Limestone Dissolution in Converter Slag: Kinetics and Influence of Decomposition Reaction

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Dissolution rate of limestone in converter slag is a key to evaluate the feasibility of limestone slagging mode during steelmaking process. In this work, kinetics of limestone dissolution in converter slag at 1 300–1 400°C were studied and the influence of decomposition reaction were investigated. The results showed that the dissolution process of limestone in converter slag can be divided into three stages: stagnation stage, coupling stage and sole dissolution stage. Higher slag temperature and lower slag basicity were conducive to reduce the duration time of stagnation stage and obtain higher dissolution degree. The coupling stage of limestone dissolution was confirmed to be controlled by the chemical reaction, whereas diffusion through the boundary layer as well as combination of controlling steps was the rate limitation at the sole dissolution stage under different slag basicities. The kinetics parameters were determined. In addition, CO₂ bubbles generated from decomposition reaction could provide a certain enhancement of limestone dissolution and inhabit the formation of 2CaO·SiO₂ phase at the coupling stage of limestone dissolution in converter slag.

KEY WORDS: limestone; dissolution; converter slag; kinetics; decomposition reaction; coupling stage.

1. Introduction

During converter steelmaking process, fast dissolution of lime is conducive to rapid formation of a proper and stable slag for purifying molten steel, which can facilitate dephosphorization and desulphurization reaction rates, reduce flux amount and increase productivity. In view of its importance, many studies on the dissolution of lime into the converter slag have been carried out, including reaction mechanism and the factors affecting the dissolution rate such as lime property, slag composition and temperature, dynamic condition and so on. Maruoka et al. investigated the dissolution rate of dense and porous lime respectively and found that the influence of lime porosity on the dissolution rate was different with or without formation of the reaction layer. Guo et al. studied the lime dissolution behavior in the molten metallurgical slags by using a confocal scanning laser microscope and concluded that temperature and slag chemistry played a significant role on the dissolution rate. Moreover, they evaluated the dissolution mechanism quantitatively by using a defined dissolution factor. Deng et al. examined the lime-slag interface layer and clarified the main mechanism for the lime dissolution under different dynamic conditions.

It is well known that lime is normally produced in a rotary kiln by calcination of limestone at 1 000–1 300°C for a few hours and then the cooled calcined lime is transported and charged into a converter, leading to a sensible heat loss and excessive CO₂ emission from limestone calcination. In recent years, with the requirement of lower production cost and CO₂ emission reduction in steelmaking industry, using limestone directly instead part of lime as slagging flux in converter steelmaking process has been proposed, and some industrial trials on the limestone slagging mode under practical converter conditions have been conducted. In the limestone steelmaking mode, the decomposed lime from limestone under converter steelmaking condition is speculated to be highly reactive and would dissolve into the molten slag quickly. Nevertheless, the experimental results conducted in converter slag at 1 600°C by Deng et al. showed that the lime produced from limestone was not porous and the dense CaO layer would greatly hinder the dissolution into the slag. In addition, some doubts and debates about the practical application of limestone in converter steelmaking still exist. Therefore, more fundamental research works are really essential for better understanding the features of limestone dissolution during converter steelmaking process.

By comparing with the dissolution of lime in converter slag, one should be aware of the fact that the so-called “limestone dissolution” is essentially the dissolution of the lime in situ decomposed from limestone, and thus the decomposition reaction would play a considerable role on the dissolution rate, such as the inevitable temperature drop of slag bath caused by the endothermic decomposition reaction, stirring effect of numerous CO₂ bubbles generated from decomposition reaction and so on. In addition, micro-structure of the decomposed lime is supposed to be various at different steelmaking temperatures, which could affect...
greatly the dissolution rate of the produced lime in converter slag. Therefore, more evidences are needed to clarify the decomposition and dissolution behaviours of limestone in converter slag as well as the interaction between each other.

In the authors’ previous study,24 the kinetics of limestone decomposition in converter slag was studied and the results indicated that the decomposition process in molten slag at 1300–1400°C was a mixed rate control of chemical reaction and heat conduction through the decomposed lime layer. Thus, the present work is mainly focused on the kinetics of limestone dissolution in converter slag and the influence of decomposition reaction on the dissolution rate will be discussed, aiming at clarifying the influence of decomposition reaction on the limestone dissolution in converter slag and confirming the rate-limiting step. Moreover, effects of slag temperature and basicity on the dissolution rate would also be investigated, which are essential for the practical application of limestone to the converter steelmaking process.

