Feedback System of Ion Transfer through Cracks During Deterioration of Mortar Due to Sulfate Attack Evaluated by RBSM-Truss Network Model

Taito Miura, Ippei Maruyama, Hikaru Nakamura, Yoshihito Yamamoto
Journal of Advanced Concrete Technology, volume 15 (2017), pp. 610-626

Related Papers Click to Download full PDF!

Time-Dependent Structural Analysis Considering Mass Transfer to Evaluate Deterioration Process of RC Structures
Hikaru Nakamura, Worapong Srisoros, Ryosuke Yashiro, Minoru Kunieda
Journal of Advanced Concrete Technology, volume 4 (2006), pp. 147-158

Numerical Approach towards Aging Management of Concrete Structures: Material Strength Evaluation in a Massive Concrete Structure under One-Sided Heating
Ippei Maruyama, Go Igarashi
Journal of Advanced Concrete Technology, volume 13 (2015), pp. 500-527

Modeling of corrosion-induced damage in reinforced concrete considering electro-mechanical coupling
Di Qiao, Hikaru Nakamura, Yoshihito Yamamoto, Taito Miura
Journal of Advanced Concrete Technology, volume 14 (2016), pp. 664-678
Scientific paper

Feedback System of Ion Transfer through Cracks During Deterioration of Mortar Due to Sulfate Attack Evaluated by RBSM-Truss Network Model

Taito Miura1*, Ippei Maruyama2, Hikaru Nakamura3 and Yoshihito Yamamoto4

Received 13 May 2017, accepted 19 October 2017 doi:10.3151/jact.15.610

Abstract

In this paper, the transformation of solid phase and expansion cracking behaviors due to sulfate attack were evaluated by using RBSM-Truss Network Model. This analysis was constructed by combining a hydration model, a diffusion-reaction model, and a crack propagation model in order to evaluate the influence of feedback system of ion transfer through cracks on transformation of solid phase and expansion cracking behavior due to sulfate attack. As a result, the proposed model can predict the change in phase assemblage and physical properties due to hydration process and the change in the transformation of solid phase and the distribution of sulfate ion due to sulfate attack. It was found that expansion crack can affect the diffusion process and expansion cracking behavior as the crack behaves as a buffer of sulfate ion.

1. Introduction

It is well-known that cementitious materials constructed in certain environments including sulfate ions chemically react with sulfate ions which either weakens the cement hardened body or causes an expansion cracks, or both. These phenomena are generally called by external sulfate attack and this deterioration mainly comes from sulfate salt such as gypsum and ettringite. The mechanisms of sulfate attack have been understood as follows (Taylor 1997; Skalny et al. 2002).

1) Infiltration of sulfate ion from external environment.
2) Sulfate ion, monosulfate and Ca ion can be chemically reacted and ettringite can precipitate.
3) After that monosulfate was completely consumed by the production reaction of ettringite, gypsum could be produced due to the reaction of sulfate ion and Ca ion.

The reaction of ettringite and gypsum due to sulfate attack has been understood to be a topo-chemical reaction which occurs in the pore solution around the original reactants (Mehta 1973; Odler et al. 1999). It has also been observed that ettringite tends to expand and is attributed to expansion cracks in cementitious material. Two hypotheses were suggested to explain how to expansion pressure is generated. The swelling theory proposed by Mehta (1973) said that expansion pressure can generate as ettringite absorbs water molecule which increases the volume of ettringite. On the other hand, the crystallization pressure theory proposed by Wellman et al. (1965) and applied to sulfate attack by Flatt and Scherer (2008), explains the expansibility due to ettringite as process in which after that ettringite becomes supersaturated in pore solution and crystallization starts, ettringite crystal grows in a pore and expansion pressure generates since it gets in contact with pore wall. In these two hypotheses, the concept of precipitation process and precipitation location of ettringite is different. Many researchers have contributed in order to judge which hypothesis is adequate and consistent with the experimental results under several conditions. To date, there is no consensus on which theory is more applicable. This further suggests that sulfate attack is a complicated phenomenon that is linked to diffusion, reaction (dissolution and precipitation), and mechanics.

Several numerical analyses that attempt to reconstruct sulfate attack have been developed for decades. Prior to that, degradation prediction methods that modeled the relationships between ettringite and expansion rate based on experimental data have been proposed. Diffusion-reaction model for predicting the amount of ettringite and the volume change in solid phase and expansion model for estimating expansion rate have also been proposed. In general, the proposed diffusion-reaction model is composed of a mass transfer term and a reaction term. With regard to mass transfer modeling, diffusion model considers interaction of coexistence ion (Maltais et al. 2004; Glasser et al. 2008; Schmid et al. 1999a, 1999b) or brief diffusion model of sulfate ion (Krajcinovic et al. 1992; Tixier et al. 2003a, 2003b; Idiart et al. 2011; Ikumi et al. 2014). In addition, some

1Assistant Professor, Graduate School of Civil Engineering, Nagoya University, Nagoya, Japan.
*Corresponding author, E-mail: t.miura@civil.nagoya-u.ac.jp
2Professor, Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan.
3Professor, Graduate School of Civil Engineering, Nagoya University, Nagoya, Japan.
4Associate Professor, Graduate School of Civil Engineering, Nagoya University, Nagoya, Japan.
researcher take account for the effect of moisture transfer against sulfate attack in order to evaluate the influence of drying condition (Maltais et al. 2004; Glasser 2008,). On the other hand, in terms of reaction modeling, thermodynamic modeling for reconstructing the dissolution and precipitation phenomena in cementitious system, and chemical reaction model described by exponent function as an index of time using reaction rate constant were proposed. Thermodynamic model can predict the change in solid-liquid phase due to dissolution and precipitation from thermodynamic equilibrium condition based on thermodynamic data (Maltais et al. 2004; Glasser et al. 2008; Schmid et al. 1999a, 1999b; Lothenbach et al. 2010). In comparison, chemical reaction model can calculate the change in reactant and precipitation from molar ratio of chemical reaction equation. In this approach, chemical reaction is defined by certain minerals and sulfate ion, and reaction rate constant is set to fit in actual phenomena (Krajcinovic et al. 1992; Tixier et al. 2003a, 2003b; Idiart et al. 2011; Ikumi et al. 2014).

