Immobilization of Hexavalent Chromium in Aqueous Solution through the Formation of 3CaO·(Al,Fe)2O3·Ca(OH)2·xH2O Phase, Ettringite and C–S–H Gel

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1. Introduction

Chromium has primarily two oxidation states in nature: Cr3+ and Cr6+. The trivalent is relatively benign and immobile, whereas the hexavalent is toxic and more mobile, and has long been an environmental concern. Besides steelmaking process, Cr6+ containing waste is generated from electroplating, tanning, wood preservation, production of chromate compounds, and so on. The safety discharge of these wastes into the environment demands a proper immobilization treatment of Cr6+ waste.

Chemical reduction of Cr6+ to Cr3+ followed by the precipitation of Cr(OH)3 offers an alternative to immobilize Cr6+. In this case reduction agents such as bisulphites and sulphides are used. The drawback with this approach is high cost, as well as potential reoxidation of Cr3+ to Cr6+, which can occur in the existence of species of high chemical potential in the environments, such as Mn–oxide,1,2) under certain condition. In addition, this remediation strategy appears appropriate only for the immobilization of liquid form of Cr6+ waste.

Another alternative to the immobilization of chromium waste is to immobilize Cr into cement base matrix through cementitious reaction. This approach has been drawing an increasing attention because cement or/and slag affords physical and chemical potentials for immobilization of waste elements, and usually produces a stable waste form. Since a variety of hazardous species can be fixed at the same time and the treatment cost is low, this method seems to be more applicable in practice. The cement base materials used in stabilizing Cr usually have complex constituents which make it difficult to characterize immobilization mechanisms. Especially, the knowledge related to the behavior of Cr6+ in stabilized matrix is far from complete. In this study, therefore, an attempt is made to direct to this problem.

Even though a variety of phases appear in the hydration of cementitious materials, the following types of compounds are of great interest in the immobilization of waste elements: A/Fm phase, ettringite and C–S–H gel.

The immobilization of hexavalent chromium in aqueous solution is found to occur through the formation of Cr6+-bearing A/Fm phase, ettringite and C–S–H gel, which are formed by calcium aluminate or ferrite, a mixture of lime and Al2(SO4)3 or Fe2(SO4)3, and calcium silicate, respectively. In the case of A/Fm phase, which is most effective one to the immobilization of Cr6+, the Cr6+ concentration in aqueous solution decreases from initial 50 ppm to below 0.05 ppm. The Cr6+-containing A/Fm phases identified are 3CaO·Al2O3·Ca(OH)2·Cr2O3·18H2O, 3CaO·(Al,Fe)2O3·Ca(OH)2·Cr2O3·18H2O, 3CaO·Fe2O3·CaCO3·Cr2O3·12H2O and 3CaO·Al2O3·CaCrO4·12H2O. The immobilization occurs through the OH− or CO32− site substitution with CrO42−. No significant amount of Cr6+ is identified in either ettringite phase or C–S–H gel, indicating that these two phases do not play an important role for the immobilization of Cr6+ in cement-based solidification/stabilization process. The immobilization takes place by the substitution of SO42− site in the case of ettringite, while in the case of C–S–H gel the sorption mechanism is more possible.

KEY WORDS: hexavalent chromium; immobilization; A/Fm phase; ettringite; C–S–H gel.

The A/Fm phase refers to the group of compounds whose prototype is C3A·Ca(OH)2·xH2O (C and A represent CaO and Al2O3, respectively). A/Fm is an abbreviation of (tricalcium)-Aluminate Ferrite: mono (sulfate, -hydroxide, etc.)·(hydrate)-phase.3) It is usually generated from the hydration of calcium aluminates and ferrite, such as C3A and Ca2(Al,Fe)2O5. It has already been found in the previous study4) that an A/Fm phase, C3A·Ca(OH)2·18H2O can immobilize fluorine ion.

