Synthesis and characterization of sulfate-iodate ettringite; and their potential role in immobilization of ^{129}I

Takeshi Iwaida*　Kazuki Yano*　Satoru Tanaka*　Shinya Nagasaki**

To improve the reliability of safety assessment of radioactive waste disposal system, it needs to elucidate the retention mechanism of radioactive nuclides by cementitious barrier material. In this study, iodate immobilization mechanism by ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$), which is one of the cement hydrated phases, was investigated. The sulfate-iodate ettringite which has various iodate concentration was synthesized by mixing KIO_3 and the crystal structure and the chemical composition of synthesized sample were investigated by using XRD and ICP-OES. In addition the sorption mechanism of IO_3^- onto ettringite was examined by comparing the characterization result of sulfate-iodate ettringite with the solid and liquid analyze result of iodate sorption experiment.

Keywords: cement, ettringite, iodate, sorption, solid solution

1 Introduction

In a geological disposal of TRU radioactive wastes, the ^{129}I is thought as the most important radioactive nuclide due to its remarkable long half-life (1.57×10^7 [y]) and its low efficiency for sorbing onto the bentonite and the mineral surface [1]. It is, therefore, significant to develop the technologies on the disposal and the treatment of wastes containing ^{129}I. Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$), which is one of the hydrated cement phases, is known as an anion substitutable crystal phase and expected for a host phase of radioactive anionic elements in a geological disposal condition [2]. In this study we scoped on the ettringite as a fixation material of ^{129}I.

Ettringite forms a trigonal-hexaganal crystal [3-4]. The columns of composition $\{Ca_6[Al(OH)_6]_2\cdot 24H_2O\}^{6+}$ build crystal structures through electrostatic interactions with the $\{(SO_4)_3\cdot 2H_2O\}^{6-}$ in the channels between columns (Fig.1). The columns are composed of $Al(OH)_6$ octahedra alternating with triangular groups of edge-sharing CaO_8 polyhedra, with which they share OH^- ions. Each calcium atom is also coordinated by four H_2O molecules, and the hydrogen atoms of coordinated H_2O form the nearly cylindrical surface of the column. The columns are parallel to the c-axis of crystal unit cell. Per formula unit with six calcium atoms, the channels contain four sites, of which three are occupied by sulfate ions and one by two water molecules. It has been reported that the channel site can host varieties of oxyanions (AsO_4^{3-}, $B(OH)_4^-$, CrO_4^{2-}, SeO_4^{2-}, and VO_4^{3-}) [5-9].

Although it needs to elucidate sorption mechanism for the long-term safety assessment of radioactive waste disposal, the immobilization process of iodate by ettringite is not fully understood. It is expected that a study of the synthesis and characterization of iodate-containing ettringites provides useful information correlated with iodate immobilization.

In this paper, the sulfate-iodate ettringite which has various iodate concentration was synthesized by mixing KIO_3. From the characterization of the prepared samples, the solid solution of the iodate-sulfate ettringite was confirmed and the uptake form of iodate was studied. The sorption experiment of iodate onto the pure ettringite was also carried out to examine the sorption mechanism of the iodate. The crystal structure and the chemical composition of synthesized sample were analyzed by using XRD (X-ray diffractometry), SEM (scanning electron microscope), ICP-OES (Inductively coupled radio frequency plasma optical emission spectrometry), and TG/DTA (thermogravimetry / differential thermal analysis).

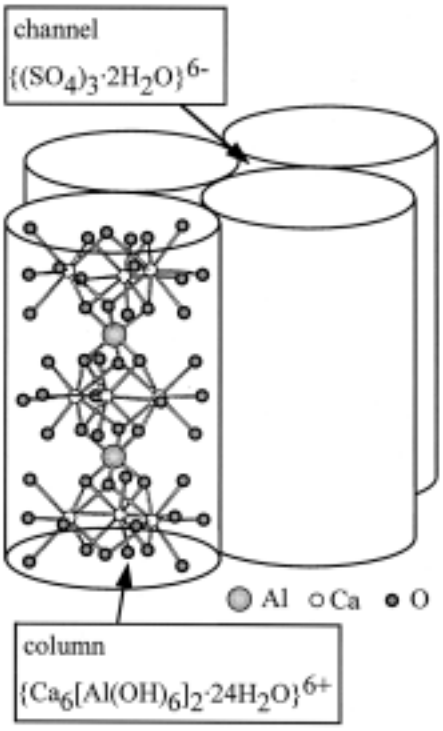

Fig.1 Structure of ettringite [3-4].

