In previous study, fluorine in hot metal pretreatment slags was found to be immobilized through the formation of Ca₃Al₂(OH, F)₁₂ (cubic hydrate) by the addition of 3CaO · Al₂O₃ or secondary refining slag (SR slag, hereinafter), which contains 3CaO · Al₂O₃ as a mineral phase, to aqueous solution in shaking test. Furthermore, in the case of SR slags with middle content of SiO₂ and low content of total Fe whose mineral phase is 12CaO · Al₂O₃, fluorine can be immobilized in aqueous solution by the precipitation of AFm (tricalcium aluminate ferrite · mono-sulfate (-hydroxide, etc.) hydrate) phase such as 3CaO · Al₂O₃ · Ca(OH, F)₂ · 18H₂O. In the shaking test where hot metal pretreatment slag (HM slag, hereinafter) is mixed with 3CaO · SiO₂, fluorine is stabilized in the form of C–S–H–F gel (C₃H₁₁₀₀₅CaO, S₃H₁₁₀₀₅SiO₂ and H₂H₁). It was found that fluorine is immobilized by hydrothermally treating the mixture of hot metal pretreatment slag, secondary refining slag with high SiO₂ and low total Fe contents and gypsum at 80°C for 3 h.

KEY WORDS: fluorine; immobilization; gypsum; calcium aluminate; calcium silicate; calcium aluminum silicate; secondary refining slag; C–S–H–SO₄ gel; hydrothermal treatment.

Immobilization of fluorine by using calcium aluminate, calcium silicate, calcium aluminum silicate and secondary refining slag as a stabilizing agent has been studied by focusing on the effect of gypsum addition on fluorine dissolution from hot metal pretreatment slags in shaking test. When gypsum is added to aqueous solution in which calcium aluminate or secondary refining slag with low contents of both SiO₂ and total Fe are present, fluorine immobilization does not occur due to the formation of ettringite and monosulfate on particle surface of added stabilizing agent. In the case of the mixture of calcium silicate and gypsum, calcium aluminum silicate or secondary refining slag with high SiO₂ and low total Fe contents, fluorine ion in solution can be immobilized through the formation of C–S–H–F–SO₄ gel, Ca₁₀(SiO₄)₃(SO₄)₃(OH, F)₂ and Ca₅[(Si, S)O₄]₃(OH, F).

It is well known that the composition of C–S–H gel prepared by hydrothermal treatment depends on temperature. On the basis of aforementioned experimental findings, hydrothermal treatment by incorporating fluorine into hydration products seems to be one of the most potential methods for solid waste treatment. In the present study the immobilization of fluorine in HM slags has been first investigated by incorporating fluorine into AFt, AFm phases and C–S–H gel containing SO₄²⁻ and the results for the effect of hydrothermal treatment on fluorine stabilization are reported.

1. Introduction

In previous study, fluorine in hot metal pretreatment slags was found to be immobilized through the formation of Ca₃Al₂(OH,F)₁₂ (cubic hydrate) by the addition of 3CaO · Al₂O₃ or secondary refining slag (SR slag, hereinafter), which contains 3CaO · Al₂O₃ as a mineral phase, to aqueous solution in shaking test. Furthermore, in the case of SR slags with middle content of SiO₂ and low content of total Fe whose mineral phase is 12CaO · Al₂O₃, fluorine can be immobilized in aqueous solution by the precipitation of AFm (tricalcium aluminate ferrite · mono-sulfate (-hydroxide, etc.) hydrate) phase such as 3CaO · Al₂O₃ · Ca(OH, F)₂ · 18H₂O. In the shaking test where hot metal pretreatment slag (HM slag, hereinafter) is mixed with 3CaO · SiO₂, fluorine is stabilized in the form of C–S–H–F gel (C₃H₁₁₀₀₅CaO, S₃H₁₁₀₀₅SiO₂ and H₂H₁). It was expected that fluorine in HM slags can be stabilized through AFt (tricalcium aluminate ferrite · tri-sulfate (-hydroxide, etc.) hydrate) phase such as 3CaO · Al₂O₃ · 3CaSO₄ · 3H₂O (ettringite), AFm phase such as monosulfate and C–S–H–SO₄ gel. It is well established that hydration reaction depends on temperature, pressure, concentration of reactants, pH value and in particular depends strongly on temperature. In our previous study, in which the mixture of heavy metal compound and iron- and steelmaking slags is treated in autoclave, the stabilization of heavy metal is dependent on hydrothermal treatment temperature. Moreover, it is well known that the composition of C–S–H gel prepared by hydrothermal treatment depends on temperature.

