Immobilization of fluorides from spent carbon cathode in a copper smelting slag

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Abstract: The fluorides from spent carbon cathodes could be effectively solidified in a molten copper smelting slag (FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃) in forms of CaF₂ and Ca₄Si₂F₅O₇. The results of thermodynamic analysis, chemical analysis, and XRD and EPMA analyses showed that the F solidification efficiency increased with the CaO amount and decreased with the addition of Al₂O₃ and SiO₂. In addition, it was noteworthy that the F solidification efficiency decreased with an excessive CaO amount, which could be ascribed to the consumption of SiO₂ through forming CaSiO₃ and Ca₃Si₂O₇. It restricted the solidification of the fluoride into Ca₄Si₂F₅O₇. Under the conditions of melting temperature of 1300°C, residence time of 60 min and N₂ flow rate of 40 ml/min, the optimum CaO and NaF amounts were found to be 20 wt.% and 6 wt.% respectively, in which the F solidification efficiency in the copper smelting slag of FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃ obtained 98.35%.

Key words: Spent carbon cathode; Fluorides; Copper smelting slags; Slag system of FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃; Immobilization

1. Introduction

Spent carbon cathode is a hazardous solid waste that generated from the aluminium electrolysis process, which mainly contains carbon, fluorides (NaF, Na₃AlF₆, and CaF₂ etc.) and other aluminium and cyanide compounds (Al₂O₃, AlN, NaCN, and Na₃Fe(CN)₆ etc.) [1-4]. Approximately 10 kg of spent cathode carbon are generated while produced per ton of primary aluminium, and approximately 360,000 tons of spent cathode carbon are generated annually in China in recent years [5]. The fluoride and cyanide components in it cause serious soil and water pollution if the spent carbon cathode is landfilled and exposed to air for a long time, and further threaten the growth and health of animals, plants, and human [6-7]. A harmless treatment of it is urgently needed.

Currently, massive methods for harmless and resource treatment of the spent cathode carbon have been developed, which could be divided into three methods of pyrometallurgical, hydrometallurgical, and pyro and hydro metallurgical corporation.
processes. The pyrometallurgical process, mainly referring to methods of combustion and vacuum evaporation [8-11], shows advantages on big processing capacity, simple operation and efficiently detoxification of fluoride and cyanide components. In the combustion process, some calcium compounds (e.g., CaO, CaCO₃, and Ca(OH)₂) are added to transform and solidify the soluble fluoride into CaF₂, Ca₅Si₂F₁₀ and Ca₁₂Al₁₄F₂O₂₂, and meanwhile the cyanide is oxidative decomposed into N₂ and CO₂ [12-14]. However, the massive consumption of high-quality graphite carbon from the spent cathode carbon causes it difficult to be carried out in an industrial application. In the vacuum evaporation process, the temperature and vacuum pressure affects the fluoride and cyanide removal rates greatly [10, 11, 15]. The soluble fluoride content could be reduced to 3.5 mg/L and the cyanide was completely decomposed under the conditions of vacuum pressure of 3000 Pa and temperature of 1700℃. However, the huge energy consumption restricts this vacuum evaporation process for an industrial application [15]. Through a hydrometallurgical method, the carbon and electrolyte components can be effectively recovered from the spent cathode carbon, and in additional the purity of the obtained carbon exceeds 95% [16-19]. However, massive acid or alkaline wastewater is generated, causing a secondary pollution. The carbon can also be recovered through a combined process of molten salt roasting (Na₂CO₃-Na₂O) and water leaching [20, 21]. The Na₃AlF₆ and CaF₂ were converted to NaF in the molten salt-assisted roasting process, and then could be separated efficiently through the followed water leaching process. Meanwhile, most cyanide was converted into Na₂CO₃, N₂, and CO. As a result, the leachable concentrations of fluoride and cyanide could be decreased to 8.17 mg/L and 0.18 mg/L respectively, and a graphite carbon with the carbon content of 95.41% was obtained [21]. But the Na₂CO₃ consumption is large, and the soluble fluoride in the leaching water needs a further separation for decreasing a secondary pollution.