2. Experimental

2.1. Preparation of Limestone Sample and Synthetic Slag

Raw limestone lumps supplied by a steelmaking company in China were cut into the cubic shape samples with the size of 10×10×10 mm. To prepare the synthesized converter slag, CaO powder was obtained by calcining the reagent grade CaCO₃ powder at 900°C for 24 hours. And wustite (FeO) powder was obtained by decarburizing the reagent grade powder of FeC₂O₄ at 600°C for 2 hours under flowing Ar atmosphere. Then, reagent grade SiO₂ and the obtained CaO and FeO powders were well mixed according to the proportion shown in Table 1 and used as starting materials for preparation of the synthetic converter slags. Next, the mixed powders were pressed into tablets and heated to 1600°C for 2 hours in a pure iron crucible to prepare the pre-melted slag under pure argon gas atmosphere. To investigate the effect of slag basicity (CaO/SiO₂) on the dissolution rate, the contents of FeO were maintained the same in the two synthesized slags A and B.

2.2. Experimental Procedure

Experimental apparatus used in the present work is similar to that in the previous study,24 and the schematic diagram of experimental set-up for evaluating dissolution rate of limestone is presented in Fig. 1. A vertical furnace with MoSi₂ heating elements and alumina tube (100 mm in diameter) was employed. Argon gas was introduced through the inlet at the lower part of the reaction chamber and led out at the top with a flow rate of 0.2 L/min. The slag temperature was controlled by a PtRh30–PtRh6 thermocouple located at the bottom of the crucible. Eighty grams of the pre-melted synthesized slag were charged into a platinum crucible and heated to the required temperature under argon flowing electron microscope (SEM) after Au coating and the element distribution was analyzed by energy dispersive spectrometer (EDS).

3. Results and Discussion

3.1. Dissolution Rate

Figure 2 presents the mean length (defined as \((l_1 + l_2)/2\)), \(l_1\) and \(l_2\) represent the sizes in two perpendicular directions of the cross section respectively) of limestone sample as a function of reaction time under different slag temperatures. Figure 2(a) shows the variation of mean length in the synthetic converter slag A, whereas Fig. 2(b) shows those in slag B. It can be noted that the effect of slag temperature on the limestone dissolution is remarkable in the two slags. For instance, at 1300°C in slag A, the mean length of limestone sample decreases from 10.0 mm for 60 seconds to 9 mm for 360 seconds, whereas at 1400°C it decreases from 10.0 mm for 60 seconds to 6.6 mm for 360 seconds. Besides, it is found that the decreasing rate of mean length in slag A is higher than that in slag B, indicating that the dissolution rate is faster in the slag with lower basicity.

In order to make a better quantitative evaluation on the dissolution rate of limestone in the slag, dissolution degree (\(X\)) is defined as the ratio of mean length of the residual sample to the initial one, expressed by Eq. (1). Figure 3 presents the dissolution degree profiles under different slag temperatures in slags A and B respectively. Figure 3(a) shows the dissolution degrees vs. reaction time at 1300–1400°C in slag A, and Fig. 3(b) shows the ones in slag B.

![Schematic diagram of experimental set-up for evaluating dissolution rate of limestone.](image-url)
where, $X$ is the dissolution degree ($\%$), $l_0$ and $l_2$ are the sizes in two perpendicular directions of the cross section ($m$), the subscripts of “0” and “re” represent the initial and residual sizes of limestone sample respectively.