On the basis of aforementioned experimental findings, hydrothermal treatment by incorporating fluorine into hydration products seems to be one of the most potential methods for solid waste treatment. In the present study the immobilization of fluorine in HM slags has been first investigated by incorporating fluorine into AFt, AFm phases and C–S–H gel containing SO₄²⁻ and the results for the effect of hydrothermal treatment on fluorine stabilization are reported.

2. Experimental

The chemical compositions and mineral phases for hot metal pretreatment (HM slag-51, S, L, U, D) and secondary refining (SR slag-A, C, D) slags are listed in Table 1, which were already given in previously cited articles. The compositions of blast furnace (BF, hereinafter), water granulated blast furnace (w.g.BF, hereinafter) and basic oxygen furnace (BOF, hereinafter) slags are 41%CaO–33%SiO₂–14%Al₂O₃–0.1%F, 43%CaO–33%SiO₂–15%Al₂O₃–0.1%F and 42%CaO–10%SiO₂–19%Fe–9%MgO–0.2%F in mass%, respectively.

The preparation methods for synthetic compounds in CaO–Al₂O₃ and CaO–SiO₂ systems and 2CaO · SiO₂ · Al₂O₃ are described in detail elsewhere. The hydrothermal treatment was carried out by the following procedure: HM, SR, BF or w.g.BF slags were ground to powders below 0.1 mm.
The synthetic compounds or slags and gypsum (CaSO$_4$·2H$_2$O) were mixed in an appropriate proportion and were pressed in cylindrical shape at 40 to 200 kg/cm$^2$. Thereafter, the pressed sample was enclosed in a glass bottle in which distilled water was contained in proper amount. A glass bottle containing a sample was capped and was put into autoclave (120°C) or airbath (80°C), followed by hydrothermal treatment for 3 to 6 h. Then, a sample was dried at room temperature for 12 h, followed by grinding to powders below 0.1 mm.

In order to evaluate the fluorine contamination dissolved from steelmaking slag, which is reused as road construction materials or subjected to landfill, to the groundwater, a shaking test is considered to be useful. The shaking test was carried out at room temperature according to the method described in previous article, which is basically followed by the Japanese standard test procedure (codified as Environment Agency Notice 46). The solid sample and aqueous solution were charged in 500 ml polyethylene bottle and were shaking horizontally at a speed of 200 times per min at the solid to liquid ratio of 1/10 (g/ml).

X-ray diffraction analysis and electron microprobe analysis were used for the identification of mineral phases. More details concerning the shaking test, identification of mineral phases after shaking test and chemical analysis are explained in previous articles.

3. Results and Discussion

3.1. Gypsum Addition

3.1.1. Calcium Aluminate, Calcium Silicate and Calcium Aluminum Silicate

a) Calcium Aluminate (C$_3$A, C$_{12}$A$_7$, and CA)

The shaking test was carried out by mixing HM slag (HM slag-51, (%CaO)/(%SiO$_2$)=1.67, (%F)=1.9, 0.5–2.0 mm), calcium aluminate (C$_3$A, C$_{12}$A$_7$, and CA, A=Al$_2$O$_3$, ≤0.1 mm) and gypsum (≤0.1 mm) at the weight ratio of 3.0 : 1.4 : 0.6. The results are shown in Fig. 1, along with those for the mixture of HM slag and calcium aluminate at the weight ratio of 3 : 2 which are already reported in previous article. The F content decreases considerably in the case of the mixture of HM slag and C$_3$A, as shown in Fig.
This has been already explained by the formation of Ca₃Al₂(OH)₁₂ on C₃A particles and/or in aqueous solution into which F is substituted. However, the mixture of C₃A and gypsum has an adverse effect on the F immobilization due to the formation of ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) on C₃A particle surface which prevents the continuous dissolution of Ca and Al. As a result, dissolved F in aqueous solution cannot be immobilized through the formation of Ca₃Al₂(OH,F)₁₂ phase.

