

# INFLUENCE OF DISTRIBUTION BEHAVIOUR OF PHOSPHORUS BETWEEN P-RICH AND MATRIX PHASE IN $\text{CaO-SiO}_2\text{-Fe}_t\text{O-P}_2\text{O}_5$ SLAG

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## Introduction

The cumulative amount of slag has increased to more than 200 million tons, which affects the environment. Owing to the dephosphorisation in steel-making process and the past use of phosphorus-rich ore in recent years, high phosphorus slags are being produced. If  $\text{P}_2\text{O}_5$  in the slag can be enriched and separated, the separated  $\text{P}_2\text{O}_5$  phase may be used as phosphoric fertiliser or phosphoric fertiliser additives, while the rest of the ingredients may be recycled in the iron- and steel-making processes, e.g., sintering, hot metal desiliconisation, and hot metal dephosphorisation process. If steel slag recycling is realised, the utilisation of converter slag will minimise environmental pollution and create financial benefit.

The fertiliser efficiency of slag phosphate fertiliser depends on  $\%(\text{P}_2\text{O}_5)$  and  $\text{P}_2\text{O}_5$  solubility. The  $\%(\text{P}_2\text{O}_5)$  in slag phosphate fertiliser is related to the phosphorus enrichment and separation from the slag, while the degree of phosphorus enrichment is dependent on the phosphorus distribution among the different phases in the slag.<sup>1-3</sup> Therefore, to efficiently recover phosphorus resources from slag to use as fertiliser, it is critical to study the phosphorus distribution between the P-rich and matrix phase in slag<sup>4-7</sup>. In the paper, the effect of  $\text{P}_2\text{O}_5$  content and slag basicity on the phosphorus existence form in the slag was studied systematically, the activity coefficient of  $\text{P}_2\text{O}_5$  and phosphorus capacity in P-rich and matrix phase were analysed. Additionally, the effect of  $\text{P}_2\text{O}_5$  content on distribution ratio of  $\text{P}_2\text{O}_5$  between P-rich and matrix phase in the slag was discussed, which provides the theoretical foundation for phosphorus enrichment and separation in the slag.

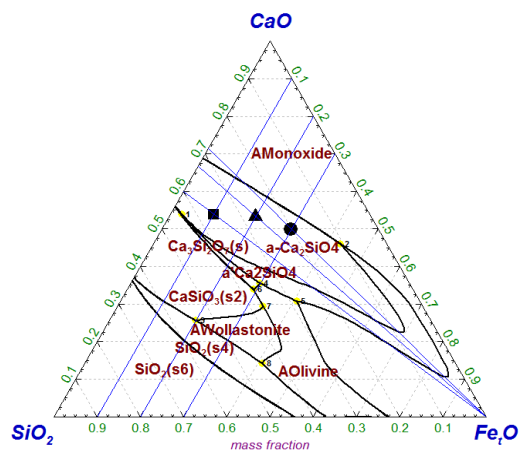
## Research method

Reagent-grade CaO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub> were used to produce experimental slag, as shown in Table 1. Figure 1 shows the compositional range of slags in the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> ternary phase diagram calculated by using the FactSage 6.3 for tagging as ■, ▲ and ●. All experimental slags were in the dicalcium silicate (C<sub>2</sub>S) primary zone, C<sub>2</sub>S precipitated first during the cooling process, and then nC<sub>2</sub>S-C<sub>3</sub>P solid solution (mainly Ca<sub>15</sub>(PO<sub>4</sub>)<sub>2</sub>(SiO<sub>4</sub>)<sub>6</sub> and Ca<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>SiO<sub>4</sub>) formed.

