



# A Review of Multi-phase Slag Refining for Dephosphorization in the Steelmaking Process

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Dephosphorization has always been a challenging task in the steelmaking process. In the traditional studies, CaO-based steelmaking slag was usually treated as a homogeneous liquid phase to analyze the dephosphorization equilibrium between molten slag and hot metal (slag/metal). In fact, the slag shows a coexisting state of both liquid and solid at steelmaking temperature. In recent years, multi-phase slag refining has been proposed and proved to be an efficient technique to improve the utilization of solid lime and the dephosphorization efficiency in steelmaking practices. The present review focuses on hot issues for the multi-phase slag refining, including the dissolution of solid lime to the molten slag, the formation of  $2\text{CaO}\cdot\text{SiO}_2$  and phosphorus-rich solid solution of  $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ , as well as the phosphorus distribution ratio between the solid and liquid phases in the multi-phase slag. In addition to the discussion on thermal and kinetic factors of dephosphorization, the necessity of further research is proposed on the dissolution behavior of phosphorus-rich solid solution and phosphorus redistribution in the slag of high temperature, high basicity and high FeO in the final stage of converter steelmaking. Then, a more applicable dynamic model of dephosphorization could be expected considering the equilibrium not only between molten slag and liquid metal but also among the phases of the multi-phase slag in steelmaking process. Furthermore, the modelling work is beneficial for the fine control of the BOF process and the development of intelligent manufacturing in steelmaking industry.

**Keywords:** steelmaking dephosphorization, multi-phase slag, lime dissolution, phosphorus-rich solid solution, distribution ratio of phosphorus

## INTRODUCTION

Dephosphorization is always the major but challenging task in the steelmaking process. CaO-based fluxes are widely used in hot metal pretreatment process and basic oxygen steelmaking process to form dephosphorization slags, which consist of  $\text{CaO}\text{-SiO}_2\text{-P}_2\text{O}_5\text{-Fe}_2\text{O}_3\text{-}(\text{MgO}, \text{MnO}, \text{Al}_2\text{O}_3, \dots)$  systems. Dephosphorization reaction in the steelmaking process and phosphorus equilibrium between liquid iron and molten slag have been extensively studied since the 1940's (Assis et al., 2015). On the basis of studies on the relationship between phosphorus distribution and slag composition as well as temperature, different phosphorus partition ( $L_p$ ) equations were obtained (Turkdogan and Pearson, 1953a; b; Healy, 1970; Gaskell, 1982; Mori, 1984; Suito and Inoue, 1984a; Bergman, 1988; Ogawa et al., 2001; Lee and Fruehan, 2005). Since the physicochemical effects of the

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solid-liquid coexisting phase in the slag have not been clarified yet, the slag was regarded as a homogeneous liquid phase to analyze the two-phase slag-metal equilibrium in those researches.

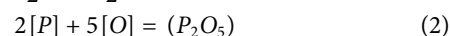
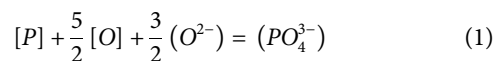
It is well known that tricalcium phosphate ( $3\text{CaO}\cdot\text{P}_2\text{O}_5$ ) is the main product of the dephosphorization reaction in the steelmaking process, as well as  $2\text{CaO}\cdot\text{SiO}_2$  is the main calcium silicate in the CaO-based steelmaking slag. According to the phase diagram of the CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> system, a solid solution can be easily formed by  $2\text{CaO}\cdot\text{SiO}_2$  (C<sub>2</sub>S) and  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  (C<sub>3</sub>P) in a wide composition range at the steelmaking temperature (Fix et al., 1969). Since a large phosphorus partition ratio between the C<sub>2</sub>S-C<sub>3</sub>P solid solution and the liquid slag has been observed (Ito et al., 1982), the importance of solid phase in the slag for dephosphorization has been taken a growing attention by Japanese researchers. The concept of multi-phase slag refining was firstly proposed by Japanese researchers, and the multi-phase slag was also called multi-phase flux or meso-phase slag (Inoue and Suito, 2006a; Hamano et al., 2006). The Iron and Steel Institute of Japan (ISIJ) organized a research group on the multi-phase slag refining for dephosphorization in the steelmaking process, which consisted of 11 university professors and 10 industry researchers. Researches on this subject were conducted from year 2005 to 2009, and the results were published in Tetsu-to-Hagané as a special issue on the “Innovative Development of Refining Processes in Steelmaking by Multi-Phase Fluxes” (Tsukihashi, 2009). A new reaction model for hot metal dephosphorization was proposed by Kitamura et al. (2009), taking into account the effects of C<sub>2</sub>S solid phase and lime dissolution, as well as the interactions of the solid and liquid phases in molten slag, in addition to the reaction between hot metal and liquid slag. Finally, the MPSR (Multi-Phase Slag Refining) model for simulation of hot metal dephosphorization process was developed, and applied to five steelmaking companies with good performance (Kitamura et al., 2014). Furthermore, the commercial thermodynamic software FactSage was also used for modelling of dephosphorization process in BOF converter (Jung et al., 2014; Khadhraoui et al., 2018).

The present review focuses on hot issues for the multi-phase slag refining, including the lime dissolution into the molten slag, the formation of  $2\text{CaO}\cdot\text{SiO}_2$  and  $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$  solid solution, and the distribution ratio of phosphorus between the solid and liquid phases in the slag, as well as the modeling of dephosphorization by multi-phase slag. Moreover, the necessity of some further researches is proposed by the authors.

## FUNDAMENTAL OF DEPHOSPHORIZATION IN THE STEELMAKING PROCESS

### Dephosphorization Reaction and the Thermodynamics

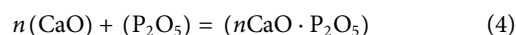
Phosphorus removal from liquid metal can be described by the ionic or molecular reactions, as shown in **Equations (1)** and **(2)**, respectively (Drain et al., 2017).



Known from the equations, the phosphorus removal is affected by [P] activity, oxygen potential [O] and basicity ( $\text{O}^{2-}$ ). And the temperature also has a significant effect on the reaction, as given in **Equation (3)** (Turkdogan, 2000a).

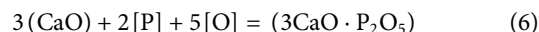
$$\Delta G^\theta = -832384 + 632.65T \quad \text{J/mol} \quad (3)$$

The incorporation of liquid phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) into the CaO and FeO containing steelmaking slags can be represented by **Equation (4)** or **Equation (5)**.



The enrichment possibility  $N_{ij}$  of five probable structural units containing  $\text{P}_2\text{O}_5$  as  $2\text{CaO} \cdot \text{P}_2\text{O}_5$ ,  $3\text{CaO} \cdot \text{P}_2\text{O}_5$ ,  $4\text{CaO} \cdot \text{P}_2\text{O}_5$ ,  $3\text{FeO} \cdot \text{P}_2\text{O}_5$ , and  $4\text{FeO} \cdot \text{P}_2\text{O}_5$  in CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> slags were calculated by (Li et al., 2014) using the developed IMCT- $N_i$  model. The results showed that  $\text{P}_2\text{O}_5$  can be bonded as  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  more easily than the others in the slags. This finding agrees with the experimental results reported by (Ito et al., 1982; Nozaki et al., 1983).

Consequently, the dephosphorization reaction in the steelmaking process can be described as **Equation (6)** by combining **Equation (2)** and **Equation (4)**, and the equilibrium constant for this reaction is given as **Equation (7)**.



$$K_P = \frac{a_{3\text{CaO}\cdot\text{P}_2\text{O}_5}}{[a_P]^2 [a_O]^5 (a_{\text{CaO}})^3} \quad (7)$$

In most cases, hot metal dephosphorization slag and BOF slag consist of CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>, and the industrial operations are carried out in the C<sub>2</sub>S saturated region (Pahlevani et al., 2010). A solid solution of C<sub>2</sub>S with C<sub>3</sub>P can be formed at steelmaking temperature over a wide composition range (Fix et al., 1969). Lv and Wang (Lv et al., 2017) considered that the dephosphorization process could be composed of two segments as “oxidation dephosphorization” and “solid phosphorus”. Though, the “oxidation dephosphorization” indicates the reaction between liquid metal and molten slag given by **Equation (6)** in traditional studies, and the “solid phosphorus” may indicate the formation of phosphorus-rich solid solution C<sub>2</sub>S-C<sub>3</sub>P in the multi-phase slag.

