Dissolution Behavior and Stabilization of Fluorine in Secondary Refining Slags

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(Received on January 22, 2002; accepted in final form on April 6, 2002)

Dissolution of fluorine in secondary refining and synthetic $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-(P}_2\text{O}_5\text{)}$ slags has been studied by using the shaking test and its behavior is discussed based on the results for the time dependence of Ca, Si, Al and F contents in aqueous solution. It was found that fluorine dissolution is affected by the contents of SiO_2 , F and total Fe in slag and particularly its effect is obvious in synthetic slags. The dissolved fluorine from slags with low contents of SiO_2 and total Fe can be immobilized through the incorporation of fluorine into precipitated hydrates such as $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ compound and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ gel. In the case of slags with high SiO_2 and low total Fe contents, the dissolved fluorine can be immobilized through the formation of $\text{CaO-SiO}_2\text{-H}_2\text{O-SO}_4\text{-F}$ gel by the addition of gypsum to aqueous solution. The dissolution behavior of fluorine in seawater has been also studied.

KEY WORDS: secondary refining slag; fluorine; immobilization; $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ compound; $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ gel; gypsum; $\text{CaO-SiO}_2\text{-H}_2\text{O-SO}_4\text{-F}$ gel; seawater.

1. Introduction

Fluorine-bearing mineral phases in secondary refining slags have been previously studied by using X-ray diffraction and microprobe analysis.¹⁾ It was found that fluorine is contained in calcium aluminates such as $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $12\text{CaO} \cdot (7-x)\text{Al}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ phases and is present at fluoride minerals such as $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ and $(2\text{CaO} \cdot \text{SiO}_2)_2 \cdot \text{CaF}_2$. Furthermore, the saturated value of fluorine in aqueous solution dissolved from $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ was considerably small in comparison with that from other F-containing mineral phases.¹⁾ It was shown in previous study²⁾ that fluorine dissolved from hot metal pretreatment slags can be stabilized by using secondary refining slags. In this case the fluorine immobilization process by using secondary refining slag (SR slag hereinafter) with low contents of SiO_2 and total Fe, namely high content of Al_2O_3 , proceeds rapidly, while that by using SR slags with high SiO_2 and low total Fe contents proceeds slowly. The rapid immobilization by the former SR slag is explained by the fact that F ion dissolved from hot metal slags is substituted by OH^- site in calcium aluminum hydrates such as $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH})_2 \cdot 18\text{H}_2\text{O}^{2,3)}$ precipitated during shaking test.

Hot metal pretreatment slags containing F demonstrated higher dissolution tendency in seawater, and it was found that fluorine was immobilized by the formation of $\text{Mg}(\text{OH}, \text{F})_2$.⁴⁾

In the present study the dissolution behavior of fluorine in SR and synthetic $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2(\text{P}_2\text{O}_5)$ slags has been

studied by using the shaking test and F-bearing hydration products have been identified by using X-ray diffraction and electron microprobe analysis. Furthermore, the immobilization of F in SR slags through the formation of $\text{CaO-SiO}_2\text{-SO}_4\text{-H}_2\text{O-F}$ gel has been discussed based on the results for the shaking test where gypsum is added. The dissolution behavior of fluorine in seawater is also reported.

2. Experimental

The synthetic slag of secondary refining was prepared as follows: Analytical grade CaCO_3 , SiO_2 , Al_2O_3 and CaF_2 were mixed to have the compositions of $\text{CaO/Al}_2\text{O}_3$ molar ratio=3.0, 0 to 15 mass% SiO_2 and 1.5 to 8.0 mass% F and was melted at 1550°C under Ar atmosphere in a graphite crucible. Then it was quenched rapidly using water cooled Cu mold in order to obtain glassy slag. For the preparation of slowly cooled slag, the melt was cooled to 800°C at a rate of 150°C/h, followed by quenching using water cooled Cu mold. For the slag with high SiO_2 content, P_2O_5 (1 mass%) was added to prevent the dusting of $2\text{CaO} \cdot \text{SiO}_2$ by the transformation from $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$ to $\gamma\text{-}2\text{CaO} \cdot \text{SiO}_2$.