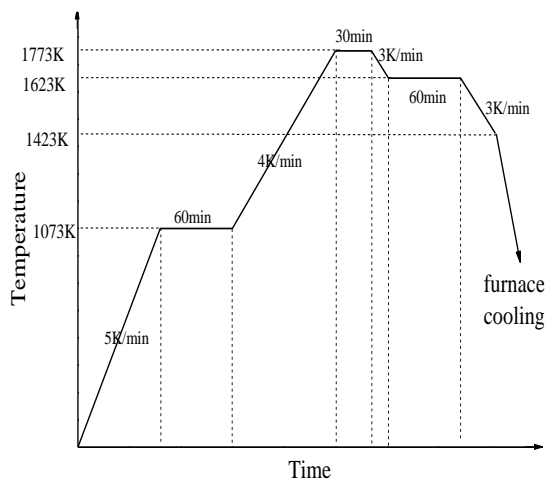
**Table 1:** Composition of the synthetic slag samples (mass fraction, % R= CaO/SiO<sub>2</sub>)

No.	R	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	No.	R	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
A	2.5	45.71	18.29	30	6	F	2.0	41.33	20.67	20	18
B	2.5	42.86	17.14	30	10	G	1.5	50.40	33.60	10	6
C	2.5	37.14	14.86	30	18	H	1.5	48.00	32.00	10	10
D	2.0	49.33	24.67	20	6	I	1.5	43.20	28.80	10	18
E	2.0	46.67	23.33	20	10						

The mixed slags (200 g) were placed in MgO crucible that was placed inside graphite crucibles and heated in a MoSi<sub>2</sub> electric resistance furnace up to 1773 K. The temperature was maintained for 30 minutes to ensure the slag fully melting. Then, the slags were cooled to 1623 K at 3 K/min and maintained at this temperature for 1 hour to fully promote the precipitation of 3CaO·P<sub>2</sub>O<sub>5</sub>. Then, the slag samples were cool in the furnace (Figure 2). The phase morphology, composition and mineralogical phases of the slag were observed by SEM, EDS and XRD respectively.

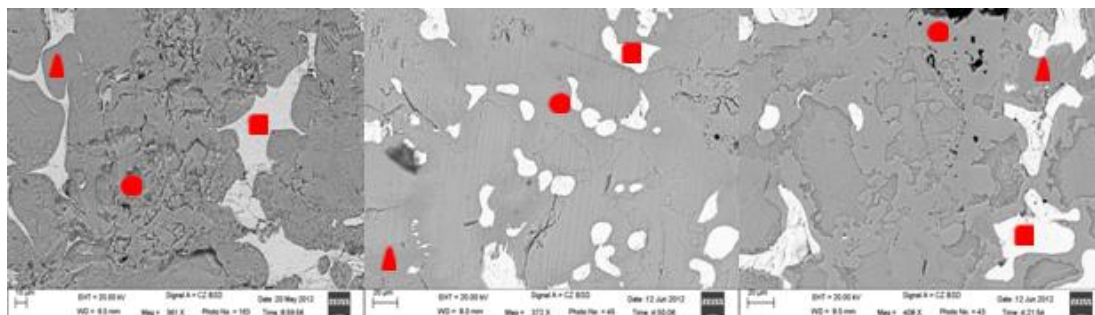


**Figure 1:** Observed slag composition in the ternary phase diagram of the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> system