### Phosphorus Equilibrium Between Liquid Metal and Molten Slag

The limit of dephosphorization reaction is determined by the phosphorus equilibrium between liquid metal and molten slag, which can be expressed in several forms, such as equilibrium constants ( $K_P$ ), phosphate capacities ( $C_{\text{PO}_4^{3-}}$ ) or phosphorus partition ( $L_P$ ). Whereas, the phosphorus partition ( $L_P$ ) is the most widely used in previous studies, and it is defined in **Equation (8)**.

**TABLE 1** | Representative formulas for  $L_P$  calculation in CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-Fe<sub>2</sub>O<sub>3</sub>-X systems.

No.	$L_P$ calculation formula	Conditions	Refs
1	$\log L_P = \frac{2625}{T} - 7.787 + \frac{1}{2} \log(\%P_2O_5) + 2.5$	(X: MgO, MnO) 1,550–1,660°C	(Turkdogan and Pearson, 1953a; Turkdogan and Pearson, 1953b)
2	$\log L_P = \frac{22350}{T} - 16.0 + 0.08 \cdot (\%CaO) + 2.5 \cdot \log(\%T.Fe) \pm 0.04$	(X: MgO, MnO, Al <sub>2</sub> O <sub>3</sub> ) 1,580–1,669°C	(Healy, 1970)
3	$\ln L_P = \Lambda \left( -588.874 + \frac{2175100}{T} - \frac{1930041500}{T^2} \right) - 24.3 + 2.5 \ln[\%O] + 0.36$	(X: MgO <sub>sat</sub> ) 1,550–1,650°C	(Gaskell, 1982)
4	$\log L_P = \frac{11570}{T} - 10.52 + 0.072 \cdot \left[ \frac{(\%CaO) + 0.3(\%MgO) + 0.6(\%MnO) + 0.6(\%P_2O_5)}{0.6(\%MnO) + 0.6(\%P_2O_5)} \right] + 2.5 \cdot \log(\%T.Fe)$	(X: MgO <sub>sat</sub> , MnO) 1,550–1,650°C	(Suito and Inoue, 1984b)
5	$\log L_P = 17.55\Lambda + 5.72 - \frac{21680}{T} - 1.87 + \log[\%P] + 2.5 \log[\%O]$	(X: MgO, MnO) 1,550–1,660°C	(Mori, 1984)
6	$\log L_P = 21.55\Lambda + \frac{32912}{T} - 27.90 + 2.5 \log[\%O]$	(X: MgO <sub>sat</sub> ) 1,550–1,650°C	(Bergman, 1988)
7	$\log L_P = 0.0715 \times \left[ \left( \frac{\%CaO}{1 + \%SiO_2} \right) \left( 80 - \frac{71.85}{55.85} (\%T.Fe) \right) - 3.23 \right] + 2.5 \log(\%T.Fe)$	(X: MgO, MnO, Al <sub>2</sub> O <sub>3</sub> ) 1,350°C	(Ogawa et al., 2001)
8	$\log L_P = -12.24 + \frac{20000}{T} + 2.5 \log(\%Fe_2O_3) + 6.65 \log \frac{(\%CaO) + 0.8(\%MgO)}{(\%SiO_2) + (Al_2O_3) + 0.8(\%P_2O_5)}$	(X: MgO <sub>sat</sub> ) 1,550–1,580°C	(Lee and Fruehan, 2005)

$$L_P = \frac{(\%P)}{[\%P]} \quad (8)$$

Where, (%P) is the phosphorus content in molten slag, and [%P] is the phosphorus content in liquid metal.

Some representative formulas for  $L_P$  calculation in CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-Fe<sub>2</sub>O<sub>3</sub>-X(X: MgO, MnO, Al<sub>2</sub>O<sub>3</sub>, ...) systems are selected from literatures, as shown in **Table 1**.

As shown in **Table 1**, the influence of slag composition on  $L_P$  mainly represents in three forms, i.e., component concentration, basicity and theoretical optical basicity.

Turkdogan *et al.* (Turkdogan and Pearson, 1953a; Turkdogan and Pearson, 1953b) considered that the Fe<sub>2</sub>O<sub>3</sub> content in the slag has a decisive influence on the degree of steel dephosphorization, and the slag-metal reactions in steelmaking practices are far from the equilibrium states (Turkdogan, 2000b). The effect of Fe<sub>2</sub>O<sub>3</sub> on the phosphorus partition was taken into account for all of the  $L_P$  calculation formulas shown in **Table 1** in different forms. Since the CaO content has a notable effect on the activity of P<sub>2</sub>O<sub>5</sub> in the slag, it was introduced to correct the  $L_P$  calculation by (Healy, 1970). In addition, the effects of MgO and MnO content on the dephosphorization equilibrium were studied by Suito and Inoue (1984b). Besides, some other  $L_P$  calculation formulas were proposed using the optical basicity of the slag (Gaskell, 1982; Mori, 1984; Bergman, 1988). In the studies of Ogawa et al. (2001) and Lee and Fruehan (2005),  $L_P$  was calculated using the binary or multi-basicity of the slag. There are also some other  $L_P$  calculation formulas obtained in different researches (Suito and Inoue, 1995; Monaghan et al., 1998; Basu et al., 2007), but represented in the same three forms.

In the above studies, the slag was treated as a homogeneous single phase and tended to be in a state of thermodynamic equilibrium. However, since the actual slag is not a

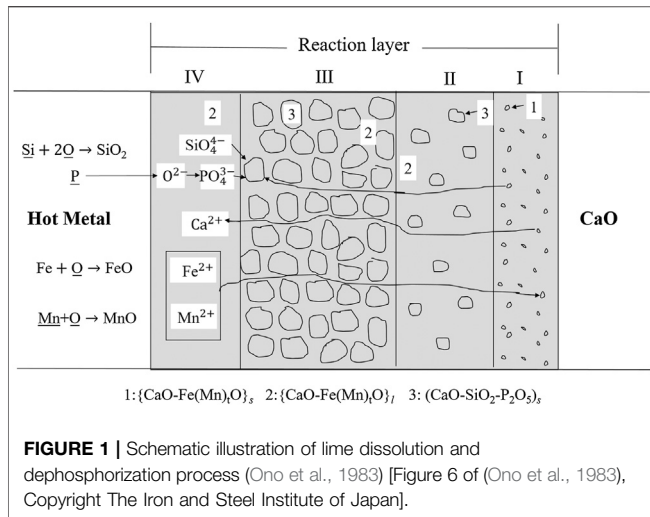
completely homogeneous liquid phase, and the industrial process is often difficult to reach the theoretical equilibrium. Therefore, it is obviously not enough to study the phosphorus equilibrium between liquid metal and molten slag. The thermodynamics and kinetics of the interactions between the solid and liquid phases in the multi-phase slag should also be considered.

## THERMODYNAMICS AND KINETICS IN MULTI-PHASE SLAG REFINING

The multi-phase slag refining was firstly proposed by Tsukihashi, and most of the relative researches were conducted by Japanese researchers, due to the popularization of hot metal pretreatment technology in Japan since the 1980s, the restricted use of fluorspar for environmental reasons (Ogawa and Maruoka, 2014; Sone et al., 2019). The researches mainly focus on the lime dissolution and the formation of phosphorus-condensed solid solution, as well as the phosphorus distribution between solid solution and liquid slag, and dephosphorization models including multi-phase slag interactions.

### Lime Dissolution and Formation of Phosphorus-rich Solid Solution

As well known, the melting temperature of CaO is over 2,500°C, which is an indispensable component for the high melting point phase in the steelmaking slag. The progress of slag-metal reactions in steelmaking process is largely influenced by the CaO content in the molten slag, and therefore by the dissolution rate of solid lime. Consequently, aiming to clarify the dissolution behavior of solid lime to the molten slag, laboratory experiments were conducted in the dynamic or static conditions.



When a lime particle dissolves into the CaO-SiO<sub>2</sub> or CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or CaO-SiO<sub>2</sub>-FeO melt, a layer of 2CaO·SiO<sub>2</sub> is confirmed to be formed on the periphery of lime particle, and the increasing temperature and the addition of CaF<sub>2</sub> or TiO<sub>2</sub> can accelerate the dissolution rate of CaO as well as that of the 2CaO·SiO<sub>2</sub> layer (Kimura et al., 1974; Amini et al., 2007; Deng and Du, 2012).