To synergistically reutilize the carbon and fluoride components, the spent cathode carbon was used as a reductant in a dilution process of copper converter slags or smelting slags for recovering Cu and/or Co [22-24]. During these processes, the increase of spent cathode carbon both increased the metal recovery and the fluorides solidification efficiency in the final slag [25], and simultaneously the cyanides were transformed to N₂ and CO₂. The leachable F⁻ and CN⁻ contents in the final slag were less than 5 mg/L and 0.1 mg/L respectively. It provides a new thought for reusing the spent cathode carbon, but the transformation behaviour of fluorides in the copper slag system was focused little. Based on the thermodynamic analysis, chemical analysis, XRD and EPMA analyses, the transformation of fluorides from the spent carbon cathode in a copper smelting slag of FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃ was researched in this study.

2. Materials and methods
2.1 Materials
2.1.1 Basic slag

Referenced to the chemical and phase compositions of copper smelting slags (Table 1 and Fig.1(a)) obtained from a copper plant locating in Yunnan province of China, a basic slag of FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃ was synthesized using pure reagents
of FeO, Fe₃O₄, SiO₂, CaO and Al₂O₃ through a melting process in a N₂ atmosphere. The chemical and phase compositions of this synthesized slag are shown in Table 2 and Fig.1(b) respectively. Figs.1(a) and (b) show that the main phases in the copper smelting slag and synthesized slag are both Fe₂SiO₄ and Fe₃O₄.

### 2.1.2 Spent cathode carbon

The spent cathode carbon, which was the first cut of the spent pot liner, was obtained from Yunnan Aluminum Co., Ltd of China. The proximate analysis result in Table 3 shows that it contains 73.24wt.% fixed carbon, 25.81wt.% ash and 0.85wt.% volatile matters. Furthermore, the ash is mainly composed of 9.49wt.% F, 8.44wt.% Na, 3.59wt.% Al₂O₃ and a small amount of CN⁻ (Table 3). Fig.1(c) identifies the C, NaF and CaF₂ as main phases in the spent cathode carbon. Considering the low leachability and little environmental risk of CaF₂ [3], the transformation of NaF was mainly focused in this research. The NaF with a purity of 99% was used in this research instead of the spent cathode carbon, and the high-purity nitrogen used with purity of 99.999% was procured from local suppliers.

**Table 1. Chemical composition of the copper smelting slag (wt.%)**

| Component | CaO | MgO | Al₂O₃ | SiO₂ | Fe₃O₄ | FeO | others |
|-----------|-----|-----|-------|------|-------|-----|--------|
| Contents  | 6.01| 3.27| 3.49  | 23.40| 1.93  | 54.82| 7.08   |

**Table 2. Chemical composition of the synthesized basic slag (wt.%)**

| Components | FeO | Fe₃O₄ | CaO | SiO₂ | Al₂O₃ | others |
|------------|-----|-------|-----|------|-------|--------|
| Contents   | 60.52| 2.13  | 6.63| 25.83| 3.85  | 1.04   |

**Table 3. Proximate analysis result of the spent cathode carbon and chemical composition of the ash in the spent cathode carbon (wt.%)**

| Proximate analysis | Chemical composition of the ash in the spent cathode carbon |
|--------------------|----------------------------------------------------------|
| FCₐd | Mₐd | Aₐ | Vₐ | F | Na | SiO₂ | Al₂O₃ | Fe | S | Ca | CN(mg/kg O) |
| 73.2 | 0.1 | 25.8 | 0.8 | 9 | 4 | 1.45 | 3.59 | 0.6 | 0.0 | 1.86 | <0.1 |

**2.2 Methods**

The experiments were carried out in a vertical resistance furnace (GSL-1700X-VTQ, Hefei Kejing Materials Technology Co. Ltd., China), and the experimental apparatus is presented in Fig.2. The temperature was precisely measured by a KSY
intelligent temperature controller connected to a Pt-Rh thermocouple (accuracy of ±1 °C), which has been corrected by a movable Pt-Rh thermocouple before. For the experimental procedure, the dried synthesized basic slag, NaF and other additives were firstly pre-ground and sieved to below 74 μm respectively, and then mixed thoroughly at proper mass ratios. After that, the mixture was loaded into a corundum crucible and further placed in the constant-temperature zone of the furnace tube to be heated to 1300 °C in a high-purity N₂ with the flow rate of 40 ml/min. Referenced to a dilution process of copper slags using waste cathode carbon in previous researches [22, 24], the melting temperature, residence time and N₂ flow rate were controlled at 1300°C, 60 min and 40 ml/min respectively in all experiments. Then the samples were cooled down to room temperature in the alumina tube under a high-purity N₂ atmosphere with the flow rate of 40 ml/min, pulled out, weighed and ground to prepare for analysis. The F solidification efficiency (S_F) in these experiments was calculated using Eq. (I):