The degree of F immobilization by C₃A, C₁₂A₇, and CA decreases in the order of C₃A>C₁₂A₇>CA, although the F contents at initial period are nearly the same. The F contents for C₁₂A₇ and CA decrease initially and then increase with shaking time. This different behavior of F dissolution is attributed to the formation of different hydration products of C–A–H–F, as described in previous article. The addition of gypsum to C₁₂A₇ and CA does not improve the F immobilization, although the F contents at initial time are smaller than those for C₁₂A₇ and CA, as shown in Figs. 1(b) and 1(c).

The contents of Al, Ca and S for the mixture of HM slag-51, calcium aluminate and gypsum are plotted against shaking time in Fig. 2. It is seen in the case of C₃A that the Al content is nearly zero and the S content keeps high level of about 400 mass ppm. Ettringite and monosulfate (3CaO·Al₂O₃·CaSO₄·12H₂O) containing F were identified by XRD and EPMA-WDX for the filtered residue after shaking test. These results suggest that ettringite and monosulfate were formed on C₃A particle from the beginning of shaking test, thus leading to the prevention of dissolution of Ca and Al from C₃A particles. This phenomenon is called as the ‘cement bacillus’, which has a delaying effect on cement solidification. This is the reason that the F content for the mixture of C₃A and gypsum is high from the beginning.

In the case of C₁₂A₇ and CA, the F content which is initially very low, increases rapidly on logarithmic scale after the S content reaches zero, and the contents of Al and Ca reach the maximum values. It follows from these results that at the initial period ettringite and monosulfate moderately precipitate in aqueous solution due to slow dissolution of C₁₂A₇ and CA. This results in the F incorporation by these hydration minerals. However, since these hydration products are formed on the surface of calcium aluminate particles, the dissolution of Ca and Al is retarded, thus leading to the increase of F content. The hydration products on film filter after shaking test were analyzed by XRD and EPMA-WDX and the results are summarized in Table 2.

**Table 2.** Hydration products observed after shaking test for the mixture of HM slag, various stabilizing agent and gypsum.

| Stabilizing agent | C₃A (or SR-A) + Gyp. | C₁₂A₇ (or SR-B) + Gyp. | CA + Gyp. | SR-C + Gyp. | C₃S + Gyp. | C₃S + Gyp. | C₃AS (or SR-D) + Gyp. | SR-D + Gyp. | BF + Gyp. | w.g.BF + Gyp. |
|------------------|----------------------|------------------------|----------|-------------|-----------|-----------|----------------------|-------------|---------|---------------|
| Ettringite        |                      |                        |          |             |           |           |                      |             |         |               |
| C₆A·3CaSO₄·F₂·32H₂O |                      |                        |          |             |           |           |                      |             |         |               |
| Ettringite        |                      |                        |          |             |           |           |                      |             |         |               |
| C₆A·3CaSO₄·F₂·32H₂O |                      |                        |          |             |           |           |                      |             |         |               |
| Monosulfate       |                      |                        |          |             |           |           |                      |             |         |               |
| C₆A·CaSO₄·F₂·12H₂O |                      |                        |          |             |           |           |                      |             |         |               |
| Monosulfate       |                      |                        |          |             |           |           |                      |             |         |               |
| C₆A·CaSO₄·F₂·14H₂O |                      |                        |          |             |           |           |                      |             |         |               |
| Hydroxy-Aluminosilicate |                  |                        |          |             |           |           |                      |             |         |               |
| Ca₆(SiO₄)₂(OH)₂(H₂O) · F₂ |                  |                        |          |             |           |           |                      |             |         |               |
| C₆A(Si₂O₇)(OH,F)₂ |                      |                        |          |             |           |           |                      |             |         |               |
| C₆A·S·H·SO₄·F gelp |                      |                        |          |             |           |           |                      |             |         |               |
| Reinhardtsmite, fluorspar |            |                        |          |             |           |           |                      |             |         |               |
| Ce₆(SiO₄)₂(OH,F)₂ |                      |                        |          |             |           |           |                      |             |         |               |
| Hiltebrandite |                      |                        |          |             |           |           |                      |             |         |               |
| Ca₆SiO₇(OH,F)₂ |                      |                        |          |             |           |           |                      |             |         |               |
| C₆A·S·H·F gelp |                      |                        |          |             |           |           |                      |             |         |               |
| C₆A(Si₂O₇)(OH,F)₂ |                      |                        |          |             |           |           |                      |             |         |               |
| C₆A·S·A·H·F gelp |                      |                        |          |             |           |           |                      |             |         |               |

C = CaO, A = Al₂O₃, S = SiO₂, F = F₂O₅, SR = secondary refining slag, Gyp. = gypsum, w.g.BF = water granulated blast furnace slag.