According to the variation of dissolution degree profile with reaction time, it is concluded that the dissolution process can be divided into three stages, i.e., stagnation stage, coupling stage and sole dissolution stage. During the stagnation stage from the starting time to 60–90 seconds at different slag temperatures, the dissolution degree is almost zero and an obvious stagnation status of limestone dissolution actually exists, implying that only the decomposition reaction of limestone in the slag is involved during this stage. Moreover, it can be found that the duration time of stagnation stage decreases with the increment of slag temperature. During the coupling stage from 90 seconds to 180–360 seconds, the dissolution rate increases remarkably with reaction time and it is also noted that the ending time of coupling stage is approximately equal to the complete decomposition time of limestone sample reported in the previous work.24) Thus, both the limestone decomposition reaction and dissolution of the decomposed lime are considered to occur.

\[
X = 1 - \left( \frac{(l_1 + l_2)_{\text{0}}} {(l_1 + l_2)_{\text{re}}} \right) \tag{1}
\]
simultaneously during this stage. Finally, during the sole dissolution stage, the dissolution degree grows continuously with reaction time, which is thought to correspond to the sole dissolution of decomposed lime. In addition, by comparing the corresponding dissolution profiles in Fig. 3, it can be found that the dissolution degrees decrease with the increment of slag basicity due to a bigger mass transfer resistance in the slag, indicating that the limestone dissolution in the slag is greatly affected by a mass transfer step.

3.2. Influence of Decomposition Reaction

3.2.1. Temperature Drop in Slag Bath
As we know, limestone decomposition is a process with strong endothermic reaction and thus the temperature of slag bath would inevitably be affected by the decomposition reaction. On the basis of the decomposition degree reported in the authors’ previous work,24 Fig. 4 shows the predicted drop rate of slag temperature as well as the variation of slag temperature caused by the endothermic decomposition reaction. The detailed calculation procedures and corresponding equations are as follows.

Heat consumption rate of limestone decomposition reaction

\[ q = \Delta H \cdot n_{\text{CaCO}_3} \quad \text{.......................... (2)} \]

\[ n_{\text{CaCO}_3} = \frac{dX_{\text{dec}}}{dt} \cdot m_{\text{CaCO}_3} \quad \text{........................ (3)} \]

where, \( q \) is the rate of heat consumption caused by limestone decomposition (J·s\(^{-1}\)), \( \Delta H \) is the enthalpy of decomposition reaction (J·mol\(^{-1}\)), \( n_{\text{CaCO}_3} \) is the rate of limestone decomposition reaction (mol·s\(^{-1}\)), \( X_{\text{dec}} \) is the decomposition degree of limestone (−), \( m_{\text{CaCO}_3} \) is the mass of CaCO\(_3\) of limestone sample (mol), \( t \) is the reaction time (s).

Drop rate of slag bath temperature

\[ \frac{d(\Delta T)}{dt} = \frac{q}{C_p \cdot m_{\text{slag}}} \quad \text{........................ (4)} \]

where, \( d(\Delta T)/dt \) is the drop rate of slag bath temperature (°C·s\(^{-1}\)), \( m_{\text{slag}} \) is the mass of molten slag (kg), \( C_p \) is the constant-pressure capacity of molten slag (J·kg\(^{-1}\)·°C\(^{-1}\)).

Based on Eqs. (2)–(4), under the conditions of three slag temperatures, the drop rates of slag temperature can be calculated for different reaction time by combining with the decomposition degrees of limestone (the green color solid dots in Fig. 4), and the drop rate equations are slao obtained by fitting these calculated results, as expressed by Eqs. (5)–(7). The green color lines in Fig. 4 represent the drop rate profiles of slag temperature.

\[ \frac{d(\Delta T)}{dt} = 0.59e^{(-148.2/ t)} - 0.093 \quad \text{(at 1300°C)} \quad \text{...... (5)} \]

\[ \frac{d(\Delta T)}{dt} = 0.84e^{(-118.8/ t)} - 0.165 \quad \text{(at 1350°C)} \quad \text{...... (6)} \]

\[ \frac{d(\Delta T)}{dt} = 1.13e^{(-74/0.1)} - 0.161 \quad \text{(at 1400°C)} \quad \text{...... (7)} \]

Moreover, the equations of slag temperature can be obtained based on Eqs. (5)–(7), which are expressed by Eqs. (8)–(10). The purple color lines in Fig. 4 present the predicted temperatures profiles of slag bath with reaction time.