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2 Experimental

2.1 Synthesis of ettringite

Ettringite was synthesized by mixing $Ca(OH)_2$ and $Al_2(SO_4)_3 \cdot 18H_2O$ in a 0.1M NaOH solution (liquid-solid ratio of 0.01 m^3/kg), to give a $Ca:SO_4$ mole ratio of 2:1.

$$6\,Ca(OH)_2 + Al_2(SO_4)_3 \cdot 18H_2O \xrightarrow{aq.} Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O \quad (1)$$

The slurry was aged for two days, and filtrated using a membrane filter with a pore size of 0.45μm. The slurry on the filter was flushed to remove NaOH. A mild vacuum was applied to take away excess water from solid products with hygroscopic P_2O_5.

2.2 Synthesis of sulfate-iodate ettringite

To synthesize sulfate-iodate ettringites, various amounts of $Ca(OH)_2$, KIO_3, $Al_2(SO_4)_3 \cdot 18H_2O$, and $Al(OH)_3$ were mixed in a 0.1M NaOH solution (0.01 m^3/kg). The amount of $Al_2(SO_4)_3 \cdot 18H_2O$ in Eq. (1) was alternated as following:

$$Al_2(SO_4)_3 \cdot 18H_2O \xrightarrow{aq.} (1\text{-}x)Al_2(SO_4)_3 \cdot 18H_2O + 6xKIO_3 + 2xAl(OH)_3 \quad (2)$$

The samples were so prepared that the iodate compositions in one mole of iodate-sulfate ettringite became 0.6, 1.2, 1.8, 2.4, and 3.0 mol. The slurries were aged for two days, separated from water, washed, and dried in the same way as section 2.1.

For synthesizing the different ettringite solid solutions, two methods have been chiefly used.

1. *Paste reaction* [7, 8, 10-12]: The sample is prepared by mixing lime-water, aluminum salt, and salts containing the different anions.
2. *The saccharat-method* [5, 7, 9]: A solution of aluminum salt and salts containing the different anions are mixed with the soluble calcium complex consisting of lime dissolved in a 10% sucrose solution.

Poellmann *et al* [10]. reported that the crystal shapes and cell volumes of ettringite solid solutions containing $B(OH)_4^-$ and CrO_4^{2-} were depended on the preparation methods. In this paper, paste reaction method was chosen for preparation of iodate-sulfate ettringite to avoid the effect of the sucrose (e.g. complexation of sucrose with iodate).

2.3 X-Ray diffraction

The MAC science M03X was used to obtain X-ray diffractograms. XRD patterns of solid products were collected with Cu-$K\alpha_1$ radiation at 35kV/20mA. The diffraction angle scans ranged from 8.5 to 40° (2θ) with a speed of 0.5° (2θ) per 1min. The positions of seven peaks (see Fig.2-a) were measured and corrected with mica (NIST Standard Reference Material SRM 675). Lattice constants were refined by a least squares method [13]. For hexagonal crystal, flowing relationship was known.

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2 + hk + k^2}{a_0^2} + \frac{l^2}{c_0^2} \quad (3)$$

Where, d nm is the interplanar spacing which have Miler indices (hkl). In addition, a_0 and c_0 are the lattice constants of a axis and c axis, respectively. The lattice constants of the samples were obtained by fitting d's into Eq.3 at the seven peaks.

2.4 Chemical analysis

The prepared samples were dissolved in a 0.5N HNO_3 solution at liquid-solid of 1m^3/kg. Quantitative elemental analyses were performed for Ca, Al, S, I, Na, and K using ICP-OES (ICPS-10004, Shimadzu). We carried out the experiments in oxidizing environment and there is no reducing agent. It was considered, therefore, I in solution and solid existed as IO_3^-. The amount of impurities ($Al(OH)_3$, and $Ca(OH)_2$) in the solids and water content of each sample were determined by gravity changes from 25°C to 1000°C using TG/DTA (DTG-30, Shimadzu). The weight reduction at 270°C and 420°C were measured to determine the amount of $Al(OH)_3$ and $Ca(OH)_2$, respectively. We had already confirmed that the weight reductions corresponded with each compound by analyzing TG/DTA of $Al(OH)_3$ and $Ca(OH)_2$ reagents. The weight reduction corresponded with $CaCO_3$ was not observed by TG/DTA. Therefore it is considered that the amounts of $CaCO_3$ in the samples are negligible.