* hydrothermally treated (80°C, 3 h), amount: ⊡ ⊠ ⊢, not observed
In order to study the F immobilization through the formation of ettringite, the shaking test was made by using the mixture of HM slag-U (\(\%\text{CaO}/\%\text{SiO}_2=3.57, \%\text{F}=7.1, 0.5–2.0 \text{ mm}\)), Ca(OH)\(_2\) and Al\(_2\)(SO\(_4\))\(_x\) \(\cdot\) \(x\)H\(_2\)O at weight ratio of 15 : 4 : 6 or 20 : 2 : 3. The Ca(OH)\(_2\)/Al\(_2\)(SO\(_4\))\(_x\) \(\cdot\) \(x\)H\(_2\)O weight ratio corresponds to the stoichiometric Ca/Al ratio in ettringite and in this case the corresponding HM slag/ettringite ratio in weight percent is 15/11 or 20/5.6. The results for the mixture of calcium hydrate and aluminum sulfate and synthetic ettringite are shown in Fig. 3. As is clear in Fig. 3 showing an increase of F content with shaking time, the amount of precipitated ettringite is large. The result that the contents of Al and S decreased rapidly at the initial period indicates that the reaction rate of ettringite formation is fast, namely, fluorine is rapidly substituted into the SO\(_4\)\(^2-\) site of ettringite during precipitation.\(^{14}\) From the results for the mixture of HM slag and ettringite, it is said that dissolved F in aqueous solution incorporates into ettringite to some extent, but its degree is much less than that observed during the formation of ettringite.

b) Calcium Silicate (C\(_3\)S and C\(_2\)S)

The shaking test was made by using the mixture of HM slag-51, calcium silicate (C\(_3\)S and C\(_2\)S) and gypsum at weight ratio of 3.0 : 1.4 : 0.6. The results shown in Fig. 4 reveal that the addition of gypsum to C\(_3\)S or C\(_2\)S improves the F immobilization compared with those for the mixture of HM slag-51 and calcium silicate,\(^1\) and its degree by C\(_3\)S (Fig. 4(a)) is higher than that by C\(_2\)S (Fig. 4(b)). The hydration products analyzed by XRD and EPMA-WDX for the filtered residue obtained at 36 h are summarized in Table 2. The improvement of F immobilization in the case of calcium silicates may be explained as follows: The main hydration products formed on C\(_3\)S or C\(_2\)S particle surface is C–S–H–SO\(_4\)–F gel and this gel layer is easy to detach from the particle surface. Then, fresh surface of C\(_3\)S or C\(_2\)S particles can continuously react with F\(^-\) and SO\(_4\)\(^{2-}\) ions in solution. This is the reason why the F immobilization by calcium silicates occurs more effectively in comparison with that by calcium aluminates.

The F immobilization can be expected by the addition of gypsum to HM slag, since main mineral phase of HM slag is C\(_2\)S. The results for shaking test are shown in Fig. 5, along with the results for the mixture of HM slag, C\(_2\)S and gypsum. It can be seen that the degree of F immobilization is very low compared with that for the mixture of HM slag, C\(_2\)S and gypsum. The reason for this can be explained as follows: It was found in mineralogical study for HM slag that main mineral phase of C\(_2\)S contains 0.2 to 8 mass% CaF\(_2\). The F content in aqueous solution is determined by the offset of the incorporation rate of F in C–S–H–SO\(_4\)–F gel and the F dissolution rate from the C\(_2\)S–CaF\(_2\) solid solution phase. As a result of dissolution of this solid solution on the particle surface of HM slag, the F content increases. On the other hand, the precipitation of C–S–H–SO\(_4\)–F gel on particle surface and/or in solution decreases the F content. It should be noted that in addition to the C\(_2\)S–CaF\(_2\) solid solution phase which contains 1 to 6 mass% CaF\(_2\), fluorine-bearing mineral phases in HM slag are CaF\(_2\), Ca\(_2\)(PO\(_4\))\(_3\), 3CaO·2SiO\(_2\); CaF\(_2\), (2CaO·SiO\(_2\))\(_2\); Ca\(_5\)F\(_2\) (0.5–12 mass% F).\(^{11}\) Therefore, the F content in solution is also affected by the dissolution from these minerals existing on particle surface of HM slag.
c) Calcium Aluminum Silicate