Secondary refining and synthetic $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-(P}_2\text{O}_5\text{)}$ slags were ground to 0.5–2.0 and below 0.1 mm, and these samples were used for the shaking test. The solid sample and aqueous solution were charged in 500 ml polyethylene bottle and were shaken horizontally at a speed of 200 times per min at the solid to liquid ratio of 1/10 (g/ml). More detailed description is given elsewhere.²⁾ The seawater used in the present study was sampled from Pacific Ocean near the coast of Japan. The chemical composition of this seawater

Table 1. Chemical compositions and mineral phases containing fluorine in secondary refining slags.

SR slag	13	D	53 (53r*)	54 (54r*)	B	32	52	A	51r*	50r*	E	C
	powder					block					block	
(% F)	0.64	0.30	0.11	0.11	0.80	2.81	1.27	1.31	1.86	2.50	0.68	0.12
(% SiO ₂)	16.2	13.5	15.5	15.4	8.9	8.7	5.3	4.9	5.2	5.1	6.4	7.6
(% Al ₂ O ₃)	27.2	30.2	24.4	27.1	28.7	35.1	35.2	33.1	30.5	31.0	29.5	15.3
(% T.Fe)	0.6	1.4	1.3	2.9	0.6	0.3	1.4	1.6	0.2	2.1	5.3	14.3
11CaO·7Al ₂ O ₃ · CaF ₂	△	△	—	—	○	⊙	○	○	—	—	○	—
(2CaO·SiO ₂) ₂ ·CaF ₂	△	△	—	△	—	△	—	—	—	—	○	—
12CaO·7Al ₂ O ₃	△	△	○	○	⊙ (0-1.3)	○ (0.3-1.9)	⊙ (0-1.1)	⊙ (0-1.4)	—	—	⊙ (0-0.7)	○ (0-0.5)
12CaO·(7-x) Al ₂ O ₃ ·xFe ₂ O ₃	—	—	—	—	—	—	—	△	—	—	○ (0-0.2)	⊙ (0-0.4)
3CaO·Al ₂ O ₃	—	—	—	—	—	—	○ (0-0.4)	○ (0-0.5)	—	—	—	—
3CaO·2SiO ₂	○	○	○	○	—	—	—	—	—	—	—	—
2CaO·SiO ₂	○	○	○	○	△ (0-0.8)	△ (0-1.0)	△ (0-0.8)	△ (0-0.8)	—	—	△ (0-0.3)	△ (0-0.3)
2CaO·SiO ₂ ·Al ₂ O ₃	⊙	⊙	○	○	—	—	—	—	—	—	—	—

* rapidly quenched (glassy), amount : ⊙ > ○ > △, — not observed, (): F content in mass%.

ter sample was 0.54%Na–0.02%K–0.02%Ca–0.05%Mg–0.86%Cl–0.13%SO₄–0.00005%F in mass%.

Sampling was made with a polyethylene whole pipette of 5 ml, followed by filtration using the membrane filter (0.1 mm open pore size). The filtrate was introduced into two polycarbonate measuring flasks for analyzing the contents of F, Ca, Al, Si, S and Cl. A buffer solution (40 ml) with the composition of 0.4w/v%CyDTA–5.8w/v%NaCl–5.7v/v acetic acid was added to the sample solution for the F analysis, and 5 ml HNO₃ (1+1) was added for the Ca, Al, Si, S and Cl analysis. The F content was determined by the selective ion-electrode method (JIS-K-0101) and the contents of Ca, Al, Si and S were determined by using inductively coupled plasma (ICP) atomic emission spectrometry. The Cl content was determined by using ICP mass spectrometry. X-ray diffraction analysis and electron microprobe analysis with energy dispersive X-ray (EDX) were used for the identification of mineral phases. The correction was made by ZAF method for EDX analysis. The F content in F-containing minerals was determined by using EPMA-wavelength dispersive X-ray (WDX) spectroscopy with the help of the Bence-Albee correction method.

