1. Introduction

One of the effective ways to utilize a huge amount of slags which are generated from iron and steelmaking industry is to reuse as road construction materials. Recently, an idea of using these slags as foundation materials of marine blocks to build the coast or the bottom of beach has cast a new light on the solution to the problem on slag utilization. However, since some of these slags contain F due to the use of fluorspar in iron and steelmaking process, this attempt will expose the biota in marine environment to the potential threat of F contamination, which largely depends on the concentration of free F ion in seawater. Therefore, the study on the leaching behavior of these F-containing slags takes a specific significance on the health of marine environments.

In this study, the leaching behavior of iron and steelmaking slags containing F in seawater has been studied and the dominating factors have been clarified. Furthermore, the F solubility of F minerals contained in those slags has also been evaluated.

2. Experimental

2.1. Materials

A hot metal dephosphorization slag (HM-slag) with the composition given in Table 1 was used for the present leaching test. After crushing, the sample was classified to the particles size of 0.5–2.0 mm. The F minerals in the slag sample are CaF₂, F-apatite (Ca₅(PO₄)₃F), cuspidine (Ca₄Si₂O₇F₂) and Ca₅(SiO₄)₂F₂, and the major phase is 2CaO·SiO₂ (C₂S) which contains a small amount of F, as confirmed by electron microprobe analysis.

The 2CaO·SiO₂ containing 2 mass% CaF₂ was prepared by sintering a mixture of CaCO₃, SiO₂, and CaF₂ at 1100°C. Cuspidine and Ca₅(SiO₄)₂F₂ were synthesized by heating a mixture of CaO, amorphous SiO₂ and CaF₂ at 1200 and 600°C, respectively. All mixtures were subjected to mechanochemical treatment for 5 h before heating. The sinter process was made under dehydrated Ar gas flowing atmosphere. The total heating time was up to 3 days. The synthesized solid samples were finely ground and particle size was less than 0.1 mm in diameter. All the prepared compounds were confirmed by X-ray diffraction analysis.

Chemical composition of the standard seawater is given in Table 2. The sum of major elements accounts for 99.5% of the dissolved solids and their concentrations in seawater.
are generally more than several hundred mg·l⁻¹ (ppm). Minor elements are present in much lower concentrations than the major elements, usually at few ppm level. The seawater used in the present study was obtained from two sources. One was sampled from Pacific Ocean near the coast of Japan (codified as #1 in Table 2) in order to simulate the practical condition in which HM-slags was used as foundation materials for the coast. The concentrations of major elements in this seawater sample, which were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES method), were about the half of those in the standard seawater (Table 2), as confirmed by ICP analysis. The other (codified as #2) was prepared, based on the chemical composition of the standard seawater listed in Table 2, by dissolving NaCl (25.07 g), MgCl₂ (5.09 g), Na₂SO₄ (1.98 g), K₂SO₄ (0.85 g) CaSO₄·2H₂O (1.72 g) and NaF (0.0022 g) in 1 l distilled water. It contains one minor element F and all major elements except for bicarbonate ion. The seawater samples were slightly acidic. The chemical composition of #2 seawater sample was analyzed by ICP method.

The Mg solution of 1.3 g/l was prepared by dissolving MgO (21.67 g) with 20 cm³ of HNO₃ (1+1), and then diluted to 1 l by distilled water. The preparation was conducted in a CO₂-free condition. The Cl solution of 19 g/l was prepared by dissolving NaCl (31.8 g) in 1 l distilled water.

2.2. Observation of Solid/Liquid Reaction Interface

The sample for the microscopic observation of solid/liquid reaction interface was prepared by dipping a solid tablet into a leaching solution at 20°C. The tablet is in cylindrical shape with the geometric size of φ13×4 mm. After a certain period of reaction time, the solid sample was taken out, washed with analytical grade methanol, and then carefully dried in a CO₂-free condition. The observation by SEM coupled with electron microprobe analysis was carried out for the obtained sample.

2.3. Shaking Test

The leaching behavior of F-containing slags and the F solubility of the F compounds observed in these slags were studied by using the shaking test at 20°C whose procedure has already been described in a previous article. The solid/liquid mass ratio was 1/10 for the HM-slag sample, and 1/100 for others. The F content was determined by the selective fluoride ion electrode method according to JIS-K-0101, where the buffer solution 0.4 w/v% CyDTA–5.8w/v%NaCl–5.7v/v% acetic acid was added.