\[ T = 4.0 \times 10^{-8} t^4 - 3.0 \times 10^{-5} t^3 \quad +8.3 \times 10^{-3} t^2 - 0.7t + 1300 \quad \text{(at 1300°C)} \quad \text{...... (8)} \]

\[ T = 2.0 \times 10^{-7} t^4 - 9.0 \times 10^{-5} t^3 \quad +1.6 \times 10^{-2} t^2 - 1.1t + 1350 \quad \text{(at 1350°C)} \quad \text{...... (9)} \]

\[ T = 4.0 \times 10^{-7} t^4 - 2.0 \times 10^{-4} t^3 \quad +2.1 \times 10^{-2} t^2 - 1.2t + 1400 \quad \text{(at 1400°C)} \quad \text{...... (10)} \]

By comparing the three green color profiles in Fig. 4, the greatest temperature drop rate is observed under the temperature condition of 1 400°C. Moreover, the appreciable temperature drop rates ranging from 0.97°C/s to 0.25°C/s are found mainly during the first 0–90 seconds and the corresponding lower temperature of slag bath (the three purple color profiles in Fig. 4) is concentrated at the stagnation stage of dissolution process. As a result, the aforementioned dissolution degrees in Figs. 3(a) and 3(b) respectively are almost zero. Although the temperature drop of slag bath could be compensated quickly in the present experiment, the influence of transitory lower slag temperature on the limestone dissolution is still appreciable. Therefore, the stagnation stage of limestone dissolution in converter slag could be attributed to the local lower temperature in the slag bath around the limestone particle surface caused by the intensive endothermic decomposition reaction. Therefore, for a feasible limestone slagging mode, sufficient heat supply in converter bath is required to maintain the slag bath temperature for limestone decomposition and dissolution, especially at the early stage of converter steelmaking process.

3.2.2. Effect of Generated CO\(_2\) Bubbles
Stirring from gas jets or bubbling is effective to accelerate the metallurgical reaction rate, especially for the mass–transfer–controlled reactions. In order to evaluate the intensity of stirring power, the stirring power supplied for unit mass liquid (or unit volume liquid) is extensively used, which is also called stirring energy density \( e \), (W·kg\(^{-1}\) or

![Fig. 4. Temperature drop rate in slag bath and variation of slag temperature with reaction time. (Online version in color.)](image-url)
W·m$^{-3}$). As for the stirring power caused by gas jet or bubbles, probable works done by the gas jet or bubbles can be estimated from the following four aspects: kinetic energy of the gas jet per unit time, expansion work done by the sudden change of temperature at the nozzle outlet during high pressure gas jetting, expansion work done by the sudden change of pressure at the nozzle outlet during high pressure gas jetting, and work done by the gas bubbles during rising through the melt bath. In this case, if the work done by CO$_2$ bubbles during rising through the slag bath is mainly considered, the stirring power supplied by CO$_2$ bubbles can be obtained by summing the contribution due to the work done by the buoyancy fore and the volumetric expansion work, expressed by Eq. (11). Thus, the stirring power supplied for unit mass slag (stirring energy density $\varepsilon$) is calculated by Eq. (12).

Figure 5 shows the variation of stirring energy density with reaction time at different slag temperatures. For example, it can be noted that during the first 60 seconds at 1400°C, the stirring energy density decreases rapidly with reaction time from 4.1 W/(kg slag) to 1.80 W/(kg slag) at the stagnation stage of dissolution, and then the stirring energy density decays to a smaller value in the coupling stage and approaches to almost zero at approximately 300, 200 and 150 s respectively under the three slag temperatures. By comparing Figs. 5 and 3, it can be noted that a greater stirring energy density is supplied by CO$_2$ bubbles at the stagnation stage of limestone dissolution, whereas the stirring energy density are below 2.0 W/(kg slag) during the coupling stage from 60 to 300 s. In view of the fact that limestone dissolution in converter slag proceeds mainly in the coupling and sole dissolution stages, the CO$_2$ bubbles generated from decomposition reaction could provide a certain enhancement of limestone dissolution, which is similar to the reports about enhancement of quicklime dissolution rate by CO$_2$ from residual lime.

3.2.3. Microstructure of the Decomposed Lime

In the authors’ previous work, the microstructure evolution of limestone decomposing in converter slag was investigated at 1300–1400°C, and the decomposed lime was confirmed to possess smaller grain size of 0.63–0.84 $\mu$m and lower apparent porosity of 30.0–34.0% than the calcined lime. Figure 6 presents the microstructure of the decomposed lime as well as the interface region across CaO-slag boundary. The typical microstructure of the lime produced at 1300°C for 180 s is shown as in Fig. 6(a), which is found to be in the dominance of CaO crystals surrounded by both the micropores and macropores. The microphotograph in the CaO–slag boundary region of limestone sample reacted at 1300°C for 270 s is presented in Fig. 6(b), and the molten slag is found to penetrate into the lime layer more easily along the macropores.