3. Results and Discussion

3.1. Behavior of Fluorine Dissolution

3.1.1. Dependence of Slag Composition and Cooling Rate

a) Slag Composition

The secondary refining slags whose chemical compositions and identified mineral phases containing F are given in Table 1, are classified into three groups depending on i) high SiO₂ and low T.Fe contents (SR-13, -D, -53 and -54), ii) low SiO₂ and low T.Fe contents (SR-B, -32, -52, and -A) and iii) low SiO₂ and middle or high T.Fe contents (SR-E and -C). For the slags containing high SiO₂ contents (14 to 16 mass%) no block sample could be obtained due to the dusting phenomenon of α' or β-Ca₂SiO₄ to γ-Ca₂SiO₄ in-

Fig. 1. Variation with shaking time of solute contents dissolved from conventionally cooled secondary refining slags with high SiO₂ and low T.Fe contents: grain size ≤ 0.1 mm.

version during cooling. Therefore, the particle size below 0.1 mm was used for the shaking test. Variations of F, Al and Ca contents with shaking time are shown in Figs. 1 through 3. The F contents for the slags with low SiO₂ and low T.Fe contents shown in Fig. 2 decrease more rapidly at initial time, as compared with those for the slags with high SiO₂ and low total Fe contents and those for the slags with low SiO₂ and middle or high total Fe contents shown in Figs. 1 and 3, respectively. High F content for SR-B slag in Fig. 2 can be explained by the fact that 3CaO·Al₂O₃ is not present in this slag, as given in Table 1. More details for this reason will be explain later in this section.

Fig. 2. Variation with shaking time of solute contents dissolved from conventionally cooled secondary refining slags with low SiO_2 and low T.Fe contents: grain size ≤ 0.1 mm.

Fig. 3. Variation with shaking time of solute contents dissolved from conventionally cooled secondary refining slags with low SiO_2 and middle T.Fe (SR-E) and low SiO_2 and high T.Fe (SR-C) contents: grain size ≤ 0.1 mm.

In general, the dissolution behavior of F in aqueous solution depends on the amount and size of F-containing mineral phases located at the particle surface, the solubility limit of corresponding hydrate, pH value and other aspects. However, the present results in which the F content decreases with shaking time suggest that the precipitation of F-containing hydrates on particle surface and/or in aqueous solution affects the F content, which will be described later.

Most of F dissolution curves show that the F content is high at initial period, followed by continuous decrease. However, some SR slags have the maximum (SR-C), the

Table 2. F-containing hydrates observed in the filtered residue after shaking test of SR slags.

SR slag	F-containing hydrate
high SiO_2 and low T.Fe	C-S-H-F gel, C-S-A-H-F gel $\text{C}_{1.5-2.0}\text{SH}_2\text{-F}$, $\text{C}_2\text{SH-F}$, $\text{C}_3\text{S}_2\text{H-F}$
low SiO_2 and low T.Fe	$\text{Ca}_3\text{Al}_2(\text{OH}, \text{F})_{12}$ $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH}, \text{F})_2 \cdot 18\text{H}_2\text{O}$
low SiO_2 and low T.Fe	$\text{Ca}_3(\text{Al}, \text{Fe})_2(\text{OH}, \text{F})_{12}$ $3\text{CaO} \cdot (\text{Al}, \text{Fe})_2\text{O}_3 \cdot \text{Ca}(\text{OH}, \text{F})_2 \cdot 18\text{H}_2\text{O}$
high SiO_2 and low T.Fe (with gypsum)	C-S-H- SO_4 -F gel, C-S-A-H- SO_4 -F gel $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH}, \text{F})_2$ $\text{Ca}_5(\text{SiO}_4)_2\text{SO}_4(\text{OH}, \text{F})$ $\text{Ca}_3\text{Si}(\text{SiO}_4)_2(\text{OH}, \text{F})_6 \cdot 9\text{H}_2\text{O}$
low SiO_2 and low T.Fe (with gypsum)	$\text{Ca}_6[\text{Al}(\text{OH}, \text{F})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ $\text{Ca}_4[\text{Al}(\text{OH}, \text{F})_6]_2(\text{SO}_4)_m \cdot m\text{H}_2\text{O}$ ($m = 6, 8$)
low SiO_2 and low T.Fe (with gypsum) (hydrothermal)	C-S-H- SO_4 -F gel, C-S-A-H- SO_4 -F gel $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH}, \text{F})_2$ $\text{Ca}_5(\text{SiO}_4)_2\text{SO}_4(\text{OH}, \text{F})$ $\text{Ca}_2\text{Al}_2\text{SiO}_6(\text{OH}, \text{F})_2$

C: CaO, S: SiO_2 , A: Al_2O_3 , H: H_2O .

minimum (SR-B) and both (SR-32). It can be said that the measured F content is determined as a result of the offset of the F dissolution from slag and the precipitation of F-containing hydrates. Such effect is influenced by kind of mineral phase and particle size which will be explained in Sec. 3.1.2.

