A better understanding of phosphorus distribution in slag is necessary to develop an effective way to treat dephosphorization slag formed during steelmaking. Here, previous studies on the enrichment, separation, and recovery of phosphorus from dephosphorization slag are reviewed, along with their influencing factors. The results suggest that a proper heat treatment can promote the selective enrichment and growth of P-rich phases. Further, adding P_2O_5 and Fe_2O facilitates phosphorus enrichment. Also, Ca_3(PO_4)_2 is precipitated from slag containing 18 wt% P_2O_5. MnO and MgO in the slag barely affect the phosphorus recovery. In contrast, the addition of Al_2O_3 and TiO_2 significantly affects phosphorus enrichment and magnetic separation. A phosphorus recovery rate of more than 70% is achieved with the addition of 10 wt% Al_2O_3 or 10 wt% TiO_2. New phases (Na_2Ca_4(PO_4)_2SiO_4, Na_3PO_4, and Ca_5(PO_4)_3F) tend to be formed on the addition of Na_2O and CaF_2, which promote phosphorus enrichment. However, the addition of Na_2O and CaF_2 results in the incomplete separation of phosphorus and iron, as CaF_2 and Na_2O improve slag metallization and the magnetism of iron-rich phases. 

**Keywords:** phosphorus enrichment, selective enrichment and growth, P-rich phase, magnetic separation

1. Introduction

Dephosphorization is a critical step in steelmaking. Dephosphorization slag based on CaO-Fe_2O-SiO_2 has high basicity (R) and Fe_2O content. However, the recycle/reuse of this slag is greatly limited by the circulation and enrichment of phosphorus, generating possible contamination in the liquid steel. Therefore, a better understanding of the phosphorus distribution and separating P are very important to promote the reutilization and treatment of dephosphorization slag formed during steelmaking.

Previous studies have proposed many methods of dephosphorization, such as gasification, addition of reductants [1], and floating separation [2]. Additionally, phosphorus is reduced and dissolved in liquid iron to decrease its content in slag [3]. However, few studies have focused on the effective recovery of phosphorus. Furthermore, the phosphorus content in slag is low (4-7%) and dispersed, making it difficult to recover phosphorus for other applications, such as the production of phosphate fertilizers [4]. Therefore, it is necessary to promote the enrichment, growth, and effective recovery of phosphorus from dephosphorization slag. Sui [5-6] has proposed the selective enrichment and separation of phosphorus based on the extraction of valuable components. According to this mechanism, by selectively gathering the dispersed components in the target phase, the efficiency of separating valuable components increases. Similarly, phosphorus is selectively gathered in the P-rich phase. This process improves the enrichment rate and separation efficiency of phosphorus. Most recent studies [7-12] have focused on the effect of slag basicity, slag composition (MgO, MnO, P_2O_5, Fe_2O), and additives (Na_2O, CaF_2, Al_2O_3, TiO_2) on the selective enrichment, growth, and separation of phosphorus along with the mechanism of phosphorus enrichment [18-21]. However, most of the above studies have focused on laboratory investigations. Therefore, research on the resource utilization of P in industrial production is scarce.

To effectively recycle Fe and P of dephosphorization slag, the effects of slag basicity, slag composition, and additives on the enrichment, separation, and recovery of phosphorus are reviewed. Besides, the challenges and factors associated with “phosphorus enrichment and growth – separation – recycling” have been considered.

2. Properties of dephosphorization slag

2.1. Phase structure of dephosphorization slag

CaO-Fe_2O-SiO_2 slag consists of a P-rich phase, matrix phase, and RO phase [18,19]. As shown in Fig. 1, the P-rich phase in the slag is mainly in the form of a \( nCa_3SiO_4Ca_2(PO_4)_2 \) solid solution (\( nC_2S-C_3P \)) and the P_2O_5 content in this solid solution is more than 20% [20,21]. The white RO phase is mainly composed of iron oxides or Fe-Mn oxides. Extra phosphorous is present in the matrix phase.
Fig. 1. Main phases in slag (1: matrix phase, 2: RO phase, 3: P-rich phase) [19]

2.2. Factors influencing phase structure

2.2.1. Slag Basicity

Slag basicity mainly affects the formation of $\gamma$CaO·SiO$_2$ phase. Then the following phenomenon will happen. Firstly, the $C_3S$ phase is formed in high-basicity slag [8]. Meanwhile, the $C_3S$ reacts with P$_2$O$_5$ and CaO in slag to form $nC_3S$-$C_3P$. With decreasing slag basicity, the $C_3S$ content decreases and the $C_2S$ phase is formed. Similarly, solid $C_3S$ particles dissolve in the slag, and the $nC_2S$-$C_3P$ phase is generated. Subsequently, the $C_2S$ phase disappears in low-basicity slag, and a new $C_3P$ phase is generated, which leads to a decrease in the $nC_3S$-$C_3P$ content. The P$_2$O$_5$ content in the phases gradually increases in the order of $nC_2S$-$C_3P < nC_3S$-$C_3P < C_3P$ [8,36].

