Note

Effect of Fluorine on the Minerals Phase and Citric Acid Solubility of CaO–SiO2–Fe2O3–P2O5–CaF2 System

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1. Introduction

Fluorspar is a commonly used additive to lower the melting point and viscosity of slag in steelmaking processes.1,2 There exists extensive literature on effect of CaF2 on dephosphorization of hot metal. It has been found that in slags with CaF2 additions between 1–4 wt%, the phosphate capacity could be increased up to a factor of three.3 The reason was explained by the experimental results that the addition of CaF2 decreased the activity coefficient of P2O5, and increased the activity coefficient of FeO in the slag.4–6 Sen et al. reported that CaF2 had a positive effect on the reaction kinetics, and can increase the mass transfer coefficient of phosphorous in the slag.9 It is also been suggested that CaF2 facilitated the solubility of CaO.9,10

Although CaF2 promotes the dephosphorization process, however, it must be reduced in order to lessen the negative environmental effect and corrosion of refractory. Moreover, it is well known that the citric acid solubility of Thomas slag is small when the phosphorus is present as fluorine-containing apatite. Depending upon slag composition after dephosphorization, it may have highly desirable properties for soil sweetening and acid neutralizing as well as soil conditioning. The quality of iron ore products, which relates to phosphorus content, will lower gradually in the long run, and there have been reports of increasing levels of phosphorus in steelmaking over the past couples of decades.11,12 This situation may leads to higher phosphorus contents in hot metal. Meanwhile, the dephosphorized slag containing high P2O5 content can be used as phosphate fertilizer. Therefore, the effect of fluorine on the minerals phase and citric acid solubility of CaO–SiO2–Fe2O3–P2O5–CaF2 system is investigated in present study in order to keep the high citric acid solubility of the slag.

2. Experimental

The initial composition of slag samples is listed in Table 1. These slags were prepared from reagent grade CaO, SiO2, FeO, Fe2O3 and CaF2. FeO was prepared by mixing of Fe2O3 and FeO. The later was added by the form of FeC2O4·2H2O. Although most of the iron oxide would be in the form of FeO in steelmaking condition, however, the distribution behavior of P2O5 between solid solution and liquid phases was not different, when the iron oxide was changed from FeO to Fe2O3.13 Therefore, considering the crucible dimension (φ50 mm×75 mm) in present study, the Fe2O3/FeO ratio was increased to 1:1 to avoid the slag escape caused by FeC2O4·2H2O decomposition. The variation of Fe2O3/FeO concentration caused by air oxidation doesn’t take into account it in the present study. The slag sample was pre-melted at 1 773 K in a corundum crucible and then taken out from the furnace with the crucible at 1 673 K in the cooling step. The mineralogical phases of slag are identified by XRD. The available phosphorus of the slag in citric acid was calculated by gravimetric method. The major reaction in the experiment is presented as follows:

\[
\begin{align*}
H_2PO_4^- + 12MoO_4^{2-} + 24H^+ &= H_4(PO_4)^- + 12MoO_4^- \cdot H_2O + 11H_2O \quad \text{(1)} \\
H_4(PO_4)^- + 12MoO_4^- \cdot H_2O + 3C_2H_2N &= (C_2H_2N)_4H_4(PO_4)^- + 12MoO_4^- \cdot H_2O \quad \text{(2)}
\end{align*}
\]

The solubility of slag sample in citric acid is calculated as:

\[
P_{2O_5}^{Solubility} = \frac{P_{2O_5}^{Available}}{P_{2O_5}^{Total}} \quad \text{..........(3)}
\]

