SiO}_2$  and  $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$

phases are found (see Figure 9(b)). In the inner layer, the majority of the phases is unreacted lime (see Figure 9(a)). It is well known that  $2\text{CaO} \cdot \text{SiO}_2$  is the primary phase with high melting temperature, which can slow down CaO diffusion across the interface according to the previous studies [2, 14]. However, the important finding in the current study is that a large quantity of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel is formed in the reacted interface region.  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel has high



melting temperature (2,373 K (2,100 °C)) which is similar to the melting temperature (2,403 K (2,130 °C)) of  $2\text{CaO} \cdot \text{SiO}_2$  [22]. Penetration of  $\text{FeO}_x$  breaks the  $2\text{CaO} \cdot \text{SiO}_2$  layer but on the other hand  $\text{FeO}_x$  participates in the formation of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel. These high melting temperature phase  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  was distributed in the discontinuous  $2\text{CaO} \cdot \text{SiO}_2$  and mixed with them. Consequently, the formation of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel will play the similar role as  $2\text{CaO} \cdot \text{SiO}_2$  to inhibit lime dissolution together with  $2\text{CaO} \cdot \text{SiO}_2$ . With further increase of  $\text{Cr}_2\text{O}_3$  in the test slag L3 ( $\text{CaO}/\text{SiO}_2 = 0.4$ , 8 %  $\text{Cr}_2\text{O}_3$ ), more  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel are found in slag/lime interface as shown in Figure 10, which will further slow-down lime dissolution.

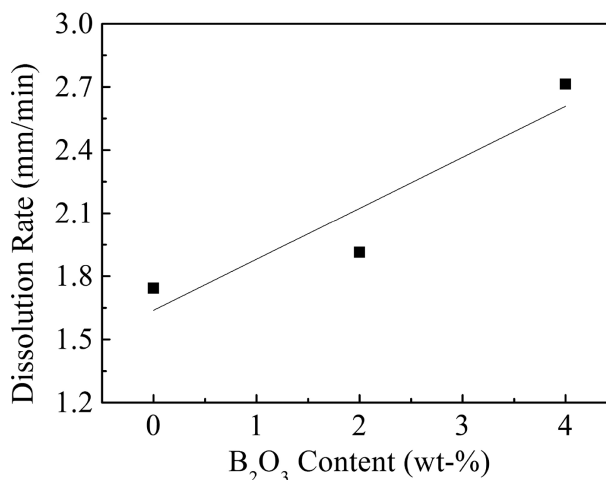


**Figure 10:** Phase morphology and compositions in the slag/lime reacted interface after dissolution in slag L3 (8 %  $\text{Cr}_2\text{O}_3$ ), phase 1 is listed in Table 3.

The above analysis reveals that during lime dissolution in the conventional  $\text{CaO-FeO-SiO}_2$  converter slag,  $2\text{CaO} \cdot \text{SiO}_2$  phase can form on the surface of lime particles and it inhibits lime dissolution. Addition of  $\text{Cr}_2\text{O}_3$  in the molten slag promotes the formation of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel with high melting temperature and slows down lime dissolution. Meanwhile, an increase of  $\text{FeO}_x$  in molten slag still accelerated lime dissolution but addition of  $\text{Cr}_2\text{O}_3$  also weakens the positive effect of  $\text{FeO}_x$  on lime dissolution due to formation of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel. Therefore, what is the different from the common  $\text{Cr}_2\text{O}_3$ -free  $\text{CaO-FeO-SiO}_2$  slag is  $\text{FeO}_x$  is not the optimal option to promote lime dissolution due to its participation into the formation of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel. An additive which promotes lime dissolution by inhibiting the formation of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel should be considered.