Ettringite (C3A·3CaSO4·32H2O) is formed during the early stage of hydration of most Portland cements. Ettringite is the prototype of another important group of compounds called Aft phase (Aluminate Ferrite·tri) which is designated to distinguish from the A/Fm phase.5)

C–S–H is a generic name for any amorphous or poorly crystallized calcium silicate hydrate. The dashes indicate that no particular compositions are implied. It is the major constituent of most cement pastes which provide physical,
as well as chemical immobilization to many waste ions. C–S–H gel is formed during hydration reaction of C₃S and C₂S.

In this study, the immobilization of Cr⁶⁺ in aqueous solution has been studied through the formation of AFm phase, ettringite and C–S–H gel. After interacting the Cr⁶⁺-containing aqueous solution with calcium aluminates, ferrites, a mixture of lime and Al₂SO₄ (or Fe₂SO₄), and calcium silicates under shaking condition, the Cr⁶⁺-containing hydration products have been identified by a combination of X-ray diffraction and electron microprobe analysis. The immobilization ability of different phases has been compared from the behavior of Cr⁶⁺ content in aqueous solution. The present results are considered useful not only for the immobilization of Cr⁶⁺ in wastewater, but also for the understanding of the Cr⁶⁺ immobilization mechanism in cementitious matrix, which is essential to the development of the effective remediation process.

2. Experimental

2.1. Materials

Calcium aluminates of CaO·Al₂O₃ (CA), 12CaO·7Al₂O₃(C₁₂A₇), 3CaO·Al₂O₃(C₃A) and ferrites of 2CaO·Fe₂O₃ (C₂F, F=Fe₂O₃) and Ca₂Al₁.₃₆Fe₀.₆₄O₅ were made by heating a mixture of analytical grade CaCO₃, Al₂O₃ and Fe₂O₃ in an appropriate amount at 1300, 1100 and 1280°C for aluminates, 2CaO·Fe₂O₃ and Ca₂Al₁.₃₆Fe₀.₆₄O₅, respectively, with repeated intermediate grinding, mixing and compressing.

It has been reported that the stabilizer such as P₂O₅ in the formation of β-2CaO·SiO₂ (β-C₂S) affects the hydration behavior of β-C₂S.(1,6) Therefore, stabilizer-free β-C₂S was prepared by the following method. A mixture of freshly calcined CaO and analytical grade amorphous SiO₂ in stoichiometric proportion was ground for at least 5 h before subjected to sintering, by using a planetary ball mill with two agate pots of 45 cm³ inner volume. Rotational speed of the mill was kept constant at 700 rounds per minute. The grinding operation was interrupted every 15 min to cool down the mill. Then, the mixture was pressed to a cylindrical shape and fired at 1100°C for 1 d. The formation of β-C₂S was confirmed by XRD. 3CaO·SiO₂ (C₃S) was prepared by sintering a mixture of analytical grade CaCO₃ and SiO₂ in appropriate proportion at 1500°C for total 6 d, with repeated intermediate grinding and compressing.

Calcium sulfoaluminate, 3CaO·3Al₂O₃·CaSO₄, was prepared by sintering a fully ground mixture of analytical grade CaCO₃, CaSO₄·2H₂O and Al₂O₃ at 1300°C. More detailed description is given elsewhere.(7) All compounds obtained were confirmed by XRD analysis.

2.2. Preparation of Cr⁶⁺-loaded C₃S Paste

C₃S powder (≤0.1 mm) pressed in a cylindrical shape (ϕ16×12 mm) was spiked in Cr⁶⁺ solution of 1000 ppm for 3 weeks. The solid to liquid ratio is 1/2. Then, it was cured in a CO₂-free glove box at room temperature for another 3 weeks. The Cr⁶⁺ uptake in the C₃S paste was evaluated by measuring the difference in the concentration of Cr⁶⁺ before and after the reaction. After dried over P₂O₅, the hardened Cr⁶⁺-containing C₃S paste was crushed and ground to less than 0.1 mm in diameter. Then, its Cr⁶⁺ leaching behavior at different pH was studied by interacting 1 g Cr⁶⁺-containing C₃S paste with 100 ml distilled water under stirring condition in a CO₂-free atmosphere.