In another laboratory experiment of sintered CaO rod rotating in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or CaO-SiO<sub>2</sub>-FeO slag, the thickness of the C<sub>2</sub>S layer was obviously affected by the FeO content in the slag, and the dissolution rate of solid lime in FeO-containing slag was much greater than that in FeO-free slag (Matsushima et al., 1976; Matsushima et al., 1977; Yang et al., 2007). Meanwhile, the formation of Al<sub>2</sub>O<sub>3</sub> or FeO rich slag layer between solid lime and the C<sub>2</sub>S layer were also observed, due to the penetration of Al<sub>2</sub>O<sub>3</sub> and FeO into solid lime. But in these studies, the formation and dissolution of the C<sub>2</sub>S layer had not been paid enough attention, until it was found by (Yang et al., 2007) to have a significant inhibitory effect on the dissolution of lime, and the removal of the C<sub>2</sub>S layer by mechanical erosion was proved to be the main mechanism for the lime dissolution (Deng and Du, 2012). The residual stress caused by formation of C<sub>2</sub>S-C<sub>3</sub>P on the C<sub>2</sub>S surface was also considered to be one of the possible reasons for C<sub>2</sub>S peeling (Xie et al., 2016).

As reported by (Ono et al., 1983), in hot metal dephosphorization by simultaneous lime and oxygen injection, CaO starts to dissolve due to the penetration of Fe<sub>2</sub>O and Mn<sub>2</sub>O. Then, the phosphorus reacted with CaO-Fe(Mn)<sub>2</sub>O in the reaction layers, and finally fixed as CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> solid solution, the process is shown in **Figure 1**. This inference is consistent with the results of (Hamano et al., 2006), in which a CaO-FeO layer was observed nearby the solid CaO, as well as a reaction layer of solid CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> coexisting with liquid slag besides the CaO-FeO phase.

The reaction product of hot metal dephosphorization was proved to be 3CaO·P<sub>2</sub>O<sub>5</sub> in the laboratory scale experiments, which coagulated with other SiO<sub>2</sub>-bearing particles in the slag to form a solid solution phase (Nozaki et al., 1983). The phosphorus-rich solid solution phase is confirmed to consist mainly with 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub>, or sometimes the mixture

of 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub> and 3CaO·SiO<sub>2</sub>, according to the mineralogical analysis results of the slag (Sasaki et al., 2002; Gao et al., 2012). Thermodynamically stable CaO-FeO phase was confirmed by using the chemical equilibration method, which can enhance the phosphorus condensation from liquid slag to solid solution (Gao et al., 2012).

By analyzing the reaction interface of the solid CaO and the CaO-SiO<sub>2</sub>-FeO-P<sub>2</sub>O<sub>5</sub> slag at 1,573 and 1,673 K, the formation of the CaO-FeO layer and the P-rich solid solutions were determined (Hamano et al., 2006), and the reaction mechanism of solid CaO and the molten slag was clarified as follows (Saito et al., 2009).

- (1) The solid CaO dissolves into the molten slag and the solid phase of 2CaO·SiO<sub>2</sub> is formed in the melt, then a reaction zone with solid and liquid phases coexisting appears between the bulk slag and the solid CaO (**Figure 2A**).
- (2) With the continuous generation of 2CaO·SiO<sub>2</sub> in the melt, the concentration of CaO and SiO<sub>2</sub> decreases and FeO increases. Owing to the activity gradient of FeO, Fe<sup>2+</sup> diffuses from FeO rich zone to both solid CaO and bulk slag, and CaO-FeO layer is formed adjacent to solid CaO (**Figure 2B**).
- (3) Ca<sup>2+</sup> diffuses to the bulk slag through the CaO-FeO layer, owing to the activity gradient of Ca<sup>2+</sup>. By repeating this process, the CaO-FeO phase grows, and the dissolution of CaO proceeds (**Figure 2C**).
- (4) The P<sub>2</sub>O<sub>5</sub> in the liquid phase reacts quickly with the 2CaO·SiO<sub>2</sub>, and the phosphorus rich phase of 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub> solid solution is formed (**Figure 2D**).
- (5) With the P<sub>2</sub>O<sub>5</sub> diffusing from the molten slag to the reaction interface and reaction with 2CaO·SiO<sub>2</sub> continuously, the phosphorus is further condensed as 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub> solid solution with high P<sub>2</sub>O<sub>5</sub> content (**Figure 2E**).

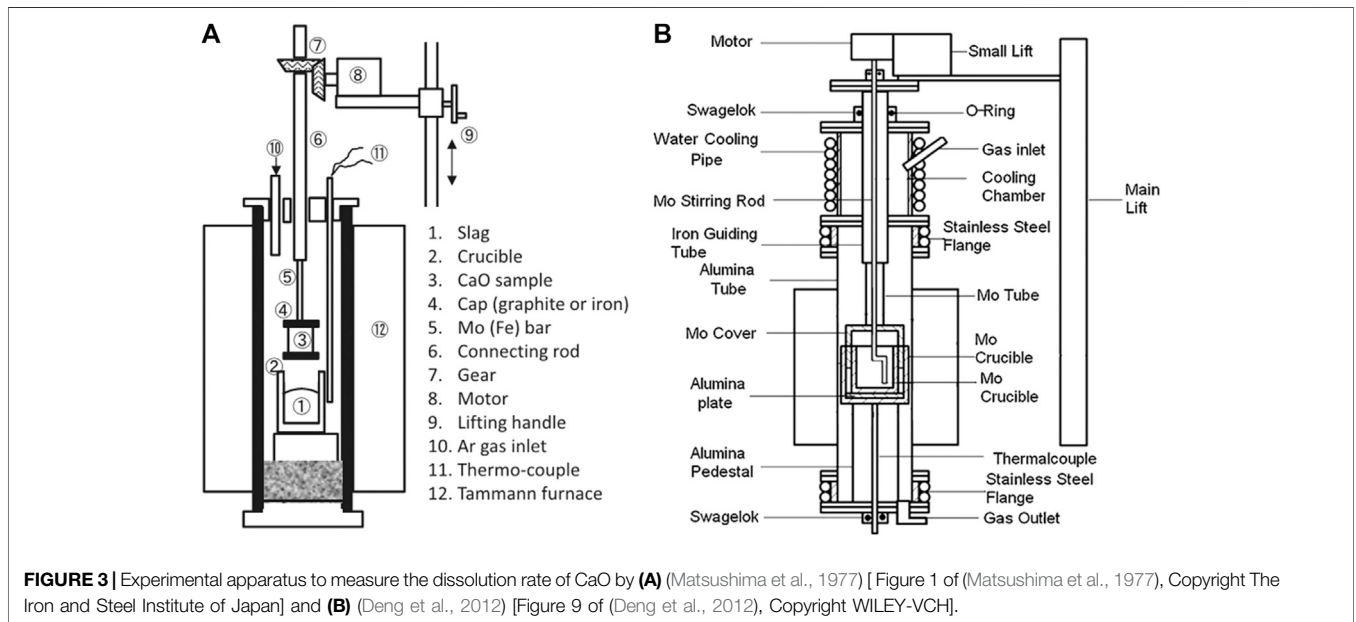
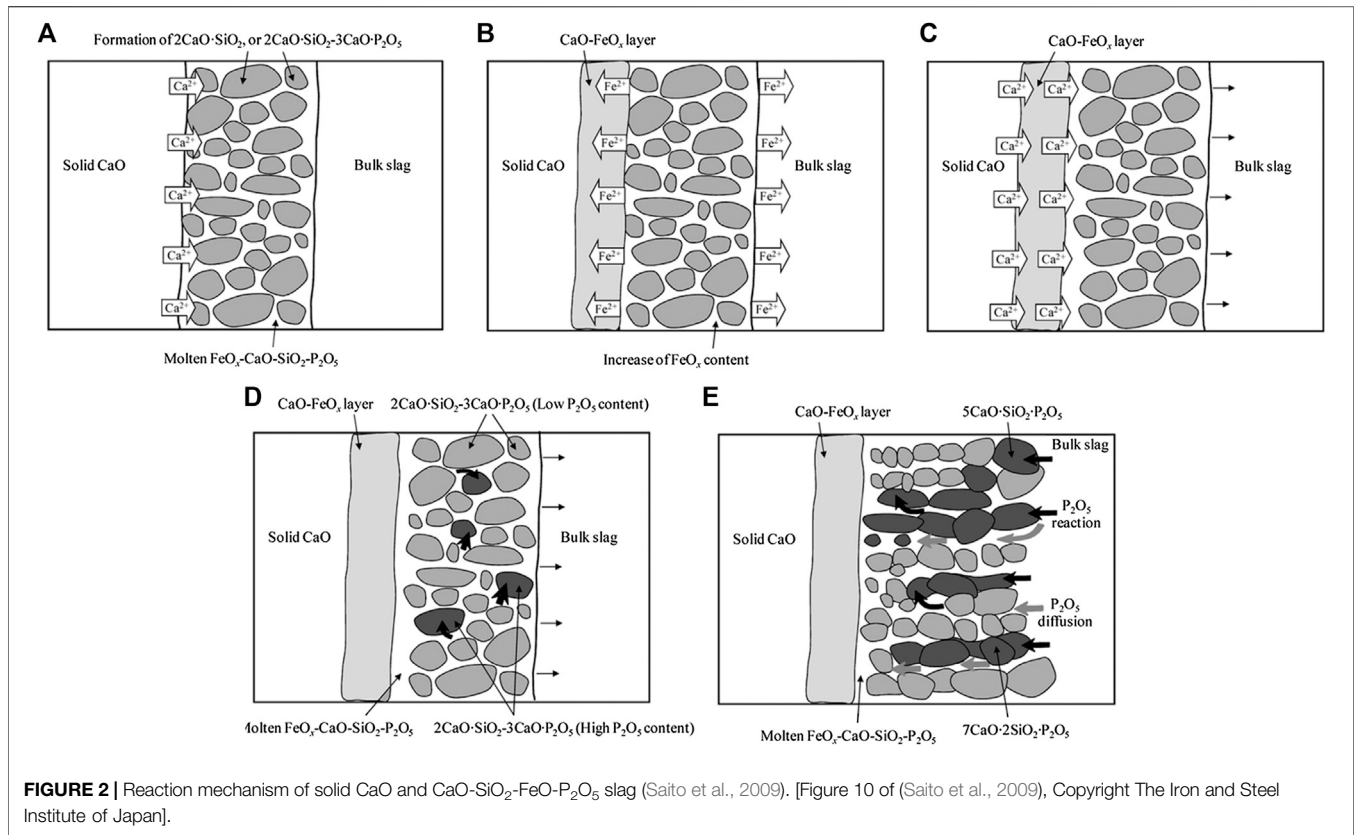
Because the transfer rate of phosphorus from molten slag to a 2CaO·SiO<sub>2</sub> particle is significantly fast, the particle changes into C<sub>2</sub>S-C<sub>3</sub>P solid solution in less than 5 s (Inoue and Suito, 2006b). Thus, the formations of C<sub>2</sub>S and C<sub>2</sub>S-C<sub>3</sub>P solid solution can be considered to be simultaneously, as shown in **Figure 2**.