2.5 Sorption experiments

The pure ettringite samples were weighted in polypropylene bottles. The 0.01M KIO_3 solutions (0.1 m^3/kg) of which pH was adjusted to be 12 by dissolving NaOH were poured into the bottles. We chose this high pH to avoid solid alteration occurring at low pH [12]. After 1, 3, 7, 14, 21, and 49 days, the solids were separated from the solutions by filtration using a membrane filter with a pore size of 0.45μm.

Concentrations of I in the filtrates were determined by ICP-OES. The solids of 21days on the filter were dried and analyzed in the manner as sections 2.2 and 2.3.

In this study, the pure water (Millipore, Milli-Q plus) was decarbonated by purging N_2 gas, and the experiments were carried out in a glovebox filled with N_2 gas (N_2 purity>99.99%) at room temperature. All reagents were analytical grade and supplied by Wako Pure Chemical Industries.

3 Results and discussion

3.1 SEM and XRD characterization

In Fig.2 (a), every peak position of XRD patterns of solid products without KIO_3 matched well to reported values [12]. The XRD patterns of the samples prepared with KIO_3 were shown in Fig.2 (b-f). The peak positions except those of

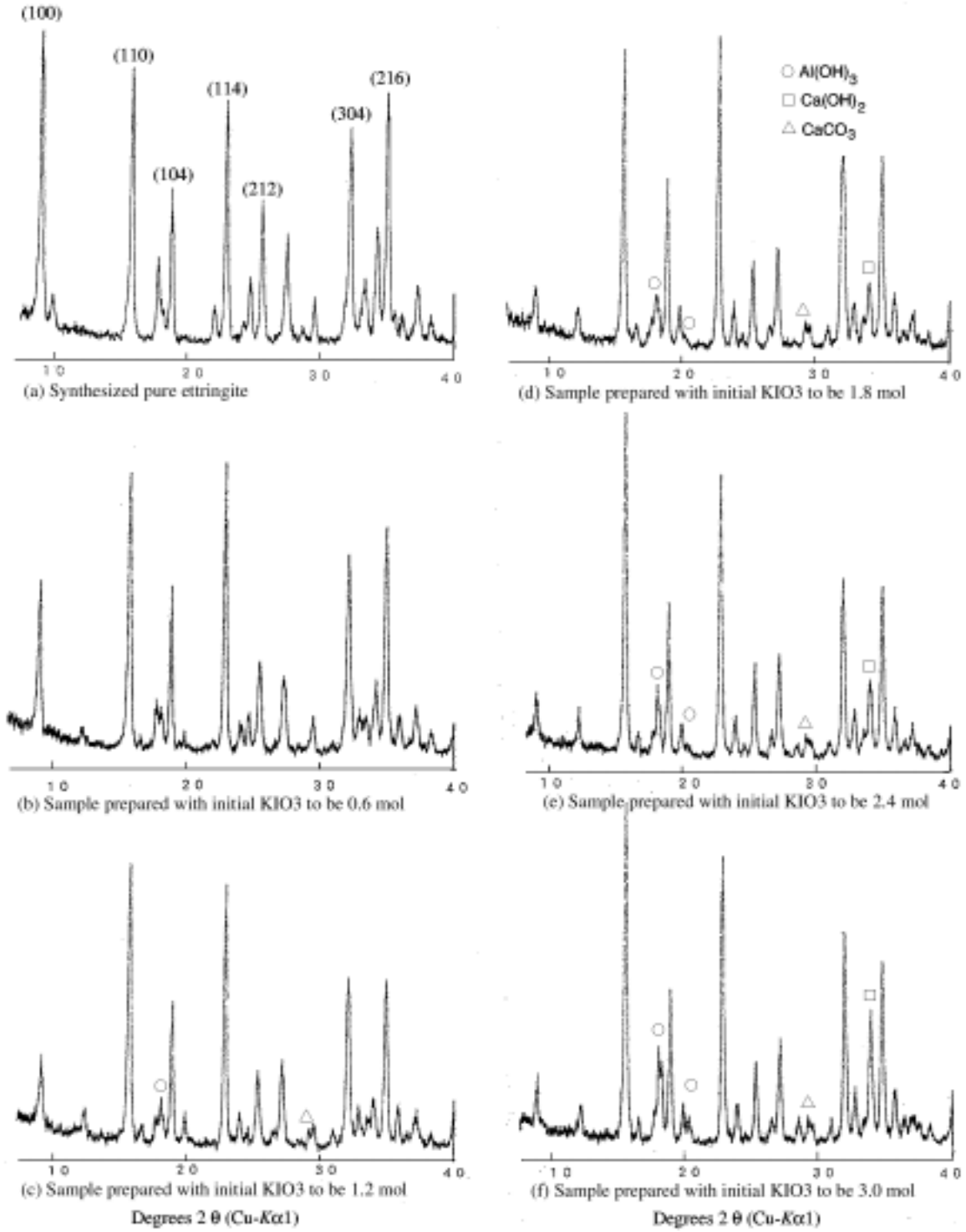
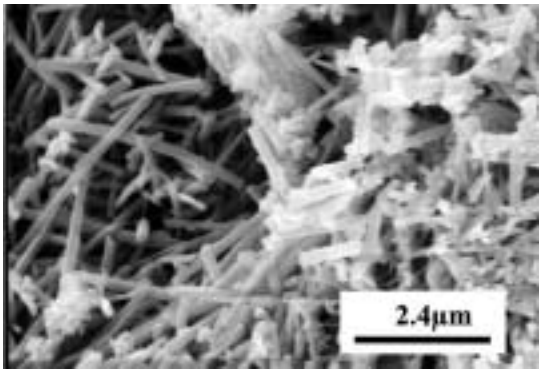
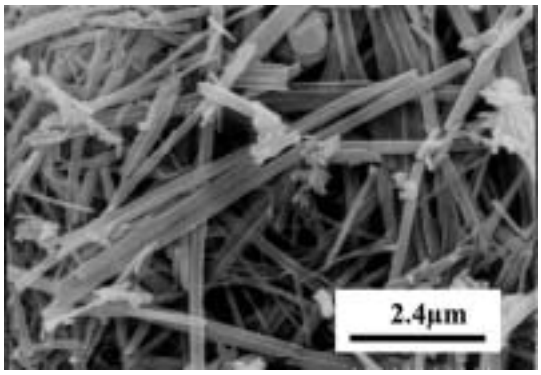