The pH was controlled by a pH controller coupled with a peristaltic pump through which 5 w/v% NaOH or 2 v/v% HNO₃ was introduced to adjust the pH value.

2.3. Preparation of Cr⁶⁺-AFm Phase

CaCrO₄·2H₂O was prepared by crystallization from the solution of 20 g CaCl₂ and 43.7 g Na₂CrO₄ in 100 ml distilled water at 0°C for a week. The product was freeze-dried after rinsing several times to remove chloride, and then further dried at 60°C to obtain CaCrO₄.

The Cr⁶⁺-containing AFm phase, C₃A·CaCrO₄·12H₂O, was synthesized by reacting C₃A with CaCrO₄ obtained in CO₂-free distilled water at room temperature. The reaction system was sealed in a 500 ml polyethylene bottle and shaken for a week. The product was finally freeze-dried. Both CaCrO₄ and C₃A·CaCrO₄·12H₂O were identified by XRD.

2.4. Shaking Test

The shaking test described in the previous article(6) was used to study the interaction between the solid sample and Cr⁶⁺ aqueous solution. The solid sample was ground to fine powders which were screened through a 160 mesh sieve. The resulting particles were all less than 100 μm in diameter. Then, the particles, along with 250 ml of 50 mass ppm Cr⁶⁺ aqueous solution were charged into a 500 ml polyethylene bottle. The solid to liquid ratio is 1/100 for aluminates and silicates, and 1/50 for ferrites and ettringite. The Cr⁶⁺ aqueous solution was prepared by dissolving an appropriate amount of K₂Cr₂O₇ in distilled water. The polyethylene bottles were then placed on a shaker table and shaken horizontally at 200 times per minute. The temperature was kept constant at 20°C for the duration of the experiment.

2.5. Analytical Method

After reacting the sample powders with Cr⁶⁺ aqueous solution for a certain period of time, sampling was made using a polyethylene whole pipet of 5 ml, followed by filtration through the membrane filter with an open pore size of 0.1 μm. The filtrate was introduced into a 100 ml polycarbonate measuring flask precharged with 5 ml HNO₃ (1+1). The Cr⁶⁺ content was determined by inductively coupled plasma (ICP) atomic emission spectrometry. The lower limit and the accuracy of Cr⁶⁺ analysis were evaluated as 0.002 ppm and ±5%, respectively.

The analytical method for fluoride was described in previous article.(6) The lower limit and the accuracy of fluoride analysis were evaluated as 0.003 ppm and ±3%, respectively.

The hydration products were identified by XRD and the Cr⁶⁺ uptake in the hydrates was evaluated by microprobe analysis (energy-dispersive spectrometry). The morphology of hydration products was observed by SEM.
3. Results and Discussion

3.1. Immobilization of Cr\(^{6+}\) by AFm Phase

The results for Cr\(^{6+}\) immobilization by calcium aluminates and ferrites are shown in Figs. 1 and 2, respectively. The initial Cr\(^{6+}\) content is 50 ppm and the solid to liquid ratios are 1/100 and 1/50 for calcium aluminates and ferrites, respectively. The particle sizes of all reactants are less than 0.1 mm. Particular attention was paid to reduce the contamination of CO\(_2\) to the hydration of calcium aluminates and Ca\(_2\)Al\(_{1.36}\)Fe\(_{0.64}\)O\(_5\) by using CO\(_2\)-free distilled water and sealing them in a reaction vessel. On the other hand, in the case of C\(_3\)F and C\(_2\)F\(+\)CaO (1:2, molar ratio), the reaction system was intentionally exposed to air atmosphere.