Lin [8] has analyzed the influence of SiO$_2$ modification on phosphorus enrichment in P-bearing steelmaking slag (P$_2$O$_5$ = 10 wt%). According to Fig. 2a, $C_3S$ appears at $R$ = 4 and disappears when $R$ = 1-3. Then, $C_3S$ and $nC_2S$-$C_3P$ are formed at 1623 K ($R$ = 2.5) as shown in Fig. 2b-d. Finally, CS is formed when $R < 1.5$. Son [36] has also reported that $nC_2S$-$C_3P$ is generated in CaO-Fe$_2$O$_3$-SiO$_2$-5 wt% P$_2$O$_5$ slag (Fe$_2$O$_3$ = 15-20 wt %) at $R$ = 1 and $R$ = 1.5. Therefore, the optimal basicity for generating $nC_2S$-$C_3P$ is 1.5-2.5. Under favorable dynamics conditions, more P$_2$O$_5$ accumulates near $C_2S$ particles at higher temperatures [31]. Therefore, the phosphorus content in the P-rich phase at 1400°C is higher than that at 1350°C [15].

2.2.2 Slag Composition

Previous studies have reported that MnO and MgO mainly enter into the RO phase to form MgFe$_2$O$_4$ and MnFe$_2$O$_4$, and different P$_2$O$_5$ and Fe$_2$O$_3$ contents affect the form of the $C_3S$ phase [9-11,36].
Son [36] has reported the effect of elemental compositions on CaO-FeO-SiO2-5 wt% P2O5 slag (CaO/SiO2 = 1.5). Fig. 3a shows that CS and C2S are generated at FeO = 10 wt%. However, according to Fig. 3b, C3P and nC2S-C3P are formed when the FeO content is high (FeO = 15-20 wt%).

Compared with FeO, the initial P2O5 content in the slag changes the form of the P-rich phase [7,9-11]. Li [7] has examined the behavior of phosphorus enrichment in CaO-FeO-Fe2O3-SiO2-P2O5 slag and has found that the initial P2O5 content promotes the generation of nC2S-C3P. Meanwhile, C3P is formed when more than 18 wt% P2O5 is added [9-11]. The results in Fig. 4 show that CaO15(P2O5)2(SiO2)6 is generated with the addition of less than 18 wt% P2O5, and C3P is formed when the P2O5 content is up to 18 wt%. C3P has lower Gibbs free energy than C3S; therefore, it is more stable in the temperature range 400-1800°C. Further, compared to SiO2, P2O5 can more easily combine with CaO. Hence, CaO preferentially combines with P2O5 and C3P is formed [9].

In summary, MgO and MnO have little effect on the P-rich phase. Appropriate P2O5 and FeO contents promote the precipitation of the P-rich phase. nC2S-C3P and C3P are formed with the addition of more than 15 wt% FeO and 18 wt% P2O5, respectively.

2.2.3. Addition of CaF2 and Na2O

Many studies have shown that adding CaF2 and Na2O changes the primary phase and phosphorus form, respectively [40,41]. Fig. 5 shows that 6C2S-C3P and C2S-C3P are generated in fluorine-free modified slag. A new phase, Ca5(PO4)3F, is generated on the addition of 6 wt% CaF2. Therefore, the nC2S-C3P and Ca5(PO4)3F phases are mainly considered to be P-rich phases [40]. Fig. 6 shows that Na2O-free modified slag consists of 6C2S-C3P, C2S-C3P, C3S, and RO phases. However, Na3Ca4(PO4)2SiO4 is formed in Na2O-bearing slag. Meanwhile, Na3PO4 is generated in slag containing 6 wt% Na2O [41].
2.2.4. Addition of Al$_2$O$_3$ and TiO$_2$

Most studies have revealed that Al$_2$O$_3$ and TiO$_2$ modification are beneficial to increase the phosphorus content in the P-rich phase [42-45]. Jiang [43] has examined the effect of Al$_2$O$_3$ on the phosphorus form existing in CaO-SiO$_2$-10 wt% FeO-6 wt% MgO-4 wt% MnO-10 wt% P$_2$O$_5$-Al$_2$O$_3$ slag. According to Fig. 7b, Ca$_2$Al$_2$SiO$_7$ is generated in Al$_2$O$_3$-bearing slag, along with the matrix, RO, and P-rich phases. Further, C$_3$P is formed on adding 11 wt% Al$_2$O$_3$.

Lin [45] has reported the effect of TiO$_2$ modification on phosphorus enrichment in industrial slag by adding 10 wt%
P₂O₅. As shown in Fig. 8a, TiO₂-free modified slag consists of the matrix, RO, and CaO₁₅(P₂O₅)₂(SiO₂)₆ phases. However, new phases (CaTiO₃, CaSiTiO₄) are generated after adding 10 wt% TiO₂ (Fig. 8b). [TiO₄], an important part of MgFe₂O₄-Mg₂TiO₄ and CaTiO₃, is formed after adding TiO₂. Furthermore, [TiO₄] and [SiO₄] can be copolymerized to form CaSiTiO₄, and C₂S in nC₂S-C₃P is robbed CaSiTionO₄ to generate yC₂S-C₃P (y < n) [4]. Therefore, new phases are generated on adding Al₂O₃ and TiO₂.

2.2.5. Temperature and cooling conditions

Su [33] has reported the distribution of phase structure in CaO-SiO₂-FeO-P₂O₅ slag under 1350°C and 1400°C. After holding 600s, the slag consists of C₂S-C₃P phase and matrix phase. However, Fig. 9 shows that C₂S-C₃P phase is blocked under 1350°C. Therefore, the lower temperature promotes the enrichment of P₂O₅.