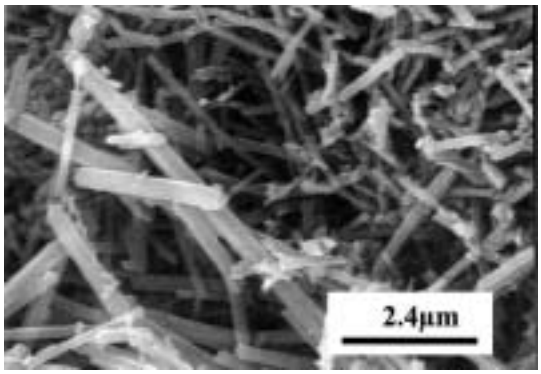
Fig.2 X-ray diffraction pattern characteristic of the synthesized solid products: (a) pure ettringite; (b-f) the samples prepared with initial KIO_3 to be 0.6, 1.2, 1.8, 2.4, and 3.0 mol, respectively.



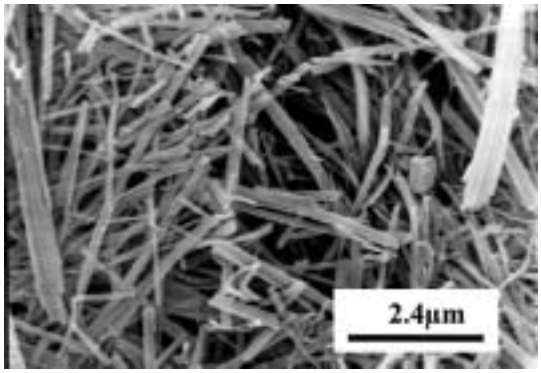
(a) SEM image of sample prepared with no KIO_3 reagent



(b) SEM image of sample prepared with initial KIO_3 to be 0.6 mol.



