Analysis of Dephosphorization Reaction Using a Simulation Model of Hot Metal Dephosphorization by Multiphase Slag

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In most cases, the slag used in hot metal dephosphorization is saturated with dicalcium silicate in the solid phase and the partition ratio of phosphorus between dicalcium silicate and the liquid slag is high. This indicates the important role of dicalcium silicate in dephosphorization. To understand the reaction kinetics and identify optimum treatment conditions, it is very important to know the influence of the solid phases in the slag. In this study, a new reaction model for hot metal dephosphorization that considers the effects of dicalcium silicate and the dissolution rate of lime is applied to simulate laboratory-scale experiments.

The calculated results are in good agreement with the experimental results for various slag compositions and methods of flux and oxidizer addition. The influence of various factors on the reaction efficiency is discussed using this simulation model. The optimum basicity and combination of stirring energy and oxidizer supply rate are found. The importance of the precipitation behavior of the solid phase in slag is clarified.

KEY WORDS: hot metal pretreatment; slag; dephosphorization; reaction kinetics.

1. Introduction

In the hot metal dephosphorization reaction, most of the slag is solid and liquid coexisting conditions. From the phase diagram for the CaO–SiO2–P2O5 system, it is well known that dicalcium silicate (C2S) and tricalcium phosphate (C3P) form a solid solution at the steelmaking or hot metal dephosphorization temperature. This phase diagram implies that the main products of the dephosphorization reaction are soluble in the main solid phase in the slag. Ito et al.1) found that the partition ratio of phosphorus between C2S and the liquid slag was very high. Thus, it can be said that phosphorus is more stable in the solid solution of C2S and C3P than in the liquid slag. Inoue and Suito2) showed that the transfer rate of phosphorus from the liquid slag to the solid solution was very high.

Assuming that the rate-controlling steps of the dephosphorization reaction are the mass transfers at the boundary layers of the metal and slag phases, the dephosphorization rate can be expressed as

\[ -d(\%P)/dt = ( Ak/V ) \times \left[ (\%P) - (%P)_L/K \right] \] ........(1)

where \( [\%P] \) and \( (%P)_L \) are the phosphorus content in the metal and liquid slag phases, respectively, (mass%); \( t \) is time (s); \( A \) is the interfacial area (m²); \( V \) is the volume of molten iron (m³); \( k \) is the overall mass transfer coefficient (m/s); and \( K \) is the equilibrium distribution ratio of phosphorus between the liquid slag and metal phases.

As the dephosphorization reaction proceeds, phosphorus moves from the metal to the liquid slag; that is, \((%P)_L\) increases and the term in the curly brackets in Eq. (1) decreases. However, when C2S precipitates in the slag, \((%P)_L\) does not increases because C2S can remove the phosphorus from the liquid slag and form the solid solution. As a result, the term in the curly brackets in Eq. (1) does not decrease much, and suppressing the decrease in the dephosphorization rate.

Sasaki et al.3) studied the effect of C2S precipitation on dephosphorization efficiency; they found that, the efficiency increased considerably when the slag was saturated with C2S. It can be considered that the dephosphorization rate increased in the C2S saturated region because the phosphorus content in the liquid slag phase decreased due to the absorption of phosphorus into the solid solution. As a result, the term in the curly brackets in Eq. (1) does not decrease much, and suppressing the decrease in the dephosphorization rate.

Hoshikawa et al.4) reported that the addition of artificially made C2S as a flux did not improve the dephosphorization efficiency. Thus, to utilize the effect of the solid solution, the optimum route for the slag-composition change during dephosphorization should be clarified.

Hot metal dephosphorization occurs under nonequilibrium conditions as it takes place of slag with a high oxygen potential with hot metal with a low oxygen potential. Analysis of the process by the reaction kinetics is ongoing, and the most important model is a “coupled reaction
model". The application of this model to the slag with coexisting solid and liquid phases is limited as the slag is assumed to be uniform liquid phase. In addition, the added flux is assumed to melt into the slag instantaneously, although the dissolution rate of flux can be considered to have a great influence on the reaction rate.