It is clear from Fig. 1 that C\(_3\)A and C\(_12\)A\(_3\) are more effective to the immobilization of Cr\(^{6+}\) compared with CA. The Cr\(^{6+}\) content in aqueous solution for C\(_3\)A and C\(_12\)A\(_3\) drastically decreases below 0.05 ppm within 6 h and becomes undetectable thereafter. On the other hand, in the case of CA the Ca and Al contents are extremely low, and the pH value of the reaction system was slightly below 7. This indicates that the hydration of CA was retarded in the presence of Cr\(^{6+}\). The pH value obtained for C\(_3\)A and C\(_12\)A\(_3\) were 12.5 and 12.0, respectively. The results obtained by XRD demonstrate that the major hydration product for C\(_3\)A is Ca\(_2\)Al\(_{1.36}\)Fe\(_{0.64}\)O\(_5\)·18H\(_2\)O, and that for C\(_12\)A\(_3\) is C\(_3\)A·Ca(OH)\(_2\)·18H\(_2\)O. It has already been found that these two phases are able to immobilize fluorine ion.\(^4\) However, only the C\(_3\)A·Ca(OH)\(_2\)·18H\(_2\)O phase contains Cr\(^{6+}\), as confirmed by a microprobe analysis. This will be shown later. It was also identified by XRD that when the initial concentration of Cr\(^{6+}\) increased to 400 ppm, C\(_3\)A·CaCrO\(_4\)·12H\(_2\)O was present in solid.

The results for Ca\(_2\)Al\(_{1.36}\)Fe\(_{0.64}\)O\(_5\) shown in Fig. 2 indicate a similar behavior to those of C\(_3\)A and C\(_12\)A\(_3\) shown in Fig. 1 for the immobilization of Cr\(^{6+}\), although the immobilization rate by Ca\(_2\)Al\(_{1.36}\)Fe\(_{0.64}\)O\(_5\) is slightly slower. However, the immobilization of Cr\(^{6+}\) by C\(_3\)F proceeds very slowly in the first 12 h and is accelerated thereafter, as shown in Fig. 2. With the addition of CaO to C\(_3\)F, a significant improvement in immobilization is observed although CaO alone does not contribute to the stabilization of Cr\(^{6+}\). The pH value measured in the case of C\(_3\)F increased with shaking time from 11 at the beginning to about 13 at the end of shaking test, but that for the C\(_3\)F+CaO mixture was nearly constant around 13 through the experimental period of time. The pH value for Ca\(_2\)Al\(_{1.36}\)Fe\(_{0.64}\)O\(_5\) was 12.5. As revealed by the results of XRD analysis, a phase of C\(_3\)F·CaCO\(_3\)·12H\(_2\)O was formed under air atmosphere in the case of C\(_3\)F, and its amount increased with the addition of lime. As indicated by a microprobe analysis described later, this compound uptakes Cr\(^{6+}\). A Cr\(^{6+}\)-containing iron complex of C\(_3\)A·Ca(OH)\(_2\)·18H\(_2\)O phase which was confirmed by a microprobe analysis, was formed in the case of Ca\(_2\)Al\(_{1.36}\)Fe\(_{0.64}\)O\(_5\).

The results for SEM observation of the Cr\(^{6+}\)-containing complexes of C\(_3\)A·Ca(OH)\(_2\)·18H\(_2\)O, C\(_3\)F·CaCO\(_3\)·12H\(_2\)O, and C\(_3\)A·CaCrO\(_4\)·12H\(_2\)O are shown in Figs. 3(A)–3(C), respectively. The C\(_3\)A·Ca(OH)\(_2\)·18H\(_2\)O and C\(_3\)F·CaCO\(_3\)·12H\(_2\)O were obtained by reacting 50 mass ppm Cr\(^{6+}\) aqueous solution with C\(_3\)A and C\(_3\)F+CaO powders, respectively, for 30 h at the same experimental conditions as those shown in Figs. 1 and 2. The C\(_3\)A·CaCrO\(_4\)·12H\(_2\)O was prepared by the method described in Sec. 2.3. It can be seen that the C\(_3\)A·Ca(OH)\(_2\)·18H\(_2\)O phase (a) shows a morphology of a thin hexagonal plate, while the C\(_3\)F·CaCO\(_3\)·12H\(_2\)O phase (b) appears to be a rosette crystal. The C\(_3\)A·CaCrO\(_4\)·12H\(_2\)O phase (c) is also hexagonal crystal, but thicker than the C\(_3\)A·Ca(OH)\(_2\)·18H\(_2\)O phase (a). The Ca\(_3\)Al\(_{1.36}\)Fe\(_{0.64}\)O\(_5\) phase (d) containing no Cr\(^{6+}\) appears to be an octahedron crystal which is different from the fluorine-containing