\[
S_F = \frac{m_2 \times w_2 - m_1 \times w_1}{m_1 \times w_1}
\]

where \( m_1 \) and \( m_2 \) represent the masses of the NaF and final slag respectively, g; \( w_1 \) and \( w_2 \) correspond to the F mass contents in the NaF and final slag (wt. %) respectively, and \( w_3 \) corresponds to the leachable F mass content in the final slag (wt. %).

![Fig.2 Schematic diagram of the experimental system](image)

2.3 Characterization

The chemical composition of the sample was analysed using chemical titration and atomic absorption spectroscopy, and the leachable F content in the final slag was detected via an ion chromatography method. All these measurements were conducted three times and the average value was taken as the final result. Phase transformation and microstructure of the sample were detected by X-ray diffraction analysis (XRD, Rigaku, TTR-III) and electron probe microanalysis techniques (EPMA, JXA82, JEOL). For the XRD analysis, the diffraction was measured in 10 to 90 deg 2θ using a Cu Ka radiation at 40kV and 40mA and a step size of 0.01 deg. The thermodynamic analysis
was carried out using the FToxid, FTmisc, and FactPS databases in the FactSage 7.2 software.

3. Thermodynamic analysis

To detect the transformation of NaF in the molten synthesized basic slag of FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃, the FactSage 7.2 software was used to calculate equilibrium phases for the reaction system of 100 g synthesized basic slag + 8 g NaF with different addition amounts of CaO, Al₂O₃ and SiO₂ at 1300 °C based on minimizing Gibbs free energy under isothermal, isobaric and fixed-mass conditions. The results are shown in Fig.3.

With no addition of CaO, Al₂O₃ and SiO₂, Figs.3(a), (b) and (c) show that the NaF was mainly transformed to CaF₂ (s), NaAlSiO₄ (l) and Na₄CaSi₂O₉ (l) through reactions (1) and (2) when it was melted with the synthesized basic slag. The CaF₂ (s) was then converted into Ca₄Si₂F₂O₇ (s) through reaction (3) with the CaO addition amount increasing from 0 to 20 wt.% as shown in Fig.3(a). Simultaneously with it, the Fe₂SiO₄ (l) amount decreases and the FeO (s) amount increases. Increasing the CaO amount further, the amount of Ca₄Si₂F₂O₇ (s) decreases while the amounts of NaF (g) and Ca₂SiO₄ (s) increase. The reason might be that massive SiO₂ in the basic slag are combined with CaO forming Ca₂SiO₄ (s) through reaction (4), and then the formation of Ca₄Si₂F₂O₇ (s) through reactions (1) and (3) is restricted.

In Fig.3(b), as the SiO₂ addition amount increases from 0 to 15 wt.%, the reaction (5) is promoted, resulting the FeO (s) amount decreases and Fe₂SiO₄ (l) amount increases. Simultaneously, the NaF is mainly transformed to CaF₂ (s). With the SiO₂ addition amount ranging from 10 to 20 wt.%, the Ca₄Si₂F₂O₇ (s) is generated through reactions (5) and (3) and increased. Then with more SiO₂ added, the ‘F’ is transferred from the Ca₄Si₂F₂O₇ (s) into the CaF₂ (s), causing the amount of Ca₄Si₂F₂O₇ (s) decreases and that of CaF₂ (s) increases.

In Fig.3(c), with the increase of Al₂O₃ addition amount from 0 to 4 wt.%, the amounts NaF (g) and Fe₂SiO₄ (l) decrease accompanied by the increase of NaAlSiO₄ (l) and FeO (s) amounts, and the ‘F’ in the NaF is mainly transformed to CaF₂ (s) and Ca₄Si₂F₂O₇ (s) through reactions (2) and (3). With the Al₂O₃ addition amount exceeding 8 wt.%, more CaO (s) and Fe₂SiO₄ (l) might be reacted with Al₂O₃ (s) forming CaAl₂Si₂O₈ (l) and FeO (s) through reaction (6), causing the reaction (3) to be restricted and the Ca₄Si₂F₂O₇ (s) amount decreases.