In order to evaluate expansion behavior, several expansion models were proposed which are normally based on the relationship between the change in solid volume and expansion strain. The difference in the proposed models can be observed in their method of estimating macroscopic expansion rate. In one of the approaches, stress-strain curves are changed in association with damage factor defined by an expansion strain and expansion rate which can be calculated from stress and elastic modulus at certain expansion strain and averaged area (Krajcinovic et al. 1992; Schmid et al. 1999a, 1999b; Tixier et al. 2003a, 2003b). Another approach is that, expansion rate is calculated by structural analysis introduced by expansion strain as initial strain (Idiart et al. 2011). In addition, a model that provides a relationship between expansion strain and pore distribution was also proposed in order to consider that smaller pore diameter potentially has bigger expansion pressure (Schmid et al. 1999a, 1999b; Ikumi et al. 2014). Furthermore, models that considered the change in diffusivity and mechanical behaviors after degradation were also developed. In terms of the model considering the change in diffusivity, the diffusivity of degradation area was evaluated from the change in porosity (Maltais et al. 2004; Glasser et al. 2008; Schmid et al. 1999a, 1999b; Lothenbach et al. 2010; Idiart et al. 2011) or damage factor (Krajcinovic et al. 1992; Tixier et al. 2003a, 2003b; Ikumi et al. 2014). With regard to model that considers the change in mechanical behaviors, material strength of degradation area can be estimated based on the relationship between porosity and strength (Schmid et al. 1999a, 1999b).

The presented studies which attempt to evaluate the transformation of solid phase and expansion behavior due to sulfate attack by numerical analysis have contributed to the clarification of degradation mechanisms. These analyses have been able to consider the different environmental and material factors needed to evaluate long-term durability. Prediction methods—applied to design and maintenance—used to determine the extent of degradation need to carry out the exposure test for construction environment in order to fit the parameters. The tasks that elaborate numerical analysis cannot describe still remained although those analytical models have proposed for the reconstruction of the mechanisms and prediction method of sulfate attack. One was the treatment of diffusivity in deterioration area. For example, Lothenbach et al. (2010) confirmed that the amount of SO$_2$ in solid phase was independent of immersion time and sulfate ion concentration of outer solution in experiment but numerical simulation cannot calculate those tendencies. As described before, proposed model has modeled the change in diffusivity in deterioration area by means of modification of diffusion coefficient corresponding to the reduction of porosity due to transformation of solid phase or diffusion coefficient of cracking area modeled by the diffusion coefficient in dilute solution. That these attempts cannot reconstruct the transformation of solid phase seems to important information related to accuracy of prediction methods of cementitious material damaged by sulfate attack. It could be supposed that sulfate ion can penetrate into crack from cracking surface and transfer through crack after cracking and sulfate ion concentration in crack increases and decreases corresponding to crack propagation and crack width. That is to say, there is possibility of change in mass balance of sulfate ion corresponding to expansion cracking propagation. Moreover, considering that ettringite crystal growth at large space is earlier, sulfate ion in expansion crack, which has larger space, is easily consumed by crystal growth of ettringite and sulfate transfer inward from expansion crack is supposed to be retarded. In fact, proposed models cannot accurately evaluate the mass balance of sulfate ion at expansion cracking area. Another task was the modeling of expansion rate. In most of proposed models, macroscopic expansion rate have modeled by expansion strain and the change in solid volume. Those modeling seem to have limited range of application because they had been defined by expansion rate observed certain experiment. For instance, expansion rate is depending on specimen size and constraint condition. Thereby, proposed models should not directly introduce to structural member which has complicated boundary condition and constraint condition. Therefore, the evaluation and prediction of macroscopic expansion rate should be discussed by structural analysis not only mathematical model. In terms of ASR, many researchers have attempted the development of prediction method for both of structural performance and durability by means of coupled with deterioration prediction model and structural analysis. However, those discussions seem to be very few in terms of sulfate attack. This is because sulfate attack have been regarded that expansion crack due to sulfate attack cannot influence to deterioration process in com-
parison to ASR. However, as expansion crack is supposed to influence to diffusion phenomena such as the former task, it should be necessary to evaluate manifestation and propagation of expansion crack itself.

In this study, an analytical approach for verifying the influence of expansion crack on diffusivity of sulfate ion was investigated. The authors have developed a three-dimensional crack propagation analysis named Rigid-Body-Spring-Model (RBSM). Moreover, mass transfer through the cracks such as moisture transport and chloride ion penetration can be evaluated by means of coupling RBSM with Truss Network Model (Nakamura et al. 2006). Using RBSM-Truss Network Model, we have conducted several attempts to reconstruct transformation of solid phase, macroscopic expansion rate and expansion cracking behavior (Miura et al. 2016). In this paper, the numerical analytical system, which can reconstruct hydration process, transformation of solid phase and manifestation and propagation behavior of expansion crack, is proposed based on previous model (Miura et al. 2016). This analytical system is composed of a hydration model using Computational Cement-Based Material model (CCBM) (Maruyama 2015) that can predict the change in solid phase, porosity, and mechanical behaviors due to hydration; a diffusion-reaction model that can predict transportation of sulfate ion and transformation of solid phase due to sulfate attack; and RBSM which can evaluate expansion cracking behavior.