In order to obtain the dissolution rate of CaO into molten slags (Matsushima et al., 1976; Matsushima et al., 1977), measured the diameter of sintered CaO rod in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and CaO-SiO<sub>2</sub>-FeO slags using a rotating rod test (**Figure 3A**). Assuming the mass transfer in the slag is the rate-determining step, the dissolution rate can be obtained by **Equation (9)**.

$$\frac{dr}{dt} = \frac{k}{100\rho_{\text{Lime}}} \{ (\% \text{CaO})_i \rho_i - (\% \text{CaO})_b \rho_b \} \cong \frac{k\rho_b}{100\rho_{\text{Lime}}} \Delta(\% \text{CaO}) \quad (9)$$

Where,  $k$  is the mass transfer coefficient of CaO in the slag (m/s),  $(\% \text{CaO})_i$  and  $(\% \text{CaO})_b$  are the content of CaO in the interface and in bulk slag, respectively.  $\rho_{\text{Lime}}$  is the density of lime (kg/m<sup>3</sup>),  $\Delta(\% \text{CaO})$  is the difference between the actual CaO content and the CaO solubility in the slag. As represented in **Equation (10)**, a dimensionless J-factor was proposed to represent the mass



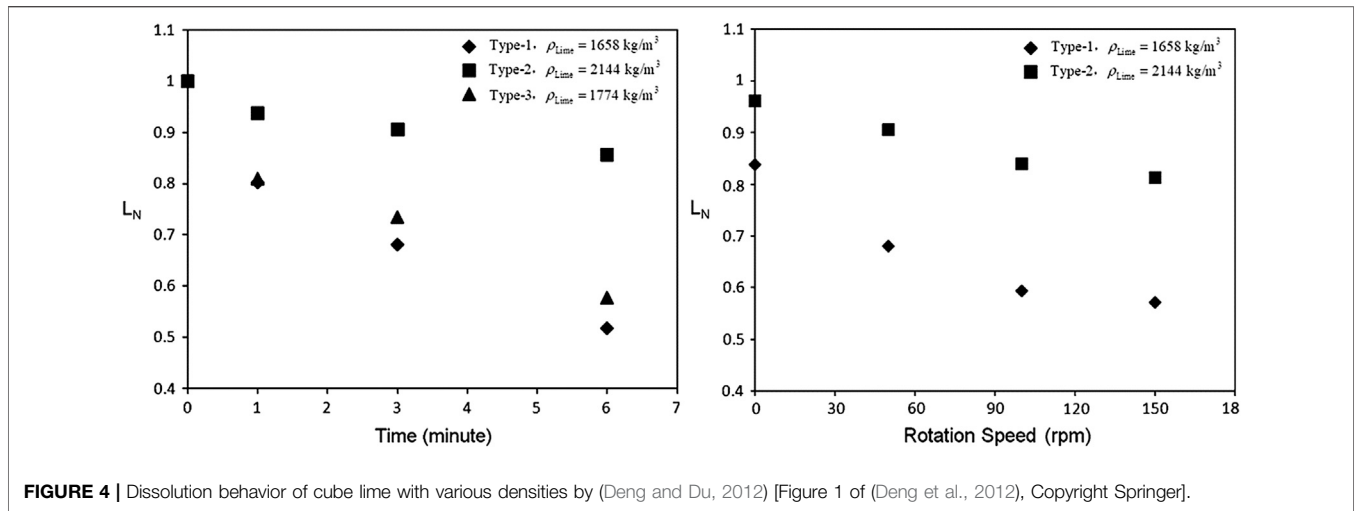


transfer rate under the convection flow, using the Stanton number ( $St = k/u$ ), Reynolds number ( $Re = d \cdot u/\nu$ ), and Schmidt number ( $Sc = \nu/D$ ).

$$J = St \times Sc^{2/3} = 0.384 \times Re^{-0.31} \quad (10)$$

Where,  $u$  and  $\nu$  are the relative velocity (m/s) and kinematic viscosity ( $\text{m}^2/\text{s}$ ), respectively.  $d$  is the diameter of the rod (m), and  $D$  is the diffusion coefficient of CaO in the slag ( $\text{m}^2/\text{s}$ ).

The dissolution rates of solid CaO in  $\text{CaO}\cdot\text{SiO}_2\cdot\text{Fe}_i\text{O}$  slags at hot-metal temperatures with different additives of X (X:  $\text{CaF}_2$ ,



**FIGURE 4** | Dissolution behavior of cube lime with various densities by (Deng and Du, 2012) [Figure 1 of (Deng et al., 2012), Copyright Springer].

CaCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>) were studied by using the same method (Hamano et al., 2004). It was considered to be well controlled by the mass transfer in the bulk slag, and increases with Fe<sub>2</sub>O concentration and decreases with basicity of the slag. Since the enhancement factors of each additives were obtained by laboratory experiments, the comprehensive dissolution rate of CaO to CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O-X slag can be expressed by **Equation (11)**. The comparison on the effect of different of additives on raising the dissolution rate was CaF<sub>2</sub> > CaCl<sub>2</sub> > B<sub>2</sub>O<sub>3</sub> > Al<sub>2</sub>O<sub>3</sub>.

$$\left(\frac{dr}{dt}\right)' = \frac{dr}{dt} \times \left\{ 1.0 + \sum E_{dis}^X \cdot (\text{mass}\%X) \right\} \quad (11)$$

Where,  $\frac{dr}{dt}$  is the dissolution rate of CaO into CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O melt without any additives, and  $E_{dis}^X$  is the enhancement factor of additive X (X: CaF<sub>2</sub>, CaCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>), which was defined in the study of (Hamano et al., 2004).

On the other hand, Du. Sichen and his group (Deng and Du, 2012; Deng et al., 2012) proposed a different method, with the experimental facility as shown in **Figure 3B**. In this method, the molten slag was stirred instead of rotating the solid CaO, and a lime cube was used instead of sintered CaO rod. The forced convection around the lime cube was considered to be much greater, and about half of the lime could be dissolved within 6 min, that was more consistent with the industrial operation. The dissolution rate of the CaO cube was represented by **Equation (12)**.

$$L_N = \frac{(L_1 + L_2)}{(L_1 + L_2)_{initial}} \quad (12)$$

Where,  $(L_1 + L_2)_{initial}$  is the sum of the initial length and width of the cube, and indicates that after the experiment. It was found that density and rotation speed have a significant effect on the dissolution rate, as shown in **Figure 4**. It was deduced that the exfoliation of the C<sub>2</sub>S layer has decisive influence to the lime dissolution.