## Effect and mechanism of $\text{B}_2\text{O}_3$ on lime dissolution in $\text{Cr}_2\text{O}_3$ -containing slag

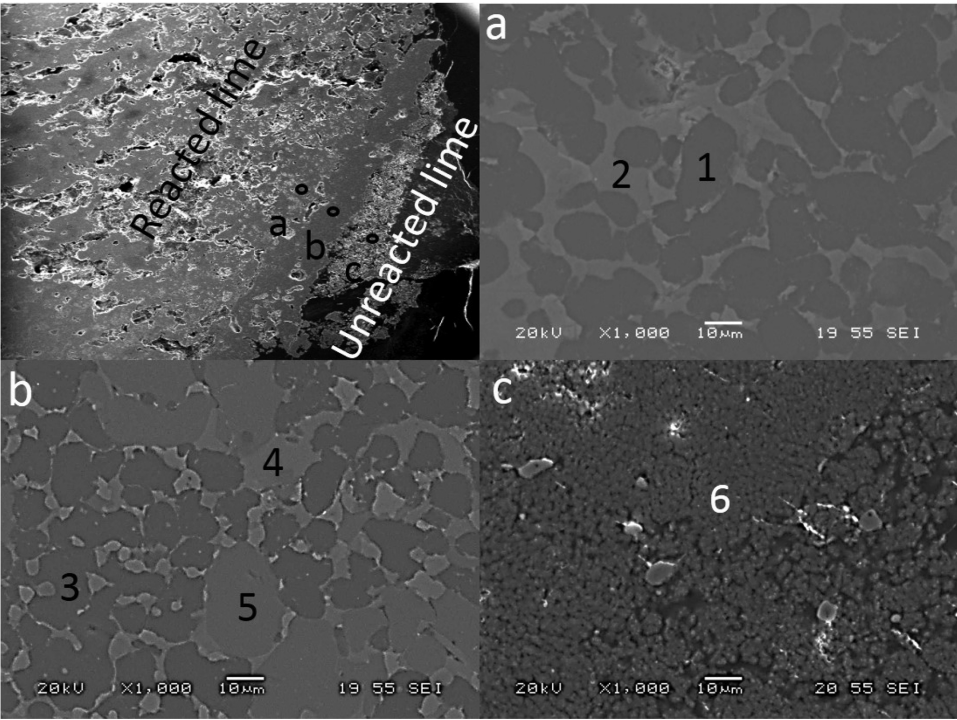
Based on the above analysis and consideration on potential application of low-cost and abundant paigeite in China, 0–4 %  $\text{B}_2\text{O}_3$  was firstly tried to be added into 8 %  $\text{Cr}_2\text{O}_3$ -containing converter slag (master slag L3) to experimentally investigate its effect on lime dissolution. The observed effect of  $\text{B}_2\text{O}_3$  on dissolution rate was shown in Figure 11. It can be seen the dissolution rate increases with the addition of  $\text{B}_2\text{O}_3$  from 0 to 4 %. On the one hand, addition of  $\text{B}_2\text{O}_3$  will decrease the slag viscosity which benefits for the diffusion of lime into slag according to eqs (12) and (13). On the other hand, it also can be seen from SEM image of slag/lime reacted interface shown in Figure 12 and Table 4 addition of 4 %  $\text{B}_2\text{O}_3$  suppresses the precipitation of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel. No  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  can be found in the SEM analysis of reaction layer of lime and slag (master slag L3 + 4 %  $\text{B}_2\text{O}_3$ ). It can be concluded  $\text{B}_2\text{O}_3$  promotes lime dissolution by combination of decreasing viscosity and suppressing formation of  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  spinel.



**Figure 11:** Effect of  $\text{B}_2\text{O}_3$  on lime dissolution rate.

## Consideration on solutions to the problems

As mentioned above, the low dephosphorization, sticking lance, bad flow ability and high melting temperature of converter slag can be contributed to poor lime dissolution and excess increase of  $\text{Cr}_2\text{O}_3$  in slag during the blowing period. Meanwhile, increase of  $\text{Cr}_2\text{O}_3$  also restricted the lime dissolution. These poor BOF performance instead may increase the cost. Based on these



**Figure 12:** Phase morphology and compositions from reacted layer after lime dissolution in slag L2. (8 % Cr<sub>2</sub>O<sub>3</sub> + 4 % B<sub>2</sub>O<sub>3</sub>), (a) outer layer, (b) middle layer and (c) inner layer, phases 1–6 are listed in Table 4.