As mentioned above, the ‘F’ in the NaF could be efficiently solidified in the molten slag of FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃ in forms of CaF₂ (s) and/or Ca₄Si₂F₂O₇ (s). However, with CaO addition amount over 20 wt.%, the F solidification decreases due to the more formation of Ca₂SiO₄ (s) which restricts the formation of Ca₄Si₂F₂O₇ (s).

\[
\begin{align*}
4\text{NaF (g) + 3CaO (s) + 3SiO}_2\text{ (s) = 2CaF}_2\text{ (s) + Na}_4\text{CaSi}_3\text{O}_9} & \quad (1) \\
2\text{NaF (l) + Al}_2\text{O}_3\text{ (s) + 2SiO}_2\text{ (s) + CaO (s) = 2NaAlSiO}_4\text{ (l) + CaF}_2\text{ (s)} & \quad (2) \\
3\text{CaO (s) + 2Fe}_2\text{SiO}_4\text{ (l) + CaF}_2\text{ (s) = Ca}_4\text{Si}_2\text{F}_2\text{O}_7\text{ (s) + 4FeO (s)} & \quad (3) \\
2\text{CaO (s) + SiO}_2\text{ (s) = Ca}_2\text{SiO}_4\text{ (s)} & \quad (4) \\
2\text{FeO (s) + SiO}_2\text{ (s) = Fe}_2\text{SiO}_4\text{ (l)} & \quad (5) \\
\text{Al}_2\text{O}_3\text{ (s) + CaO (s) + 2Fe}_2\text{SiO}_4\text{ (l) = CaAl}_2\text{Si}_2\text{O}_8\text{ (l) + 4FeO (s)} & \quad (6)
\end{align*}
\]
Fig. 3 Effects of CaO, SiO$_2$ and Al$_2$O$_3$ addition amounts on the equilibrium amounts of species in the reaction system of 100 g synthesized basic slag + 8 g NaF at 1300°C

4 Results and discussion

4.1 Effects of CaO addition amount

Based on the thermodynamic analysis above, the effects of CaO addition amount ranging from 0 to 24 wt.% with an interval of 4 wt.% on the F solidification efficiency were firstly assessed under the condition of melting temperature of 1300°C, NaF amount of 10 wt.%, residence time of 60 min and N$_2$ flow rate of 40 ml/min.

In Fig. 4(a), the Fe$_2$SiO$_4$ diffraction intensity decreases with the CaO amount from 0 to 12 wt.% and disappears at CaO amount of 20 wt.% while the FeO and Ca$_4$Si$_2$F$_2$O$_7$ appear at CaO addition of 12 wt.% and increase with the CaO amount. Fig. 5 also shows that the Fe and F elements are mainly distributed in the phases of Fe$_2$SiO$_4$ and CaF$_2$ respectively with no addition of CaO, and the Ca$_4$Si$_2$F$_2$O$_7$ appears at 12 wt.% CaO added. These transformations accord well with the thermodynamic calculation results in Fig. 3(a), indicating that the reactions (1)-(3) could be carried out in the
roasting process.

More addition of CaO leads to more formation of CaF$_2$ and Ca$_3$Si$_2$F$_2$O$_7$ through reactions (1)-(3), as a result of which the F solidification efficiency ($S_F$) increases with the CaO amount from 0 to 20 wt.% as shown in Fig.4(b). However, increasing the CaO amount further to 24 wt.% the $S_F$ decreases. It might be due to the consumption of SiO$_2$ through forming Ca$_2$SiO$_4$ by reaction (4) restricts the occurrence of reactions (1)-(3) and some NaF (g) volatilizes into the gas phase as presented in reaction (7) and Fig.3(a). However, the Ca$_2$SiO$_4$ cannot be detected in the final slag according to Fig. 4 (a), the reason for which might be that it transforms to CaSiO$_3$ and Ca$_3$Si$_2$O$_7$ during the sample cooling process inferred from Fig. 6 and confirmed by Fig. 4(a). In Fig.6, during the cooling process of Ca$_2$SiO$_4$ from 1300°C to 50 °C, the Ca$_2$SiO$_4$ is decomposed and transformed to CaSiO$_3$ (“B” and “D” points), Ca$_3$Si$_2$O$_7$ (“B” and “D” points) and CaO (“C” and “E” points). To increase the F solidification efficiency, the CaO addition amount should be controlled at 20 wt.%.