With this background, we propose herein a new hot metal dephosphorization model that takes into account the solid phase in the slag and the dissolution rate of the flux. We also discuss the optimum dephosphorization conditions and compare the predictions of this model with experimental results.

2. Hot Metal Dephosphorization Model

2.1. Modeling of Slag with Coexisting Solid and Liquid Phases

In this model, three phases—solid slag, liquid slag, and liquid metal—and the reaction between the solid and liquid slag are considered besides the reaction between the liquid slag and liquid metal. As details of the model may be found elsewhere, we only describe it in brief below.

To calculate the phase diagram, slag is simplified as a CaO–SiO₂–FeO system and the compositions at the boundary lines between the various coexisting solid and liquid regions at 1673 K are numerically formulated. The solid fraction in the solid–liquid coexisting region is calculated by the law of the lever. When C₂S is precipitated in slag, the P₂O₅ content is distributed between the solid and liquid phases as a function of the FeO content, based on the results of Ito et al. But when the other solid phase is precipitated, P₂O₅ is pushed out into the liquid phase. As P₂O₅ dissolves in C₂S and forms a C₂S–C₃P solid solution, when 1 mol of P₂O₅ is dissolved as C₃P, 1.5 mol of SiO₂ must move from the solid solution into the liquid phase to maintain stoichiometric conditions. In this model, the boundary lines between each region where solid and liquid phases coexist are considered on the basis of the CaO–SiO₂–FeO system. When the SiO₂ content in the liquid slag increases as a result of P₂O₅ dissolution as C₃P, the liquid slag becomes unsaturated in C₂S, which contradicts the existence of the solid solution. Therefore, in this model, phosphorus is assumed to be solved as P₂O₅ instead of C₃P.

In the case where C₂S precipitates because of a change in the slag composition, the distribution of phosphorus between the liquid slag and newly precipitated C₂S is calculated. Although the phosphorus content in each C₂S particle is different from that in the industrial slag, the average phosphorus content in C₂S is calculated and the differences between individual particles are not considered.

On the other hand, in the case where a fraction of C₂S melts because of a change in the slag composition, the increase in the P₂O₅ content of the liquid phase is calculated on the basis of the weight of C₂S melted and the average phosphorus content in C₂S. In this model, the mass transfer of phosphorus into the precipitated C₂S particles by diffusion is not considered.

2.2. Modeling of Reaction Kinetics between Molten Slag and Metal Phases

A coupled reaction model is used to calculate the reaction kinetics between the molten slag and metal phases. In this model, the reactions are described by the double boundary theory assuming equilibrium conditions at the interface. For example, for the oxidation reaction of element "M" in Eq. (2), the molar flux density is described by Eq. (3), and the equilibrium relation at the interface is represented as in Eq. (4).

\[
[M] + n[O] = (MO_n) \quad \text{..................................(2)}
\]

\[
J_M = (k_m \cdot \rho_m/(100M_{MO_n})/([%M]_L - [%M]_L) = (k_r \cdot \rho_r/(100M_{MO_n}))([(MO_n)]_L - ([MO_n])_L) \quad \text{..........................(3)}
\]

\[
E_M = ([MO_n])^n/([%M]_L \cdot \alpha_0 \gamma_{MO_n}) = 100 \cdot C \cdot N_{MO_n} \cdot J_M \cdot K_M/(\rho \cdot \gamma_{MO_n}) \quad \text{..................................(4)}
\]

where, \(J_M\) represents the molar flux density of element M (mol/(m²·s)); \(k_m\) and \(k_r\) represent the mass transfer coefficient in the boundary layer of the liquid metal and slag phases, respectively (m/s); \(\rho_m\) and \(\rho_r\) are the densities of the liquid metal and slag, respectively (kg/m³); \(M_{MO_n}\) and \(M_{MO_n}\) are the atomic weight of M and molecular weight of \(MO_n\), respectively; \(\alpha_0\) is the oxygen activity; \(C\) is the total number of moles in the liquid slag phase; \(f\) is the activity coefficient; \(K_M\) is the equilibrium constant of Eq. (4); \(\gamma_{MO_n}\) is the activity coefficient of \(MO_n\); and the superscripts b and * indicate the bulk and interface concentrations, respectively, while the subscript L indicates liquid slag. In this calculation, the composition of each component in the liquid slag phase was used instead of the average over the liquid and solid slag phases.

