Immobilization Mechanism of Fluorine in Aqueous Solution from Road Material Containing Synthetic Hot Metal Pretreatment Slag by Shaking Test

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The ability of immobilization of fluorine dissolved from the fluorine containing slag with the calcium compound was evaluated by the shaking test. In the calcium compounds which have the ability of immobilization of fluorine, the $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ was found to be the largest ability. From the results of evaluating the stability of immobilization with $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, it was shown that the dissolved fluorine from slag was immobilized for 100 h in shaking time. It was confirmed from the experimental results of X-ray analysis and the equilibrium thermodynamic calculation for aqueous solution that the generation of fluorite which was hard to dissolve in aqueous solution enabled the immobilization of fluorine dissolved from slag. Moreover, the $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ of 5–15 mass% could be used for the road construction material which consisted of fluorine containing slag and blast furnace slag and as a result the immobilization of fluorine was confirmed.

KEY WORDS: slag; fluorine; immobilization; road material; calcium aluminate; shaking test.

1. Introduction

The depression of dissolution of fluorine from the slag is important for the utilization of slags which contain fluorite. When the fluorine is contained in the steelmaking slag, the technology of immobilizing fluorine from slag and utilizing fluorine containing slag has been developed and the mechanism of immobilization of fluorine has been elucidated.^{1–5)} As one of the applications of fluorine containing slag is to use as the road construction material, it is necessary to find out the proper immobilization method for fluorine containing slag in advance.

In this study, to clarify the mechanism of immobilization of fluorine from slag containing fluorite, the systematic experiments were done using various synthetic slags, and the immobilization method was applied to road construction material.

2. Experimental Procedures

2.1. Sample

The experiments of immobilization of fluorine dissolved from slag using the synthetic slag were done using the same method reported previously⁶⁾ to eliminate the factors such as slag composition and cooling rate during solidification, and the mechanism of immobilization of fluorine was examined.

The chemical composition of synthetic slag samples is listed in **Table 1**. The reagent chemicals were mixed and

charged in a dense magnesia crucible, and then were melted and solidified at a fixed cooling rate. The furnace was put in the vacuum vessel, and the regents were melted and solidified under argon gas atmosphere. From this method, the oxidation of slag was prevented during melting and cooling. The cooling rate during solidification was similar to that at slag pot used in practical operation.

As the dissolution of fluorine from slag depended on the distribution of particle size, that is, specific surface area of slag,⁶⁾ the distribution of slag particle size was fixed to that of plant slag which was crushed by using the jaw crusher. After crushing, the slag was riddled by sieves machine for twenty minutes using six kinds of sieves with opening screen from 0.1 to 2.0 mm, and the distribution of particle size of slag was controlled by mixing these riddled slags.

There were two types of the blast furnace slag such as the granular slag and the air cooled slag. In this study, the plant blast furnace slags were used. The results of the shaking test for the fluorine containing hot metal pretreatment slag which was prepared from reagents indicate that the amount of fluorine from slag depended on the diameter of slag. Though the fluorine is not contained in blast furnace slags, the slag diameter was controlled as shown in **Figs. 1(b)** and

Table 1. Slag composition for shaking test (mass%).

Slag	CaF ₂	CaO	SiO ₂	Al ₂ O ₃	FeO	P ₂ O ₅	C/S
F6	6.2	46.0	24.4	5.5	3.0	5.7	1.9
F13	13.3	46.7	24.7	4.8	2.7	5.5	1.9

Fig. 1. Distribution of slag diameter. (a) Fluorine containing synthetic slag, (b) granulated blast furnace slag and (c) air cooled blast furnace slag.

1(c). The constitution of fluorine containing synthetic slag was shown in this Fig. 1(a) for comparison. The constitution of diameter for both the blast furnace slag and the fluorine containing slag are different.

2.2. Method for Immobilization of Fluorine

The evaluation of both dissolution and immobilization of fluorine from slag was made from the results obtained by using the shaking test which was based on the Environmental Agency Notice 46.