\[ \text{Ca}_2\text{Al}_{1.36}\text{Fe}_{0.64}\text{O}_5 \]
Ca₃Al₂(OH,F)₁₂ phase in the previous observation. The Cr⁶⁺ uptake in C₃A·Ca(OH)₂·18H₂O is up to 1.52 mass%, but the Cr⁶⁺ uptake in C₃F⁻·CaCO₃·12H₂O is lower, only 0.96 mass%.

Both C₃A·Ca(OH)₂·18H₂O and C₃F⁻·CaCO₃·12H₂O belong to the AFm phase group. The structure of the prototype of the AFm phase, C₃A·Ca(OH)₂·xH₂O, is based on the structural element [Ca₂Al(OH)₆](OH)₂ according to Buttler et al. The seventh OH⁻ in the last term of [Ca₂Al(OH)₆](OH)₂ is situated above the aluminum position to balance the charge, and is exchangeable. Calcium aluminum sulfate hydrate C₃A·CaSO₄·12H₂O is an example of SO₄²⁻ substitution for this exchangeable OH⁻ site. It has already been found in the previous study that the immobilization of F by the C₃A·Ca(OH)₂·18H₂O phase occurs on this seventh OH⁻ site. Similarly, it is considered that the immobilization of Cr⁶⁺ also takes place through the substitution on this site. Since the pH for all the reaction systems in this study is higher than 6.4, the hexavalent Cr exists in the form of CrO₄²⁻ in aqueous solution. Therefore, this Cr⁶⁺-containing C₃A·Ca(OH)₂·18H₂O phase can be expressed as C₃A·[(OH)ₓ]₁₋ₓ(CrO₄)ₓ·18H₂O, where x indicates the solubility of Cr⁶⁺ in this complex.

Since the properties such as ionic radius and charge are very different between OH⁻ and CrO₄²⁻ ions, it can be expected that C₃A·Ca[(OH)ₓ]₁₋ₓ(CrO₄)ₓ·18H₂O phase can be present only in a narrow range, that is, the x value is small. When the initial concentration of Cr⁶⁺ is 50 mass ppm, the formation of the C₃A·Ca[(OH)ₓ]₁₋ₓ(CrO₄)ₓ·18H₂O phase with x ranging from 0 to 0.2 was confirmed by a micro-probe analysis.

The C₃F⁻·CaCO₃·12H₂O phase itself is another example of complete CO₃²⁻ substitution for the exchangeable OH⁻ sites in the AFm phase. Therefore, it is considered that the Cr⁶⁺ immobilization can be obtained by the CrO₄²⁻ substitution for CO₃²⁻ sites.

### 3.2. Immobilization of Cr⁶⁺ by Formation of Ettringite

The results for the stabilization of Cr⁶⁺ by CaO·Al₂(SO₄)₃ (6:1, molar ratio) and CaO·Fe₂(SO₄)₃ (6:1, molar ratio) mixtures are shown in Fig. 4, where the results for a mixture containing 3CaO·3Al₂O₃·CaSO₄, CaSO₄·2H₂O and Ca(OH)₂ (2:4:3 molar ratio) are also included for comparison. These immobilization reactions were carried out in 50 mass ppm Cr⁶⁺ aqueous solution under shaking condition.