As the compositions of the liquid metal and the liquid slag phases changed widely, \(E_M\) is not constant during the calculation. In this model, the empirical equations derived by Suito and Inoue are adapted for Mn and Fe, where the activity coefficients for MnO and FeO are described as being functions of the slag composition and temperature. To suppress the divergence of the calculation, the maximum and the minimum values for the activity coefficient are set as 1.0 and 0.1, respectively. According to the relation between the FeO activity and CaO/SiO₂ (basicity), the activity is the maximum when the basicity is around one. Therefore, when the basicity is smaller than one, the equation in which the FeO activity decreases with basicity is used.

For the dephosphorization reaction, empirical equations derived by Suito and Inoue are used. To ensure agreement with the experimental results, the influence of the slag composition is revised as the following equation.

\[
\log([P]_L/([P]_L)_{T,Fe}) = 11.570/7 - 10.52 + 0.0720 \times 0.8/([CaO])_L + 8/23([FeO])_L - 2/23/[P_2O_5]) \quad \text{..........................(5)}
\]

The mass transfer coefficient in the metal phase (\(k_m\)) is formulated as a function of the stirring gas flow rate \(q_{Ar}^0 \quad Nm^3/s\) below, where the superscript 0 indicates the standard condition in Table 2.

\[
k_m = \alpha(q_{Ar}^0/q_{Ar}^0)^{1/2} \quad \text{..................................(6)}
\]

The mass transfer coefficient in the slag phase (\(k_r\)) is formulated by considering the effect of the CO gas formation rate \((q_{CO}^0 \quad Nm^3/s)\) and slag volume \((W_s \quad kg)\):
\[ k = \frac{k^*}{(q_\text{Ar} + 3 \times q_\text{CO})/q_\text{Ar} \times (W^0_\text{CaO}/W^0_s)} \]  

Also, \( k_s \) is considered as a function of the solid fraction in the slag, because a change in the slag viscosity would affect the boundary layer thickness, although the diffusion rate would not change. Equation (8) is assumed to hold, and the value of \( n \) is defined such that the calculated results match the experimental results, where \( f_{\text{solid}} \) is solid fraction in slag.

\[ \log(k_s/k^0_s) = -f_{\text{solid}} \]  

The interfacial area for the reaction (A) changes in proportion to the 2/3 power of the liquid fraction of the slag, as it can be considered that \( A \) is the contact area between the liquid metal and the liquid slag. In the coupled reaction model, the decarburization reaction is expressed with mass transfer rate in the metal phase and the CO gas formation rate, as shown in Eq. (9), where \( P^*_{\text{CO}} \) denotes the partial pressure of CO at the interface, and \( G_{\text{CO}} \) denotes the formation rate of CO gas bubbles (mol/(m²·s)).

\[ J_{\text{CO}} = k_m \rho_m/(100M_{\text{CO}}) \{ [\%\text{CaO}]^* - [\%\text{CaO}] \} = G_{\text{CO}}(P^*_{\text{CO}} - 1) \]  

Although \( G_{\text{CO}} \) is normally treated as a constant defined such that the equation fits the experimental results, the reduction rate of iron oxide by CO gas is known to decrease with slag basicity. Therefore, an equation that considers this dependence of the reduction rate on slag basicity is formulated:

\[ G_{\text{CO}} = C_{\text{CO}} \times ((q_\text{Ar} + 3 \times q_\text{CO})/q_\text{Ar} \times (W^0_\text{CaO}/W^0_s))^{-1} \]  

### 2.3. Dissolution Rate of Lime

Matsushima et al. measured the dissolution rate of sintered lime rotating in molten slag and derived Eq. (11) for the mass transfer coefficient \( k^* \), m/s, assuming that the dissolution rate was controlled by the mass transfer in the slag. The rate of the decrease in weight of lime can be expressed as in Eq. (12).