In addition, the cooling conditions have effect on phase structure. Li [18] has reported the P-rich phase in steel slag under water quench process and hot splash process. The P-rich phase under water quench process is nC₂S-C₃P, while it is C₃P under hot splash process. Wu [23] has reported the distribution in SiO₂ modified slag. The results show that P is gathered to C₂S phase when the cooling rates are 1°C min⁻¹ and 3°C min⁻¹. The C₂S phase are spherical and arborization. However, the C₂S phase is arborization and punctate when the cooling rate is 5°C min⁻¹.

3. Phosphorus enrichment in dephosphorization slag

3.1 Mechanism of phosphorus enrichment

The mechanism of phosphorus enrichment can be concluded from the following process. First, solid C₂S particles dissolve in the slag. Then nC₂S-C₃P is generated in the multi-phase area where solid and liquid phases coexist. Finally, the solid-solution layer is extended and completely changes into the nC₂S-C₃P layer with the shrinking of the solid C₂S particles [21-27].

According to the slag ionic structure theory [22], slag consists of oxides, compounds, and charged protons (ions). As the SiO₂ content in basic dephosphorization slag is higher than the P₂O₅ and Al₂O₃ contents, C₂S and C₃S based on SiO₄²⁻ are generated during solidification, and SiO₄²⁻ is more easily replaced by P₂O₅ and Al₂O₃. Then, phosphorus is precipitated as PO₄³⁻ and coexists with SiO₄²⁻. Therefore, it is difficult to generate C₃P in dephosphorization slag. The formation reaction of nC₂S-C₃P can be expressed as Eq. (1).

\[
2n\text{CaO} + n\text{SiO}_2 + \text{Ca}_3\text{(PO}_4)_2 \rightarrow n\text{Ca}_2\text{SiO}_4 \cdot \text{Ca}_3\text{(PO}_4)_2
\]

It is well known that C₃S and C₂S react with C₃P to form a solid solution. Hence, the phosphorus in the slag is distributed in multiple phases [23]. Stable C₂S changes to spherical C₂S at 1300°C. Therefore, the P-rich phase mainly occurs in the nC₂S-C₃P phase as C₃S cannot react with C₂S at any ratio.

Most researchers have reported the behavior of mass transfer between single C₂S particles and slag [24-27]. C₂S particles are regarded as a multi-layered filter paper. Here the phosphorus in the slag is filtered and the phosphorus content gradually decreases in the direction of the C₂S particles. Therefore, nC₂S-C₃P is generated until the C₂S particles disappear. Fig. 10 shows the reaction between C₂S particles and CaO-SiO₂-FeO-P₂O₅ slag at 1500°C for 300 s. It reveals that a solid-solution layer is formed between the slag and the C₂S particles after 1 s (Fig. 10a), and after 60 s (Fig. 10b, c), the number of C₂S particles decrease with increasing area of this solid-solution layer [27]. Ono [24] has reported that ferrous and iron oxides increase the activity coefficient of C₃P in CaO-SiO₂-FeO/Fe₂O₃ slag. Most of the P₂O₅ in the slag reacts with C₂S particles to generate a solid solution. Moreover, the products float to the top of the slag. Ito [25] has measured the distribution ratio between CaO-SiO₂-FeO/Fe₂O₃ slag and C₂S particles. The results reveal that 80% P₂O₅ is transferred from the slag to the surface of the C₂S particles to form nC₂S-C₃P. Wang [26] has analyzed the enrichment be-
behavior of CaO-SiO$_2$-FeO-P$_2$O$_5$ slag at 1400°C and has found that C$_2$S particles provide space for phosphorus enrichment. Therefore, phosphorus diffuses from the slag to the surface of the C$_2$S particles.

Furthermore, a macro-process for phosphorus enrichment has been proposed. Yang et al. [28-30] have reported the reaction between C$_2$S particles and CaO-SiO$_2$-FeO$_2$P$_2$O$_5$ slag at 1400°C for 60 s. The mechanism is illustrated in Fig. 11.

1) C$_2$S particles dissolve into the slag and the slag penetrates into the solid sample (Fig. 11a).
2) The edge of the solid C$_2$S particles changes into a multi-phase area where solid and liquid phases coexist (Fig. 11b).
3) In this multi-phase area, CaO and P$_2$O$_5$ react with the C$_2$S particles to form nC$_2$S-C$_3$P (Fig. 11c).
4) The multi-phase area shifts toward the side of the C$_2$S particles to form a new P-rich phase (Fig. 11d).
5) The previously formed P-rich phase is either retained (Fig. 11e1), partly dissolved (Fig. 11e2), or fully dissolved into the slag (Fig. 11e3). The P-rich phase region is gradually extended.

Suito [31] has examined the behavior of phosphorus diffusion from CaO-Fe$_2$O-P$_2$O$_5$(-SiO$_2$) slag to CaO particles at 1400°C. The results show that nC$_2$S-C$_3$P is generated at the surface of CaO particles within 30 s. After 5 min, CaO-Fe$_2$O is produced between the nC$_2$S-C$_3$P and CaO particles. Inoue [32] has reported the phosphorus distribution between CaO-Fe$_2$O-P$_2$O$_5$ slag and C$_2$S particles. The results show that all the phosphorus in C$_2$S particles (20-50 μm) is converted into nC$_2$S-C$_3$P in less than 5 s. Only the rim part of the particles (5 μm) and the small particles (3-8 μm) change to nC$_2$S-C$_3$P within 5 s when the particles are clustered. However, this phenomenon is not observed in CaO-SiO$_2$-FeO-P$_2$O$_5$ slag.