The hydration products after the shaking test were identified by using XRD and EPMA for the filtered residue and the F-containing hydration products are summarized in **Table 2**. Fluorine was observed in C-S-H gel for the slags with high SiO_2 and low T.Fe contents whose main mineral phases are C_3S , C_2S and C_2AS (C, S, A and H represent CaO, SiO_2 , Al_2O_3 and H_2O , respectively). Fluorine for the slags with low SiO_2 and low T.Fe contents was stabilized in the form of $\text{Ca}_3\text{Al}_2(\text{OH}, \text{F})_{12}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH}, \text{F})_2 \cdot 18\text{H}_2\text{O}$.³⁾ These hydrates are the hydration products of C_3A and C_{12}A_7 , respectively, which are main minerals in the slags with low SiO_2 and low T.Fe contents. In the case of the slags with low SiO_2 and middle or high T.Fe contents whose main mineral phase is $12\text{CaO} \cdot 7(\text{Al}, \text{Fe})_2\text{O}_3$, fluorine was stabilized in the form of $\text{Ca}_3(\text{Al}, \text{Fe})_2(\text{OH}, \text{F})_{12}$ and/or $3\text{CaO} \cdot (\text{Al}, \text{Fe})_2\text{O}_3 \cdot \text{Ca}(\text{OH}, \text{F})_2 \cdot 18\text{H}_2\text{O}$.

It was confirmed in the previous study^{3,5)} that the degree of F immobilization through the formation of $\text{Ca}_3\text{Al}_2(\text{OH}, \text{F})_{12}$ was higher than that of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH}, \text{F})_2 \cdot 18\text{H}_2\text{O}$, and that of $\text{Ca}_3(\text{Al}, \text{Fe})_2(\text{OH}, \text{F})_{12}$ was lower than that of the aforementioned two hydrates. Furthermore, the degree of F immobilization by C-S-H gel decreases with increasing SiO_2 content in SR slags. This is due to the fact that the hydration rate of calcium aluminum silicate is lower than that of calcium aluminate. The behavior of Ca and Al contents in aqueous solution will be described in detail in Sec. 3.1.3.

The major hydrates after the shaking test by using the synthetic slags containing 5 mass% F whose analyzed compositions and mineral phases are given in **Table 3**, are shown in **Fig. 4**. The particle size is in the range between

Table 3. Chemical compositions and mineral phases of synthetic $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-(P}_2\text{O}_5\text{)}$ slags and major hydrates after shaking test.

	S-1	S-2	S-3	S-4	S-21	S-22	S-41	S-42
(% F)	5.0	5.0	5.1	5.0	2.0	8.0	1.5	8.0
(% CaO)	59.2	56.0	53.3	49.2	57.9	54.2	50.9	47.3
(% SiO ₂)	0	5.0	9.3	15.0	5.0	5.0	15.2	15.0
(% Al ₂ O ₃)	35.8	34.0	31.4	29.8	35.1	32.8	31.3	28.7
(% P ₂ O ₅)	0	0	1.0	1.0	0	0	1.1	1.0
$11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$	○	○	○	△	△	◎	—	△
$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	◎	○	△	—	○	○	—	—
$12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$	△	○	○	△	○	○	△	△
$2\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$	—	—	—	◎	—	—	◎	◎
$2\text{CaO} \cdot \text{SiO}_2$	—	△	△	○	△	△	○	○
$\text{Ca}_3\text{Al}_2(\text{OH}, \text{F})_{12}$	◎	○	○	△	○	—	△	—
$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH}, \text{F})_2 \cdot 18\text{H}_2\text{O}$	△	◎	◎	○	◎	◎	○	○

Amount : ◎ > ○ > △, — not observed.