(c) SEM image of sample prepared with initial KIO_3 to be 1.2 mol.



(d) SEM image of sample prepared with initial KIO_3 to be 1.8 mol.

Fig.3 SEM image of the synthesized sulfate-iodate ettringites.

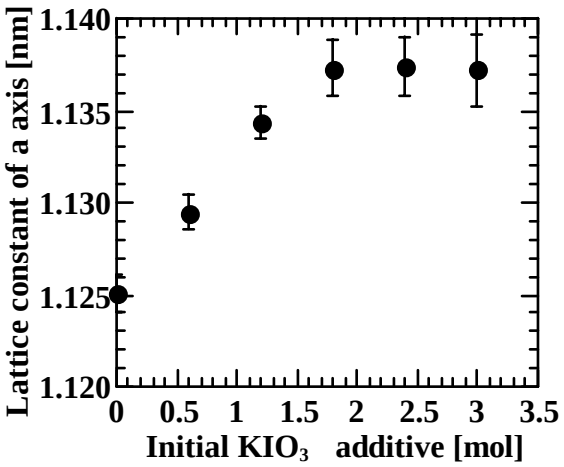
impurities ($Al(OH)_3$, $Ca(OH)_2$, and $CaCO_3$) were close to the values of ettringite. Figure 3 are SEM (S-4100, Hitachi) images of synthesized sulfate-iodate ettringite. Crystal formed typical needle-shape of ettringite. From these results, it was confirmed that the ettringite was indeed formed by the methods mentioned in section 2.1and 2.2.

In Fig.4, lattice constants of ettringite were plotted against initial KIO_3 additive. It was observed that lattice constant of a-axis increased linearly and that of c-axis decreased linearly along with increasing IO_3^- concentration till 1.5 mol. According to Vegard role[13], it is known that lattice constant linearly changes along with increasing concentration of solute end-member. It was considered that the change of lattice constants was caused by increasing concentration of end-member IO_3^- in ettringite. The changes stop around initial content of 1.5 mol. Thus, it was revealed that the solid-solution of IO_3^- in ettringite had a limitation at 1.5 of initial KIO_3 additive.

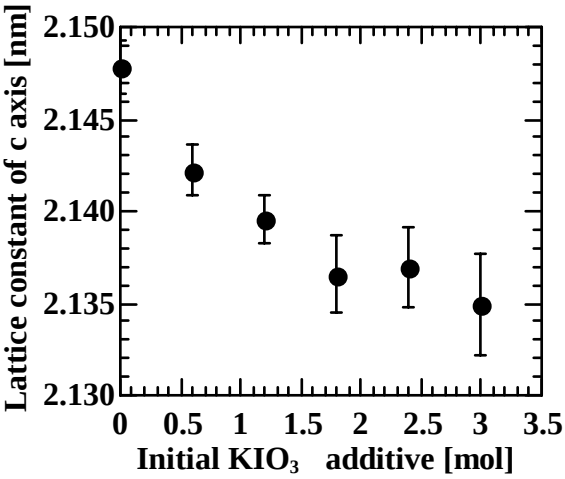
3.2 Chemical Characterization

Table 1 gives structural formulae of prepared samples in which all elements are normalized to Ca = 6. Structural formulae have been calculated from the analyses using the following procedure [5]: The composition of solid products was determined in the way as section 2.3. However, XRD analysis showed that remarkable quantitative impurities remained in the products. The amount of impurities with prepared sample was measured using TG/DTA. We made the assumption that the composition of solid products without impurities corresponded to only one phase, sulfate-iodate ettringite, in which all initial additive iodate was included. The composition of sulfate-iodate ettringite was determined by subtracting impurity contribution from total composition of solid products. Whole charge balance was adjusted by adding OH^-. Finally the H_2O content determined by weight reduction at 100~140 °C which was corresponded with strong endtherms of DTA curves of synthesized pure ettringite.