2.4. Solubility of F-containing Minerals

The F solubilities of Ca₄Si₂O₇F₂, Ca₅(SiO₄)₂F₂, CaF₂ and Ca₅(PO₄)₂F were evaluated as a function of pH under the shaking condition at 20°C. The particle sizes of synthesized Ca₄Si₂O₇F₂ and Ca₅(SiO₄)₂F₂ samples were below 0.1 mm in diameter, and those of CaF₂ and Ca₅(PO₄)₂F were less than 2 μm. The #2 seawater was used as a leaching solution. The solid to liquid mass ratio was kept at 1 to 100. In actual marine environment, the concentration of Ca remains nearly constant at a certain level as a result of the dynamic equilibrium between the formation and decomposition of calcite. However, since the amount of seawater is fixed as 250–500 cm³ in the present experimental conditions, the contact of seawater with CO₂ will significantly vary the composition of the seawater sample due to the formation of CaCO₃. Therefore, the experiment was carried out in a CO₂-free condition.

The pH was controlled by a pH controller coupled with a microtube pump, which is of control margin of ±0.1. NaOH or HNO₃ aqueous solution with an appropriate concentration were used in pH adjustment.

3. Results and Discussion

3.1. Leaching Behavior of HM-Slag

One of the representative results for the leaching test of HM-slag in distilled water and seawater are shown in Fig. 1 in which the variations of solute contents are plotted against shaking time. The seawater was the #1 sample given in Table 2. In the case of distilled water, the F concentration increases gradually and reaches a nearly constant value around 6 mass ppm at 24 h. In the case of seawater, the F content demonstrates a rapid decrease at the beginning, and then increases gradually after reaching a minimum at 2 h. Within the experimental period of time, the F content in seawater is lower than that in distilled water. On the other hand, the Ca content increases more rapidly and is higher in the case of seawater, indicating an accelerated dissolution. This is an opposite trend with respect to the behavior of F content. The Mg content in seawater decreases continuously. These results suggest that the formation of Mg-containing precipitates occurs.

For HM-slag samples in seawater, the formation of Mg(OH)₂ was confirmed by XRD which was carried out on the filtered residues obtained after the shaking test. Electron microprobe analysis revealed that the Mg(OH)₂ phase contains F up to 3.2 mass%, as well as a small amount of CaO.
and SiO₂ (3 and 1.7 mass%, respectively). Since the Mg(OH)₂ phase is solely formed in seawater for a given pH value. This indicates that the dissolution behavior of F from HM-slags in seawater is related to the formation of Mg(OH)₂.

3.2. Leaching Behavior of F-containing 2CaO·SiO₂

To clarify the cause of the different leaching behavior of HM-slags in seawater, the leaching test of synthesized C₂S–2%CaF₂ solid solution powder (≤0.1 mm) which is the major phase of HM-slags (Table 1) was carried out in distilled water, Mg solution and seawater at 20°C. The pH value was kept constant at 9.5 throughout the leaching test. The results are shown in Fig. 2.

The F content in distilled water is higher and the behavior of F in Mg solution whose initial content is 1.3 g Mg/l, is similar to that in seawater, thus suggesting that Mg is responsible for the different behavior of F in seawater.

Figure 3 shows the SEM images for the cross section of a hydrated tablet of C₂S–2%CaF₂ solid solution treated in distilled water, Cl solution (19 g Cl/l), Mg solution (1.3 g Mg/l) and synthesized seawater (#2) for 24 h under static condition. In both cases of distilled water (a) and Cl solution (b), only a small amount of amorphous CaO–SiO₂–H₂O (C–S–H gel) is observed, which does not form a protective surface layer. The C–S–H gels formed in the case of Cl solution contain a small amount of NaCl and the F uptake in both cases is low, not more than 0.6 mass%. The pH values in bulk solutions are 11.5 in both cases, indicating a high hydration degree. On the other hand, the Mg(OH)₂ layer was observed on the C₂S–2%CaF₂ tablets treated in Mg solution (c) and seawater (d). Electron microprobe analysis demonstrates that Mg(OH)₂ phase formed in Mg solution can be expressed as Mg(OH)₂xFₓ (x=0–0.04) and that formed in seawater has the composition of Mg(OH)₂xFₓClᵧ (x=0–0.08, y=0–0.08).