**Figure 2:** T Experimental conditions for precipitation of C<sub>2</sub>S-C<sub>3</sub>P solid solution

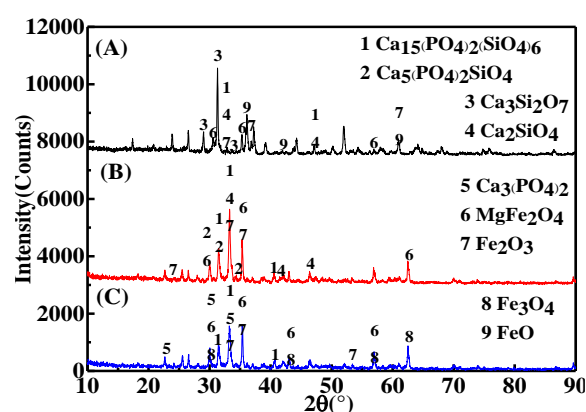
## Analysis and discussion



**Figure 3:** SEM-BSE image of experimental samples (●-P-rich phase, ■-RO phase, ▲-Base phase)

**Table 2:** Chemical compositions of each phase from sample in Figure 1 by EDS (mass fraction, %)

No.	Main phase	MgO	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>
A	P-rich phase	0	11.69	14.96	70.04	3.31
	RO phase	16.93	0.20	0	0	82.87
	Matrix phase	0	24.01	6.67	68.68	0.64
B	P-rich phase	2.95	15.24	20.75	58.90	2.16
	RO phase	5.30	0.07	0.17	0.61	93.85
	Matrix phase	11.46	31.29	3.56	53.68	0
C	P-rich phase	0	6.53	34.91	58.56	0
	RO phase	2.58	0	0	0	97.42
	Matrix phase	9.18	28.41	2.84	54.68	4.88



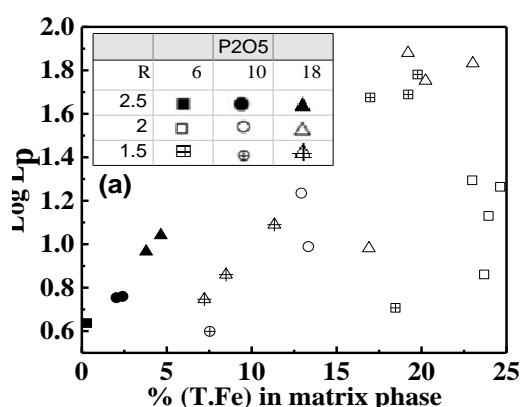
**Figure 4:** XRD results of different slag composition (sample A, B and C)

As shown in Figure 3, Figure 4 and Table 2, the results suggest that the P-bearing slag mainly consists of P-rich phase, matrix phase and RO phase. The phosphorus in the slag is mainly in the form of  $n2\text{CaO} \cdot \text{SiO}_2 \cdot 3\text{CaO} \cdot \text{P}_2\text{O}_5$  (for short  $n\text{C}_2\text{S} \cdot \text{C}_3\text{P}$ ) solid solution, the matrix phase mainly comprises of  $n\text{CaO} \cdot \text{SiO}_2$ , and the RO phase mainly consists

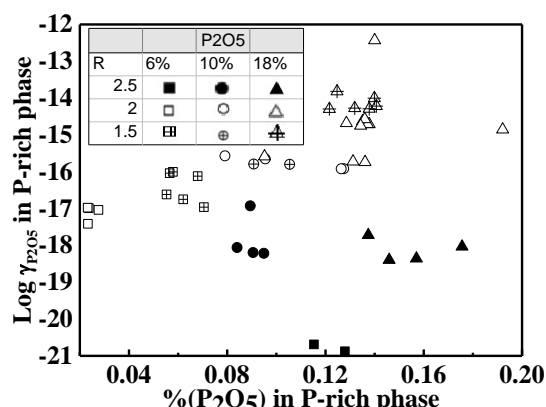
of iron oxide or iron and magnesium oxide. In the slag A, the phosphorus in P-rich phase is mainly in the existence of  $5\text{C}_2\text{S}-\text{C}_3\text{P}$  solid solution. When  $\text{P}_2\text{O}_5$  content in slag is increased to 10% for slag B, the P-rich phase is mainly  $5\text{C}_2\text{S}-\text{C}_3\text{P}$  and  $\text{C}_2\text{S}-\text{C}_3\text{P}$ . The  $\text{SiO}_2$  content in P-rich phase is obviously reduced or even disappeared in slag C, and the P-rich phase is mainly  $\text{Ca}_3(\text{PO}_4)_2$  and also a small amount of  $5\text{C}_2\text{S}-\text{C}_3\text{P}$ . So the  $\text{P}_2\text{O}_5$  content in slag has a certain effect on the phosphorus enrichment, but has little effect on the occurrence form of phosphorus.