**Table 3:** Phase and their chemical compositions in the vicinity of slag/lime interface.

Samples (Figures)	Label	Primary phase	Chemical compositions of phases						
			CaO	SiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	MgO	MnO	Al <sub>2</sub> O <sub>3</sub>
L2 (Figure 9)	1	2CaO · SiO <sub>2</sub>	56.88	34.15	0	4.48	4.49	0	0
	2	FeO · Cr <sub>2</sub> O <sub>3</sub>	4.05	1.68	12.02	64.21	6.17	8.8	3.06
	3	3CaO · SiO <sub>2</sub>	75.3	17.44	0	4.37	2.89	0	0
	4	2CaO · SiO <sub>2</sub>	56.32	34.79	0	3.35	5.54	0	0
	5	3CaO · SiO <sub>2</sub>	80.57	12.38	0	7.05	0	0	0
	6	CaO · MgO · SiO <sub>2</sub>	32.11	17.79	0	6.35	25.31	17.5	0.95
	7	2CaO · SiO <sub>2</sub>	66.69	28.5	0	0	0	0	4.82
	8	CaO	100	0	0	0	0	0	0
L3 (Figure 10)	1	FeO · Cr <sub>2</sub> O <sub>3</sub>	1.91	2.67	38.43	54.51	2.48	0	0

analyses, some initial measures can be taken from the technical and economic perspectives to alleviate these issues for achieving application of low-cost laterite and meanwhile good BOF performance as far as possible, such as increasing the activity of lime to promote its dissolution in early blowing, reducing the addition of laterite to restrict Cr content to less than 0.5-wt % in hot

metal, adding some bauxite to decrease melting temperature, adjusting the lance height to change the FeO content in slag. The above measures have been taken and achieved positive effect. Effectiveness of paigeite addition in alleviating these problems is expected to be examined next during BOF process to achieve more utilization of low-cost laterite.



**Table 4:** Phase and their chemical compositions in the vicinity of slag/lime interface.

Samples (Figures)	Label	Primary phase	Chemical compositions of phases					
			CaO	SiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	MgO	MnO
L3 + 4 %B <sub>2</sub> O <sub>3</sub> (Figure 12)	1	2CaO · SiO <sub>2</sub>	67.71	30.22	0	2.08	0	0
	2	CaO · FeO	45.99	1.46	1.56	48.50	0	0
	3	3CaO · SiO <sub>2</sub>	71.43	28.57	0	0	0	0
	4	CaO · FeO	48.63	0	0	48.29	0	0
	5	CaO	84.9	0	0	8.67	1.45	4.98
	6	CaO	98.85	0	0	0	1.15	0

## Conclusions

Lime dissolution behavior and dissolution mechanism in Cr<sub>2</sub>O<sub>3</sub>-containing converter slags were studied by rotating cylinder method at 1,673K (1,400 °C), the phases formed in the slag/lime reacted interface were examined using SEM/EDS analysis. The results obtained are summarized as follows:

1. Lime dissolution and slagging rate decreased with increasing Cr<sub>2</sub>O<sub>3</sub> content and slag basicity, but increased with increasing FeO<sub>x</sub> content in Cr<sub>2</sub>O<sub>3</sub>-containing converter slag.
2. A linear relationship between logarithms of lime dissolution rate and revolution speed of the lime cylinder was found and it demonstrated that mass transfer is the rate control step in slag phase for lime dissolution in Cr<sub>2</sub>O<sub>3</sub>-containing slag.
3. Addition of Cr<sub>2</sub>O<sub>3</sub> into the converter slag promoted the formation of high melting temperature phase FeO · Cr<sub>2</sub>O<sub>3</sub> in the lime/slag reacted interface and slowed down lime dissolution in the Cr<sub>2</sub>O<sub>3</sub>-containing converter slag. Addition of FeO<sub>x</sub> promoted lime dissolution but also participated in formation of FeO · Cr<sub>2</sub>O<sub>3</sub> spinel. Addition of B<sub>2</sub>O<sub>3</sub> into Cr<sub>2</sub>O<sub>3</sub>-containing converter slag promoted the lime dissolution and meanwhile suppressed formation of FeO · Cr<sub>2</sub>O<sub>3</sub> spinel.
4. Measures such as improving lime property, adjusting BOF operation and adding low-cost fluxing agent were tried and suggested to alleviate the issues and achieve more utilization of low-cost laterite ore.

## References

- [1] T.F. Deng and S.C. Du, *Metall. Mater. Trans. B*, 43 (2012) 578–586.
- [2] T.F. Deng, J. Gran and S.C. Du, *Steel Research Int.*, 81 (2010) 347–355.
- [3] T.F. Deng, B. Glaser and S.C. Du, *Steel Research Int.*, 83 (2012) 259–268.
- [4] T. Hamano, M. Horibe and K. Ito, *ISIJ Int.*, 44 (2004) 263–267.
- [5] T. Hamano, S. Fukagai and F. Tsukishashi, *ISIJ Int.*, 46 (2006) 490–495.
- [6] S.H. Amini, M.P. Brungs, S. Jahanshahi and O. Ostrovski, *Metall. Mater. Trans. B*, 37 (2006) 773–780.
- [7] S. Amini, M. Brungs and O. Ostrovski, *ISIJ Int.*, 47 (2007) 32–37.
- [8] J. Yang, M. Kuwabara, T. Asano, A. Chuma and J. Du, *ISIJ Int.*, 47 (2007) 1401–1408.
- [9] Z.S. Li, M. Whitwood, S. Millman and J. Boggelen, *Ironmaking Steelmaking*, 41 (2014) 112–120.
- [10] M. Matsushima, S. Yadoomaru, K. Mori and Y. Kawai, *Trans. ISIJ*, 17 (1977) 442–449.
- [11] N. Maruoka, A. Ishikawa, H. Shibata and S.Y. Kitamura, *High Temp. Mater. Process.*, 32 (2013) 15–24.
- [12] R. Tang, Y. Wang, C.J. Zhang, B. Xie and J. Diao, *Ironmaking Steelmaking*, 42 (2014) 169–175.
- [13] M. Umakoshi, K. Mori and Y. Kawai, *Trans. ISIJ*, 24 (1984) 532–539.
- [14] S. Taira, K. Nakashima and K. Mori, *ISIJ Int.*, 33 (1993) 116–123.
- [15] M. Kosaka and S. Minowa, *Tetsu to Hagane*, 52 (1966) 1748–1762.
- [16] H.A. Kooijman, *Ind. Eng. Chem. Res.*, 41 (2002) 3326–3328.
- [17] K. Hirota, *Kinetics of Reaction*, Kyoritsu Shuppan Press, Tokyo (1964).
- [18] K.C. Mills, Y. Lang and R.T. Jones, *J. S. Afr. I. Min. Metall.*, 11 (2011) 649–658.
- [19] S. Tunezo and S. Keizo, *Tetsu to Hagane*, 51 (1965) 1851–1854.
- [20] S. Tunezo and S. Keizo, *Tetsu to Hagane*, 51 (1965) 1855–1857.
- [21] S. Glasstone, K.J. Laidlev and H. Eyring, *The Theory of Rate Processes: The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena*, McGraw-Hill, New York (1941).
- [22] V.D. Eisenhüttenleute, *Slag Atlas* (2nd edition), Verlag Stahleisen GmbH, Düsseldorf (1995).