NaF (l) = NaF (g)

(7)

Fig.4 (a) XRD patterns of the final slag with different CaO addition amounts; (b) Effects of CaO addition amount on the F solidification efficiency in the synthesized basic slag.
Fig. 5 (a) EPMA mappings of the final slag with no CaO addition; (b) EPMA mappings of the final slag with 12 wt.% CaO added

Fig. 6 Phase diagram of CaO-SiO$_2$ at different temperatures

4.2 Effects of NaF addition amount

Almost all the F from the NaF could be immobilized in the molten slag of FeO-
Fe₃O₄-SiO₂-CaO-Al₂O₃ as deduced from Fig.3, but the F solidification efficiency in Fig.4(b) is low around 75%. The equilibrium amounts of species for 100 g synthesized basic slag and 20 g CaO roasted with different NaF amount at 1300 °C were calculated and the results are shown in Fig.7. Fig.7 shows that with the NaF amount from 0 to 14 wt.%, almost all the F could be solidified in forms of Ca₅Si₂F₂O₇ (s) and CaF₂ (s) thermodynamically. In details, with the increase of NaF amount from 0 to 3 wt.%, the Ca₅Si₂F₂O₇ (s), Ca₃Si₂O₇ (l) and NaAlSiO₄ (l) are formed and increased accompanied by the decrease of Ca₅Al₂SiO₇ (l) and CaSiO₃ (l), which might be due to the occurrence of reaction (8). Increasing the NaF amount over 9 wt.%, some Ca₅Si₂F₂O₇ (s) can be transformed to CaF₂ (s) through reaction (9), causing the amounts of Ca₅Si₂F₂O₇ (s) and Fe₂SiO₄ (l) decrease and that of Na₄CaSi₃O₉ (l), CaF₂ (s) and FeO (s) increase. The EPMA results in Fig.8 accord well with this F transformation, in which the Ca₅Si₂F₂O₇ amount decreases and CaF₂ amount increases with the NaF amount from 8 to 10 wt.%. While the NaF amount increases over 14 wt.%, except for solidification by the synthesized basic slag, some NaF can evaporate into the gas phase through reaction (7).

The effect of NaF amount ranging from 2 to 12 wt.% on the F solidification efficiency was then experimentally researched under the conditions of melting temperature of 1300°C, CaO addition amount of 20 wt.%, residence time of 60 min and N₂ flow rate of 40 ml/min, and the results are shown in Fig.9. The increase of NaF amount promotes the formation of Ca₅Si₂F₂O₇ and CaF₂ through reactions (1)-(3), (8) and (9), as a result of which their intensities in the XRD analysis results increase with NaF amount as shown in Fig.9(a). However, the F solidification efficiency (SF) decreases greatly from 98.35% to 56.90% with the NaF amount from 6 to 12 wt.% as shown in Fig.9(b), which isn’t consistent with the thermodynamic results in Fig.7. The reason might be that some NaF have been evaporated into the gas phase before a solidification, which could be confirmed by the more formation of gas pores in the final slag at a more NaF addition as shown in Fig.10. To decrease the environmental pollution caused by the F evaporation, the NaF amount should not be higher than 6 wt.%.

![Figure 7](image1.png)

Fig. 7 Effects of NaF amount on the equilibrium amounts of species in the reaction system of 100 g synthesized basic slag + 20 g CaO at 1300°C

Ca₅Al₂SiO₇ (l) + 5CaSiO₃ (l) + 2NaF (l) =

Ca₅Si₂F₂O₇ (s) + Ca₃Si₂O₇ (l) + 2NaAlSiO₄ (l) (8)

Ca₅Si₂F₂O₇ (s) + 4NaF (l) + Fe₂SiO₄ (l) = 3CaF₂ (s) + Na₄CaSi₃O₉ (l) + 2FeO (s) (9)
Fig. 8 (a) EPMA mappings of the final slag with 20 wt.% CaO and 8 wt.% NaF addition; (b) EPMA mappings of the final slag with 20 wt.% CaO and 10 wt.% NaF addition.