### The effect of $\text{P}_2\text{O}_5$ on $L_p'$ between P-rich phase and matrix phase

The phosphorus in slag is transferred from the matrix phases to the  $2\text{CaO}\cdot\text{SiO}_2$  particles to form  $n\text{C}_2\text{S}-\text{C}_3\text{P}$  solid solution. The bigger the  $L_p'$  is, the more phosphorus is transferred from the matrix to the P-rich phase. Based on SEM and EDS data, the distribution ratio of  $\text{P}_2\text{O}_5$  ( $L_p' = \frac{\%(\text{P}_2\text{O}_5)_{\text{SS}}}{\%(\text{P}_2\text{O}_5)_{\text{M}}}$ ) is used to represent the degree of phosphorus enrichment in the slag in this study,  $\%(\text{P}_2\text{O}_5)_{\text{SS}}$  and  $\%(\text{P}_2\text{O}_5)_{\text{M}}$  respectively stands for the  $\text{P}_2\text{O}_5$  mass fraction in the P-rich and matrix phase.



**Figure 5:** The effect of  $\%(\text{T.Fe})$  in matrix phase on  $L_p'$  of different slag system



**Figure 6:** The effect of  $\%(\text{P}_2\text{O}_5)_{\text{SS}}$  on the  $\gamma_{\text{P}_2\text{O}_5(\text{SS})}$  in different slag systems

As shown in Figure 5, when the  $\text{P}_2\text{O}_5$  content in slag is constant, appropriate reduction of slag basicity can increase  $L_p'$  in the slag. For slag system with basicity of 2.0 and 2.5,  $L_p'$  increases with increasing  $\%(\text{P}_2\text{O}_5)$ . But for slag system with basicity of 1.5, when the  $\text{P}_2\text{O}_5$  content in slag is 6%,  $L_p'$  is the largest. That is because  $2\text{CaO}\cdot\text{SiO}_2$  precipitation amount is reduced in the low basicity slag, and when  $\text{P}_2\text{O}_5$  content in slag is high, the  $n\text{C}_2\text{S}-\text{C}_3\text{P}$  solid solution is supersaturated and even precipitated in the form of  $3\text{CaO}\cdot\text{P}_2\text{O}_5$ . At the same time, there is also a considerable amount of phosphorus in the matrix phase which cannot migrate, thus the phosphorus distribution ratio decreases.

### The effect of $\text{P}_2\text{O}_5$ on the activity coefficient of $\text{P}_2\text{O}_5$

As the P-rich and the matrix phase of the final slag are in equilibrium, the activities of  $\text{P}_2\text{O}_5$  in both phases are the same, thus,  $L_p'$  is proportional to the ratio of the activity

coefficient of  $P_2O_5$ , as shown in Equation (1), where  $a$  is the activity;  $\gamma$  is the activity coefficient, and  $k$  is the coefficient for converting the mass to mol fraction.

$$L_P = \frac{(\%P_2O_5)_{SS}}{(\%P_2O_5)_L} = k \frac{a_{P_2O_5(SS)} \times \gamma_{P_2O_5(L)}}{a_{P_2O_5(L)} \times \gamma_{P_2O_5(SS)}} = k \frac{\gamma_{P_2O_5(L)}}{\gamma_{P_2O_5(SS)}} \quad (1)$$

As shown in Figure 6, the  $\gamma_{P_2O_5(SS)}$  increases with increasing  $\%(P_2O_5)$  in the slag and decreasing slag basicity. In the regular model, the interaction energy between other cations and  $Ca^{2+}$  is negative, and the  $\gamma_{P_2O_5(SS)}$  and  $Ca^{2+}$  content in the slag is a negative correlation, which results in  $\gamma_{P_2O_5(SS)}$  increasing with decreasing slag basicity.