3.3. Formation of Interfacial Layer during Limestone Dissolution

Some research works reported that the dissolution rate
of lime would be limited by the formation of 2CaO·SiO$_2$ layer between the lime and molten slag.\textsuperscript{4,5,29} In the present work, no C$_2$S phase is found at the interface between the decomposed lime and the synthetic slag with the basicity of 0.5 (slag A), mainly due to the lower ratio of CaO to SiO$_2$ in the slag. On the other hand, for the limestone dissolution in the synthetic slag with the basicity of 1.0 (slag B), the interfacial layers formed at 1350°C for 240 s and 900 s respectively are shown in Fig. 7. It can be noted that for the dissolution of limestone sample reacted at 1350°C for 240 s, only the CaO–FeO layer is observed adjacent to the produced lime, as shown in Fig. 7(a). But for the limestone sample reacted for 900 s, a continuous C$_2$S layer is found produced lime, as shown in Fig. 7(b). Thus, the dissolution process of limestone in converter slag displays these features: at the coupling stage of dissolution process from 90 seconds to 180–360 seconds, generation of CO$_2$ gas from decomposition reaction is considered to inhabit the formation of C$_2$S layer, whereas C$_2$S layer can be formed at the sole dissolution stage of dissolution process.

### 3.4. Kinetics Analysis

Dissolution of limestone in converter slag is considered to involve the following three elementary steps, i.e., chemical reaction of decomposed lime from solid to liquid phase (expressed by Eq. (13)) at the interface between the slag and lime, diffusion through the product layer (2CaO·SiO$_2$), and diffusion through the boundary layer (in the Stokes regime) to the bulk slag. Under the assumption of chemical reaction controlling process, the relationship between dissolution degree $X$ and reaction time $t$ can be expressed by Eq. (14).\textsuperscript{30}

If the dissolution process is controlled by the boundary layer diffusion, a relationship between dissolution degree and reaction time is expressed by Eq. (15).\textsuperscript{30} If the resistance to diffusion through the product layer controls the whole process, the progression of dissolution process in terms of fractional conversion is given in Eq. (16).\textsuperscript{30}

\[
CaO_{(\text{decomposed, solid})} = (CaO) \quad (13)
\]

\[
\frac{1}{2}(1-x)^{1/2} = k_{01}t = \frac{2b(C_{CaO}^e - C_{CaO}^e)}{\rho_{CaO} b^2} t \quad (14)
\]

\[
\frac{1}{2}(1-x)^{1/2} = k_{02}t = \frac{2b(C_{CaO}^e - C_{CaO}^e)D}{\rho_{CaO} b^2} t \quad (15)
\]

\[
\frac{1}{2}(1-x)^{1/2} + 2(1-x) = \frac{2b(C_{CaO}^e - C_{CaO}^e)D_{eff}}{\rho_{CaO} b^2} t \quad (16)
\]

where, $t$ is the actual reaction time (s); $k_{01}$, $k_{02}$, $k_{03}$ are the apparent rate constants for the three different rate-controlling mechanisms ($s^{-1}$); $C_{CaO}^e$ is the concentration of CaO at the interface between the surface of decomposed CaO and molten slag (mol m$^{-3}$), which can be determined from that at the intersect of liquidus line with a straight line connecting the point of bulk slag composition and the CaO apex on the CaO–SiO$_2$–FeO$_2$ phase diagram; $C_{CaO}^e$ is bulk concentration of (CaO) in molten slag (mol m$^{-3}$); $\rho_{CaO}$ is the molar density of decomposed lime (mol m$^{-3}$); $k_e$ is the chemical reaction rate constant (m$^3$ s$^{-1}$); $D$ is the diffusion coefficient in the Stokes regime (m$^2$ s$^{-1}$); $D_{eff}$ is the effective diffusion coefficient through the CaO·SiO$_2$ product layer (m$^2$ s$^{-1}$).