\[ k' = 0.35 \times \rho^{0.36} \times \eta^{-0.36} \times D^{0.67} \times d^{-0.31} \times U^{0.67} \]  

where \( \eta \) is the viscosity of the slag (Pa·s), \( D \) is the diffusion coefficient of CaO in slag (m²/s), \( d \) is the diameter of the lime (m), and \( U \) is the relative velocity (m/s).

\[ -dW_{\text{CaO}}/dt = n_{\text{CaO}} \times A_{\text{CaO}} \times (k') \rho \times (\Delta(\%\text{CaO})/\rho \times \xi) \]  

where \( W_{\text{CaO}} \) is the weight of the lime (kg), \( n_{\text{CaO}} \) is the number of lime particles (calculated from the weight of lime, assuming a spherical shape), \( A_{\text{CaO}} \) is the surface area of one lime particle (m²), \( \rho \) is the density of lime (kg/m³), \( \Delta(\%\text{CaO}) \) is the difference between the lime content in the liquid slag and the saturation concentration, and \( \xi \) is a fitting parameter for the surface area (used because industrial lime is very porous). In this model, these equations are used to calculate the dissolution rate of lime, and the viscosity is assumed to be in proportion to the 3/4 power of the solid fraction of the slag.

The saturation concentration of CaS should be used as it is well known that CaS forms on the lime surface. However, slag basicity can increase in the CaS-saturated region with coexisting solid and liquid phases; that is, the lime content in slag becomes higher than the saturation concentration of CaS. The physical delamination of the CaS particles formed at the lime surface causes this phenomenon. Therefore, in this model, \( \Delta(\%\text{CaO}) \) is calculated, which is the difference between the concentration of lime and the saturation concentration of CaO, and in the CaS-saturated region of coexisting solid and liquid phases, \( k' \) is decreased to 1/10. To calculate Eq. (11), the relative velocity between the lime and slag is important. In this model, this value is set as 0.5 m/s, which is the reported value for the relative velocity between scrap and liquid iron in the scrap melting process. If lime is not added at the same time, lime particles of various sizes will exist in the slag, depending on the time after the addition. For simplicity, in this model, when lime is newly added, the average size for all lime particles—the newly added lime particles and the existing lime particles in the slag, which have already been partially dissolved—is calculated and this average is used to estimate further dissolution.

### 3. Comparison with Experimental Results

#### 3.1. Experimental Methods

Experiments were carried out using an induction furnace. About 70 kg of molten iron was melted and the bath was stirred by Ar gas from the porous brick installed at the bottom of the furnace at the flow rate of 20 NL/min. For dephosphorization, mixtures of powder lime and reagent-grade FeO and SiO₂ wrapped in paper were added on the bath surface. Hereafter, the lime and SiO₂ are called the flux, and FeO is called the oxidizer. Metal was sampled with a dip-up-type sampler and the compositions (except carbon) were analyzed by fluorescence X-ray analysis; the carbon content was analyzed by the combustion method. Slag was sampled with a steel spoon sampler. After magnetically separating the iron and grinding it, a glass bead sample was analyzed by the fluorescence X-ray analysis method. As very fine iron particles cannot be separated by magnetic separation, the metallic iron content was analyzed by chemical analysis. The content of Fe as FeO in the slag was calculated by subtracting the metallic iron content from the total iron content. During the experiments, the metal temperature was measured in approximately 4-min intervals with an immersion-type consumable thermocouple and was maintained at 1 673 ± 20 K by electric power.

In run 1, a mixture of lime, SiO₂, and FeO was added 40 times at 1-min intervals to the hot metal without containing Si. After addition, stirring was continued for 20 min. The average basicity was about 1.35. In run 2, initially, a mixture of lime and SiO₂ was added to form a slag and after that only FeO was added (40 times at 1-min intervals) on the hot metal without containing Si. The average basicity was about 0.7. In run 3, to hot metal containing 0.32 % Si, FeO was added seven times at 1-min intervals for desiliconization, followed by the addition of lime and FeO (40 times at 1-min intervals). The average basicity was about 2.6.