As confirmed by XRD analysis for the filtered residues obtained after 30 h, the Ca₆Al₂O₆(SO₄)₃·32H₂O phase was formed in both cases of CaO·Al₂(SO₄)₃ and 3CaO·3Al₂O₃·CaSO₄·2H₂O·Ca(OH)₂ mixtures, and the Ca₆Fe₂O₆(SO₄)₃·32H₂O phase was formed in the case of CaO·Fe₂(SO₄)₃ mixture. Both phases were virtually pure. The formation reactions for the two ettringite phases Ca₆Al₂O₆(SO₄)₃·32H₂O and Ca₆Fe₂O₆(SO₄)₃·32H₂O are represented as follows:

In the case of CaO+Al₂(SO₄)₃ mixture,

\[
\text{CaO}+\text{H}_2\text{O} = \text{Ca}^{2+}+2\text{OH}^- \quad \text{............(1)}
\]

\[
\text{Al}_2(\text{SO}_4)_3 + 8\text{OH}^- = 2\text{AlO}_2^- + 3\text{SO}_4^{2-} + 4\text{H}_2\text{O} \quad \text{............(2)}
\]

\[
6\text{Ca}^{2+} + 2\text{AlO}_2^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 3\text{H}_2\text{O} = \text{Ca}_6\text{Al}_2(\text{SO}_4)_3·32\text{H}_2\text{O} \quad \text{............(3)}
\]

and in the case of 3CaO·3Al₂O₃·CaSO₄·CaSO₄·2H₂O·Ca(OH)₂ mixture,

\[
3\text{CaO}·3\text{Al}_2\text{O}_3·\text{CaSO}_4 + \text{CaSO}_4·2\text{H}_2\text{O} + \text{Ca(OH)}_2 \quad \text{mixture,}
\]

\[
3\text{CaO}·3\text{Al}_2\text{O}_3·\text{CaSO}_4 = 4\text{Ca}^{2+} + 6\text{AlO}_2^- + \text{SO}_4^{2-} \quad \text{............(4)}
\]

\[
\text{CaSO}_4·2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad \text{............(5)}
\]
Ca(OH)₂ + Ca²⁺ + 2OH⁻ → Ca(OH)₃·H₂O ..........................(6)

Ettringite phase Ca₆Al₂O₆(SO₄)₃·32H₂O are formed by reaction (3).

In the case of CaO + Fe₂(SO₄)₃ mixture, CaO phase reacts with water as reaction (1), followed by

Fe₂(SO₄)₃ + 4OH⁻ → 2Fe(OH)₃ + 3SO₄²⁻ ............................(7)

6Ca²⁺ + 2Fe(OH)₃ + 3SO₄²⁻ + 8OH⁻ + 26H₂O → Ca₆Fe₂O₆(SO₄)₃·32H₂O ..........................(8)

It can be seen from Fig. 4 that the Cr⁶⁺ content decreases at the beginning of reaction, which is due to the rapid formation of ettringite. A nearly constant Cr⁶⁺ content is attained after 3 h, which is about 36 ppm for Ca₆Al₂O₆(SO₄)₃·32H₂O and 15 ppm for Ca₆Fe₂O₆(SO₄)₃·32H₂O. Figure 4 shows that the latter gives better immobilization degree than the former. The immobilization rates of Cr⁶⁺ by the formation of Ca₆Al₂O₆(SO₄)₃·32H₂O via reactions (1) to (3) and (3) to (6) agree well with each other. On the other hand, the Ca and S contents equilibrated with Ca₆Fe₂O₆(SO₄)₃·32H₂O is high, while the Fe content is extremely low.

The results for the SEM observation for Ca₆Al₂O₆(SO₄)₃·32H₂O and Ca₆Fe₂O₆(SO₄)₃·32H₂O are shown in Fig. 5. These samples were obtained from the reactions of CaO with Al₂(SO₄)₃ and Fe₂(SO₄)₃, respectively, in Cr⁶⁺ aqueous solution of an initial concentration of 200 mass ppm after 30 h shaking. It can be seen that the Ca₆Al₂O₆(SO₄)₃·32H₂O appears to be hexagonal acicular crystals, about 6 μm long, while the Ca₆Fe₂O₆(SO₄)₃·32H₂O is hexagonal prismatic crystals, about 12 μm long. The microprobe analysis revealed that the Cr⁶⁺ uptake in these ettringite phases was not more than 0.2 mass%, which was consistent with the low degree of immobilization shown in Fig. 4.