3. Results and Discussion

It is well known that dicalcium silicate (C2S) forms a solid solution with tricalcium phosphate (C3P) at the dephosphorization treatment temperature over a wide composition range.13 This implies that the phosphorus element in the dephosphorized slag would mainly exist as the form of C2S–C3P solid solutions. Figure 1 shows the X-ray diffraction pattern of the fluorine-free slag (No. 1 in Table 1). Due to the complex composition, the XRD result gives a high probability of several phases. Phosphorus is found to be distributed in (C2S–C3P)ss (both Ca0.93(P2O5)2(SiO4) and Ca5(PO4)2(SiO4)), and FeO(P2O5)2O. Figure 2 shows the X-ray diffraction patterns of the fluorine-containing slags (Nos. 2, 4 and 7 in Table 1). The diffraction intensities in the case of

| Table 1. Chemical composition of slag samples (mass%). |
|-----------------|----------|--------|--------|--------|
| No. | CaO | SiO2 | FeO | P2O5 | CaF2 |
|-----|-----|------|-----|------|------|
| 1   | 46.43 | 18.57 | 25.00 | 10.00 | 0    |
| 2   | 46.06 | 18.42 | 25.00 | 10.00 | 0.52 |
| 3   | 45.69 | 18.28 | 25.00 | 10.00 | 1.03 |
| 4   | 45.32 | 18.13 | 25.00 | 10.00 | 1.55 |
| 5   | 44.96 | 17.98 | 25.00 | 10.00 | 2.06 |
| 6   | 44.95 | 17.73 | 25.00 | 10.00 | 2.58 |
| 7   | 42.14 | 16.86 | 25.00 | 10.00 | 6.00 |
Fluorine-containing slags are obviously larger than that in the fluorine-free one shown in Fig. 1. The half peak breadth also decreased in the fluorine-containing slags. In the case of slag No. 2 with 0.52% CaF$_2$ and slag No. 4 with 1.55% CaF$_2$, the precipitated phosphorus-containing phases are Ca$_5$(PO$_4$)$_3$F, Ca$_{15}$(PO$_4$)$_2$(SiO$_4$)$_6$, and Fe$_4$(PO$_4$)$_2$O. In the case of slag No. 7 with 6% CaF$_2$, phosphorus is found to be distributed in Ca$_5$(PO$_4$)$_3$F and Ca$_{15}$(PO$_4$)$_2$(SiO$_4$)$_6$. It was found in the XRD results that some peaks match both the standard three strong lines of Ca$_{15}$(PO$_4$)$_2$(SiO$_4$)$_6$ and Ca$_5$(PO$_4$)$_3$F. Both the two phases have low FOM (figure of merit) values. It was represented in Fig. 2 that all characteristic peaks of Ca$_{15}$(PO$_4$)$_2$(SiO$_4$)$_6$ overlap with those of Ca$_5$(PO$_4$)$_3$F. It can be considered that Ca$_{15}$(PO$_4$)$_2$(SiO$_4$)$_6$ coexisted with Ca$_5$(PO$_4$)$_3$F in the fluorine-containing slags.

The phase diagram, which is obtained by the thermal analysis of Ca$_3$(PO$_4$)$_2$–CaF$_2$ system,$^{14}$ is shown in Fig. 3. Initial compositions of slag Nos. 2–4 are located in the region of primary crystalline phase of C$_3$P + ApA. The XRD results of slag Nos. 2 and 4 in Fig. 2 is in agreement with this diagram. Initial compositions of slag Nos. 5, 6 and 7 are located in the region of primary crystalline phase of (ApA, ApB)$_{ss}$ and ApB + CaF$_2$, respectively. The XRD result of slag No. 7 in Fig. 2 shows that there is only one compound containing phosphorus and fluorine Ca$_5$O$_{3}$P$_4$ and Ca$_7$O$_{4}$P$_4$F$_2$ (ApB in Fig. 3) is not observed in present study. It was found that the XRD result agreed with the phase diagram reported by Nacken.$^{15}$ To further verify the distribution of phosphorus and fluorine, the phase diagram of CaO–P$_2$O$_5$–CaF$_2$ system was calculated at 1 273 K using the thermodynamic software package FactSage. As shown in Fig. 4, the result coincides with XRD analysis and the reported phase diagram.$^{15}$ It can be considered from these results that the phosphorus and fluorine mainly precipitated as fluorapatite crystal during the slag cooling step.