Runs 4 and 5 were carried out to determine the influence...
of the lime particle size. To hot metal containing 0.37% Si, FeO was added for seven times at 1-min intervals, followed by the addition of lime and FeO (20 times at 1-min intervals). In run 4, lime particles of 1–3 mm in diameter were used; in run 5, lumpy lime particles with an average diameter of 16 mm were used. The experimental conditions are summarized in Table 1.

### 3.2. Experimental Results and Comparison with Calculations

The parameters under the standard conditions used for the calculations are summarized in Table 2. These values are based on the reported values for experiments of the same size.14)

The experimental and calculated results for runs 1–3 are shown in Figs. 1–3, respectively. For runs 1 and 2, the model simulates the change in [P], (FeO), and basicity quite well. But for run 3, although the model simulates the changes in [P] and (FeO) quite well, the calculated basicity is lower than the experimental value. In run 3, the difference in basicity between the added flux and slag was quite large, and it was difficult to match the calculated and experimental values. Nevertheless, although some mismatch still exists, this model can be used to study dephosphorization with various slag compositions and methods of flux addition.

The influence of the CO gas formation rate and slag volume is taken into account in Eqs. (7) and (10). In Fig. 4, case 1 shows the calculation results for run 1 without considering Eqs. (7) and (10). Case 2 shows the results obtained when the influence of the CO gas formation rate is considered but the influence of the slag volume is neglected in Eqs. (7) and (10). Compared with the results in Fig. 1 (case 3), we find that to simulate the phosphorus recovery behavior, the decrease in the CO gas formation rate after the addition of the oxidizer must be considered. In addition, comparing cases 2 and 3, we find that the influence of the slag volume must be considered to simulate the initial dephosphorization rate. This is because the smaller is the slag volume, the larger is the stirring intensity at the same CO gas formation rate.

In Fig. 5, the influence of the n term in Eq. (8) is shown. Compared with the case where n is set to 5 (Fig. 1, case 3), the calculated dephosphorization behavior for when n is set as 1 (case 3') is different in the lower–phosphorus–content region. This difference would be the result of the following: when the value of n is large, the mass transfer coefficient in the slag does not change until the solid fraction becomes quite large; in contrast, when the value of n is small, the mass transfer coefficient in the slag changes sensitively with the solid fraction. In this model, n was set as 5 to fit the experimental results.

The experimental and calculation results of runs 4 and 5 are shown in Figs. 6 and 7, respectively. In these calculations, the value of x in Eq. (12) was changed. If the value of x was set as 1, the calculated basicity was much smaller than actually measured even for run 4 (in which powdered lime was used). For run 5 (in which lumpy lime was used), when the value of x was set as 10 or 50, the change in basicity could be simulated. On the contrary, the calculated dephosphorization behavior became close to the measured behavior when the value of x was set as 1. Therefore, the relation between the lime dissolution behavior and the dephosphorization cannot be simulated by this model with sufficient accuracy.

### 4. Influence of the Various Factors on the Dephosphorization Behavior

Influence of the operational factors on the dephosphorization behavior was calculated using the proposed model with the parameters determined as above. For the calculation, to hot metal without containing Si, mixture of CaO, SiO₂, and FeO was added at 1-min intervals. The dissolution rate of lime was not considered. The conditions for the calculation are summarized in Table 3. In case (a), the basicity of the flux was changed and the flux and oxidizer were supplied at a constant rate. In case (b), the supply rates of flux and oxidizer was changed and the ratio of basicity was kept constant. Under the same conditions as that in case (a), in case (c), the supply rate of oxidizer was increased twofold; in case (d), the gas flowrate for stirring was increased twofold.

The influence of basicity on the dephosphorization rate (De-P) and phosphorus recovery rate (Re-P) are shown in Table 4.
Fig. 1. Comparison of the calculated and experimental results for run 1.

Fig. 2. Comparison of the calculated and experimental results for run 2.

Fig. 3. Comparison of the calculated and experimental results for run 3.

Fig. 4. Influence of stirring by CO gas and slag volume on the calculated result for run 1.