The results for shaking test obtained by using the mixture of HM slag, C\textsubscript{2}AS and gypsum are shown in Fig. 6. The degree of F immobilization is nearly the same as that for the mixture of HM slag, C\textsubscript{3}S and gypsum. The hydration products after shaking test are given in Table 2. These hydration products correspond to those for the mixture of HM slag, C\textsubscript{3}S and gypsum and that of HM slag, C\textsubscript{2}A and gypsum. In the case of mixture of HM slag, C\textsubscript{3}S and gypsum the hydration products containing SO\textsubscript{4}\textsuperscript{2-} radical are C–S–H–F–SO\textsubscript{4} gel, Ca\textsubscript{10}(SiO\textsubscript{4})\textsubscript{3}(SO\textsubscript{4})\textsubscript{3}(OH, F)\textsubscript{2} and Ca\textsubscript{5}[(Si, S)O\textsubscript{4}]\textsubscript{3}(OH, F), and in the case of mixture of HM slag, C\textsubscript{2}A and gypsum they are ettringite and monosulfate.

3.1.2. Secondary Refining Slag

SR slag (SR-D) with high SiO\textsubscript{2} (13.5 mass\%) and low T.Fe (1.4 mass\%) contents whose major mineral phases were C\textsubscript{2}AS, C\textsubscript{3}S and C\textsubscript{2}S, was used for the F immobilization in HM slags. The results for shaking test by using the mixture of HM slag-L (\%CaO)/\%SiO\textsubscript{2} = 2.0, \%F = 3.5, 0.5–2.0 mm), SR slag-D (\%SiO\textsubscript{2} = 0.1 mm) and gypsum at weight ratio of 3.0 : 1.4 : 0.6 and 4.0 : 0.85 : 0.15 are shown in Fig. 7(a), along with the results\textsuperscript{11} without gypsum addition. It is apparent that the addition of gypsum to SR slag has a significant effect on the F immobilization. The major hydration product was C–S–H–F–SO\textsubscript{4} gel and other hydration products are summarized in Table 2. Figure 7(b) shows the results for the addition of gypsum to HM slag and SR slag whose particle size is below 0.1 mm. In comparison with the behavior of F dissolution for the mixture of HM slag and SR slag, the F content for the mixture with gypsum decreases considerably at initial period and then gradually increases with shaking time. It is clear from the results shown in Fig. 6 that the favorable effect of gypsum addition is attributed to the C–S–H–SO\textsubscript{4}–F gel formed by the hydration of C\textsubscript{2}AS, C\textsubscript{3}S and C\textsubscript{2}S phases, which are the major mineral phases in SR slags with high SiO\textsubscript{2} and low T.Fe contents.

The results for the shaking test of SR slag with low SiO\textsubscript{2} and low T.Fe contents whose major phase is C\textsubscript{2}A are shown in Fig. 8(a), along with the results\textsuperscript{13} without gypsum addition. Although the F content at initial time is considerably low, it increases to the higher value than that for HM slag only in the range of shaking time longer than 6 h. Unfavorable effect of gypsum addition to this SR slag is explained by the fact that ettringite and monosulfate are formed on the particle surface of SR slags. This effect is observed for C\textsubscript{2}A particles shown in Fig. 1.