Fig. 4. Variation with shaking time of solute contents dissolved from slowly cooled synthetic slags ($X_{\text{CaO}}/X_{\text{Al}_2\text{O}_3}=3$, (%F)=5) as a function of SiO_2 content: grain size 0.5–2 mm.

0.5 and 2 mm. Fluorine contents increase initially and then decrease. However, the start of F decrease tends to be longer with an increase of SiO_2 content at constant molar ratio of $\text{CaO}/\text{Al}_2\text{O}_3=3$. With an increase of SiO_2 content from 0 to 15 mass%, main mineral phase changes as $\text{C}_3\text{A} \rightarrow \text{C}_{12}\text{A}_7 \rightarrow \text{C}_2\text{AS}$ and main hydration product containing F changes as $\text{Ca}_3\text{Al}_2(\text{OH}, \text{F})_{12} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH}, \text{F})_2 \cdot 18\text{H}_2\text{O} \rightarrow \text{C-S-H}$ (C-S-A-H) gel. The degree of F im-

Fig. 5. Variation with shaking time of solute contents dissolved from rapidly quenched secondary refining slags with high SiO_2 and low T.Fe contents: grain size ≤ 0.1 mm.

mobilization can be explained by the hydration ability of these calcium aluminates, as observed in previous study.³⁾

b) Cooling Rate

The shaking test was carried out for rapidly cooled SR slags with high SiO_2 and low T.Fe contents and the results are shown in **Fig. 5**. It can be seen that the contents of F, Al and Ca for rapidly cooled slags decrease more in comparison with those for slowly cooled slags shown in **Fig. 1**.

The dissolution behavior of F, Al and Ca for rapidly cooled synthetic slags with 0, 5 and 15 mass% SiO_2 at constant molar ratio of $\text{CaO}/\text{Al}_2\text{O}_3=3$ are shown in **Fig. 6**. The dissolution behavior is different from that for slowly cooled synthetic slags shown in **Fig. 4**. That is, in the case of the rapidly cooled slag with 15 mass% SiO_2 , the F content remains almost unchanged and the Al content is considerably lower than that for the slowly cooled slag. The reason for the different behavior with respect to cooling rate is not clear and further study is necessary.

3.1.2. Dependence of Fluorine Content and Particle Size

a) Fluorine Content

The influence of F content in slag on dissolution behavior of F was studied for slowly cooled synthetic slags with 5 and 15 mass% SiO_2 at constant molar ratio of $\text{CaO}/\text{Al}_2\text{O}_3=3$. The results are shown in **Figs. 7 and 8**. In the case of the slags with 5 mass% SiO_2 shown in **Fig. 7**, the F dissolution behavior of the slags containing F up to 5 mass% F is nearly the same. However, in the case of the slags with 15 mass% SiO_2 shown in **Fig. 8**, the behavior of F dissolution is dependent on the F content. This may be explained by different mineral phases, as shown in **Table 3**.

b) Particle Size

Influence of particle size of SR slags with low SiO_2 and low T.Fe contents on the dissolution behavior of F, Al and Ca was studied and the results are shown in **Fig. 9**. The slag

Fig. 6. Variation with shaking time of solute contents dissolved from rapidly quenched synthetic slags ($X_{\text{CaO}}/X_{\text{Al}_2\text{O}_3}=3$, (%F)=5) as a function of SiO_2 content: grain size 0.5–2 mm.

Fig. 8. Variation with shaking time of solute contents dissolved from slowly cooled synthetic slags ($X_{\text{CaO}}/X_{\text{Al}_2\text{O}_3}=3$, (% SiO_2)=15) as a function of fluorine content: grain size 0.5–2 mm.

Fig. 7. Variation with shaking time of solute contents dissolved from slowly cooled synthetic slags ($X_{\text{CaO}}/X_{\text{Al}_2\text{O}_3}=3$, (% SiO_2)=5) as a function of fluorine content: grain size 0.5–2 mm.

Fig. 9. Effect of grain size of rapidly quenched secondary refining slag on solute contents.

dissolution occurs suddenly at initial time regardless of particle size. In the case of the slags with low SiO_2 and low T.Fe contents the dissolved F is incorporated into $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and/or $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH}, \text{F})_2 \cdot 18\text{H}_2\text{O}$, which are precipitated on the particle surface and/or in aqueous solution. This is the reason that the F content in so-

lution decreases at initial period. The increase of F content after 1 h is explained by the fact that the F dissolution rate is higher than the F incorporation rate. It is apparent that the degree of F increase for small particles is higher than that for larger particles.