Consequently, the formation of the P-rich phase can be described by the following process. The phosphorus in the slag transfers to the C$_2$S particles at high temperatures and reacts with C$_2$S to generate nC$_2$S-C$_3$P, and the previously formed P-rich phase is replaced by new products.

3.2. Factors influencing selective enrichment

3.2.1. Concept of Selective Enrichment

Temperature and the size of the C$_2$S particles affect phosphorus enrichment [26,33]. Because a higher temperature improves the kinetics of slag formation, the phosphorus content in the P-rich phase at 1400°C is higher than that at 1350°C [26,33]. The size of the P-rich phase increases with increasing enrichment time [33], and C$_2$S particles, of size less than 50 μm, are completely converted to form a P-rich phase [26].
However, the phosphorus content in the P-rich phase is low and dispersed. Therefore, the selective enrichment of P is important to increase the enrichment, separation, and recovery of the P-rich phase [34,35]. In 1978, Jha [34] proposed the concept of selective precipitation to obtain nickel sulfide and cobalt sulfide. In China, Sui [35] has proposed the technology of selective enrichment and separation. “Selective enrichment” means that suitable thermodynamics and kinetics are achieved by changing...
the slag compositions and additives. Then, valuable components interspersed in each phase are selectively transferred. Eventually, the valuable components accumulate in the target phase due to chemical gradient. The slag basicity and composition, the initial content of P$_2$O$_5$, and the value of ($\%$FeO)/($\%$CaO) have effect on the selective enrichment.

3.2.2. Slag Basicity and Composition

Using a suitable slag basicity is a good method to promote selective enrichment. Zhou [11] has examined the behavior of distribution of phosphorus between the P-rich phase and the matrix phase. The results show that phosphate capacities increase with decreasing slag basicity. According to Fig. 12, the P$_2$O$_5$ content in the P-rich phase decreases with increasing slag basicity. Lin [8] has reported the influence of SiO$_2$ modification on the phosphorus enrichment in P-bearing steelmaking slag. The results show that the P$_2$O$_5$ contents in the P-rich phase were 19-25 wt%, 31-32 wt%, 32-33 wt%, and 34-37 wt% for $R$ values decreasing from 4 to 1, respectively. Son [36] has analyzed CaO-20 wt% Fe$_2$O$_3$-SiO$_2$-5 wt% P$_2$O$_5$ slag and has found that the P$_2$O$_5$ content was 37.3 wt% and 22.7 wt% at $R = 2.0$ and $R = 2.5$, respectively. Thus, a higher slag basicity is harmful to phosphorus enrichment.

Many studies have reported the effect of slag compositions (MgO, MnO, P$_2$O$_5$, Fe$_2$O$_3$) on the selective enrichment of the P-rich phase. The addition of P$_2$O$_5$ increases the phosphorus content in the P-rich phase, whereas MgO and MnO have little effect [9-11,15,36-39].

Fe$_3$O$_4$ is an inevitable component in slag and reduces polymerization and viscosity. Additionally, it contributes to mass transfer and phosphorus enrichment in dephosphorization slag [4]. Son [36] has analyzed the effect of Fe$_3$O$_4$ on CaO-Fe$_2$O$_3$-SiO$_2$-5 wt% P$_2$O$_5$ slag. As shown in Fig. 13, the P$_2$O$_5$ content in the P-rich phase is 17.6 wt% and 22.7 wt% with the addition of 10 wt% Fe$_3$O$_4$ and 20 wt% Fe$_3$O$_4$, respectively. Moreover, the common effect of Fe$_3$O$_4$ and CaO on slag is unclear [7,37,38]. Li [7] has analyzed the effect of Fe$_3$O$_4$/CaO content on CaO-Fe$_2$O$_3$-SiO$_2$-P$_2$O$_5$ slag and found that $\alpha$-$\text{C}_2$-$\text{S}$-$\text{C}_3$-$\text{P}$ decreases with increasing Fe$_3$O$_4$/CaO content.

Zhou [9] has reported the effect of initial P$_2$O$_5$ content on phosphorus enrichment in CaO-Fe$_2$O$_3$-SiO$_2$-P$_2$O$_5$ slag. According to Figure 12, when the P$_2$O$_5$ content is increased from 6 wt% to 8 wt%, the phosphorus content in the P-rich phase increases from 20.33 wt% to 33.99 wt% and reaches a maximum value (34.91 wt%) when 18 wt% P$_2$O$_5$ is added. This suggests that phosphorus content in the P-rich phase increases with increasing initial P$_2$O$_5$ content.