The structures of Ca₆Al₂O₆(SO₄)₃·32H₂O and Ca₆Fe₂O₆(SO₄)₃·32H₂O are based on two distinct structural components like other AFt phases: columns of \{Ca₆[Al(OH)₆]·24H₂O\}₆⁶⁻ and channels of \{SO₄⁴⁻·2H₂O\}₆⁶⁻. With this structure a modest deviation in composition can be tolerated without causing a change in structure. This compositional change occurs on the crystal chemical level in the form of ionic substitution. The immobilization of CrO₄²⁻ occurs through the SO₄²⁻ site substitution. However, it follows from Fig. 4 that Cr⁶⁺ is immobilized into ettringite only to a limited degree and thus soluble Cr⁶⁺ equilibrated with ettringite is higher than 10 ppm. This indicates that ettringite phase is less effective than AFm phases in term of immobilization of Cr⁶⁺.

### 3.3. Immobilization of Cr⁶⁺ by C–S–H Gel

The results for the immobilization of Cr⁶⁺ by C₃S and C₅S are shown in Fig. 6 where the initial concentration of Cr⁶⁺ is 50 ppm. Particle size of C₃S and C₅S is less than 0.1 mm and the solid to liquid ratio is 1 to 100. It can be seen that the Cr⁶⁺ content remains nearly constant at about 40 ppm after a slight decrease in the first 12 h. This indicates that the immobilization of Cr⁶⁺ by C–S–H gel does not occur to any significant degree within experimental period of time. No significant difference in the immobilization of Cr⁶⁺ has been observed between C₃S and C₅S.

The results for the Cr⁶⁺ solubility of hardened Cr⁶⁺-loaded C₃S paste which is prepared by the method described in Sec. 2.2, are shown in Fig. 7. The Cr⁶⁺ content in C₃S paste was 2.33 mg/g which was determined by measuring the difference in the concentration of Cr⁶⁺ in aqueous solution before and after the reaction. It is clear that the Cr⁶⁺ content saturated with Cr⁶⁺-loaded C₃S paste increases with decreasing pH. The Cr⁶⁺ content is about

![Fig. 5. SEM images of Cr⁶⁺-containing ettringite phases, (A) Ca₆Al₂O₆(SO₄,CrO₄)₃·32H₂O and (B) Ca₆Fe₂O₆(SO₄,CrO₄)₃·32H₂O.](image)

![Fig. 6. Immobilization of Cr⁶⁺ in aqueous solution by calcium silicates.](image)

![Fig. 7. pH dependence of leaching behavior of Cr⁶⁺-containing C₃S paste; Cr⁶⁺-content in C₃S paste is 2.33 mg/g.](image)
immobilization may occur through the crystal chemical substitution of CrO$_2^{2-}$ for the OH$^-$ site in C–S–H gel.

The other mechanism is sorption and incorporation. It occurs through two steps: (i) the CrO$_4^{2-}$ ion is adsorbed to C–S–H gel and (ii) the CrO$_4^{2-}$-containing C–S–H gel is wrapped in the hardened C$_3$S paste matrix, through which the immobilization is strengthened and improved.

The substitution mechanism seems unlikely due to the amorphous nature of C–S–H gel. The immobilization by sorption and incorporation mechanism appears to be consistent with the experimental results obtained in the present study. As shown in Fig. 6, the immobilization of Cr$^{6+}$ does not occur significantly during the experimental period of time when the hardening of C–S–H gel after C$_3$S hydration has not taken place. However, once the hardening occurs, the Cr$^{6+}$ containing C$_3$S paste shows much lower leaching tendency due to the stability of C–S–H gel at higher alkaline condition, as can be seen from Fig. 7 where the hardened C$_3$S paste containing Cr$^{6+}$ was used. It should be pointed out that the true picture about the immobilization mechanism is not completely clear and the further work is needed to clarify this mechanism.