The dissolution rates of various limes including the industrial quick lime were measured by (Maruoka et al., 2013) in the molten slag stirred by gas bubbling. In this study, it increased with the gas flowrate, but was not strongly influenced by the density of lime,

when the C<sub>2</sub>S layer formed and covered the lime surface. It is considered to be the most realistic method to simulate the actual situation in steelmaking process (Kitamura, 2017).

Consequently, the lime dissolution can be expressed by **Equation (13)** in gas stirring situation (Maruoka et al., 2013) or by **Equation (14)** in rod rotation situation (Matsushima et al., 1977; Umakoshi et al., 1984)

$$\frac{dr}{dt} = a \times Q^b \quad (13)$$

$$\frac{dr}{dt} = c \times U^d \quad (14)$$

Where,  $\frac{dr}{dt}$  indicates the change in radius of lime particle (rod) with time,  $a$  and  $b$  and  $c$  and  $d$  are all constants, the gas flowrate  $Q$  and the relative linear velocity of rotating rod  $U$  are used as stirring parameter in different forms.

Based on the above studies, the dissolution rate of lime and the mass content of CaO in molten slag can be obtained, as well as the remained mass of undissolved solid CaO. Then, the extent of dephosphorization can be concluded, by considering the phosphorus equilibrium between the metal and the slag with known compositions.

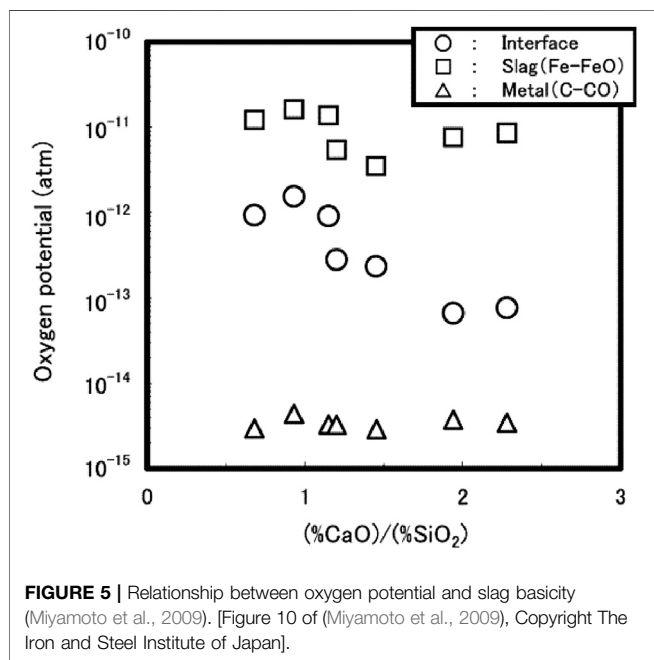
### Distribution of Phosphorus in Multi-phase Slag

Although the dephosphorization reaction have been widely studied, it is still an ongoing topic due to the continuous desire of higher efficiency for dephosphorization and lime utilization in steelmaking process.

The dephosphorization reaction in a solid and liquid coexistence slag is greatly influenced by the solid phase that precipitates in the slag. The higher efficiency of dephosphorization can be observed in the C<sub>2</sub>S crystallizing range, owing to the concentration of phosphorus in the solid phase (Sasaki et al., 2002). It was revealed that P<sub>2</sub>O<sub>5</sub> can be condensed easily in the solid solution

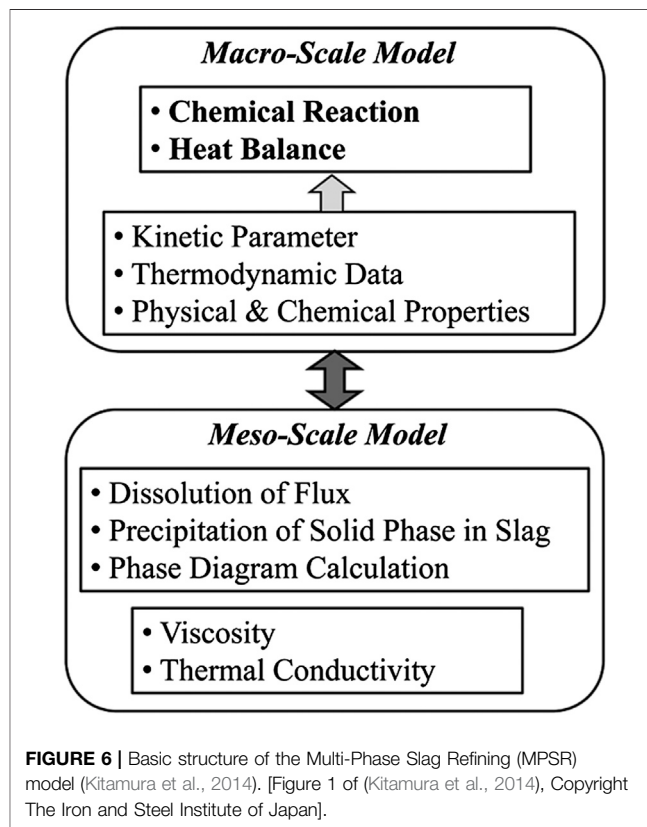
**TABLE 2** | Studies on the distribution ratio of  $P_2O_5$  between solid solution and liquid phase in multi-phase slag

Slag system	Temperature range °C	Basicity range	$L'_p$	Refs
CaO-SiO <sub>2</sub> -FeO-P <sub>2</sub> O <sub>5</sub> -Na <sub>2</sub> O	1,350	1.3–1.9	6.14–12.5	(Du et al., 2019)
CaO-SiO <sub>2</sub> -FeO-P <sub>2</sub> O <sub>5</sub> -Al <sub>2</sub> O <sub>3</sub>	1,400	1.4–12.0	3.58–106.5	(Gao et al., 2013)
CaO-SiO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -(MgO/MnO/Al <sub>2</sub> O <sub>3</sub> )	1,300/1,400	1.27–2.79	2.21–14.7	(Pahlevani et al., 2010)
CaO-SiO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -(MgO/MnO)	1,400	1.52–2.79	2–21.8	(Shimauchi et al., 2009)
CaO-SiO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -(MgO)	1,300–1,560	1.03–11.55	1.4–83	(Inoue and Suito, 2006b)
CaO-SiO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -(CaF <sub>2</sub> )	1,350–1,450	1.2–4.8	2–100	(Ito et al., 1982)



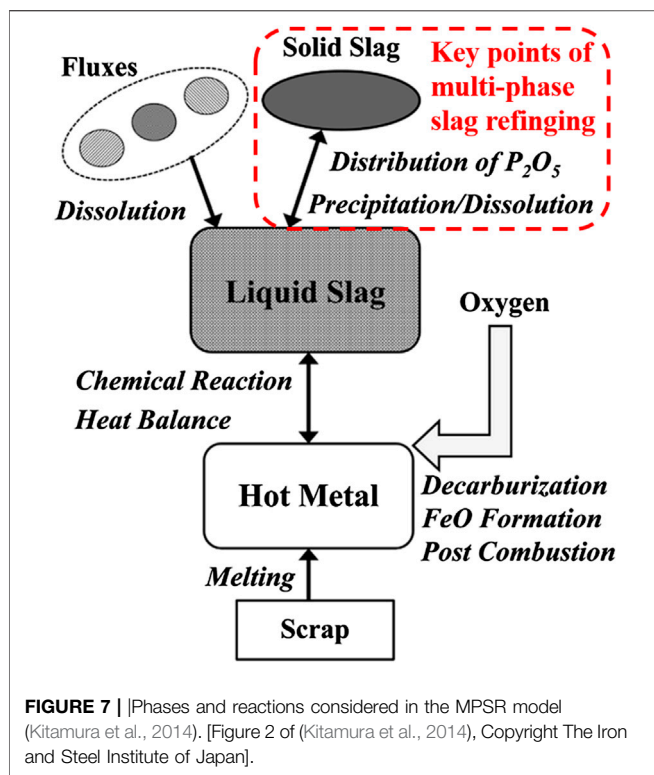
with a high distribution ratio, which was up to tens or even higher than one hundred, as shown in **Table 2**.