In this paper, the adequacy of proposed model is first discussed through validation with the experimental and analytical results from Lothenbach et al. (2010). Subsequently, we investigate the influence of feedback system of ion transfer through cracks on transformation of solid phase and expansion cracking behavior due to sulfate attack by using several transfer models.

2. Modeling of sulfate attack

The analytical flow of modeling sulfate attack is shown in Fig. 1. This analysis is composed of CCBM for hydration process, diffusion-reaction model for sulfate attack, and RBSM for manifestation and propagation behavior of expansion crack. In this analysis, the change in phase assemblage, porosity, and compression strength along with curing time based on mineral composition is derived by CCBM. Then, diffusion coefficient of sulfate ion is calculated corresponding to the change in porosity. Subsequently, the transformation of solid phase has been calculated—using a diffusion-reaction model which can predict the transportation of sulfate ion, and the reaction with sulfate ion and hydrates—at each time step. At this stage, ettringite and gypsum can be produced depending on the existence of monosulfate. After this process, the change in porosity due to the transformation of solid phase is calculated. If the calculated porosity is less than a certain value expansion pressure can be generated and the expansion strain, which takes into account the increment of ettringite that produced after the threshold value of porosity, is estimated at each time step. The expansion behavior such as manifestation and propagation of crack is then evaluated using RBSM through the introduction of expansion strains into mechanical springs of RBSM. Finally, after cracking, the diffusivity of sulfate ion in crack corresponding to crack width is introduced. The complete details of these modeling approaches will be shown in the succeeding sections.

2.1 CCBM

CCBM is one of the cement hydration model proposed by Maruyama et al. (2015). This model has been constructed by physical and chemical properties that can influence to the hydration process of cementitious material under different relative humidity and temperature based on many experimental data. CCBM can predict phase assemblage, porosity, strength of cement paste and concrete in a hydration process under several conditions. In this section, the capillary porosity, \( p_{\text{cap}} \), is estimated by subtracting gel porosity from total porosity. Indeed, gel porosity was defined as the difference between molecular volume of \( \text{C}_1.7\text{SH}_2.5 \) and \( \text{C}_1.7\text{SH}_4.0 \). The details of the physical properties can be found in Maruyama et al. (2015).

2.2 Diffusion-reaction model for sulfate attack

The authors have proposed diffusion-reaction model for
sulfate attack. This analysis is discretized by finite volume method. This model takes into account the sulfate ion diffusion, and the reactions of ettringite and gypsum by a reaction rate constant related to portlandite. In addition, the stability of ettringite due to the value of pH suggested by Gabrišova et al. (1991) is introduced in order to take into account for dissolution of ettringite at near surface. These dissolution and precipitation processes, however, should be evaluated by chemical equilibrium condition in solid-liquid phase. Considering the above problem, this study is dedicated on a simple production reaction of ettringite from monosulfate in order to describe the chemical reaction clearly.

The concise model for sulfate attack is shown in Fig. 1. As mentioned, the aluminate phase consumed by the reaction of ettringite is only monosulfate. Then, the production reaction of ettringite which reacted with sulfate ion, portlandite and monosulfate, and the reaction of gypsum should be modeled. In this analysis, sulfate attack was described by a reaction rate with regard to the reaction of sulfate ion and portlandite because dissolved portlandite involves both production reaction of ettringite and gypsum. Intrinsically, all of aluminate phase can be involved into the reaction of ettringite. These reaction rate constants, however, are not yet fully understood. Therefore, in this paper, a diffusion-reaction model is utilized as a tentative model.

Ion transfer and consumption with regards to sulfate ion in cement matrix were modeled by Eq. (1).

\[
\frac{\partial (P_{cem} \cdot C_{liquid})}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial (P_{cem} \cdot C_{liquid})}{\partial x} \right) + \frac{\partial C_{solid}}{\partial t}
\]  

(1)

where, \(C_{liquid}\) is the concentration of sulfate ion in liquid phase (mol/l); \(C_{solid}\) is the concentration of sulfate ion in solid phase (mol/l); \(D\) is the diffusion coefficient of sulfate ion (mm²/sec); and \(P_{cem}\) is the porosity in cement paste (cm³/cm³).

Based on Garboczi and Bentz (1992) study, the influence of the change in pore structure can be introduced using Eq. (2).

\[
\frac{D}{D_0} = 0.001 + 0.07 \cdot p_{cap}^2 + 1.8 \cdot H_p \left( p_{cap} - 0.18 \right)^2
\]  

(2)

where, \(D_0\) is the diffusion coefficient of sulfate ion in dilute solution (mm²/sec); \(p_{cap}\) is capillary porosity (cm³/cm³); and \(H(x)\) is the Heaviside function (if \(x > 0\), \(H(x) = 1\), if \(x \leq 0\), \(H(x) = 0\)).

The reaction with sulfate ion and portlandite is defined using Eq. (3). In this analysis, \(K_{CH}\) should be defined using experimental results as will be described later.

\[
\frac{\partial C_{solid}}{\partial t} = \sum (K_{CH} \cdot CH_{cem} \cdot C_{liquid})
\]  

(3)

where, \(K_{CH}\) is the coefficient value of reaction rate of portlandite (cm³/sec); and \(CH_{cem}\) is the amount of portlandite in cement paste (g/cm³).