### 3.4. Simultaneous Immobilization of Cr$^{6+}$ and F$^-$

A simultaneous immobilization to Cr$^{6+}$ and F$^-$ in aqueous solution was studied by using C$_3$A, C$_{12}$A$_7$ and C$_{24}$A$_1$Fe$_{0.64}$O$_{5.6}$, as shown in Fig. 9. The initial concentrations of Cr$^{6+}$ and F$^-$ are 50 mass ppm, respectively. The solid to liquid ratio is 1/100 for C$_3$A and C$_{12}$A$_7$, and 1/50 for C$_{24}$A$_1$Fe$_{0.64}$O$_{5.6}$. The particle size of solids is below 0.1 mm in diameter. It is clear that Cr$^{6+}$ and F$^-$ can be immobilized simultaneously by these minerals. The results for C$_3$A and C$_{12}$A$_7$ indicate a rapid decrease in both Cr$^{6+}$ and F$^-$ concentrations, and a good immobilization ability to these elements. It is noteworthy that in the presence of Cr$^{6+}$ in aqueous solution, the fluorine immobilization ability of C$_{12}$A$_7$ is substantially improved, comparing
with the results obtained in the previous study without Cr\(^{6+}\). On the other hand, the immobilization rate for these elements becomes slower in the case of Ca\(_{1.36}\)Al\(_{1.36}\)Fe\(_{0.64}\)O\(_5\), although the same immobilization degree can still be achieved in a longer time.

According to XRD and electron microprobe analysis, the hydration products of hydrogarnet phase Ca\(_3(\text{Al,Fe})_2(\text{OH})_12\) and AFm phase Ca\(_3(\text{Al,Fe})_2\text{O}_6\cdot\text{Ca(OH)}_2\cdot18\text{H}_2\text{O}\) were formed. The iron-containing hydrogarnet and AFm phases were identified only in the case of Ca\(_2\)Al\(_{1.36}\)Fe\(_{0.64}\)O\(_5\). The hydrogarnet phase is responsible to the F\(^2-\) immobilization, and the AFm phases is responsible to the Cr\(^{6+}\) immobilization. These results explain the phenomena observed in Fig. 9.

The stability of AFm phase which immobilizes Cr\(^{6+}\) and F\(^-\) is dependent on pH value of solution. From the results of pH dependence of Cr\(^{6+}\) dissolution from stainless sludge, it was found that the amount of Cr\(^{6+}\) dissolution in neutral aqueous solution decreases considerably compared with that in high alkaline aqueous solution. This experimental finding suggests that the amount of Cr\(^{6+}\) dissolved from AFm phase tends to decrease in neutral aqueous solution. More detail will be given in a separate article.

4. Summary

The immobilization of hexavalent Cr by the formation of AFm phase, ettringite, and C–S–H gel has been investigated. The conclusions are summarized as follows:

1. The AFm phases of C\(_3\)A·Ca[(OH)_2CrO_4]·18H\(_2\)O and C\(_3\)F·Ca(CO\(_3\),CrO\(_4\))·12H\(_2\)O are identified and the immobilization occurs through the substitution of CrO\(_4^{2-}\) ion for the seventh (OH\(^-\)) site in the structural element of AFm phase. The AFm phases show a good immobilization capacity of Cr\(^{6+}\).

2. Even though ettringite acts as a host to a number of waste ions, the immobilization of Cr\(^{6+}\) only occurs to a limited extend by substituting SO\(_4^{2-}\) sites. The soluble Cr\(^{6+}\) content equilibrated with ettringites in aqueous solution is higher than 10 ppm.

3. The immobilization mechanism by C–S–H gel appears more complicated. Two immobilization mechanisms are proposed: One is the substitution mechanism by which the OH\(^-\) ion site in the C–S–H gel is replaced by CrO\(_4^{2-}\) ion. The other is the sorption and incorporation mechanism by which CrO\(_4^{2-}\) ion is first adsorbed to the C–S–H gel, and then the Cr\(^{6+}\)-loaded C–S–H gel is wrapped into the hardened C\(_3\)S paste.

4. The stabilization ability for Cr\(^{6+}\) is in the increasing order of AFm > C–S–H > ettringite.

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