It is noted that in both cases a small amount of CaO and SiO₂ was also observed in Mg(OH)₂ layer. The contents of CaO and SiO₂ are up to 2 and 2 mass% in the case of Mg solution, and 4 and 5 mass% in the case of seawater, respectively. Therefore, it is reasonable to say that the surface layer consists of a mixture of Mg(OH)₂ and C–S–H gel.

The surface images of a C₂S–2%CaF₂ solid solution tablet hydrated in distilled water and Mg solution (1.3 g Mg/l) are shown in Fig. 4. It is clear that in the case of Mg solution (b), the sample is covered by gel-like Mg(OH,F)₂, while no obvious hydration product layer is observed on the sample treated in distilled water (a).

On the basis of the aforementioned experimental findings, it can be concluded that the different behavior of F in seawater compared with that in distilled water, as shown in Fig. 1, is due to the precipitation of Mg(OH,F)₂. The initial hydration of HM-slags in seawater results in the increase of pH, whose initial value is 8.0. At the point where the Mg(OH,F)₂ starts to precipitate, the F content decreases continuously. The immobilization of F by the formation of
Mg(OH,F)$_2$ continues until the conditions for the precipitation of Mg(OH,F)$_2$ cannot be satisfied due to the consumption of Mg content. Thereafter, the F content begins to increase with the continuous dissolution of HM-slag. Factors affecting the precipitation of Mg(OH,F)$_2$ are the pH value and Mg content. It was found that in standard seawater #2 in which Mg is about 1.3 g/l, the Mg(OH,F)$_2$ precipitation occurs in an appreciable amount at pH=10.2. This pH value was determined by adding a dilute NaOH solution into a standard seawater in an extremely slow speed. However, since the pH value at solid/liquid reaction interface is higher than that in bulk, the precipitation of Mg(OH)$_2$ can be observed on the surface of HM-slag even when the pH value measured in the bulk solution is lower than 10.2.

In the case of HM-slags, high hydration ability leads to a higher pH value which favors the formation of Mg(OH,F)$_2$. The effect of the pH value on the dissolution behavior of F was studied and the results are shown in Fig. 5. These results were obtained from the shaking test of C$_2$S–2%CaF$_2$ solid solution in Mg solution at different pH. The particle size of C$_2$S–2%CaF$_2$ solid solution is below 0.1 mm and the solid/liquid mass ratio is 1/100. It is clear that the F content decreases with an increase of pH. It is noted that the Ca and Si contents also decrease with increasing pH. This suggests that Mg(OH)$_2$ plays two roles in affecting the leaching behavior of F-containing materials: one is a F scavenger and the other is to form a retarding layer to the dissolution of F-containing minerals.

It should be pointed out that F-containing Mg(OH)$_2$ is not a stable form of F compounds. The immobilization of F and the retardation to the dissolution of F-containing slags by Mg(OH)$_2$ occur temporarily in marine environment where the typical pH value is in the range between 6.5 and 8. Therefore, it is necessary to determine the stable form of F-containing minerals and their dissolution behavior. This will be discussed in the following section.

### 3.3. Solubility of F in Seawater for F Minerals in HM-slag

In this section, the solubilities of F minerals which are identified in the HM-slags have been studied as a function of pH.

The times to attain the equilibrium for CaF$_2$ and Ca$_4$(PO$_4$)$_3$F were studied in distilled water and seawater at pH=8, and those for Ca$_4$Si$_2$O$_7$F$_2$ and Ca$_5$(SiO$_4$)$_2$F$_2$ were only studied in distilled water at pH=12. The pH was controlled by the method described in Sec. 2.4. These results are shown in Fig. 6. The F content reached a constant value after shaking for 24 h in the case of CaF$_2$ and Ca$_4$(PO$_4$)$_3$F. For Ca$_4$Si$_2$O$_7$F$_2$ and Ca$_5$(SiO$_4$)$_2$F$_2$, the equilibrium state was also attained in 24 h at pH=12.