Fig. 10. Relations among solute contents in solution during dissolution of secondary refining slags: grain size ≤ 0.1 mm.

3.1.3. Relations among F, Al and Ca Contents

The relations between F and Al, between F and Ca and between Al and Ca contents in aqueous solution are shown in Fig. 10 for the data shown in Fig. 1 (SR-53 and -54) and Fig. 2 (SR-52). The arrow mark represents the lapse of shaking time. It can be seen that the contents of Al and Ca increase initially to a considerable degree and then gradually decrease, as shown in the lower diagram. With decreasing the contents of Al and Ca, the F contents decrease continuously. As given in Table 1, major mineral phases for SR-52 are $C_{12}A_7$ and C_3A , and those for SR-53 and SR-54 are $C_{12}A_7$ and C_2AS . The dissolution behavior for the synthetic $C_{11}A_7 \cdot CaF_2$ compound, which is represented by solid square is in agreement with that for the SR slags, as shown in Fig. 10. It can be expected from these results that F is incorporated into C–A–H compounds during the hydration of $CaO-Al_2O_3$ mineral phases. Since the Si contents in all experiments are below 0.1 ppm, the hydration product of C–S–H gel is rapidly formed due to high hydration rate.

The relations between F and Al, between F and Ca and between Al and Ca contents in aqueous solution are shown in Fig. 11 for the data of synthetic slags shown in Fig. 4 (molar ratio of $CaO/Al_2O_3=3$, 5 mass% F, 0–10 mass% SiO_2). A trend of the observed relations between F and Al, F and Ca and Al and Ca contents is quite similar to that in Fig. 10; that is, the Al and Ca contents increase initially and then decrease along with the F content. The thick line in Fig. 11 indicates the corresponding results observed in Fig. 10. It can be seen that the final contents of Ca, Al and F converge onto this line. This experimental finding indicates that the behavior of the formation of C–A–H–F compounds

Fig. 11. Relations among solute contents in solution during dissolution of slowly cooled synthetic slags ($X_{CaO}/X_{Al_2O_3}=3$, (%F)=5): grain size 0.5–2 mm.

during the hydration of synthetic slags is in agreement with that during the hydration of SR slags.

3.1.4. Dissolution Mechanism of Fluorine

The F contents in aqueous solution obtained after 6 h shaking for SR (≤ 0.1 mm) and synthetic (0.5–2 mm) slags are plotted against the F contents in slag in the upper diagram of Fig. 12 and are plotted against $(\%CaO)/(\%SiO_2)$ weight ratio in the lower diagram. It can be seen from the upper diagram that the F content in solution decreases with decreasing the F content in synthetic slags, although the data for the SR slags do not show this trend. From the results shown in the lower diagram, it is clear that the F content in solution decreases with an increase of the $(\%CaO)/(\%SiO_2)$ ratio. This finding can be interpreted in the following. Calcium, Al and Si also dissolve to aqueous solution during the shaking time, thus resulting in the precipitation of C–A–H hydration compound, C–S–H gel and C–A–S–H gel, as given in Table 2. It was experimentally confirmed that the amount of C–A–H hydration compound increases with increasing the $(\%CaO)/(\%SiO_2)$ ratio. As a result, the F content in solution decreases with an increase of the amount of this hydrate, because fluorine is incorporated into this compound and is stabilized.³⁾ On the other hand, the amount of C–S–H and C–A–S–H gel increases with decreasing the $(\%CaO)/(\%SiO_2)$ ratio due to an increase of dissolved amount of Si from slag. However, the immobilization ability of F by these gels is much less than that by C–A–H hydration compound.⁶⁾ This is the reason that the F content in solution increases, as shown in the lower diagram. For the immobilization of F in SR slags the immobilization ability of hydration products is of great im-

Fig. 12. Relation between fluorine content in solution and its content in slags (upper diagram) and between that and CaO/SiO₂ weight ratio (lower diagram): ● SR slags ($X_{\text{CaO}}/X_{\text{Al}_2\text{O}_3}=2.6\text{--}4.7$, grain size ≤ 0.1 mm), ○ synthetic slags ($X_{\text{CaO}}/X_{\text{Al}_2\text{O}_3}=3$, grain size 0.5–2 mm).

portance because not only the F dissolution occurs, but also the F incorporation by precipitation occurs simultaneously during the shaking test.