The results for SR slags with low SiO\textsubscript{2} and high T.Fe contents whose major mineral phases are 20CaO·Al\textsubscript{2}O\textsubscript{3}, 3MgO·SiO\textsubscript{2} and 12CaO·7(Al, Fe)\textsubscript{2}O\textsubscript{3} are shown in Fig. 8(b). Ettringite and monosulfate were identified as major hydration products by using XRD and EPMA-EDX. Since the hydration rate of 12CaO·7(Al, Fe)\textsubscript{2}O\textsubscript{3} is smaller than that of C\textsubscript{2}A or C\textsubscript{12}A\textsubscript{7,14,15}, ettringite and monosulfate are gradually precipitated in aqueous solution compared with
the case for C$_3$A or C$_{12}$A$_7$. Consequently, the formation of F-containing compound occurs effectively even in the case of SR slag with low SiO$_2$ content if the T.Fe content is reasonably high.

3.1.3. BF Slag, BOF Slag and Cement

a) BF Slag

The mixture of HM slag, BF slag and gypsum was used to immobilize F in HM slag. The major phases for BF slag are 2CaO·Al$_2$O$_3$·SiO$_2$, 2CaO·MgO·2SiO$_2$ and 2CaO·SiO$_2$. The F contents are plotted against shaking time for the mixtures of HM slag-51 (0.5–2.0 mm), BF slag (0.5–2.0 mm) and gypsum at weight ratio of 3.0:1.7:0.3 and 1.0:3.4:0.6 in Fig. 9(a), together with the results of the mixture of HM slag and BF slag at weight ratio of 1:4. It is clear that the F immobilization becomes favorable with an increase of the amount of BF slag and gypsum against the amount of HM slag. The effect of particle size of BF slag (≤0.1 mm) on the F dissolution was studied and the results are shown in Fig. 9(b), indicating that the degree of F immobilization is slightly improved.

The results obtained by w.g.BF slag (≤0.1 mm) are compared with those by conventionally cooled BF slag in Fig. 9(c). It is seen that the former is less effective to the F immobilization. The hydration products are given in Table 2.

b) BOF Slag

Main mineral phase of BOF slag is C$_2$S, and C$_3$S is observed in the case of high CaO/SiO$_2$ ratio. The F immobilization using the mixture of HM slag-51 (0.5–2.0 mm), BOF slag (≤0.1 mm) and gypsum was studied and the results of the shaking test are shown in Fig. 10, in which the results for the mixture of HM slag, BF slag and gypsum are included for comparison. The slightly higher degree of F immobilization than that for the mixture of HM slag, BF slag and gypsum can be explained by the favorable condition for the formation of the C–S–H–F–SO$_4$ gel. This is supported by the results that the contents of Ca and S are considerably smaller than those by the mixture of HM slag, BF slag and gypsum, as shown in Figs. 9(b) and 9(c).

c) Cement

The effect of portland cement whose major phases are C$_3$S and C$_2$S$^8$ on F immobilization was studied in the previous article. In the present study, portland cement is mixed with HM slag and gypsum. The results are shown in Fig. 11. It can be seen that the degree of F immobilization is improved by the addition of gypsum. This is due to the acceleration of the formation of C–S–H–F–SO$_4$ gel on the surface of C$_3$S or C$_2$S particle and/or in aqueous solution, similar to the results shown in Fig. 4.

3.2. Hydrothermal Treatment

3.2.1. HM Slag

In order to accelerate the incorporation of fluoride in AFI and AFm phases and C–S–H–SO$_4$ gel and to produce rapidly harmless materials for construction, the effect of hy-
drothermal treatment was examined.

The HM slag-D (≤0.1 mm) was hydrothermally treated at 120°C for 6 h by the method described in Sec. 2. The results for shaking test are shown in Fig. 12 by open circles. It is seen that the F immobilization occurs and the Ca content is about two times higher than that without hydrothermal treatment. A similar trend is observed in the hydrothermally treated mixture of HM slag-D (≤0.1 mm) and BF slag (≤0.1 mm) whose results are shown by cross marks. The decrease of F content can be explained as follows: From XRD and EPMA analyses of the samples after the hydrothermal treatment, it was observed that fluorine incorporated into C–S–H gel. It was found that fluorine was also stabilized by the precipitation of CaF$_2$ because CaF$_2$ was confirmed from the XRD analysis of the filtered residue after shaking test.