The diameter of slag for shaking test is 2.0 mm or less in diameter and the weight of slag is 50 g. The initial pH value of the aqueous solution is adjusted to 5.8–6.3 and the volume of aqueous solution is 500 mL which corresponds to ten times of slag weight. The shaking time is 6 h, and the frequency of shaking is 200 times per minute. The fluorine dissolution from slag was analyzed according to the JIS method in which the aqueous solution after filtering using a membrane filter with open pore size of $0.45 \mu\text{m}$ was analyzed by absorption spectroscopy after regular treatment.

3. Results and Discussion

3.1. Mechanism of Immobilization of Fluorine

3.1.1. Selection of Immobilization Method

To immobilize the dissolved fluorine there is a method of exchanging the ion in compound for the fluorine ion in slag by the following equation.⁷⁾ As the ability of immobilization of fluorine by the reaction (1) is not clear, the shaking test was done. In addition to this the method of addition of calcium compounds to slag is reported by He and his coworkers.^{1,2)}

Though the effect of immobilization of fluorine from

Fig. 2. Comparison of compounds used in the immobilization method of dissolved fluorine from slag.

slag by addition of calcium compound had been confirmed, the effect of ion exchange method is uncertain. Therefore, the effect of immobilization of fluorine from synthetic slag by ion exchange method was examined using apatite reagents by the shaking test. The amount of fluorine dissolved from sample containing several apatite reagents in 10 mass% and slag F6 was measured after the shaking test.

Figure 2 shows the experimental results for the exchange and absorption method. The immobilization ability of fluorine from the slag is different depending on the kind of the apatite. The amount of dissolved fluorine is $1.6 \text{ mg} \cdot \text{L}^{-1}$ at the most and is hard to clear the $0.8 \text{ mg} \cdot \text{L}^{-1}$ value which corresponds to the drinking water quality standard even if apatite HAP ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is used. The ability of immobilization of fluorine of C12A7 is larger than that of HAP. Thus, in this study, the method of immobilization using the calcium compound was examined for the road construction material.

3.1.2. Thermodynamics of Aqueous Solution

From the thermodynamic calculation for aqueous solution, it is possible to evaluate the stability of mineral phase which contains fluorine. The thermodynamic calculation for aqueous solution was made at the temperature of 298 K and the relationship between stability phase and pH was examined for the Ca, Fe, Al, and Si components which made up the slag.

Though there were several stable phases^{8,9)} which contained fluorine, the stable phase in this calculation is fluorite regardless of Fe, Al and Si ion as shown in Fig. 3, indicating that the immobilization of fluorine was dominated by the Ca ion. From these results, it follows that the Ca ion contributes to the fluorine ion mainly and the Fe, Al and Si ions do not contribute to the immobilization of the fluorine ion significantly.

To confirm this, CaO or $\text{Ca}(\text{OH})_2$ which would dissolve the Ca ion in aqueous solution was added to slag F6 in 10 mass% and the shaking test was done followed by the measurement of the amount of fluorine in aqueous solution.

Figure 4 shows the relationship between the amount of dissolved fluorine from the sample and shaking time. The ability of immobilization of fluorine is different depending on the kind of mineral phase containing Ca ion. When C12A7 or $\text{Ca}(\text{OH})_2$ is mixed with slag F6, the amount of dissolved fluorine decreases monotonously with shaking

Fig. 3. Fluorine containing phase by thermodynamic calculation for aqueous solution. (a) F-Ca-H₂O system, (b) F-Ca-Al-H₂O, (c) F-Ca-Si-H₂O and (d) F-Ca-Fe-H₂O.