3.2. Stabilization of Fluorine

It was found that fluorine in the slags with low SiO₂ and low T.Fe contents whose mineral phases are C₃A and C₁₂A₇ are stabilized in the precipitation of Ca₃Al₂(OH, F)₁₂ and 3CaO·Al₂O₃·Ca(OH, F)₂·18H₂O, as shown in Table 2. Fluorine in the slags with high SiO₂ and low T.Fe contents is immobilized mainly by C–S–H–F gel, but the degree of F immobilization is not satisfactory. Therefore, the gypsum addition and hydrothermal treatment were made in order to stabilize F in the slags with high SiO₂ and low T.Fe contents.

3.2.1. Gypsum Addition

Gypsum was added to the solution containing the SR slags with high SiO₂ and low T.Fe contents (SR-D) or with low SiO₂ and low T.Fe contents (SR-52) at the ratio of slag/gypsum=1/4 in weight. The results for these slags are shown in Figs. 13 and 14, respectively. It can be seen from the results shown in Fig. 13 that the addition of gypsum to the slags with high SiO₂ and low T.Fe contents is very effective to the F immobilization by the formation of C–S–H–SO₄–F gel and other hydration products given in Table 2. These hydration products were identified by XRD and EPMA-WDX for the filtered residue after the shaking test. However, the addition of gypsum to the solution containing the SR slag with low SiO₂ and low T.Fe contents whose major mineral phases are C₃A and C₁₂A₇, has an adverse effect on F immobilization, as shown in Fig. 14. This is due to the fact that SO₄²⁻ ion in solution reacts with C₃A and C₁₂A₇ phases on the particle surface, leading to the formation of ettringite (3CaO·Al₂O₃·3Ca(SO₄, F)₂·32H₂O) and monosulfates (3CaO·Al₂O₃·Ca(SO₄, F)₂·12H₂O and

Fig. 13. Variation with shaking time of F content in solution dissolved from the mixture of secondary refining slag with high SiO₂ and low T.Fe contents (grain size ≤ 0.1 mm) and gypsum, and that after hydrothermal treatment.

Fig. 14. Variation with shaking time of F content in solution dissolved from the mixture of secondary refining slag with low SiO₂ and low T.Fe contents (grain size ≤ 0.1 mm) and gypsum.

3CaO·Al₂O₃·Ca(SO₄, F)₂·14H₂O). This protective reaction layer prevents the continuous dissolution of Al and Ca from SR slag surface, which contributes to the F immobilization by precipitation of C–A–H hydrate. The behavior that low content of F at initial period, followed by an increase of F

Fig. 15. Variation with shaking time of solute contents in seawater dissolved from conventionally cooled secondary refining slag with high SiO_2 and low T.Fe contents: grain size ≤ 0.1 mm.

content, as shown in the upper diagram of Fig. 14, can be explained by the behavior of sulfur content in solution. The decrease of F content after 24 h is explained by peeling-off of the ettringite layer on particles, which prevents the F immobilization.

3.2.2. Hydrothermal Treatment

The mixture of slag containing high SiO_2 and low T.Fe slag with gypsum (4:1 in weight) was pressed (200 kg/mm²) and treated hydrothermally at 80°C for 3 h, followed by crushing under 0.1 mm. The results for the shaking test are shown by plus marks in Fig. 13. It can be seen that the F content is extremely low at initial time, but starts to gradually increase after 6 h. The XRD and EPMA-WDX analysis for the filtered residue after the hydrothermal treatment reveals that major hydration products are C-S-H-SO₄-F gel and C-S-A-H-SO₄-F gel, and minor ones are $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH}, \text{F})_2$, $\text{Ca}_5(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH}, \text{F})$ and $\text{Ca}_2\text{Al}_2\text{SiO}_6(\text{OH}, \text{F})_2$, as listed in Table 2. These hydration products except for $\text{Ca}_2\text{Al}_2\text{SiO}_6(\text{OH}, \text{F})_2$ are also identified for the filtered residue obtained after the shaking test in the mixture of SR slag and gypsum without hydrothermal treatment. It is clear from these results that C₂AS is easily hydrated under the hydrothermal condition.