MgFe$_2$O$_4$ and MnFe$_2$O$_4$ generated by MgO, MnO, and Fe$_2$O$_3$ enter into the RO phase, as shown in Eq. (2) [11,15,39]. Lin [15] has analyzed the effect of MgO and MnO on phosphorus enrichment in CaO-SiO$_2$-30wt%Fe$_2$O$_3$-MgO-MnO-10wt%P$_2$O$_5$ slag. According to Figure 12, when the MgO content increases from 5 wt% to 10 wt%, the P$_2$O$_5$ content in the P-rich phase changes from 20.76 wt% to 19.66 wt%. Similarly, when the MnO content increases from 5 wt% to 10 wt%, the P$_2$O$_5$ changes from 22.62 wt% to 19.66 wt%. Thus, P$_2$O$_5$ content in the P-rich phase does not change significantly.

\[
\begin{align*}
\text{MgO} + \text{Fe}_2\text{O}_3 &= \text{MgFe}_2\text{O}_4 \\
\text{MnO} + \text{Fe}_2\text{O}_3 &= \text{MnFe}_2\text{O}_4
\end{align*}
\] (2)

In summary, MgO and MnO have little effect on the selective enrichment of the P-rich phase. In contrast, the P$_2$O$_5$ content in the P-rich phase reaches 20 wt% and 35 wt% on the addition of 15 wt% Fe$_3$O$_4$ and 18 wt% P$_2$O$_5$, respectively.

3.2.3. Addition of CaF$_2$ and Na$_2$O

CaF$_2$ and Na$_2$O can significantly reduce the melting point of slag and promote phosphorus enrichment [4,11,40,41]. Wang [4] has analyzed the effect of CaF$_2$ on crystallization in CaO-
SiO$_2$-Fe$_2$O$_3$-MgO-P$_2$O$_5$-CaF$_2$ slag. The results show that the P$_2$O$_5$ content in Ca$_5$(PO$_4$)$_3$F reduces to 28.35 wt% with the addition of 3 wt% CaF$_2$. According to Fig. 14, on adding 3 wt% CaF$_2$ into the slag, the P$_2$O$_5$ content in the P-rich phase is 32.5 wt%, and on adding 6 wt% CaF$_2$ into the slag, the P$_2$O$_5$ content in the P-rich phase increases to 35.65 wt% [11]. Meanwhile, Lin [40] has reported the phosphorus enrichment behavior in CaO-SiO$_2$-Fe$_2$O$_3$-MgO-P$_2$O$_5$-CaF$_2$ slag. The results reveal that the P$_2$O$_5$ content in the P-rich phase is 20.75 wt% in fluorine-free modified slag. On increasing the CaF$_2$ content from 3 wt% to 6 wt%, the P$_2$O$_5$ content in the P-rich phase increases from 34.0 wt% to 37.75 wt%. Furthermore, it is necessary to control the CaF$_2$ content to avoid lining erosion and environmental pollution.

![Fig. 14. Effect of addition of CaF$_2$ and Na$_2$O on selective enrichment of phosphorus](image)

The form of phosphorus in the P-rich phase changes on the addition of Na$_2$O according to Eqs. (3-5) [41].

\[
12\text{CaO} + 6\text{SiO}_2 + \text{Ca}_3(\text{PO}_4)_2 \rightarrow 6\text{Ca}_2\text{SiO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2 \tag{3}
\]

\[
\text{Na}_2\text{O} + 6\text{Ca}_2\text{SiO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2 \rightarrow \text{Na}_2\text{Ca}_4(\text{PO}_4)_2 \cdot 3\text{SiO}_4 + 5\text{Ca}_2\text{SiO}_4 + \text{CaO} \tag{4}
\]

\[
3\text{Na}_2\text{O} + \text{Na}_2\text{Ca}_4(\text{PO}_4)_2 \cdot 3\text{SiO}_4 \rightarrow 2\text{Na}_3\text{PO}_4 + \text{Ca}_2\text{SiO}_4 + 2\text{CaO} \tag{5}
\]

As shown in Eq. (3), 6C$_2$S-C$_3$P is precipitated in the previous stage of cooling. Then Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$ is generated by the reaction of 6C$_2$S-C$_3$P and Na$_2$O at 1623 K (Eq. (4)). Moreover, Na$_3$PO$_4$ is formed in the presence of excess Na$_2$O content (Eq. (5)). Lin [41] has reported the influence of Na$_2$O on phosphorus enrichment in CaO-SiO$_2$-Fe$_2$O$_3$-MgO-P$_2$O$_5$ slag. As shown in Fig. 14, the P$_2$O$_5$ content in the P-rich phase is 21 wt% in Na$_2$O-free modified slag. When the Na$_2$O content is increased from 3 wt% to 6 wt%, the P$_2$O$_5$ content in the P-rich phase increases from 24 wt% to 32 wt%. According to the slag ionic structure theory, the combination of Na$^+$ and phosphorus ions is stronger than that of Ca$^{2+}$ and phosphorus ions. Moreover, Ca$^{2+}$ in 6C$_2$S-C$_3$P or Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$ is replaced by Na$^+$. Further, Na$_3$PO$_4$ is generated when sufficient Na$_2$O is added.

Thus, the P$_2$O$_5$ content in the P-rich phase increases to 30 wt% on adding 3 wt% CaF$_2$ or 6 wt% Na$_2$O. Furthermore, considering the limitations of CaF$_2$, it can be replaced by Na$_2$O to promote the selective enrichment of phosphorus.