3.2.2. HM Slag and 3CaO·Al$_2$O$_3$

The HM slag-D (≤0.1 mm) mixed with C$_3$A (≤0.1 mm) in weight ratio of 3 : 2 was pressed (200 kg/cm$^2$) and was hydrothermally treated at 120°C for 3 h. This sample ground to powders below 0.1 mm was used for the shaking test. As shown in Fig. 13, the hydrothermal treatment has an adverse effect on F immobilization. The F contents in Ca$_3$Al$_2$(OH)$_12$ and 3CaO·Al$_2$O$_3$·Ca(OH)$_2$·18H$_2$O of the filtered residue after shaking test were much lower than those obtained without hydrothermal treatment. This is due to the fact that once C$_3$A is hydrated during the hydrothermal treatment, the hydration product of C–A–H does not contribute to the F immobilization during shaking test.

3.2.3. HM Slag, SR Slag and Gypsum

The mixture of HM slag-S (%CaO)/(%SiO$_2$) = 1.99, (%F) = 3.2, ≤0.1 mm), SR slag-D (≤0.1 mm) with high SiO$_2$ and low T.Fe contents and gypsum in weight ratio of 3.0 : 1.4 : 0.6 was pressed and was hydrothermally treated at 80°C for 3 h. This sample ground to powders below 0.1 mm was used for shaking test and the results are shown in Fig. 14. It can be seen that the F content is extremely low from the beginning of shaking test in comparison with that observed without hydrothermal treatment. This is due to the fact that hydration products containing SO$_4^{2-}$ radical after hydrothermal treatment are C–S–H–F–SO$_4$ gel, Ca$_{10}$(SiO$_4$)$_3$(SO$_4$)$_3$(OH, F)$_2$ and Ca$_5$(Si, S)O$_4$(OH, F), which are the same as those observed after shaking test for the sample without hydrothermal treatment, as given in Table 2.

3.2.4. HM Slag, SR Slag, BF Slag and Gypsum

Using the hydrothermally treated mixture of HM slag-S, SR slag-D, BF slag, w.g.BF slag and gypsum with various mixing ratios, the shaking test was carried out and the results are shown in Fig. 15. Although the initial F contents in these mixtures are not low, the F contents decrease suddenly at initial period of shaking test and remain at very low level for the mixtures containing large amount of SR slag and gypsum against the amount of HM slag.

4. Conclusions

The F immobilization in HM slag by the formation of AFm, AFt and C–S–H gel containing SO$_4^{2-}$ ion has been studied by adding gypsum to aqueous solution in which calcium aluminate, calcium silicate, calcium aluminum silicate and SR slag are present in shaking test. The effect of hydrothermal treatment on F immobilization is also studied. The following conclusions are summarized.

(1) Fluorine ions dissolved from HM slag are stabilized by the formation of ettringite when Ca(OH)$_2$ and Al$_2$(SO$_4$)$_3$...
are added in stoichiometric ratio for ettringite to aqueous solution in shaking test.

(2) When the mixture of calcium aluminate and gypsum or that of SR slag containing low contents of SiO₂ and T.Fe and gypsum is used as a F stabilizing agent, it was found that ettringite and monosulfate are rapidly formed on stabilizing agent surface. This protective layer retards the formation of the compound containing F.

(3) When the mixture of 3CaO·SiO₂ and gypsum, 2CaO·SiO₂ and gypsum, 2CaO·Al₂O₃·SiO₂ and gypsum, or SR slag and gypsum with high SiO₂ and low T.Fe contents and gypsum is added to stabilize the F dissolved from HM slag, fluorine ions are stabilized by incorporating through the precipitation of C–S–H–F–SO₄ gel, Ca₁₀(SiO₄)₃·(SO₄)₃·(OH,F)₂ and Ca₅[(Si,S)O₄]₃·(OH,F).

(4) In the case of hydrothermal treatment of the mixture of 3CaO·Al₂O₃ and HM slag, the hydration reaction of 3CaO·Al₂O₃ occurs very rapidly. Fluorine ions are not substituted by OH⁻ site in already formed C–A–H compounds, thus resulting in low degree of F immobilization.

(5) In the case of hydrothermal treatment of the mixture of SR slag with high SiO₂ and low T.Fe contents, gypsum and HM slag, fluorine ions are immobilized during this treatment by the formation of C–S–H–F–SO₄ gel, Ca₁₀(SiO₄)₃·(SO₄)₃·(OH,F)₂ and Ca₅[(Si,S)O₄]₃·(OH,F).

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