Considering that the reduction of pH value started after CH completely disappeared, expansion cracking behavior cannot be dramatically changed by the change in pH because the CH disappeared area is narrow surface area and ettringite already precipitated before CH disappeared in the objective analysis. Therefore, this analysis didn’t consider the influence of pH on ettringite precipitation. Furthermore, in this analysis, the author proposed the balance of solid-liquid phase by only sulfate ion in diffusion-reaction model as distinct from multiphase system such as thermodynamic phase equilibrium calculation. In particular, the influence of interaction of cation and anion and pH in liquid phase on ettringite precipitation was assumed as the brief reaction-diffusion system in association with sulfate ion by first approximation. As described later, it was confirmed that this analysis can describe the presumable expansion cracking behavior.

2.3 Expansion pressure model

It is known that the manifestation and propagation behavior of expansion crack due to sulfate attack would be influenced by several factors. With respect to precipitation process of ettringite, Odler et al. (1999) observed that the expansion does not occur so much by through-solution reaction, but expansion occurs in case of that crystallization of ettringite occurs at the surface of original phase because the crystal has directional characteristics. Mehta (1973) mentioned in his swelling theory that ettringite has colloid-like behavior and it could absorb many water molecules which results to swelling. In contrast, Flatt and Scherer (2008) developed crystal growth theory that ettringite crystal could push pore wall and expansion pressure could be generated. Still in relation to the precipitation area of ettringite, Tosun et al. (2010) investigated the effect of morphology of ettringite and mentioned that ettringite produced in entrapped air does not generate expansion but ettringite produced in narrow area such as micro crack could have expansibility. In this connection, Flatt and Scherer (2008) mentioned that expansion pressure become bigger as pore diameter is smaller and they proposed interpretation in association with the relationship between pore shape and expansion pressure. Thus, the expansion mechanism of ettringite is not yet fully understood because of those complicated influences of precipitation process and/or precipitation location. In addition, the macroscopic expansion behavior can be changed by internal constraint effect due to different specimen size even though deterioration area is same (Cheng et al. 2013). Therefore, the adequate expansion model considering internal stress state should be constructed to evaluate how microscopic transformation is related to macroscopic expansion behavior. To solve this problem, the combined application with experiment and structural analysis seems to be available.
From the point of view of engineering aspect, a prediction method has been proposed. According to proposed model, expansion strain can be defined by the amount of ettringite or the change of solid volume although the modeling method of macroscopic expansion rate is different. In this analysis, the expansion model is represented such that the expansion strain can generate the corresponding amount of ettringite. In addition, it is known that after the supersaturation of ettringite, ettringite crystal is produced in the pore solution and expansion pressure is generated whenever the crystal gets into contact with pore wall as described in the crystal growth theory. Then, the introduced time lag in the expansion model which suggests that expansion pressure will begin to generate when the ratio of temporal porosity to certain porosity at averaged volume becomes lower than threshold porosity ratio named as \( p_{TH} \) by reference to Tixier et al. (2003a, 2003b) and Ikumi et al. (2014). The expansion strain was calculated by the precipitation amount of ettringite after \( p_{TH} \). In particular, as shown in Eq. 4, the increment of ettringite named by effective ettringite: \( ETT - ETT_{pre} \) in every time steps can contribute to expansion strain.

\[
\varepsilon_{ex} = \alpha \left( ETT - ETT_{pre} \right) \tag{4}
\]

where, \( \varepsilon_{ex} \) is the expansive strain, \( \alpha \) is the conversion factor of expansive strain (cm/g); \( ETT \), the temporal amount of ettringite in cement paste (g/cm\(^3\)), \( ETT_{pre} \), the amount of ettringite in cement paste at previous time step (g/cm\(^3\)).

### 2.4 The change in porosity

Porosity should be changed corresponding to the change in solid phase such as portlandite, monosulfate, ettringite, and gypsum. The calculation equation of porosity in cement paste and capillary porosity is provided in Eqs. (5) and (6). In addition, after cracking, in calculating the total porosity to compare it with the experimental results, the volume of crack has to be considered. Using RBSM, the volume of crack can be calculated from the change in crack width and the area of boundary surface of each element as shown in Eq. (7). Then, the total porosity can be calculated using Eq. (8).

\[
p_{con} = p_{con0} + (V_{CH} + V_{AFm} - V_{ETT} - V_{GYP}) \tag{5}
\]

\[
V_{con} = \sum_{i} w_i \cdot A_i \tag{7}
\]

\[
p_{total} = p_{con0} \cdot p_{vol} + V_{con} \tag{8}
\]

where, \( p_{con0} \) is the initial porosity in cement paste (cm\(^3\)/cm\(^3\)); \( p_{cap0} \) is the initial capillary porosity calculated by CCBM (cm\(^3\)/cm\(^3\)); \( V_{CH} \) and \( V_{AFm} \) are the solid volume reduction in cement paste due to consumption of portlandite and monosulfate (cm\(^3\)/cm\(^3\)), respectively; \( V_{ETT} \) and \( V_{GYP} \) are the solid volume increment due to precipitation of ettringite and gypsum (cm\(^3\)/cm\(^3\)), respectively; \( V_{con} \) is the volume ratio of crack to total volume of specimen (cm\(^3\)/cm\(^3\)); \( w_i \) is the crack width of \( i \)th boundary surface (mm); \( A_i \) is the area of \( i \)th boundary surface (mm); \( V \) is the volume of each element(cm\(^3\)); \( p_{total} \) is the total porosity in mortar (cm\(^3\)/cm\(^3\)) ; and \( p_{vol} \) is the coefficient factor of the amount of cement paste.