Table 1 shows that samples prepared with initial KIO_3 to be less than 1.2 mol had Ca:Al ratio of 6:2. The ratio equals to that of column in pure ettringite. It is considered that the samples have those column structures. It is also observed that sulfate decreased with increasing iodate, and decreasing of sulfate was compensated by twice iodate ions. As shown in Fig. 1, ettringite has four sites in a channel for three SO_4^{2-} ions. Thus, total negative charge in a channel is six. Figure 5 showed the sum of anionic charges in the prepared samples. The samples of which initial additive were lesser than 1.2 mol maintained six negative charges in a channel. It can be considered one SO_4^{2-} in the structure of ettringite substitute with two IO_3^-s, considering charge difference between SO_4^{2-} and IO_3^-. That is, because the stoichiometry of solid products



(a) attice constant of a axis of synthesized sulfate-iodate ettringite



(b) Lattice constant of c axis of synthesized sulfate-iodate ettringite

Fig.4 Variation of lattice constants of synthesized sulfate-iodate ettringite.

Table 1 Chemical compositions of prepared samples

Initial KIO_3 Additive	Chemical Formula[a]					
	Ca	Al	SO_4	IO_3	OH	H_2O
Ideal ettringite	6	2	3	0	12	26
0	6	2.01	2.94	0.00	12.15	26.40
0.6	6	2.09	2.71	0.67	12.18	26.31
1.2	6	2.05	2.19	1.50	12.27	27.00
1.8	6	1.44	2.00	1.80	10.52	27.54
2.4	6	1.35	1.70	1.85	10.64	26.70
3	6	1.34	1.52	1.65	11.33	17.60

a. Normalized to Ca = 6

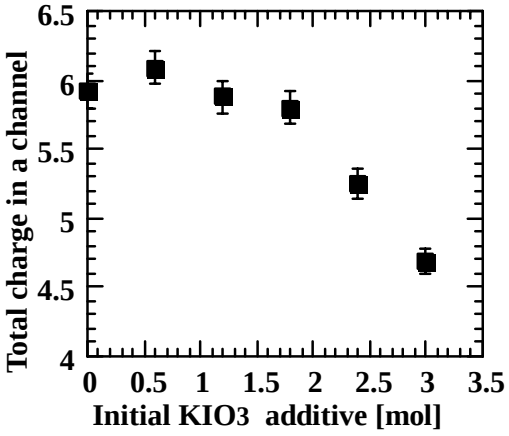


Fig.5 Total charge of anions in a channel of sulfate-iodate ettringite

satisfied $Ca_6Al_2(SO_4)_{3(1-x)}(IO_3)_{6x}$, it was suggested that the sulfate-iodate ettringite have the column structure and the IO_3^- existed in the channel of ettringite at low concentration samples.

If one SO_4^{2-} was completely substituting with two IO_3^-s, final Ca:SO_4^{2-}: IO_3^- ratio becomes 6:2:2. Nevertheless, the entering of IO_3^- stops at 1.2 mol of initial additive. From XRD analysis, the similar limitation of lattice constants change was observed at the same initial additive. In the samples which have more than 1.8 mol of initial KIO_3, Ca:Al ratio became 6:1.4, thus the structure of column could not maintain. The size and geometric differences between IO_3^- and SO_4^{2-} are considered as one candidate of the cause. At high iodate concentration samples, much defects in the Al site of ettringite was observed. One of the possibilities for defects in the Al site is direct sorption of IO_3^- ion onto the column of ettringite. In the case of arsenate sorption onto ettringite [7], it was said that the arsenate ion existed in the channel of etrringite with hydrated water molecules at low concentration of arsenate. At high concentration of arsenate, however, the arsenate ion sorbed directory onto the column of ettringite by distorting Ca polyhedra. If same kind of mechanism were occurred, Al that connected to Ca polyhedra must remove from the structure of the ettringite. However, exact solution to the cause could not be obtained. Further detailed study is necessary with a proof.

3.3 Sorption experiment

In this work, the distribution coefficient, K_d m^3/kg, is defined as

$$K_d = \frac{C_{sorbed}}{C_{liq}} = \frac{(C_{init} - C_{liq}) \times R}{C_{liq}} \qquad (4)$$

where C_{init} mol/m^3 is the IO_3^- concentration in initial solution. C_{sorbed} mol/kg and C_{liq} mol/m^3 are the IO_3^- concentrations in solid and liquid phases after certain periods, respectively. R m^3/kg is the liquid-solid ratio of the samples. In Fig. 6, the K_d values of IO_3^- for sulfate ettringite were plotted against time. The K_d value increased gradually with increasing time, and became seemingly stable at about 0.3 m^3/kg after 21 days.