Fig. 5. Influence of the mass transfer coefficient of slag and the solid fraction on the calculated result for run 1.
De-P increases significantly when the basicity is larger than 1.2, when C\textsubscript{2}S starts to precipitate; this matches the experiment results reported by Sasaki et al.\textsuperscript{3)} When the basicity is too high, De-P decreases because the solid fraction of the slag is too large. An optimum basicity can be found to minimize Re-P, although this value is higher than the optimum value that maximizes De-P. In Fig. 9, the influence of basicity on the solid fraction and on the oxygen activity at the interface (\textit{aor}) at the time just before the start of phosphorus recovery is shown. The \textit{aor} value decreases with increasing basicity; this matches the experiment results of Miyamoto et al.\textsuperscript{15)} The reason for the occurrence of this phenomenon would be the change induced in the FeO activity and CO gas formation rate by the change in basicity. According to these results, for efficient dephosphorization, the basicity should be controlled to be an optimum value by considering the precipitation of the solid phase. This optimum value would change with the operational

<table>
<thead>
<tr>
<th>Unit consumption of flux and FeO, kg/t</th>
<th>CaO/SiO\textsubscript{2} of flux</th>
<th>Stirring Condition</th>
<th>Rate of addition, kg/min/t</th>
<th>Method of Addition*\textsuperscript{**}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case</td>
<td>Flux</td>
<td>FeO</td>
<td>Ar flow rate</td>
<td>(v)</td>
</tr>
<tr>
<td>a</td>
<td>20.28</td>
<td>50.71</td>
<td>0.8-2.1</td>
<td>25</td>
</tr>
<tr>
<td>b</td>
<td>20.28</td>
<td>50.71</td>
<td>1.56</td>
<td>25</td>
</tr>
<tr>
<td>c</td>
<td>20.28</td>
<td>101.43</td>
<td>1.56</td>
<td>25</td>
</tr>
<tr>
<td>d</td>
<td>20.28</td>
<td>50.71</td>
<td>1.56</td>
<td>50</td>
</tr>
</tbody>
</table>

\*\*; C(n) means that flux or FeO is added continuously for n times at intervals of 1 min.

Fig. 6. Influence of the surface area of lime on the calculated result for run 4.

Fig. 7. Influence of the surface area of lime on the calculated result for run 5.

Fig. 8. Change in dephosphorization rate and phosphorus recovery rate with slag basicity.
conditions, i.e., the FeO content and temperature. The influence of the flux supply rate on the dephosphorization ratio is shown in Fig. 10 for cases (b), (c), and (d). The optimum flux supply rate is found. At lower flux supply rates, the supply rate of the oxidizer is also low; therefore, as the oxygen potential decreases, the dephosphorization rate decreases. At overly high flux supply rates, although the oxygen potential increases, the dephosphorization rate decreases. The reason for this would be the decrease in the dephosphorization capacity of the slag as the increase in FeO content causes a decrease in the CaO content. Comparing cases (b) and (c), we find that an increase in the oxidizer supply rate causes an increase in the dephosphorization ratio and the optimum supply rate changes to a lower value. In case (c), even at low flux supply rate, the oxygen potential does not decrease as the oxidizer supply rate is high. Comparing cases (b) and (d), we find that an increase in the stirring energy causes a decrease in the dephosphorization ratio. Therefore, for efficient dephosphorization, an optimum combination of stirring energy and flux and oxidizer supply rates would be necessary.

5. Conclusions

We proposed a new reaction model for hot metal dephosphorization that considers three phases—solid slag, liquid slag, and liquid metal—and the reaction between the solid and liquid slag, besides the reaction between the liquid slag and liquid metal and the dissolution rate of lime. It was used to simulate laboratory-scale experimental results. The following results were obtained:

(1) The calculated results are in good agreement with the experimental results for various slag compositions and methods of flux and oxidizer addition.

(2) With this simulation model, we discussed the influence of various factors on the reaction efficiency. The optimum basicity and the optimum combination of stirring energy and oxidizer supply rate were found.

In this model, some parameters are determined such that the equation fits the experimental results and no theoretical reasons are provided. To develop a more precise model, empirical or theoretical equations that describe these parameters are necessary.

REFERENCES