By analyzing the experimental results in slag A with model–fitting method based on Eqs. (14), (15) and (16) respectively, it can be noted in Fig. 8, that the plots of $1-(1-X)^{1/3}$ and $t$ during the coupling stage present the best linear relationship with the variance value ($R^2$) above 0.992, whereas the plots of $1-(1-X)^{1/3}$ versus $t$ during the sole dissolution stage give the best linear relationship. On the other hand, the results in slag B show that the kinetic plot of chemical reaction control also present a better linear relationship in the coupling stage, whereas the kinetic plots of mixed control (diffusion through the product layer and diffusion through the boundary layer) shows the best linear relationship during the sole dissolution stage, as shown in Fig. 9.

The kinetic analysis results indicate that chemical reaction controlling is considered to limit the process at the coupling stage of limestone dissolution in slags A and B. However, during the sole dissolution stage, boundary layer diffusion is thought as the rate controlling step in slag A, whereas a combination of controlling step including diffusion through the product layer and diffusion through the boundary layer, must be considered when predicting the limestone dissolution rate. As discussed in section 3.2, during the limestone dissolution process especially at the coupling stage, limestone decomposition and dissolution of decomposed lime proceed simultaneously. Thus, decomposition reaction does play a significant role on the chemical
Fig. 8. Kinetics plots of limestone dissolution in slag A under different slag temperatures during (a) coupling stage and (b) sole dissolution stage. (Online version in color.)

Fig. 9. Kinetics plots of limestone dissolution in slag B under different slag temperatures during (a) coupling stage and (b) sole dissolution stage. (Online version in color.)
reaction of the lime from solid to liquid phase. For example, lower slag temperature around the limestone sample surface and smaller surface area due to the lower apparent porosity of the lime would slow down the chemical reaction rate (Eq. (13)). As a result, a controlling step of chemical reaction must be considered to predict the limestone dissolution rate at the coupling stage.

Furthermore, the kinetic parameters including chemical reaction rate constant \(k_r\), effective diffusion coefficient \(D_{eff}\) and diffusion coefficient through boundary layer are obtained respectively from the line slopes, as shown in Table 2. It is found that the chemical reaction rate constant \(k_r\) ranges from \(8.39 \times 10^{-6}\) to \(3.49 \times 10^{-5}\) m/s in slag A and from \(6.43 \times 10^{-6}\) to \(3.25 \times 10^{-5}\) m/s in slag B respectively. On the other hand, the diffusion coefficient through boundary layer varies from \(1.43 \times 10^{-7}\) to \(2.59 \times 10^{-7}\) m\(^2\)/s in slag A and from \(1.16 \times 10^{-7}\) to \(2.35 \times 10^{-7}\) m\(^2\)/s in slag B respectively. Moreover, the effective diffusion coefficient through product layer ranges from \(5.66 \times 10^{-9}\) to \(2.27 \times 10^{-8}\) m\(^2\)/s in slag B. The reason why \(D_{eff}\) is much smaller than other diffusivities is explained as follows. Under the present experiment condition (1 300–1 400°C), the product layer of \(2\text{CaO} \cdot \text{SiO}_2\) is thought to be solid and \(\text{Ca}^{2+}\) is considered to diffuse through the crystal lattice of \(2\text{CaO} \cdot \text{SiO}_2\) solid solution, resulting in a much smaller value of \(D_{eff}\) (depending on the crystal structure of product layer and sinuosity of the diffusion path). On the other hand, for the mass transfer in molten slag, \(D\) is the diffusion coefficient of \(\text{Ca}^{2+}\) through boundary layer (in the Stokes regime with low Reynolds number) to the bulk slag concentration, which is associated with the viscosity of molten slag. Therefore, the value of \(D_{eff}\) is much smaller than that of \(D\). In addition, it is noted that \(k_r\), \(D\) and \(D_{eff}\) increase with decreasing the slag basicity and increasing the slag temperature. Thus, higher slag temperature and lower slag basicity would provide substantial contribution to enhance the limestone dissolution process.