### 3. RBSM and coupled scheme

#### 3.1 RBSM

In this study, expansion cracking behavior was evaluated using three-dimensional RBSM which is one of the discrete analyses proposed by Kawai (1978). Figure 2 shows the voronoi particle definition of one RBSM element. The rigid body element is discretized using random voronoi mesh. One normal spring and two shear springs are set at integration points defined on element’s boundary surface in which numerical constitutive law are introduced allowing the evaluation of crack propagation and crack width with a high degree of accuracy. Figure 3 shows the material models of mortar. Tensile and compression models, and shear models are set into normal springs and shear springs, respectively, where, \( f_t \) is the tensile strength; \( E \) is the elastic modulus; \( G_f \) is the tensile fracture energy; \( \tau \) is the shear strength; \( G \) is the shear stiffness; and \( f_c \) is the compressive strength. The adopted compression model of normal spring is based on Yamamoto et al. (2014). Prior to the analytical investigation, compression test of cylindrical specimen was modeled, and compression and tensile strength were evaluated using RBSM in order to determine the mechanical properties at mesoscale. If we attained the mechanical properties of experiment, these coefficient val-
ues of mechanical properties are then decided in a way that is consistent with the compression and tensile test of experiment and analysis. Otherwise, we have to define macroscopic mechanical properties from $f_c$ calculated by CCBM and the coefficient values set based on Yamamoto et al. (2014).

The expansion strain, introduced at every normal spring as initial strain, is shown in Eq. (9). This expansion strain should be imposed uniformly to the normal springs set at every integration points on the boundary surfaces and is used to calculate by the amount of ettringite at the pyramid which consists of the center of element and boundary surface area as will be described later.

$$
\varepsilon_T = \varepsilon_N + \varepsilon_e
$$

where, $\varepsilon_T$ total strain, and $\varepsilon_N$ is the strain of normal spring, respectively.

### 3.2 Truss network model

Diffusion-reaction model for sulfate attack and RBSM can be coupled by Truss Network Model as proposed by Nakamura et al. (2006). In this model, one-dimensional pipe elements, which cannot be influenced mechanically, are set between the center of element and the center of boundary surface ($E_{p1}$), and between the center of boundary surface and the center of line constructing boundary surface ($E_{p2}$). This is done in order to describe ion diffusion between the element and a crack, and between crack to an adjacent crack as shown in Fig. 4. $E_{p1}$ represents ion transfer in element and $E_{p2}$ represents ion transfer in crack. Before cracking, sulfate ion can transfer into only $E_{p1}$. After cracking, sulfate ion can transfer not only in $E_{p1}$ but also in $E_{p2}$ corresponding to a crack width. In addition, the temporal solid phase in each pyramid is calculated from temporal sulfate ion content in $E_{p1}$.

#### 3.3 The change in ion diffusivity after expansion crack

Diffusion coefficient in $E_{p1}$ should be changed from Eq. (2) and the transportation of sulfate ion in crack should be also considered after cracking. Gerard and Marchand (2000) investigated the change in ion transportation after cracking. According to their results, the diffusivity at the deteriorated area was twice to ten times of diffusivity against non-deteriorated area as freezing-thawing cycle increased. Tixier et al. (2003a) introduced the change in diffusion coefficient at damaged area corresponding to a damage factor in reference to Gerard and Marchand (2000). In addition, Idiart et al. (2011) introduced the non-linear change of diffusion coefficient which will be closed to $D_0$ corresponding to crack width.

In those described modeling method, however, the averaged diffusivity in the element include solid-liquid phase and crack. As mentioned before, RBSM can evaluate crack width and Truss Network Model can directly describe ion transfer through crack. Therefore, the concept of averaged diffusivity model should not be applied to Truss Network Model. In this analysis, the diffusion coefficient in the pipe element, $E_{p1}$, can only be influenced by the change in porosity and the diffusion coefficient in the pipe element. $E_{p2}$ is directly set to $D_0$ as follows.

$$
D = D_0 \quad (w > 0)
$$

In addition, the boundary condition of pipe element at boundary surface of outer solution is always set to sulfate ion concentration of outer solution. The amount of sulfate ion in the crack can be defined similar as the pipe element. $E_{p2}$ is set to the boundary surface of each element.
4. Sensitivity analysis for proposed analytical model

4.1 Analytical objective and conditions

In this paper, the transformation of solid phase due to sulfate attack was verified by comparing the experimental and analytical results referred from Lothenbach et al. (2010). The description of the objective experimental and analytical condition is explained as below.

In the objective experiment, the mix proportion of mortars, which are made from mix proportion in reference to EN196-1, are shown in Table 1. The mortars were immersed in sodium sulfate solution and the mineral composition of cement (CEM I 42.5) is also shown in Table 1. The concentrations of sulfate ion were 4 and 44 g/L. The size of mortar is 10 x 40 x 160 mm and curing time was 28 days. In addition, in the analysis (Lothenbach et al. 2010), thermodynamic equilibrium calculation using GEMS and ALLIANCES, which can consider diffusivity of coexistence ion, were used to describe the change in solid-liquid phase due to sulfate attack.