#### 3.2.1. Ca$_4$Si$_2$O$_7$F$_2$ and Ca$_5$(SiO$_4$)$_2$F$_2$

The solubilities of corresponding solutes for Ca$_4$Si$_2$O$_7$F$_2$ in seawater and distilled water, which were obtained after 24 h shaking, are plotted as a function of pH in Fig. 7. In the case of distilled water, the F content increases with a decrease of pH in the range of pH>9, and shows a maximum of 38 mass ppm at pH around 9, followed by dropping with decreasing pH. The Ca and Si contents substantially increase with decreasing pH. Based on the peak heights observed by XRD analysis, the decomposition of Ca$_4$Si$_2$O$_7$F$_2$ occurred at pH<10 and the amount of precipitated CaF$_2$ increases with a decrease of pH. In the case of seawater, on the other hand, the behavior of F in the range of pH between 7 and 9 is similar to that in the case of distilled water although the F content is higher in seawater. However, the F content drops sharply at pH>10, which is due to the precipitation of Mg(OH,F)$_2$, as confirmed by XRD. The gradual decrease of the F content observed from pH=9 to 7 can be explained by an increase in the amount of precipitated CaF$_2$, as evaluated from the X-ray peak heights obtained by XRD. This is because the decomposition of Ca$_4$Si$_2$O$_7$F$_2$ is accelerated at lower pH value and this leads to the higher
Ca content which promotes the formation of CaF₂. A sharp decrease in the contents of F, Mg and Cl observed at pH 10 in the case of seawater is due to the formation of Mg(OH)₂ which contains not only F but also Cl.

SEM images of the surface of hydrated Ca₄Si₂O₇F₂ tablet in distilled water and seawater are shown on the left-hand side of Fig. 8. These samples were obtained by interacting with distilled water and seawater for 15 days under static condition. The pH values in bulk solutions were about 12 in distilled water and 9 in seawater.

The hydration products observed in the case of seawater are needle-like phases which have the CaO/SiO₂ mass ratio of 3 and contain a high amount of Cl. They are observed along the cracks on the surface of Ca₄Si₂O₇F₂ tablet. The precipitation of Mg(OH,F)₂ was also identified, but its amount was small because of a low pH condition. Electron microprobe analysis revealed that in the case of seawater, the surface of the Ca₄Si₂O₇F₂ tablet is covered by a thin layer which is rich in Si, but poor in Ca, as shown by the result of Energy Dispersive X-ray Spectroscopy (XES) shown in the diagram (b) on the right-hand side of Fig. 8. The F content is also low, while the Cl content is high. This phenomenon was not observed in the case of distilled water, as can be seen from the diagram (a) on the right-hand side of Fig. 8. This indicates that Ca₄Si₂O₇F₂ dissolves incongruently in seawater. A similar phenomenon was also observed on the surface of Ca₄Si₂O₇F₂ tablet treated in Cl solution. It can be concluded that Ca₄Si₂O₇F₂ is only stable at pH 11, decomposes with decreasing pH and converts to more stable form of CaF₂ and C–S–H gel.

The results for F solubility of cuspidine Ca₅(SiO₄)₂F₂ in distilled water and seawater are shown in Fig. 9. The solubility value was obtained after 24 h shaking. The behavior of F for Ca₅(SiO₄)₂F₂ is similar to that observed for Ca₄Si₂O₇F₂ shown in Fig. 7. The maximum of F content occurs at pH=10.

3.2.2. CaF₂ and Ca₅(PO₄)₃F

The solubilities of corresponding solutes for CaF₂ and Ca₅(PO₄)₃F in distilled water and seawater are shown as a function of pH in Figs. 10 and 11, respectively. The solubility values were obtained after 24 h shaking. The F solubility of CaF₂ is independent of pH except for the case of seawater at pH>10. The F content in seawater is 6.0 mass ppm, which is slightly higher than that in distilled water (5–4 mass ppm).

On the other hand, the F content for Ca₅(PO₄)₃F increases gradually with an increase of pH, as shown in Fig. 11. No obvious difference has been found in the solubility of F between distilled water and seawater except for pH>10. The F concentration is 4 mass ppm at pH=6–7, and increases to 9 mass ppm at pH=10.
A sharp drop of F, Mg and Cl contents in the case of seawater is observed at pH 10 due to the formation of Mg(OH)₂. The SEM images of filtered residues obtained after shaking CaF₂ (pH 5 10.4) and Ca₅(PO₄)₃F (pH 5 10.2) particles in seawater for 24 h are shown in Fig. 12. The formation of Mg(OH)₂ (a) was identified in both cases, which contains F and Cl. In the case of Ca₅(PO₄)₃F, the (Ca, Mg)₅(PO₄)₃(OH,F) phase (b) was also observed, indicating the substitution of Ca²⁺ by Mg²⁺ and F²⁻ by OH⁻.