Then the determined rate constants for the coupling and sole dissolution stages are further plotted with temperature \((1/T)\) and the results in slag A and B are shown in Figs. 10(a) and 10(b) respectively. The activation energies of limestone dissolution during the coupling stage in slags A and B are 315 kJ/mol and 376 kJ/mol respectively, and on the other hand, the activation energies for the sole dissolution stage are 139 kJ/mol and 284 kJ/mol respectively. The present activation energies during the sole dissolution stage correspond well to the reported values\(^{6,31}\) of solid lime and burnt dolomite dissolved into \(\text{FeO} \cdot \text{CaO} \cdot \text{SiO}_2\) molten slag (137 kJ/mol and 210 kJ/mol respectively).

### Table 2. Kinetic parameters for different rate-controlling mechanisms.

| Slag basicity (CaO/SiO\(_2\)) | Slag temperature (°C) | \(k_r\) (m/s) | \(D\) (m\(^2\)/s) | \(D_{eff}\) (m\(^2\)/s) |
|-------------------------------|-----------------------|-------------|----------------|------------------|
| 0.5                           | 1 300                 | 8.39 \times 10\(^{-6}\) | 1.43 \times 10\(^{-7}\) | / |
|                               | 1 350                 | 1.64 \times 10\(^{-6}\) | 1.96 \times 10\(^{-7}\) | / |
|                               | 1 400                 | 3.49 \times 10\(^{-6}\) | 2.59 \times 10\(^{-7}\) | / |
| 1.0                           | 1 300                 | 6.43 \times 10\(^{-6}\) | 1.16 \times 10\(^{-6}\) | 5.66 \times 10\(^{-9}\) |
|                               | 1 350                 | 1.10 \times 10\(^{-6}\) | 1.71 \times 10\(^{-7}\) | 1.82 \times 10\(^{-8}\) |
|                               | 1 400                 | 3.25 \times 10\(^{-6}\) | 2.35 \times 10\(^{-7}\) | 2.27 \times 10\(^{-8}\) |

**Fig. 10.** Relationship between rate constant and temperature in (a) slag A (b) slag B. (Online version in color.)

### 3.5. Practical Consideration

To promote the limestone dissolution in converter slag, the following suggestions can be made based on the present experimental results.

1. Considering the existence of stagnation stage caused by the lower slag temperature due to decomposition reaction, the replacement of lime with limestone in practical application is not advisable at the early stage of converter steelmaking, and rapidly increasing the temperature of slag bath is conducive to reduce the duration time of stagnation stage.

2. For an applicable limestone slagging mode, sufficient heat supply to the melt bath is strongly recommended to compensate the local temperature drop in slag bath and promote limestone dissolution, such us increasing the oxygen supply intensity appropriately and reducing the amounts of scrap charged into converter.

### 4. Conclusions

Kinetics of limestone dissolution in early converter slag was studied under different slag temperatures and basicities and the influences of decomposition reaction were examined. The following conclusions could be drawn.

1. Limestone dissolution process in converter slag can be divided into three stages, i.e., stagnation stage, coupling stage and sole dissolution stage. Higher slag temperature is conducive to decrease the duration time of stagnation stage and higher dissolution degree can be obtained under the conditions of lower slag basicity.

2. CO\(_2\) bubbles generated from decomposition reaction can provide a certain enhancement of limestone dissolu-
tion at the coupling stage. Formation of 2CaO·SiO$_2$ phase is not found at the coupling stage whereas a continuous 2CaO·SiO$_2$ layer is formed at the sole dissolution stage.

(3) Kinetics analysis based on the experimental results shows that the coupling stage of limestone dissolution is controlled by chemical reaction, whereas diffusion through the boundary layer or a combination of controlling step is the rate-limiting step at the sole dissolution stage under different slag basicities.

(4) Kinetics parameters for limestone dissolution in converter slag at 1300–1400°C are obtained. The chemical reaction rate constant ($k_c$) at the coupling stage ranges from 6.43×10$^{-6}$ to 3.49×10$^{-5}$ m/s, and the diffusion coefficient through boundary layer ($D_{cb}$) at the sole dissolution stage ranges from 1.16×10$^{-7}$ to 2.59×10$^{-7}$ m$^2$/s$^{-1}$. Moreover, the effective diffusion coefficient through the 2CaO·SiO$_2$ product layer in the slag with the basicity of 1.0 ranges from 5.66×10$^{-9}$ to 2.27×10$^{-8}$ m$^2$/s$^{-1}$ ($D_{en}$).

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