It is previously known that the fluorapatite is an insoluble phosphorus-containing mineral, but the phosphate must be soluble for fertilizer use. Therefore, in order to get high solubility in citric acid, i.e. high ratio of citric acid soluble P$_2$O$_5$ to total P$_2$O$_5$, it is necessary to remove the fluorine content as far as possible or to avoid the use of fluorine-containing slagging materials. It also has previously been proposed to produce such a soluble product by removal of fluorine in the slag. The defluorination reactions are expressed as follows:

$$\text{Ca}_5\text{(PO}_4\text{)}_3\text{F} + \text{H}_2\text{O} = \text{Ca}_5\text{(PO}_4\text{)}_3\text{(OH)} + \text{HF} \quad (4)$$

$$4\text{Ca}_3\text{(PO}_4\text{)}_2\text{(OH)} + \text{SiO}_2 = 6\text{Ca}_3\text{(PO}_4\text{)}_2 + \text{Ca}_2\text{SiO}_4 + 2\text{H}_2\text{O} \uparrow \quad (5)$$

$$2\text{Na}_2\text{S} + 3\text{O}_2 = 2\text{Na}_2\text{O} + 2\text{SO}_2 \quad (6)$$

$$\text{Ca}_7\text{(PO}_4\text{)}_4 + \text{Na}_2\text{O} = 2\text{CaNaPO}_4 + \text{CaO} \quad (7)$$

Although the reaction products C$_3$P and CaNaPO$_4$ have high solubility in citric acid, however, this method is uneconomic for the reason that it needs extra treatment of slags.

**Figure 5** shows the effect of fluorine content on solubility of the slag in citric acid. The solubility of the fluorine-free slag No. 1 calculated by Eq. (3) is 92.5%. By addition of CaF$_2$, the solubility of slag decreases notably: the solubility decreases to 77.7% in the slag of 0.25% F (slag No. 2), the solubility falls to 47.1% in the slag of 0.50% F (slag No. 3) and the solubility falls to 30.9% in the slag of 0.76% F (slag No. 4). When the fluorine content reach up to 2.92% (slag No. 7), the solubility of slag is only 13.7%.

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**Fig. 1.** X-ray diffraction pattern of fluorine-free slag No. 1.

**Fig. 2.** X-ray diffraction pattern of fluorine-containing slags (Nos. 2, 4 and 7).

**Fig. 3.** Phase diagram of Ca$_5$(PO$_4$)$_3$F–CaF$_2$ system (ApA: Ca$_{15}$(PO$_4$)$_2$(SiO$_4$)$_6$, ApB: Ca$_5$(PO$_4$)$_3$F)$^{14}$: • denotes the sample composition.
To obtain dephosphorized slag with a much higher solubility degree, it is better to lower the fluorine content in slag less than 0.5%.

Moreover, it can be seen from Fig. 3 that the C₃P solid has two crystal forms of α-type and β-type. α-C₃P is stable at higher temperature compared with β-C₃P. In fact, previous study indicated that the α-C₃P has a higher solubility than β-C₃P. This suggests that rapid cooling is preferable in order to keep α-C₃P phase without the transformation of α-C₃P to β-C₃P. The further and systemic study to investigate the effect of cooling rate, slag composition and other substitutes containing fluorine on citric acid solubility would be necessary to utilize dephosphorized slag as phosphatic fertilizer.

4. Conclusions
(1) Phosphorus was found to be distributed in \((C₃S–C₃P)ss\) and \(Fe₄(PO₄)₂O\) in fluorine-free slag. In the cases of fluorine-containing slags, \(Ca₅(PO₄)₃F\) phase exists along with \(Ca₃₃(PO₄)₂(SiO₄)₆\).
(2) The calculated results by FactSage indicated that the phosphorus and fluorine precipitated mainly as fluorapatite crystal during the slag cooling step.
(3) The solubility of slag in citric acid decreased notably with CaF₂ addition. To get a higher solubility slag, the fluorine content had to decrease to 0.5% or less.

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