### 3.2.4. Addition of Al$_2$O$_3$ and TiO$_2$

Previous studies have shown that Al$_2$O$_3$ and TiO$_2$ modification are beneficial to phosphorus enrichment [42-45]. The mechanism of Al$_2$O$_3$ modification can be illustrated as shown in Eqs. (6-7) [42-44].

\[
m\text{Ca}_2\text{SiO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2 + n\text{Al}_2\text{O}_3 = n\text{Ca}_2\text{Al}_2\text{SiO}_7 + y\text{Ca}_3\text{SiO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2 \tag{6}
\]

\[
y\text{Ca}_3\text{SiO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2 + x\text{Al}_2\text{O}_3 = x\text{Ca}_2\text{Al}_2\text{SiO}_7 + (y - x)\text{Ca}_3\text{SiO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2 \tag{7}
\]

First, $m$C$_2$S-C$_3$P is precipitated at 1623 K and gradually decreases with the generation of $y$C$_2$S-C$_3$P ($y < n$) (Eq. (6)). Then $(y - x)$C$_2$S-C$_3$P is produced on adding Al$_2$O$_3$ (Eq. (7)). Finally, C$_2$S in yC$_2$S-C$_3$P disappears when the Al$_2$O$_3$ content is sufficient to make $y = x$, and C$_3$P is precipitated from the slag.

As shown in Fig. 15, Diao [44] has revealed that the P$_2$O$_5$ content in the P-rich phase reached 5.1 wt% on adding 8 wt% Al$_2$O$_3$ into CaO-SiO$_2$-10wt%FeO-MgO-MnO-P$_2$O$_5$ slag ($R = 2$), whereas the content increases to 9.15 wt% on adding 11 wt% Al$_2$O$_3$. Wang [4] has also reported that the P$_2$O$_5$ content in the P-rich phase reaches 28.71 wt% with the addition of 15.17 wt% Al$_2$O$_3$ in CaO-SiO$_2$-Fe$_2$O$_3$-MgO-P$_2$O$_5$ slag.

![Fig. 15. Effect of addition of Al$_2$O$_3$ and TiO$_2$ on selective enrichment of phosphorus](image)
Similarly, the mechanism of TiO₂ modification is shown in Eqs. (8-9) [45]. CaSiTiO₅ and CaTiO₃ are generated on adding TiO₂. Lin [45] has found that the P₂O₅ content in the P-rich phase is only 13-15 wt% and increases to 24-26 wt% on adding 10 wt% TiO₂.

\[
\begin{align*}
mCa_2SiO_4 \cdot Ca_3(PO_4)_2 + 2nTiO_2 &= nCa_2SiTiO_6 + nCaTiO_3 \\
+ \gamma Ca_2SiO_4 \cdot Ca_3(PO_4)_2 & \quad (8) \\
\gamma Ca_2SiO_4 \cdot Ca_3(PO_4)_2 + 2xTiO_2 &= xCa_2SiTiO_6 + xCaTiO_3 \\
+ (y-x)Ca_2SiO_4 \cdot Ca_3(PO_4)_2 & \quad (9)
\end{align*}
\]

The effect of Al₂O₃ and TiO₂ on the selective enrichment of the P-rich phase is significant. The P₂O₅ content in the P-rich phase reaches 20 wt% on adding 15 wt% Al₂O₃ or 10 wt% TiO₂ to the slag.

4. Selective growth and precipitation in dephosphorization slag

4.1. Effect of temperature on selective growth and precipitation

According to the mechanism of selective enrichment and separation by Sui, the enrichment phase will grow up by controlling temperature, slag basicity, slag composition, and additives. Finally, the efficiency of separating valuable components is improved. The process is called as selective growth.

Heat treatment is the main factor affecting selective growth and precipitation. Most reports agree that the P-rich phase is thicker at lower cooling rates [4,5,7,23,47].

Wang [4] has analyzed the crystallization of the P-rich phase in CaO-SiO₂-Fe₂O₃-MgO-P₂O₅-Al₂O₃/TiO₂ slag by differential scanning calorimetry. The results reveal that the crystallization temperature of the P-rich phase increases with decreasing cooling rate. The diffusion of the P-rich phase is hampered at higher sub-cooling degrees. Li [7] has reported the effect of temperature on selective growth in CaO-FeO-Fe₂O₃-SiO₂-P₂O₅ slag. The results reveal that the size of the P-rich phase and its crystal fraction are 40 μm and 24% at a cooling rate of 3°C/min, respectively, and the latter reaches its maximum value within 1 h. Wu [23] has examined the average size of P-rich phases in industrial SiO₂-modified slag. On decreasing the cooling rate from 5°C·min⁻¹ to 3°C·min⁻¹ and 1°C·min⁻¹, the average size increases from 8 μm to 56 μm and 87 μm and the P₂O₅ content in the P-rich phase increases from 3.65 wt% to 7.5 wt% and 7.74 wt%, respectively. Yang [47] has analyzed the growth of the P-rich phase in CaO-SiO₂-Fe₂O₃-MgO-MnO-P₂O₅-Al₂O₃ slag at 1520°C. The statistical results show that the relationship between holding time (\(t\)) and the size of the C₃S layer (\(D\)) can be described by \(D = kt^m\). Where, \(k\) and \(m\) is constant. Thus, the size of the P-rich phase exceeds 40 μm when the cooling rate is less than 3°C·min⁻¹.

Fig. 16. Size of different phases (1: P-rich phase, 2: RO phase, 3: matrix phase) [8]
4.2. Effect of slag basicity and composition on selective growth and precipitation

Appropriate slag basicity and composition promote the selective growth and precipitation of the P-rich phase [8,9,15]. As shown in Fig. 16, the size of the P-rich phase is 10-30 μm, 20-100 μm, and 30-150 μm at \( R = 4, 3, \) and 2, respectively [8]. Further, the P-rich phase at \( R = 1 \) is rod-shaped and smaller than that at \( R = 2 \).