Fig. 4. Effect of Ca ion on immobilization of fluorine.

time. When CaO is mixed with slag F6, the amount of dissolved fluorine decrease with shaking time and reaches the minimum value in time of 2 h, and increases with time. As the heat of hydration of CaO is large, the temperature on the surface of CaO particle got in touch with water is raised, the dissolution of Ca ion is promoted and the concentration of Ca ion on the surface of CaO particle is increased locally. From these result, it is thought that the fluorine immobilization ability of CaO is higher than that of C12A7 and Ca(OH)_2 and the fluorine containing mineral phase is formed rapidly. However, the amount of dissolved fluorine increases after shaking time of 4 h. This change of amount of dissolved fluorine suggests that the dissolution of fluorine from fluorine containing mineral phase is caused.

3.1.3. Fluorine Containing Mineral Phase

To study the fluorine behavior in the immobilization reaction by mineral phase, the experiment of both reaction of immobilizing material with solid of fluorine containing slag and aqueous solution, and the reaction of fluorine containing slag with solid of immobilizing mineral phase and aqueous solution were done, and the reaction product was analyzed. The schematic diagram of experimental method is shown in Fig. 5 together with the results of analysis of fluorine containing mineral phase. The slag F6 was used for

Fig. 5. Experimental procedure to identify fluorine containing mineral and results of X-ray diffraction analysis.

fluorine containing slag and the C12A7 ($12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$) was used for immobilizing material. The samples of both slag F6 and C12A7 were thin plates of 20×20×2 mm, which were cut from the blocks melted with reagent chemicals and whose surface was polished like mirror.

The thin plate of fluorine containing slag F6 was im-

Fig. 6. Comparison of ability of immobilization of fluorine by calcium contained mineral.

mersed in solution of C12A7, which was the aqueous solution filtered by membran filter in diameter $0.45\ \mu\text{m}$ after shaking of C12A7 of the $0.1\ \text{mm}$ or less in diameter for 6 h, for 24 h to hydrate. Then, the thin plate samples were dried and the surface layer of samples were analyzed by X-ray diffraction. From these results, the mineral phase of surface layer of samples which were reacted with aqueous solution was identified.

The C12A7 plate was immersed for 24 h in the aqueous solution made by shaking with slag F6 and the surface was analyzed by X-ray diffraction. The aqueous solution was obtained by filtration using the membran filter of $0.45\ \mu\text{m}$ in diameter after shaking with slag F6 of $0.1\ \text{mm}$ or less in diameter for 6 h.

From the results of X-ray diffraction as shown in Fig. 5, the fluorite was formed on the surface layer of both slag F6 and C12A7 plate. It was confirmed that the Ca ion contributed to the immobilization of fluorine from slag and the fluorine containing mineral phase was fluorite. The concentration of Al in aqueous solution has been hardly changed before and after dipping C12A7 plate.

As it is hard to analyze the fluorine containing mineral phase on the surface layer of thin plate by X-ray diffraction below 10° or less in angle 2θ , the powder sample milled with that thin plate was analyzed by X-ray diffraction. He and Suito^{1,2)} reported in detail the hydration mechanism and identified the major hydration product for C12A7 was $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{OH})_2\cdot 18\text{H}_2\text{O}$ after the shaking test. In this study, the intensity of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{OH})_2\cdot 18\text{H}_2\text{O}$ was low and it was difficult to distinguish the peak of that mineral phase from background.

3.1.4. Evaluation of Immobilization Ability of Fluorine

The Ca ion containing mineral phase should be selected to satisfy the regulation value of fluorine. Since the order of ability of dissolution of Ca ion from mineral phase is difficult to determine, the ability of immobilization of fluorine was evaluated by shaking test. The mineral phases containing the Ca ion such as the lime-alumina and the lime-silica systems were selected, and that mineral phase of $0.1\ \text{mm}$ or less in diameter was mixed with slag F6 in 10 mass%.