### The effect of $P_2O_5$ on the phosphorus capacity

The  $C_P$  in the P-rich phase ( $C_{P(SS)}$ ) and the matrix phase ( $C_{P(M)}$ ) are studied to analyse the phosphorus distribution between P-rich phase and matrix phases. The  $C_P$  was calculated by using Equation (2)<sup>8</sup> for the  $CaO-SiO_2-Fe_tO-P_2O_5$  slag system.

$$\log C_P = 0.51 \times (23N_{CaO} + 8N_{Fe_tO} - 26N_{P_2O_5}) + \frac{29920}{T} - 19.280 + \log(\%P) / N_{P_2O_5}^{1/2} \quad (2)$$

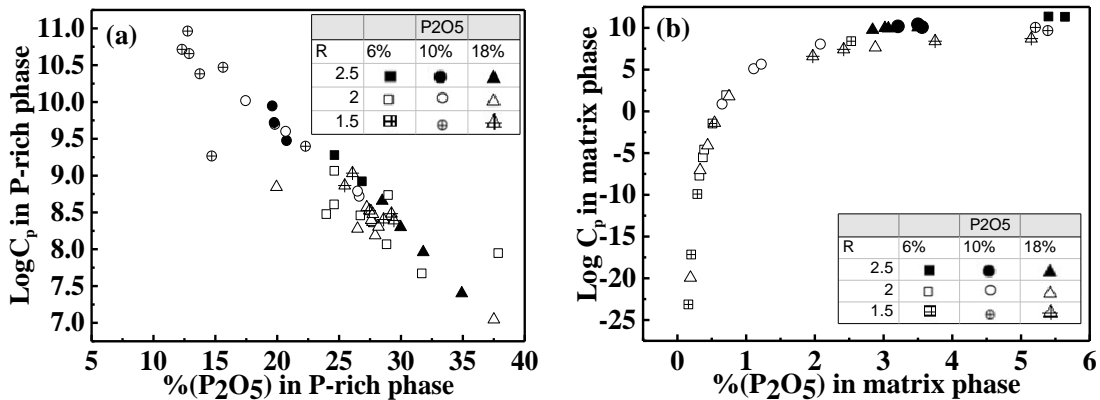


Figure 7: The effect of  $\%(P_2O_5)_{SS}$  and  $\%(P_2O_5)_L$  on  $\log C_P$  in corresponding phase

It can be seen from Figure 7a that  $C_{P(SS)}$  linearly decreases with increasing  $\%(P_2O_5)_{SS}$ . It can be seen from Figure 7b that  $C_{P(L)}$  increases with increasing  $\%(P_2O_5)_L$ . But when  $\%(P_2O_5)_L$  is more than 2%,  $C_{P(L)}$  has little change.

### Conclusions

In order to study the characters of  $P_2O_5$  distribution between the P-rich and the matrix phase in the slag, the influencing factors such as  $P_2O_5$  content in the slag, basicity of slag,  $TFe\%$  in the matrix phase and so on are analysed from the aspect of  $L_P$ , the activity coefficient of  $P_2O_5$  and phosphorus capacity. The findings are summarised as follows:

1. The slag is composed of P-rich phase, matrix phase and RO phase. Phosphorus in the slag is mainly in the form of  $n\text{C}_2\text{S}-\text{C}_3\text{P}$  solid solution in the P-rich phase. The adding of  $\text{P}_2\text{O}_5$  in the slag can increase the content of phosphorus in the P-rich phase and have no effect on the phosphorus existence form in the slag.
2. For the  $\text{CaO}-\text{SiO}_2-\text{Fe}_t\text{O}-\text{P}_2\text{O}_5$  quaternary slag system, with the increase of  $\text{P}_2\text{O}_5$  content in the slag and decrease of slag basicity,  $L_p'$  increases.
3.  $\gamma_{\text{P}_2\text{O}_5(\text{SS})}$  increases with increasing  $\%(\text{P}_2\text{O}_5)$  in the slag and decreasing slag basicity. With increasing  $\%(\text{P}_2\text{O}_5)$  in the slag,  $C_{\text{P}(\text{SS})}$  linearly decreases and  $C_{\text{P}(\text{L})}$  increases.

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