As MgO and MnO enter the RO phase, they have little effect on the selective growth and precipitation of the P-rich phase. Moreover, few studies have focused on the influence of P_2O_5 and Fe_2O_3 contents on the selective growth and precipitation of phosphorus [9,15]. Zhou [9] has measured the size of the P-rich phase in CaO-Fe_2O_3-SiO_2-P_2O_5 slag. On increasing the P_2O_5 content from 6 wt% to 10 wt% and 18 wt%, the size of the P-rich phase increases from 20-60 μm to 30-90 μm and 50-80 μm, respectively.

4.3. Effect of additives on selective growth and precipitation

Recently, some studies focusing on the effect of additives (CaF_2, Na_2O, Al_2O_3, and TiO_2) on the selective growth and precipitation of the P-rich phase have found CaF_2 and Al_2O_3 have a positive effect [40,42]. According to Fig. 17a-b, the size of the P-rich phase is 20-40 μm on the addition of 3 wt% CaF_2 and increases to 100 μm on adding 6 wt% CaF_2 [40].

Jiang [42] has reported the effect of Al_2O_3 on the selective growth of the P-rich phase in CaO-SiO_2-Fe_2O_3-MgO-MnO-P_2O_5-Al_2O_3 slag. As shown in Fig. 18, the P-rich phase is significantly accumulated on the addition of Al_2O_3, and the size of the P-rich phase increases from 20 μm (without Al_2O_3) to 30-40 μm on the addition of 8 wt% Al_2O_3.

5. Separation of phosphorus from dephosphorization slag

5.1. Magnetic separation of dephosphorization slag

5.1.1. Effect of Slag Basicity and Composition on Magnetic Separation

A common method for separating dephosphorization slag is magnetic separation. The phosphorus recovery rate can be promoted under a suitable magnetic field intensity (<0.5 T) and slag size (<50 μm) [5,7,8,12,25,40,41,54-58]. Several parameters have been suggested to characterize magnetic separation [12].

\[
L_p = \frac{a_{p_{2}O_{5}h} \cdot M_1}{a_{p_{2}O_{5}l} \cdot M_2}
\]  

(10)

Fig. 17. Effect of CaF_2 on selective growth (1: P-rich phase, 2: RO phase, 3: matrix phase) [40]
Where $M_1$ and $M_2$ are the mass of the nonmagnetic and magnetic substances (g), respectively; $\omega_{(P_2O_5)1}$ and $\omega_{(P_2O_5)2}$ are the mass fractions of $P_2O_5$ in the nonmagnetic and magnetic substances (%), respectively; $L_P$ is the phosphorus partition ratio between the nonmagnetic and magnetic substances; $\omega_{(TFe)1}$ and $\omega_{(TFe)2}$ are the mass fractions of the nonmagnetic and magnetic substances (%), respectively; $H_P$ is the $P_2O_5$ content (wt %) in the slag entering the nonmagnetic and magnetic substances; and $H_{Fe}$ is the TFe content (wt %) in the slag entering the nonmagnetic and magnetic substances. The phosphorus recovery rate and iron recovery rate are defined by the $P_2O_5$ content entering the nonmagnetic substances and Fe content entering the magnetic substances, respectively.

Suitable slag basicity and compositions promote magnetic separation. Lin [12,15] has examined the effect of slag basicity on magnetic separation in CaO-SiO$_2$-Fe$_2$O$_3$-MgO-P$_2$O$_5$-MnO Al$_2$O$_3$/TiO$_2$/CaF$_2$ slag. When the $R$ is decreased from 4 to 2, the $P_2O_5$ content in the slag entering the nonmagnetic substance increases from 64.59 wt% to 74.68 wt% and the $L_P$ changes from 2.71 to 5.48. Moreover, as shown in Fig. 19, the phosphorus recovery rate increases from 73.5% to 84.57% when the $R$ decreases from 4 to 2. Diao [58] has reported magnetic separation in CaO-10wt%SiO$_2$-Fe$_2$O$_3$-MgO-MnO-10wt%P$_2$O$_5$ slag ($R = 2.5$). According to Figure 18, the phosphorus recovery rate in the nonmagnetic substances is 74%.

MgO and MnO improve slag metallization and the magnetism of the iron-rich phase, resulting in the incomplete separation of phosphorus and iron [15,58]. As shown in Figure 18, on adding 10 wt% MgO and 10 wt% MnO to the slag, the phosphorus recovery rate in the nonmagnetic substances decreases from 65.44% to 40.43% and 35.8%. and $L_P$ decreases from 2.71 to 0.63 and 0.56, respectively [15]. Diao [58] has added 10 wt% MnO into CaO-SiO$_2$-Fe$_2$O$_3$-MgO-MnO-10wt%P$_2$O$_5$ slag and has found that the phosphorus recovery rate decreases from 46% to 40%. Thus, the phosphorus recovery rate can exceed 70% when the slag basicity is 1.5-2.5. Further, MgO and MnO decrease the phosphorus recovery rate.