In the study of (Ito et al., 1982), about 80% of the phosphorus transported from the molten slags to the precipitated solid  $C_2S$ , when the molten slag was cool down to the liquidus temperature and showed a state of liquid and solid coexisting. The equilibrium distribution ratio ( $L'_p$ ) of phosphorus between the solid solution and the liquid phase in the slag was proposed, which increased with the increment of the total Fe content, but irrelevant to the valency of Fe. In addition, no dependence of  $L'_p$  on temperature and basicity was observed (Inoue and Suito, 2006b). studied the phosphorous transfer to a  $C_2S$  particle which dispersed in CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-(MgO) slags, the isolated  $C_2S$  particles with diameters of 20 to 50  $\mu m$  completely changed to the particles of uniform  $C_2S$ - $C_3P$  solid solution within 5 s. The maximum  $L'_p$  appears at the tip of  $C_2S$  primary precipitation area in CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> phase diagram. A linear relationship was observed between the  $L'_p$  and total Fe content, but independent of the basicity and  $P_2O_5$  content, and no significant influence by the addition of MgO and MnO (Shimauchi et al., 2009). The ruling factors were clarified to be the CaO content in the liquid slag and the activity of  $P_2O_5$  in the solid solution, which was evidently affected by the total solved oxide and especially the  $P_2O_5$  content (Pahlevani



et al., 2010). The addition of  $Al_2O_3$  could enlarge the liquid phase area, but has no effect on the composition of the solid solution, because it mostly exists in the liquid phase (Gao et al., 2013). On the other hand,  $Na_2O$  was observed to facilitate the enrichment of  $P_2O_5$  in the solid solution, due to its positive effect on improving both the  $L'_p$  and the mass percentage of the solid solution in the molten slag (Du et al., 2019), while  $B_2O_3$  has the opposite effect (Xie et al., 2014). Moreover, the phosphorus-enrichment contribution ratio of  $C_2S$  solid solution ( $R_{C_2S}$ ) was confirmed by an IMCT calculation approach, while increases exponentially with the increase of basicity, and shows an asymmetric parabolic trend with the FeO increment (Xie et al., 2018).

Since the mechanisms of lime dissolution and the phosphorus enrichment in the multi-phase slag have been clarified, prediction of the phosphorus content in steel by establishing a more accurate dephosphorization model could be expected, considering the reactions of multi-phase slag refining.



## Modeling for Dephosphorization Considering the Multi-phase Slag

The dephosphorization reaction occurs under non-equilibrium conditions, due to the large difference in oxygen potentials between the metal and the slag phases, and the oxygen potential at the metal-slag interface has crucial influence on the reaction rate (Kitamura, 2014). The oxygen potentials of the two phases and their interface were calculated using a computational thermodynamics method (Miyamoto et al., 2009), as shown in **Figure 5**.

Therefore, the dephosphorization model should be established based on reaction kinetics as well as thermodynamic data. A representative model is the competitive reaction model, which was proposed by (Ohguchi et al., 1984). Based on this competitive reaction model, a computer program with the name of MACSIM was developed for the simulation of hot metal dephosphorization process in industrial scale (Kitamura et al., 1991). However, since the slag is treated as a homogeneous liquid phase in the conventional models, there is a limit for its application to the multi-phase slag refining. Since more researches on multi-phase slag refining for dephosphorization were conducted, some advanced dephosphorization models that taken into account the solid phase in the slag were proposed. In 2008, a model considering the effect of solid phase in slag and the dissolution of lime has been presented (Kitamura et al., 2008). Then, a complete computer program of Multi-Phase Slag Refining (MPSR) model with a user interface and generalized parameters was developed (Kitamura et al., 2014). The basic

structure of the MPSR model is shown in **Figure 6**. The model employed a multi-scale model, including macro-scale model and meso-scale model. All the phases and reactions considered in the MPSR model are shown in **Figure 7**.

The MPSR model involves the followings:

- (1) Chemical reactions between the liquid slag and the hot metal.
- (2) Flux dissolution and scrap melting.
- (3) Fraction of the solid phase and distribution of phosphorus in the multi-phase slag.
- (4) Direct decarburization, FeO formation, and post combustion.
- (5) Heat balance calculation.

Based on the MPSR model, a computer program was developed with a user interface and parameter setting window, as shown in **Figure 8**. This program has been applied to Sumitomo Metals, Nippon Steel, Kobe Steel and JFE, it is easy to use and enables the user to apply it to industrial on-line control as well as process simulation.

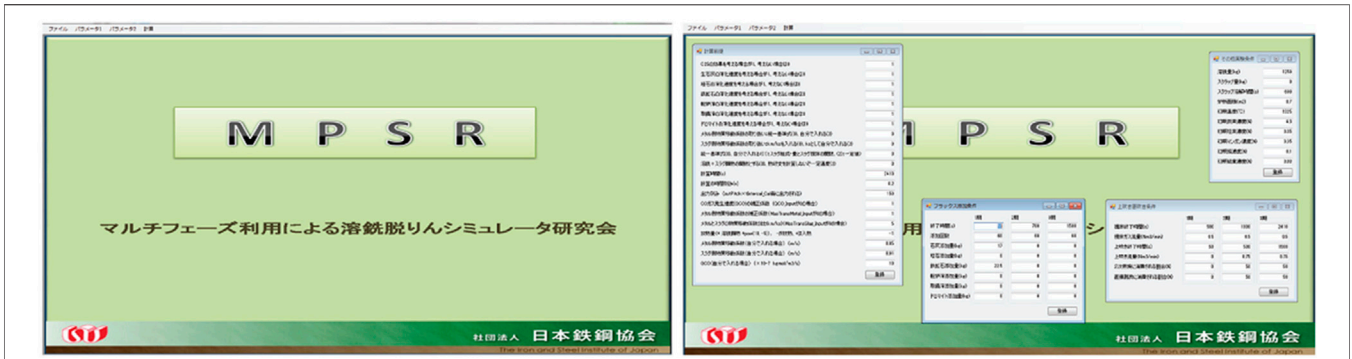
The program has been applied to laboratory furnaces and industrial top-bottom blown converter with some generalized thermodynamic parameters and specialized kinetic parameters in different operational conditions, and its availability was validated since the simulation results agreed well with the operational results, as shown in **Figure 9** (Kitamura et al., 2014).

Since the MPSR model is only applicable for the hot metal pretreatment process and the early stage of BOF process, limited in the cases of low temperature and low basicity, another reaction model was developed for simulation of the entire BOF process based on the Effective Equilibrium Reaction Zone Model by using FactSage software (Jung et al., 2014; Van Ende and Jung, 2018). In this model, the BOF process was divided into several reaction zones, in which kinetics were taken into account by varying the effective volumes of these reaction zones, and a thermodynamic database for  $P_2O_5$ -containing slag was used to calculate the equilibrium of phases and chemical reactions. The calculation results of this model are shown in **Figure 10**, with input conditions taken from a 200-ton industrial converter reported by (Cicutti et al., 2002). The amount of  $C_2S$ - $C_3P$  solid solution phase and other phases in the multi-phase slag were calculated, as well as the compositions of the liquid slag and the metal bath.

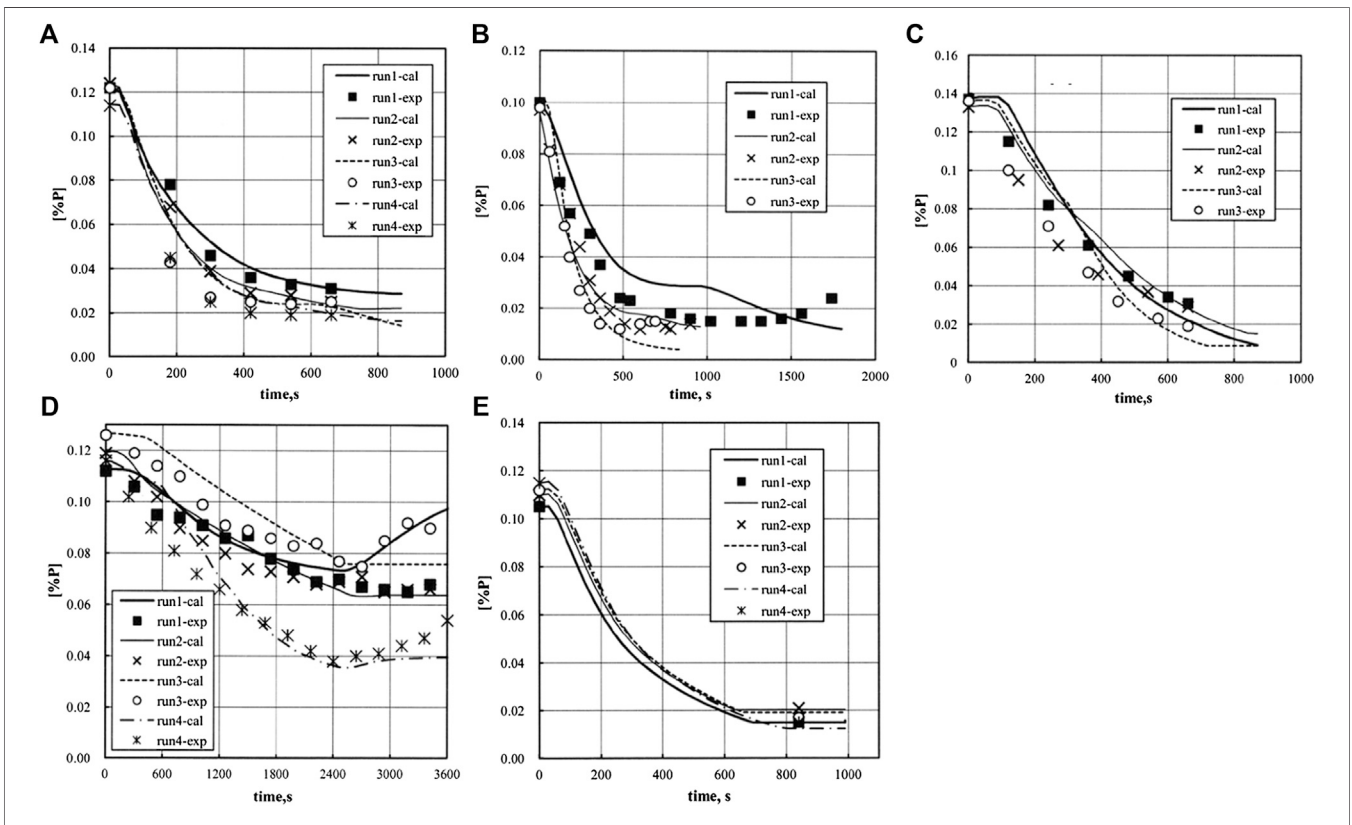
On the other hand, the researchers from SMS group and GTT company (Khadhraoui et al., 2018; Khadhraoui et al., 2019) proposed a new approach to establish a dephosphorization model, by coupling a new thermodynamic database developed for industrial steelmaking slag to FactSage for the phase equilibrium calculation, and the phosphorus distribution ( $L_p$ ) between the  $C_2S$ - $C_3P$  solid solution and the liquid slag was regressed based on the experimental data of (Ito and Sano, 1983; Suito and Inoue, 2006; Suito and Inoue, 1984b) and then introduced to the total  $L_p$  equation. Kinetics of the dephosphorization reaction which only occurs at the metal-slag interface were represented by a 2-zone reaction model.