3.3. Dissolution Behavior in Seawater

Dissolution behavior in seawater has been studied by using the SR slag (SR-D, ≤ 0.1 mm) with high SiO_2 and low T.Fe contents. The solute contents are plotted against shaking time in Fig. 15 together with those obtained in distilled water in shaking test. The Si content was found to be below the analytical limit. The hydration products, which were

identified by XRD, EPMA-EDX and EPMA-WDX for the filtered residue after the shaking test, are $\text{Mg}(\text{OH}, \text{F})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, $\text{C}_3\text{A} \cdot \text{Ca}(\text{Cl}_{1-x}\text{F}_x)_2 \cdot 10\text{H}_2\text{O}$ ($x=0-0.4$), C-S-H-Cl-F gel ($\text{Cl}=0-3\%$, $\text{F}=0-0.4\%$) and hydration products without containing F such as $\text{Mg}_5\text{Al}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_m$ ($m=1, 8$) and $\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 3\text{H}_2\text{O}$.

On the basis of these hydration products and the solute behavior shown in Fig. 15, the fluorine dissolution mechanism from SR slag in seawater can be explained as follows: Rapid decrease of F, Mg and Cl contents at initial time suggests that F is immobilized in the form of $\text{Mg}(\text{OH}, \text{F})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. Furthermore in this period the Ca content increases and the Al content remains almost zero, suggesting the precipitation of $\text{Mg}_5\text{Al}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_m$. From the results that the Ca content starts to decrease after the Mg content becomes almost zero at 2 h shaking time, it is considered that the precipitation of $\text{C}_3\text{A} \cdot \text{Ca}(\text{Cl}_{1-x}\text{F}_x)_2 \cdot 10\text{H}_2\text{O}$ and $\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 3\text{H}_2\text{O}$ occurs. However, due to low degree of F stabilization by these hydrates the F content starts to increase. The Al content increases and the Ca content decreases with increasing shaking time in the range above 6 h. This finding reveals that F cannot be stabilized because main precipitate is $\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 3\text{H}_2\text{O}$ which does not incorporate F. Although C-S-H-Cl-F gel is formed as a result of Si dissolution from SR slag, the stabilization ability of this gel is lower than that of C-S-H-SO₄-F gel.⁷⁾ Therefore, the F stabilization by this gel is considered to be small.

4. Conclusions

The dissolution behavior of fluorine in secondary refining and synthetic $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(P}_2\text{O}_5\text{)}$ slags has been studied and the immobilization of F through the formation of $\text{CaO-SiO}_2\text{-H}_2\text{O-SO}_4\text{-F}$ gel has been proposed by the addition of gypsum. The main results obtained are summarized in the following.

(1) The F content dissolved from secondary refining slags decreases with decreasing the contents of SiO_2 and F in slag due to the incorporation of F into $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ compounds precipitated in aqueous solution.

(2) For the slags containing low SiO_2 and high total Fe content where the amount of $12\text{CaO} \cdot (7-x)\text{Al}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ phase is large, the F content in solution decreases with shaking time after reaching the maximum due to slow precipitation process of $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-H}_2\text{O}$ compound containing F.

(3) For the slags containing high SiO_2 and low total Fe contents the F content in solution decreases slowly with shaking time through the incorporation of F into $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ gel.

(4) When gypsum is added to the solution containing the slags with high SiO_2 and low total Fe contents, the F content in solution decreases considerably with shaking time due to the formation of $\text{CaO-SiO}_2\text{-SO}_4\text{-H}_2\text{O-F}$ gel.

(5) When gypsum is added to the solution containing the slags with low SiO_2 and low total Fe contents, ettringite and monosulfate are formed on slag particle surface which retards the precipitation of F-containing compounds in solution.

(6) Fluorine dissolved from SR slag to seawater is sta-

bilized through the precipitation of $\text{Mg}(\text{OH}, \text{F})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}$.

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