### 5.1.2. Effect of Additives on Magnetic Separation

Many studies [40-41,58] have revealed that CaF$_2$ and Na$_2$O improve slag metallization and the magnetism of the iron-rich phase. Moreover, they can result in the incomplete separation of phosphorus and iron. However, Al$_2$O$_3$ and TiO$_2$ are beneficial to magnetic separation.

Lin [40-41] has analyzed the phosphorus recovery rate in fluorine-free modified slag. As shown in Fig. 20, the phosphorus recovery rate is 64.6% in fluorine-free modified slag, while
it decreases to 48.8% on adding 6 wt% CaF₂. In addition, the phosphorus recovery rate is 64.55% on adding less than 6 wt% Na₂O, but it is only 36.53% on adding more than 6 wt% Na₂O. Therefore, the Na₂O content should be controlled to be within 6 wt%.

According to Fig. 21, the phosphorus recovery rate is 45.51 wt% in Al₂O₃-free slag and increases to 68.47 wt% and 82.16 wt% on increasing the Al₂O₃ content from 10 wt% to 15 wt%. Furthermore, the phosphorus recovery rate increases to 74.46 wt% on adding 10 wt% TiO₂. Additionally, the Lᵣ is 4.61 and 2.91 on adding 10 wt% Al₂O₃ and 10 wt% TiO₂, respectively [12]. Simultaneously, Diao [58] has reported the effect of Al₂O₃ and TiO₂ on magnetic separation in CaO-SiO₂-Fe₂O₃-MgO-MnO-10 wt% P₂O₅ slag. The results reveal that the phosphorus recovery rate reached 87% and 70% on the addition of 10 wt% Al₂O₃ and 10 wt% TiO₂, respectively.

In summary, the phosphorus recovery rate increases to 60% either in fluorine-free modified slag or in slag containing 6 wt% Na₂O. Moreover, it reaches 70% on adding more than 10 wt% Al₂O₃ and 10 wt% TiO₂.

5.2. Separation of phosphorus from dephosphorization slag by supergravity separation

Previous studies have reported that calcium silicate in slag floats to the top due to the density difference between calcium silicate and the slag. Namely, CaO, SiO₂, and P₂O₅ accumulate at the top of the slag. Meanwhile, FeO, Fe₂O₃, and MnO accumulate at the bottom of the slag [48, 49]. However, the initial temperature must be up to 1580°C and the average cooling rate should be less than 2°C·min⁻¹. Additionally, FeO and MnO contents must be more than 30% [48]. Supergravity separation has been found to be effective for phosphorus separation [50-53].

Li [50-52] has reported the separation of Fe-bearing and P-bearing phases in industrial slag. As shown in Fig. 22, the sample obtained by centrifugal enrichment (G = 800, T = 1663 K, t = 40 min) is compared with a parallel sample (G = 1, T = 1663 K, t = 40 min). According to Fig. 22a, a uniform structure is observed under normal gravity. However, an obvious stratified boundary appears after centrifugal enrichment (as depicted in the white line in Figure 21b). The bottom of the sample is compact and tight, while the top, where the P-rich phase is formed, is loose and porous [50]. Therefore, the enrichment efficiency is proportional to the centrifugation time and gravity coefficient.

Li [50] has reported the separation of the Fe-bearing phase and P-rich phase in industrial slag (G = 800, T = 1663 K and
poor liquidity. Actually, Al2O3, Na2O, and TiO2 decrease the efficiency is greatly limited due to the higher melting point and temperature. However, an increase in the dephosphorization is favorable before decarburization because of the relatively low melting point and improve the liquidity. On the other hand, they replace parts of SiO2 and combine with CaO to generate new phases (decreasing the value of “n” in nC2S-C3P). Therefore, the process not only effectively increases the P2O5 content in the P-rich phase but also promotes the magnetic separation of this phase. Further, Na2O strengthens the magnetism of the Fe-bearing phase and has little effect on the magnetic separation. Li [61] has revealed that according to thermodynamics, Al2O3/TiO2 slightly decreases the distribution ratio between the slag and carbon-saturated iron. However, according to semi-industrial test results, Al2O3/TiO2 significantly improves the dephosphorization efficiency of the previous stage in the steelmaking process (before decarburization; [C] = 2.5-3.0%). The results show that the dephosphorization efficiency is up to 85% and the [P] content is less than 0.02% [62,63], which is beneficial to the smelting of medium and high-phosphorus-content hot metals. Additionally, it broadens the range of available iron ore resources and increases the purity of steel.

Therefore, CaO-FeO-SiO2-Al2O3/TiO2/Na2O dephosphorization slag is significant for improving production efficiency and resource utilization. Previous studies have analyzed the behaviors of phosphorus enrichment and separation under the conditions of thermodynamics/dynamics. To effectively increase the practical application of dephosphorization slag, further research concerning phosphate fertilizers are necessary. Although Al2O3/TiO2/Na2O enriches the P-rich phase, how the proportion of the P-rich phase in dephosphorization slag changes with different compositions directly affects the total P2O5 solubility in the slag. Moreover, few investigations have focused on the most direct data related to the quantity of dephosphorization slag. The P2O5 content in the slag increases with increasing dephosphorization efficiency. However, the variation in slag viscosity and slag structure caused by P2O5 content affects the liquidity and separation of the slag. Therefore, further studies on these aspects should be conducted.

**Acknowledgement**

The authors would like to thank the National Natural Science Foundation of China (No. 51474021) for financial support.

**REFERENCES**