The simulation results of both MPSR model and Jung model seem to be in good agreement with industrial experiments, but





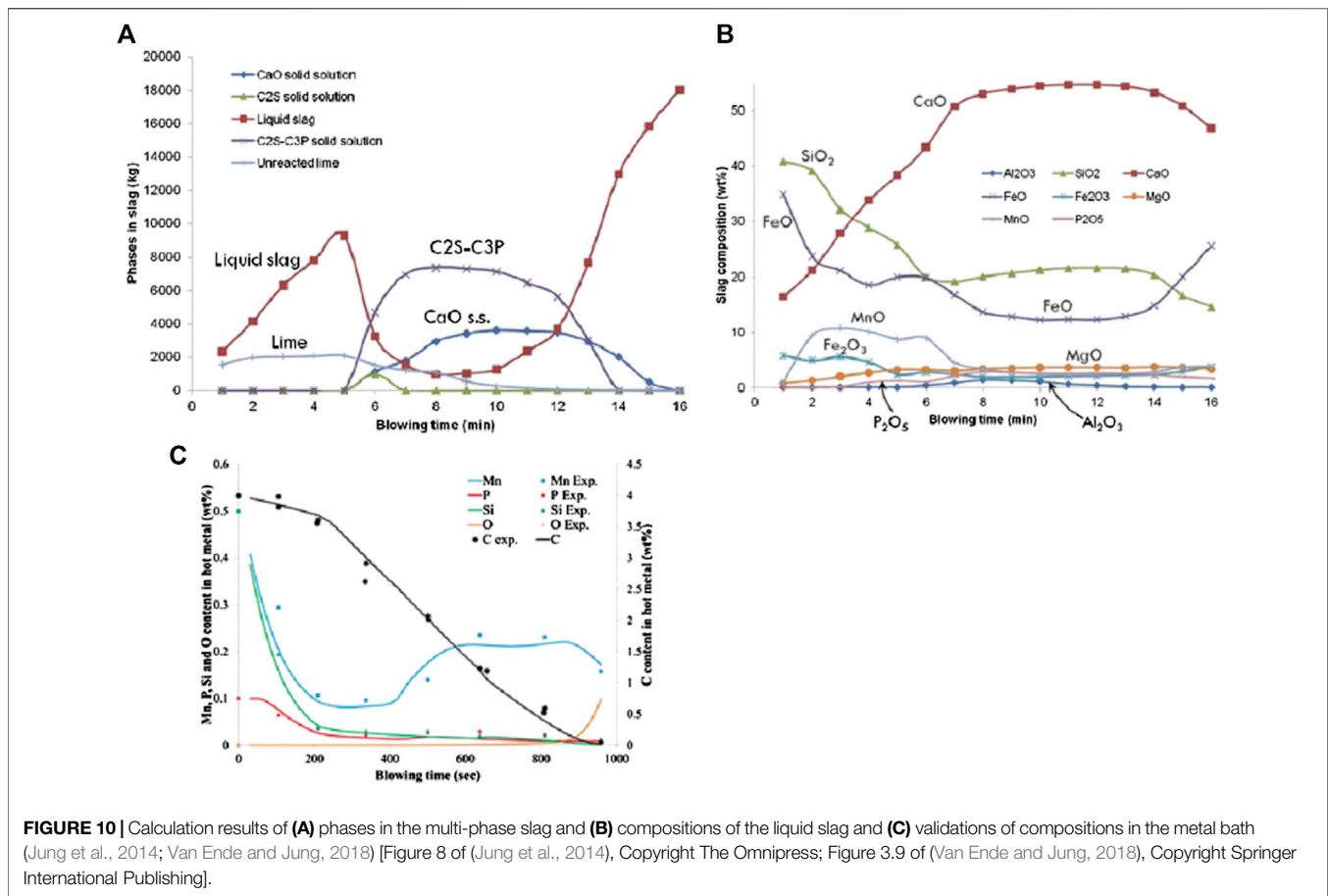
**FIGURE 8** | User interface and parameter setting window of the MPSR model (Kitamura et al., 2014) [Figures 4 and 5 of (Kitamura et al., 2014), Copyright The Iron and Steel Institute of Japan].



**FIGURE 9** | Simulation results of the MPSR model for (A) laboratory furnace with FeO feeding all at once and bottom stirring but no oxygen blown; (B) laboratory furnace with FeO feeding all at once, bottom stirring and oxygen top blown; (C) laboratory furnace with bottom stirring and oxygen top blown, but no FeO addition; (D) laboratory furnace with FeO feeding in batches, bottom stirring and oxygen top blown; (E) Industrial converter with FeO feeding all at once, bottom stirring and oxygen top blown (Kitamura et al., 2014) [Figures 7 to 11 of (Kitamura et al., 2014), Copyright The Iron and Steel Institute of Japan].

there is still a potential for improvement in accuracy, while the validation of the SMS model was not mentioned in the literature. For all of these dephosphorization models with consideration of multi-phase slag refining, the influence of solid phases, especially the  $C_2S-C_3P$  solid solution, from both thermodynamic and kinetic perspectives, has been considered. Gibbs free energy calculations were conducted for phase equilibrium and

chemical reactions in these models with generalized thermodynamic parameters, but it is not easy to determine the specialized kinetic parameters in different operational conditions, so different kinetic methods were introduced to the three models. Besides, there are some common limitations for the existing models, due to the lack of thermodynamic and kinetic details of multi-phase slag reactions in the final stage of BOF process.



## DISCUSSION

Before the concept of Multi-phase Refining being proposed, the dephosphorization slag was usually perceived as a homogeneous liquid phase in steelmaking process, including hot metal pretreatment and converter steelmaking. A lot of laboratory or industrial experiments have been conducted to clarify the mechanism of phosphorus removal from liquid metal to molten slag, in which the temperature and the composition of the slag are significantly related to the phosphorus distribution ratio. According to the principle of metallurgical thermodynamics, the temperature has an obvious effect on the equilibrium constant  $k$  in the dephosphorization reaction between the slag and hot metal, and the contents of each oxide in the slag has influence on the oxygen potential and the activity of components in the slag, thereby further affecting the distribution of phosphorus between the slag and hot metal. Although the solid-liquid coexistence state of actual steelmaking slag and its influence on dephosphorization were neglected in previous studies, most conclusions of the above studies are not inconsistent with studies on multiphase slag refining, but can be elaborated from different perspectives.