Figure 6 shows the experimental results for the evaluation of immobilization ability of fluorine by shaking test after 6 h. The ability of immobilization of fluorine changes

Fig. 7. Relationship between fluorine content in aqueous solution and heat of hydration of calcium containing minerals of cement components.

depending on the kind of mineral phase and that of C12A7 is the highest. The cement has the ability of immobilization of fluorine, because it contains C2S($2\text{CaO}\cdot\text{SiO}_2$), C3S($3\text{CaO}\cdot\text{SiO}_2$), C3A($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) and C4AF($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$) which dissolve Ca ion.

In case of cement, it is necessary to change the setting time according to the amount of these mineral phases. As the setting time is related to the rate of hydration,¹⁰⁾ the heat of hydration, which is proportional to the rate of hydration, was measured.

The relationship between heat of hydration and amount of dissolved fluorine after 6 h is shown in Fig. 7 for the experiments in which the sample is mixed with slag F6 and mineral phase of cement in 10 mass%. The amount of fluorine from sample decreases with increasing the heat of hydration. It is thought that the larger ability of dissolution of Ca ion from mineral phase in cement causes the larger heat of hydration.

3.2. Immobilization of Fluorine

To evaluate the ability of immobilization of fluorine dissolved from slag, the following experiments were done by using the synthetic slag and the slag which was used to construct the actual road.

It is necessary to evaluate the stability of immobilizing reagent of fluorine before applying the reagent to the actual road construction material which included fluorine containing slag. First of all, to evaluate the stability of immobilizing reagent, the shaking tests were done with various shaking time using by the synthetic slag and the road construction material for the immobilization method for fluorine from slag. It is necessary to examine the stability of immobilizing ability of fluorine. Then, the stability of immobilization of fluorine which depends on both time and pH value is evaluated by the shaking test using the sample mixed with the fluorine containing slag and the calcium aluminate C12A7 with the particle size $1.4/2.0\ \text{mm}$. Moreover, the accelerated tests by which the water temperature of shaking test was raised were done and the stability of immobilization of fluorine was examined.

Figure 8 shows the relationship between the amount of dissolved fluorine from the fluorine containing synthetic slag and shaking time. The amount of dissolved fluorine from slag was increased with shaking time and the dissolved fluorine reached $7.3\ \text{mg}\cdot\text{L}^{-1}$ after 100 h. When the slag was mixed with C12A7 in 10 mass%, the amount of

Fig. 8. Relationship between dissolved fluorine content from fluorine containing synthetic slag with and without C12A7, and shaking time.

Fig. 9. Relationship between dissolved fluorine content from fluorine containing synthetic slag with and without C12A7, and temperature of shaking water under two different shaking frequencies.

dissolved fluorine was $0.8 \text{ mg} \cdot \text{L}^{-1}$ after 100 h.

The mechanism of dissolution of fluorine from slag can be explained by the diffusion of fluorine ion in the surface layer of slag particle. Based on this mechanism, the stability of immobilization of dissolved fluorine from slag can be evaluated by an acceleration test in which both frequency and temperature of shaking test are increased.

Figure 9 shows the relationship between amount of dissolved fluorine from slag and water temperature of shaking test as a function of shaking frequency. When calcium aluminate C12A7 is not mixed with slag, the amount of dissolved fluorine increases with both frequency and water temperature of shaking test. It can be seen that the dissolved fluorine content can be lowered below $0.8 \text{ mg} \cdot \text{L}^{-1}$ by mixing the C12A7 even if the water temperature is raised. This is because an excessive amount of Ca ion exists in aqueous solution.

One of slag usage is thought to be a road construction material and this material is mixed with a blast furnace slag. When a road construction material is mixed with blast furnace slag, the amount of dissolution of fluorine from slag may be affected. To examine the influence of the blast furnace slag, the shaking test was done by using a slag sample containing a blast furnace slag, and the amount of dissolved fluorine from the road construction material and the ability of immobilization of fluorine by C12A7 were evaluated.