In our proposed analysis, analytical model was focused on center part of cross section area of mortar and was constructed by V oronoi element as shown in Fig. 5. The average element size is 1.0 mm. According to El-Hachem et al. (2012), they observed expansion crack in circumferential direction at the center of specimen. As well as objective experiment, expansion in a circumferential direction could be occurred by means of considering constraint stress from adjacent cross-section area. This is why the authors considered only center part of cross section area and constructed three-dimensional analytical model. Mix proportion and mineral composition shown in Table 1 were introduced to CCBM as input data and the change in phase assemblage, porosity, and $f'_c$ were predicted. In addition, the input data for diffusion-reaction model was a solid phase, and porosity calculated by CCBM and diffusion coefficient of sulfate ion is in dilute solution. $D_0$ was set to $2.0 \times 10^{-9}$ m$^2$/s in reference to Lothenbach et al. (2010). In this study, since the information about the mechanical characteristics such as $f'_c$ is not available, $f_c$ was estimated by CCBM and was introduced to RBSM. The macroscopic and mesoscopic mechanical properties are shown in Table 2. $f'_c$ is defined as one-tenth of $f'_c$. $E$ and $G_c$ were estimated using JSCE standard (2012). The coefficient values were used based on Yamamoto et al. (2014). In this paper, reaction rate, $K_{CH}$, was changed as analytical parameter of CASE 1-6 as shown in Table 3. The proposed analysis was verified with the distribution of SO$_3$ and transformation of solid phase in the direction of depth of experimental or analytical results. After that, the effect of ion diffusion in crack is discussed using CASE 7-12 as shown in Table 3. In case of CASE1-6, sulfate ion infiltration was only considered at one sur-

![Table 1 mineral composition and mix proportion of objective experiment.](image)

| CEM I 42.5 | Mineral Composition (g/100g) | EN196-1 | Mix proportion (kg/m$^3$) |
|------------|-------------------------------|---------|--------------------------|
| C$_3$S     | 62.5                          | W       | 225                      |
| C$_2$S     | 10.5                          | C       | 450                      |
| C$_3$A     | 7.1                           | S       | 1530                     |
| CaSO$_4$   | 8.2                           | W/C (%) | 0.5                      |
| CaSO$_4$   | 4.7                           | S/C (%) | 3.0                      |

![Table 2 constitutive law of RBSM.](image)

|                  | Macroscopic constitutive law | Mesoscopic constitutive law | Coefficient factor (meso/macro) | Note          |
|------------------|-----------------------------|----------------------------|---------------------------------|---------------|
| $f'_c$ (MPa)     | 59.48                       | 89.22                       | 1.5                             | CCBM          |
| $f_c$ (MPa)      | 5.95                        | 4.76                        | 0.8                             | $0.1 f'_c$   |
| $E$ (GPa)        | 34.90                       | 48.86                       | 0.5                             | JSCE standard 2012 |
| $G_c$ (N/m)      | 0.04918                     | 0.02459                     | 0.14                            | JSCE standard 2012 |
| $c$ (MPa)        | 8.33                        | 0.14                        |                                 | Yamamoto 2014 |

![Fig. 5 Analytical model and boundary condition.](image)
face and, in case of CASE7-12, it was set to four surfaces as shown in Fig. 5(c). In addition, the elements which faces are in z-directional boundary surface were constrained—as they cannot deform in z-direction—to consider the existence of adjacent mortar in experiment.

### 4.2 Phase assemblage and porosity before sulfate attack

The change in phase assemblage, total porosity, and capillary porosity in mortar and $f_c$ due to hydration process calculated by CCBM are shown in Figs. 6 and 7.

As shown in Fig. 6, in the initial stage, ettringite produced in conjunction with the consumption of C$_3$A and gypsum. After gypsum was completely consumed, ettringite decreased by the reaction of monosulfate. In addition, the amount of portlandite and C-S-H increased along with time in association with the consumption of C$_3$S and C$_2$S. These results are similar to the experimental result. As shown in Fig. 7(a), it can be confirmed that the total porosity and capillary porosity decreased with time after the curing time was about 0.15 days. After 28 days curing, total porosity and capillary porosity were found to be 0.168 and 0.080 cm$^3$/cm$^3$, respectively. However, the calculated porosity was higher and capillary porosity was lower than Lothenbach’s result in which total porosity and capillary porosity were about 0.154 and 0.105 cm$^3$/cm$^3$, respectively. In this analysis, CaCO$_3$ and MgO were not considered in the hydration process so the presence of hemicarbonate and hydrotalcite are not observed in our proposed model which is in contrast with experimental result. This seems to be one of the reasons why the calculated total porosity was higher than experimental one. Indeed, the gel porosity is defined as difference between molecular volume of C$_{1.67}$SH$_{4.0}$ and C$_{1.7}$SH$_{2.1}$ and is consistent with Lothen-

| Sulfate ion (g/L) | $K_{CH}$ (cm$^3$/g/sec) | $p_{tm}$ | $\alpha$ | Infiltration area | Ion transfer |
|------------------|-------------------------|---------|---------|------------------|-------------|
| CASE1            | 4                       | 0.005   |         |                  | Type-1      |
| CASE2            | 44                      |         |         |                  | Type-1      |
| CASE3            | 4                       | 0.01    |         |                  |             |
| CASE4            | 4                       | 0.02    |         |                  |             |
| CASE5            | 4                       |         |         |                  |             |
| CASE6            | 4                       |         |         |                  |             |
| CASE7            | 4                       |         |         |                  |             |
| CASE8            | 44                      | 0.01    | 0.9     | 4 surface of x and y direction | Type-2      |
| CASE9            | 4                       |         |         |                  |             |
| CASE10           | 44                      |         |         |                  |             |
| CASE11           | 4                       |         |         |                  |             |
| CASE12           | 44                      |         |         |                  |             |

Fig. 6 Phase assemblage of hydration process.

Fig. 7 Change in porosity and compressive strength of mortar.
bach et al. (2010). Therefore, the difference on the definition of C-S-H gel under each drying condition could also be an influence to the capillary porosity. We have also confirmed the sensitivity of porosity to the transformation of solid phase and expansion cracking behavior, and found that those tendencies were almost same although porosity was different. Therefore, in the analytical results, the used of predicted porosity can be justified. As shown in Fig. 7(b), $f'_c$ increases with time until a curing time of about 0.15 days and the increment of $f'_c$ gradually decreased as well as the porosity. The $f'_c$ after 28 days was found to be 59.48 MPa.