Since seawater is a concentrated mixed electrolyte with NaCl as the major component, the activity coefficient of F in seawater is different from that in water. Activity coefficient in a solution containing several electrolyte can be simply written by

$$\log \gamma_i = -\frac{A z_i^2 I^{1/2}}{1 + I^{1/2}} \quad \text{..................................(1)}$$

where $\gamma_i$ is the activity coefficient of the $i$-th ion in solution, $z_i$ is the $i$-th ion’s charge, $I$ is the ionic strength and $A$ is a constant of the Debye–Hückel theory, which is a function of medium and temperature. For an aqueous solution at 25°C, $A$ is reported as 0.5112 [6] and $c_i$ is the molar concentration (mol/l) of the $i$-th ion in solution. From Eqs. (1) and (2), the activity coefficient of F⁻ is 0.586 and that of Ca²⁺ is 0.118. In the case of distilled water, because the corresponding solutes for CaF₂ and Ca₅(PO₄)₃F are extremely low, the activity coefficients of F⁻ and Ca²⁺ are approximately equal to unity. Therefore, it can be explained qualitatively that the concentration of F⁻ and Ca²⁺ in seawater for both CaF₂ and Ca₅(PO₄)₃F are higher than those in distilled water.

The dissolution reaction of CaF₂ is given by

$$\text{CaF}_2 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + 2\text{F}^- \quad \text{..................................(3)}$$

From Eq. (3) we have

$$a_{F^-} = \left( \frac{K_3}{a_{Ca^{2+}}} \right)^{1/2} \quad \text{..................................(4)}$$

where $a_{F^-}$ and $a_{Ca^{2+}}$ are the activities of F⁻ and Ca²⁺ ions, respectively. $K_3$ is the equilibrium constant of Eq. (3). The results obtained in Fig. 10 in which the F content is independent of pH are interpreted from Eq. (4).

The dissolution reaction of Ca₅(PO₄)₃F is expressed by

$$\text{Ca}_5(\text{PO}_4)_3\text{F} + 6\text{H}^+ \rightarrow 5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{F}^- \quad \text{..................................(5)}$$

Similarly, that of Ca₅(PO₄)₃OH is given by

$$\text{Ca}_5(\text{PO}_4)_3\text{OH} + 7\text{H}^+ \rightarrow 5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \quad \text{..................................(6)}$$
The combination of Eqs. (5) and (6) yields
\[ \text{Ca}_5(\text{PO}_4)_3\text{F} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{F}^- + \text{H}^+ \ldots\ldots\ldots\ldots(7) \]

We have the following relation from Eq. (7):
\[ \log a_{\text{F}} = \log K_7 + \text{pH} \ldots\ldots\ldots(8) \]

where \( K_7 \) is the equilibrium constant of Eq. (7). It can be seen from Eq. (8) that the F content increases with increasing pH, which is in line with the results at pH = 10 in Fig. 11.

Comparing with Ca\(_4\)Si\(_2\)O\(_7\)F\(_2\) and Ca\(_5\)(SiO\(_4\))\(_2\)F\(_2\) shown in Figs. 7 and 9, respectively, it is clear that CaF\(_2\) and Ca\(_5\)(PO\(_4\))\(_3\)F are the stable forms of F minerals in typical marine environments where pH is in the range of 6 to 8.

4. Summary

The leaching behavior of F-containing HM-slags and C\(_2\)S–2%CaF\(_2\) solid solution and the F solubilities of F-containing minerals existing in HM-slags have been investigated. The following conclusions are summarized.

(1) Hot metal pretreatment slags containing F demonstrate higher dissolution tendency in seawater. However, fluorine can be temporarily immobilized by the formation of Mg(OH,F)\(_2\) which favorably occurs at solid/seawater interface where pH is higher than that in bulk.

(2) The F-bearing Mg(OH)\(_2\) is not a stable form of F mineral in seawater. Of the F minerals in HM-slags, only CaF\(_2\) and F-apatite are stable in typical marine environments where pH is in the range of 6 to 8.

(3) The concentrations of F and Ca in seawater for CaF\(_2\) and F-apatite are higher than those in distilled water due to strong ionic interaction.

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