The chemical structure of the sample, which contacted with IO_3^- solution during 21 days was determined as $Ca_6Al_{1.97}(SO_4)_{2.47}(IO_3)_{0.93}(OH)_{12.04}$. The lattice constants of a axis and c axis were 1.132 nm and 2.142 nm, respectively. The lattice constants of this sample (opened circle) and the synthesized samples (closed circle) are plotted in Fig.7 along with final IO_3^- concentration in solid. The lattice constants of IO_3^- sorbed sample suit well to fitting lines, which were drawn by the data of synthesized samples. It is considered that the sorbed IO_3^- is retained in the way as synthesized sample, that is IO_3^- sorbed into the channel of ettringite by substituting with SO_4^{2-}.

4 Conclusions

From the characterization of sulfate-iodate ettringite that has various iodate concentrations and the sorption experiment of iodate on ettringite, the following conclusions were drawn.

1. The lattice constants of sulfate-iodate were changed with increasing initial KIO_3 additive. It is thought that the IO_3^- entered ettringite structure as an end-member of solid solution. This solid solution had a limitation at 1.5 mol of initial KIO_3 additive.
2. From the chemical analysis of synthesized samples, it is concluded that the two IO_3^-s were entered ettringite channel by substituting with one SO_4^{2-}.
3. The sorption of IO_3^- occurred by substituting with SO_4^{2-} in an ettringite channel.

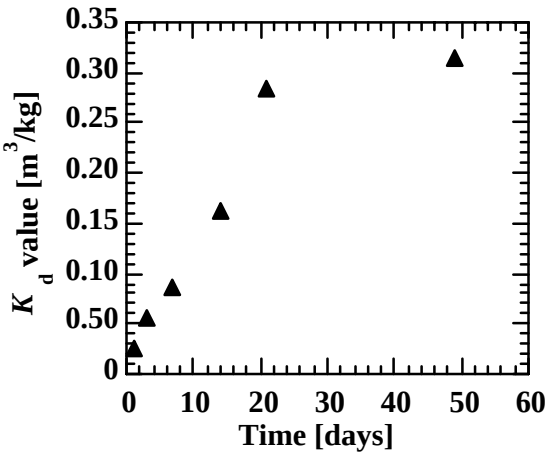
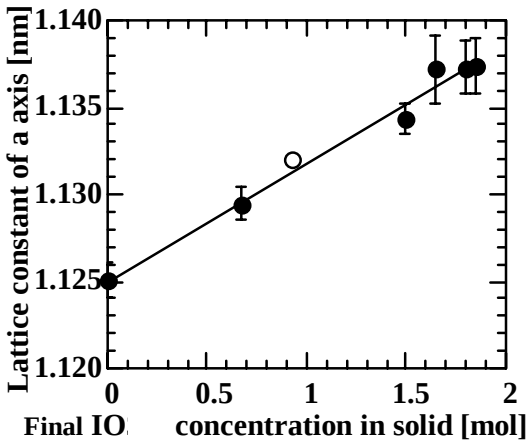
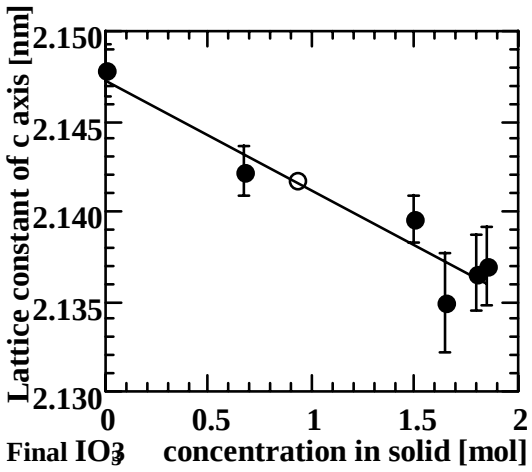


Fig.6 K_d value of IO_3^- to ettringite.



(a) Lattice constant of a axis of synthesized sulfate-iodate ettringite and IO_3^- sorbed ettringite.



(b) Lattice constant of c axis of synthesized sulfate-iodate ettringite and IO_3^- sorbed ettringite.

Fig.7 Variation of lattice constants of synthesized sulfate-iodate ettringite and IO_3^- sorbed ettringite.

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