4.3 The change in phase assemblage due to sulfate attack

In this analysis, in order to evaluate the sensitivity of $K_{CH}$, the values were set to 0.005, 0.01 and 0.02. The distribution of portlandite, gypsum, ettringite and monosulfate at the cross-section area in case of CASE1-6 are shown in Fig. 8. In particular, these distributions were extracted in the central part of cross section area as shown in Fig. 5(c). These figures show that mortar is immersed in Na$_2$SO$_4$ solutions with concentration of 4 and 44 g/L, and the immersion time is 56 days.

As shown in Fig. 8(a), the reduction of portlandite tends to be larger as $K_{CH}$ is increased, and sulfate ion concentration is higher. As shown in Fig. 8(b), gypsum was precipitated except for CASE1 (i.e., in case of low sulfate ion concentration) and the amount of gypsum increased along with increment of $K_{CH}$ (i.e., in case of high sulfate ion concentration). This tendency that gypsum mainly precipitated in case of high sulfate ion concentration seems to agree with thermodynamic model results (Lothenbach et al. 2010). Looking on the distribution of ettringite and monosulfate shown in Fig. 8(c), it was observed that ettringite precipitated corresponding to the reduction of monosulfate and these tendencies can be seen in thermodynamic model results as well. The amount of ettringite and monosulfate was, however, half of thermodynamic model result. The difference in the porosity and production reaction of ettringite can be an influence.

Next, the distribution of SO$_3$ in solid phase calculated by using each $K_{CH}$ and each sulfate ion concentration are shown in Fig. 9. The amount of SO$_3$ in solid phase was calculated by sum of SO$_3$ content of gypsum, monosulfate and ettringite. Based on the distribution of SO$_3$ in solid phase in depth direction of experiment, in case of low sulfate ion concentration, the amount of SO$_3$ were very close to each other even though immersion time is increased. In case of high sulfate concentration, it can be seen that the amount of SO$_3$ near the surface area increased locally and the amount of SO$_3$ at the inner area was almost same as that of low sulfate ion concentration cases in the experiment. In contrast, in the analytical results, the amount of SO$_3$ increased along with time in case of low sulfate ion concentration and gradually decreased along with depth. It is also difficult to reconstruct the former phenomena using thermodynamic model and Lothenbach mentioned that the diffu-
sivity at deteriorated area could affect the distribution of SO$_3$ in depth direction.

Also, there were two big differences between the proposed model and thermodynamic model. One is that the thermodynamic model and diffusion model, which consider the coexistence of ion diffusion, are able to reconstruct disappearance of portlandite and gypsum in near the surface area because the models can take into account for Ca leaching and supersaturation of gypsum. In contrast, it can be seen that portlandite still remained and gypsum could precipitate at the surface calculated by proposed analysis. This is because the model cannot account for Ca leaching and thermodynamic equilibrium condition. Another possible reason is that the boundary surface between reacted and non-reacted zone calculated by thermodynamic model was found to be clear. In our proposed model, the degree of transformation due to sulfate attack gradually decreased along with depth. This would be one of the signature behaviors of diffusion-reaction model using reaction rate constant. In this paper, $K_{CH}$ was defined from transformation area of ettringite and monosulfate, and the distribution of SO$_3$ in solid phase. Besides, the boundary of ettringite and monosulfate was defined as the cross point of both curves as shown in Fig. 8(c), and was compared with thermodynamic model results. Based on this information, it was judged that the feasible $K_{CH}$ is 0.01.

The phenomenon that is unable to describe by the proposed model is the Ca leaching and precipitation condition based on chemical equilibrium condition that consider the pH value and sulfate ion concentration. This is why gypsum precipitated from the surface and the area spread widely in this analysis, whereas it locally distributed near the surface in objective experiment. Future tasks are to develop a transfer model of coexistence ion for Ca leaching and chemical equilibrium condition to evaluate accurately the dissolution/precipitation process. In this paper, the authors assumed that the proposed simple mathematical model can evaluate the tendency of transformation of solid phase due to sulfate attack and proceeded to the discussions below.

5. The influence of ion transfer through expansion crack

As described above, previous proposed analytical models do not consider the effect of ion transfer through crack although they could evaluate the influence of the expansion crack indirectly by means of changing the diffusion coefficient. Those attempts seem not to clearly mention that expansion crack itself affects the mechanism of sulfate attack. It is possible, however, that gap in the transformation of solid phase amount of SO$_3$ exists between experimental results and analytical one as mentioned by Lothenbach et al. (2010). This gap could have an influence in the prediction of long-term durability. Furthermore, it may also influence the expansion cracking behavior because such behavior is attributed to the process of transformation of solid phase. The authors focused on the possibility that the mass balance of sulfate ion is different from actual phenomena unless we consider the efflux and influx of sulfate ion in crack. That is to say, the capacity of sulfate ion at the cracking area is supposed to increase in proportion to the expansion crack because the volume of cracking area increases. For example, in terms of ASR, the manifestation of expansion pressure due to ASR gel after cracking (e.g., see for instance Multon et al. 2009). The expansion cracking behavior of ASR can directly influence the stiffness and deformation. This is the why the concept that the influence of the crack itself affects expansion mechanism were introduced a long time ago. On the other hand, discussion about the expansion cracking behavior due to sulfate attack is not usually provided because the expansion crack occurs near the surface, and the influence of expansion mechanism affected by the crack is already included in the change in diffusion coefficient. Here, the ion transfer through crack was directly described by our proposed model and its influence in the process of transformation of solid phase and expansion cracking behavior will be discussed.