The relationship between amount of dissolved fluorine and shaking time is shown in Fig. 10 for a road construction material which are a mixture of fluorine containing

Fig. 10. Relationship between dissolved fluorine content from road construction material with and without C12A7, and shaking time.

Fig. 11. Relationship between dissolved fluorine from road construction material with and without C12A7, and temperature of shaking water under shaking frequency of 200 cycle/min.

synthetic slag and blast furnace slag. The mixing ratio of fluorine containing slag in the road construction material was 30 mass%. The amount of dissolved fluorine increases with shaking time and reached $3.2 \text{ mg} \cdot \text{L}^{-1}$ in shaking time of 100 h. The amount of fluorine from road construction material was smaller than that from fluorine containing slag, as shown in Fig. 8. When the C12A7 with the particle size 1.4/2.0 mm in 5 mass% was mixed with road material, the amount of fluorine was lowered below $0.8 \text{ mg} \cdot \text{L}^{-1}$ or less in shaking time of 100 h.

Figure 11 shows the relationship between amount of dissolved fluorine from road construction material and water temperature of shaking test. When C12A7 is not mixed with road construction material, the amount of dissolved fluorine increases with both frequency and water temperature of shaking test. From this, it is said that the dissolution of fluorine from road construction material is controlled by the diffusion in the thin layer near slag surface¹¹⁾ as well as the fluorine containing slag, and there was no influence of the blast furnace slag on dissolution of fluorine because the fluorine is not contained in the blast furnace slag. When C12A7 is mixed with road construction material, the amount of dissolved fluorine is kept slightly $0.8 \text{ mg} \cdot \text{L}^{-1}$ even if the shaking frequency and water temperature are raised.

When C12A7 is used to actual road construction material, the ability of immobilization of fluorine is influenced by pH value in soil which contacts with road construction material. Figure 12 shows the fluorine in aqueous solution

Fig. 12. Relationship between dissolved fluorine in aqueous solution from road construction material and pH value before shaking test.

Table 2. Constitution of road construction material (mass%).

Road material	Slag	A	B	C	D	E	F	G
	F6	30				0		
	F13	0				30		
	Gran.-B.F.	5						
	A.C.-B.F.	65	62.5	60	55	65	60	55
	C12A7	0	2.5	5	10	0	5	10

Fig. 13. Results of shaking test for immobilization of fluorine from road construction material under various constitutions of slags.

from actual road construction material under various pH values before shaking test. In the range of the pH value of soil in Japan (pH 4–8), the fluorine content in aqueous solution is not influenced by pH value and it is confirmed that fluorine can be immobilized by C12A7. To determine the best mixing ratio of C12A7 to fluorine containing slag, the shaking test was done by using the road construction material listed in Table 2.

Figure 13 shows the measurement results of amount of

dissolved fluorine in aqueous solution after 6 h shaking. When the concentration of fluorine in slag is high the amount of fluorine dissolved in aqueous solution becomes larger. However, the amount of fluorine can be decreased by mixing of C12A7 in 10 mass% at the maximum. By changing either the mixing ratio of fluorine containing slag or the amount of C12A7, the fluorine dissolved from road material can be controlled to the level less than a desired value.

4. Conclusions

To clarify the mechanism of immobilization of fluorine from both fluorine containing synthetic slag and road construction material which is a mixture of blast furnace slag and calcium aluminates, the shaking tests have been done under various experimental conditions. The ability and stability of immobilization by using calcium aluminates have been investigated.

(1) By mixing the calcium compounds with slag, it was found that fluorine dissolved from slag could be immobilized. It was confirmed from the experiment and thermodynamic calculation that the fluorite was one of fluorine containing mineral phases and contributed to the immobilization of fluorine.

(2) The ability of immobilization of fluorine by C12A7 was the highest in the calcium compounds.

(3) When C12A7 was added to slag, the amount of dissolved fluorine was could be controlled to $0.8 \text{ mg} \cdot \text{L}^{-1}$ or less within 100 h in the shaking test.

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