With a restricted use of fluorite resources and a large-scale application of hot metal pretreatment technology, the

coexistence of solid and liquid phases in the slag and the effect on the dephosphorization have been paid more attention. On the one hand, efforts were made to improve the “oxidation dephosphorization” of **Equation (6)** by increasing the activity of CaO in the liquid slag, which mainly includes two strategies, i.e., looking for some alternatives similar to CaF<sub>2</sub> (such as TiO<sub>2</sub>, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, etc.) or exploring some other methods used to accelerate lime dissolution (such as strengthening stirring, increasing FeO content, etc.). On the other hand, as an important part in the multiphase slag refining, the enrichment of “solid phosphorus” tends to be promoted by controlling the composition and temperature of the slag in an optimal range, thereby increasing the precipitation of the phosphorus-rich solid solution phase and the distribution ratio of phosphorus between the solid solution and the liquid slag. From the perspective of traditional research, increasing FeO content can facilitate the dephosphorization by promoting the dephosphorization reaction (**Equation 6**) which occurs at the slag-metal interface; and from the perspective of multiphase slag refining, it can be explained that the formation of CaO-FeO phase promotes the transfer of P<sub>2</sub>O<sub>5</sub> from the liquid slag to the solid phase, thereby forming more P-rich solid solution and increasing the solid-liquid phosphorus distribution ratio ( $L'_p$ ) in the slag.

The dissolution behavior of lime into the molten slag has always been the focus of research, which needs to be studied from both the thermodynamics and kinetics perspectives. The existence of the  $C_2S$  layer and its crucial role on lime dissolution is undoubted, but there are still different views on the decisive step. In the study on lime dissolution mechanism, the mass transfer from bulk slag to slag- $C_2S$  interface or the mechanical peeling of the  $C_2S$  layer on the lime surface were regarded as the determining step, respectively (Matsushima et al., 1976; Matsushima et al., 1977; Yang et al., 2007; Deng and Du, 2012). In fact, based on the previous studies, the decomposition of the  $C_2S$  layer should be treated as a comprehensive consequence of chemical reaction and mechanical erosion. Since the reactant oxides (such as  $SiO_2$ ,  $FeO$  and  $MnO$ , etc.) transfer from the bulk slag to the interface of the dense  $C_2S$  layer and the bulk slag, chemical reactions occur at the interface which is subsequently transformed into a low melting point phase. At the same time, some special oxides (such as  $FeO$  and  $MnO$ , etc.) penetrate the reaction interface and enter into the inside of dense  $C_2S$  layer or even the solid  $CaO$  layer, making the dense  $C_2S$  layer loose. Following this, the loose  $C_2S$  phase is broken and peeled off by gas stirring or other mechanical scouring, thereby promoting the dissolution of lime.

In traditional researches, the equilibrium constant  $k$  of the dephosphorization reaction (between hot metal and liquid slag) is generally obtained through thermodynamic experiments, then the phosphorus distribution ratio between the slag and hot metal can be calculated. In addition, the empirical formula of the phosphorus distribution ratio ( $L_p$ ) can be solved by a regression method using industrial experimental data. However, in multiphase slag refining, the interactions of the hot metal phase - liquid slag phase - solid solution phase and the distribution ratio of phosphorus between these three phases are considered in more details as shown in **Figure 7**. As two key points of multi-phase slag refining, the precipitation and dissolution of solid phases could be clarified by phase diagram calculation, and the distribution of  $P_2O_5$  between the solid solution and liquid slag ( $L'_p$ ) could be obtained by experimentals.

Since hot metal dephosphorization pretreatment process and dual slag BOF process have been fully applied in Japan (Ogawa and Maruoka, 2014; Kitamura et al., 2018; Sone et al., 2019), most of the researches on multi-phase slag have been carried out aiming at the process conditions of low temperature and low basicity in the hot metal pretreatment or the early stage of BOF process. In such cases, the temperature of the dephosphorization slag is usually below  $1,450^\circ C$ , and the basicity is less than 2.0. Moreover, due to a high carbon content in the hot metal, the  $FeO$  content in the slag is significantly lower than that in the final stage of BOF process with low carbon concentration. As shown in **Table 2**, many experimental studies have been conducted on the phase equilibrium and phosphorus distribution in the multi-phase slag at the temperature below  $1,560^\circ C$ . However, there is a lack of thermodynamic equilibrium data at the temperatures above  $1,600^\circ C$ , as well as the kinetic data for dissolution rate of solid solution.

Although a few literatures reported the studies on the dissolution of  $C_2S$  and  $C_2S-C_3P$  solid solution in molten slag at  $1,300-1,400^\circ C$  (Yang et al., 2010; Kobayashi and Sadamoto, 2017), but their dissolution behaviors in the final stage of BOF process with a high temperature and high basicity condition have rarely studied. For the BOF process, the endpoint temperature of molten steel and slag reaches up to  $1,600-1700^\circ C$ , and the basicity of the slag is higher than 3.0, meanwhile the  $FeO$  content is extremely high due to low carbon content in the metal bath. Although the statistical relation between the phosphorus distribution ratio and its influential factors has been studied in the final stage conditions of BOF (Wang et al., 2014), but the dephosphorization mechanism in the final stage has not been clarified yet. The dissolution of the solid solution phase and the redistribution of P in the final slag should not be neglected (Lv et al., 2017), because the phosphorus-enrichment contribution ratio of  $C_2S$  solid solution is strongly affected by the basicity and  $FeO$  content (Xie et al., 2018). Meanwhile, the liquid-solid coexisting state of the molten slag would change significantly in the final stage of BOF process. Especially for the BOF process using the single slag method, the influence is very large, because the dephosphorization slags produced in the early stage are in large amount and left in the furnace to the end of the process. Therefore, a further study should be performed to clarify the dissolution mechanism of the phosphorus-rich phase solid solution in the slag and the redistribution of phosphorus in the solid and liquid phases, which is beneficial to develop a more applicable dynamic model for the phosphorus prediction of the entire BOF process, considering the multi-phase slag reactions in the final stage conditions. For modelling the entire dephosphorization process, it is necessary to consider the influence of solid phases in the multi-phase slag from both thermodynamic and kinetic perspectives, and more details still need to be further clarified through laboratory experiments. Furthermore, the modelling work is beneficial for the fine control of the BOF process and the development of intelligent manufacturing in steelmaking industry.

## CONCLUSIONS

Molten slag in steelmaking process is usually regarded as a homogeneous liquid phase in traditional researches, which focus on increasing the slagging rate of the flux by adding co-solvents (such as  $CaF_2$ ,  $Na_2O$  . . .) or improving the  $FeO$  content, so as to promote the balance of dephosphorization between liquid slag and hot metal. On the other hand, the main concerns for multi-phase slag refining are the physical and chemical properties of solid-liquid coexisting phases, and the formation and dissolution behaviors of phosphorus-rich phase solid solution, as well as the phosphorus distribution ratio between solid and liquid phases in the slag. Thus, dephosphorization reaction models established in terms of above studies can show great

advantage over the previous ones. The main conclusions are shown as follows:

Since the molten slag in actual steelmaking process shows a coexisting state of both liquid and solid phases, the concept of multi-phase slag refining has been proposed and proved to be an effective way to improve the utilization of solid lime flux and the efficiency of dephosphorization in steelmaking practices. Multi-phase slag refining is not in opposition to the traditional researches, but gives more details about the reactions between the liquid slag and solid phases, and the importance of solid phases on dephosphorization is clarified.

The  $2\text{CaO}\cdot\text{SiO}_2$  layer on the surface of the lime particles plays a crucial role on lime dissolution. The decomposition of the  $\text{C}_2\text{S}$  layer is considered as the limiting factor for the dissolution of lime in the molten slag, including a comprehensive effect of chemical reaction and mechanical peeling; the dissolution rate of lime can be improved by adding co-solvents or strengthening stirring.

Owing to the lime dissolution and increasing of temperature and FeO content in the molten slag, the solid-liquid coexisting state of the slag will change significantly. Further researches should be conducted on the dissolution of the phosphorus-rich phase solid solution ( $2\text{CaO}\cdot\text{SiO}_2\cdot 3\text{CaO}\cdot\text{P}_2\text{O}_5$ ) in the final stage of BOF process with high temperature, high FeO content and high basicity, as well as the redistribution of phosphorus between the solid and liquid phases in the final slag.

For modelling of the dephosphorization process, it is necessary to consider the influence of solid phases in the multi-phase slag from both thermodynamic and kinetic perspectives. Some

simulation models have been developed and the results agreed well with the industrial experiments, but there is still a potential for improvement in accuracy. However, it is still necessary to develop a more applicable dynamic dephosphorization simulation model for the entire BOF process, containing more thermodynamic and kinetic details of the multi-phase slag reactions in the final stage conditions.

## AUTHOR CONTRIBUTIONS

All authors contributed to the analysis and writing of the manuscript, and approved it for publication.

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