Fig. 9 (a) XRD patterns of the final slag with different NaF amount; (b) Effects of NaF amount on the F solidification efficiency in the synthesized basic slag.
4.3 Effects of Al₂O₃ and SiO₂ addition amounts

In the conditions of melting temperature of 1300°C, residence time of 60 min, N₂ flow rate of 40 ml/min, CaO and NaF addition amounts of 20 wt.% and 6 wt.% respectively, the changes of F solidification efficiency with Al₂O₃ and SiO₂ amounts are shown in Fig.11(a) and (b) respectively.

![Fig.10 Apparent morphology of the final slag with NaF amount of 6 wt.% and 10 wt.% respectively](image)

**Fig.10** Apparent morphology of the final slag with NaF amount of 6 wt.% and 10 wt.% respectively

**Fig.11** Effects of Al₂O₃ (a) and SiO₂ (b) addition amounts on the F solidification efficiency in the synthesized basic slag

Fig.11(a) shows that the F solidification efficiency decreases greatly with the increase of Al₂O₃ addition amount, which differs greatly with the thermodynamic calculation results in Fig.3(b). The reason might be that some CaO are consumed through forming Ca₂Al₂SiO₇ (Fig.12(a)), and the solidification of F through forming CaF₂ and Ca₄Si₂F₂O₇ is restricted deduced from reactions (1)-(3). In Fig.12(a), compared to the phase composition of the final slag without extra Al₂O₃ addition, the Ca₂Al₂SiO₇ could be found at a Al₂O₃ addition of 8 wt.% and increases with the Al₂O₃ amount increased to 20 wt.%. Also due to the consumption of CaO by adding SiO₂ through forming Ca₂Al₂SiO₇ and CaSiO₃ (Fig.12(b)), the F solidification efficiency decreases obviously with the SiO₂ addition as shown in Fig.11(b). Fig.12(b) shows that the Ca₂Al₂SiO₇ and CaSiO₃ can be generated at a SiO₂ amount of 10 wt.% and increase with the SiO₂ addition amount. To increase the F solidification efficiency in the synthesized basic slag, the extra Al₂O₃ and SiO₂ should not be added.

Moreover, the value of leachable F in the final slag was detected via ion chromatography method and found to be 3.67 mg/L, which is far less than the national allowable emission concentration in China as shown in Table 4. It implies that the final
slag might be treated as a general solid waste.

Fig. 12 (a) XRD patterns of the final slag with Al₂O₃ addition amount of 0 wt.%, 8 wt.% and 20 wt% respectively; (b) XRD patterns of the final slag with SiO₂ addition amount of 0 wt.%, 10 wt% and 20 wt.% respectively.

Table 4 Detection of leaching toxicity of the final slag

| Sample | Final slag | National allowable emission concentration in China | Analytical approach |
|--------|------------|---------------------------------------------------|---------------------|
| F/mg·L⁻¹ | 3.67       | <100                                              | Ion chromatography  |

5 Conclusions

The results showed that the NaF could be effectively solidified in the molten slag of FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃.

The ‘F’ from NaF was mainly transformed to CaF₂ and Ca₆Si₂F₂O₇ in the slag of FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃. In a certain range, more addition of CaO led to more formation of CaF₂ and Ca₆Si₂F₂O₇, and the F solidification efficiency increased with it. However, with the CaO addition amount exceeding 20 wt.%, some SiO₂ in the synthesized basic slag would be consumed by forming CaSiO₃ and Ca₃Si₂O₇, which restricted the solidification of NaF into Ca₆Si₂F₂O₇. It caused some NaF volatilized into the gas phase and the F solidification efficiency decreased. Similarly, the addition of Al₂O₃ and SiO₂ also hindered the formation of CaF₂ and Ca₆Si₂F₂O₇ and decreased the F solidification efficiency through their priority combination with CaO forming Ca₂Al₂SiO₇ and/or CaSiO₃. Under the conditions of melting temperature of 1300°C, residence time of 60 min and N₂ flow rate of 40 ml/min, the optimum CaO and NaF amounts were found to be 20 wt.% and 6 wt.% respectively, in which the F solidification efficiency in the copper smelting slag of FeO-Fe₃O₄-SiO₂-CaO-Al₂O₃ obtained 98.35%.

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