Firstly, the influence of ion transfer through crack will be evaluated by three types of transfer model and then, the presence of the gap mentioned by Lothenbach et al. (2010) will be discussed. Subsequently, the change of expansion cracking behaviors calculated by each transfer model will be validated. Finally, the influence of ion transfer through crack and its relationships will be discussed by extracting results from target elements in order to precisely clarify cracking behavior, sulfate ion distribution, and transformation of solid phase.

5.1 The modeling of ion transfer through EXPANSION crack

In this analysis, three types of transfer model are introduced as shown in Fig. 10. Type-1 is a model in which sulfate ion can transfer between elements as shown in Fig. 10(a). Type-2 and Type-3 are models in which sulfate ion can transfer between elements, element and crack, and crack and adjacent crack as shown in Fig. 10(b). In case of Type-2 transfer model, sulfate ion concentration in the crack is set to zero as initial condition. This condition assumes that crack is always saturated by water. In case of Type-3 transfer model, the sulfate ion concentration in the crack is taken as the averaged value. This is calculated from sulfate ion concentration possessed by two pyramids of adjacent elements and the volume of two pyramids and crack. This condition assumes that pore solution in liquid phase instantly flow in expansion crack due to negative pressure. This is because the driving force corresponding to crack opening and sulfate ion in the crack is always held in equilibrium with two adjacent pyramids of element. Basically, in case of Type-2 and 3, sulfate ion can penetrate into expansion crack and the cracks behave the capacity of
sulfate ion which can store the penetrated sulfate ion. The authors attempted to evaluate the influence of transformation of solid phase and expansion crack propagation on ion transfer through expansion crack by means of the feedback system related to ion transfer through cracks considering the sequential change in crack information and boundary condition due to manifestation and propagation of expansion crack. The difference between Type-2 and Type-3 is the process of sulfate ion transfer into the crack. Here, the sensitivity of sulfate ion diffusion of each type was particularly verified to comprehend whether the sulfate ion transfer in crack can influence to the transformation of solid phase and expansion cracking behavior itself in case of CASE7-12 as shown in Table 3.

5.2 The evaluation of transformation of solid phase

The distributions of SO₃ in solid phase at the center of cross-section area in each case are shown in Fig. 11. As mentioned above, it was observed in objective experiment that the difference of SO₃ due to immersion time was small and the difference of SO₃ due to sulfate ion concentration in outer solution at about 1 mm deeper area was very small. As can be observed from Fig. 11(a), the distribution of SO₃ was clearly changed by the immersion time and sulfate ion concentration in outer solution. These tendencies are similar to Fig. 9(b). On the other hand, as shown in Figs. 11(b) and (c), the distribution of SO₃ after 270 day immersion in case of CASE9 and CASE11, and after 56 day immersion in case of CASE10 and CASE12, are as close to the distribution of SO₃ after 56 day immersion in case of CASE9 and CASE11, respectively.

In order to evaluate the influence of immersion time and sulfate ion concentration in the outer solution, the differences in the distribution of SO₃ were shown in Fig. 12. In this figure, the solid lines show the influence of immersion time while broken lines show the influence of sulfate ion concentration in outer solution. As can be observed at the influence of immersion time, it was confirmed that the difference of SO₃ in the case of CASE9 and CASE11 are smaller than that of CASE7, and are close to the experimental result although the difference with experimental result are still significant. In particu-

![Fig. 10 Concept of sulfate ion penetration into crack. (a) Sulfate ion transfer in only element (Type-1), (b) Sulfate ion transfer in element, between element and crack and between crack and crack (Type-2 and Type-3).](image)

![Fig. 11 Change in SO₃ in solid phase corresponding to sulfate ion transfer type.](image)

![Fig. 12 Difference of distribution of SO₃ due to immersion time and sulfate ion concentration of outer solution.](image)
lar, the amount of SO$_3$ increased near the surface area in the analytical results and the difference of SO$_3$ distributed uniformly along with depth. This is because gypsum can immediately precipitate in near the surface area. In this analytical model, sulfate ion in the system can be immediately consumed by the precipitation of gypsum after the complete consumption of monosulfate because this model does not account for the Ca leaching and equilibrium condition of solid-liquid phase, and the amount of SO$_3$ at near the surface can increase. For the influence of sulfate ion concentration in outer solution, the results of CASE9 and CASE11, which consider sulfate ion transfer into crack, shows that the difference of SO$_3$ are consistent with experimental result at the 0.5mm deeper area. Moreover, the reduction of SO$_3$ at the surface in the experiment could be due to Ca leaching. Therefore, the distribution of SO$_3$ near the surface will be closer to actual phenomena if diffusion-reaction model can account for Ca leaching and equilibrium condition in solid-liquid phase.

5.3 The evaluation of expansion cracking behavior

The distribution of expansion crack, effective ettringite—defined by the increment of ettringite which contributes to manifestation of expansion crack—and sulfate ion at the center of cross-section area are shown in Fig. 13. CASE7, CASE9, and CASE11 are results with low sulfate ion concentration, and with distributions presented after 28, 56 and 270 days. CASE8, CASE10, and CASE12 are results with high sulfate ion concentration, and with the distributions results after 7, 14 and 56 days.

As can be observed from results with low sulfate ion in outer solution cases, larger cracks distributed from the surface to inner area in case of CASE7, and smaller cracks distributed in near the surface in the case of CASE9 and CASE11. These distributions of expansion crack can be explained by the distribution of effective ettringite. It was observed that high effective ettringite distributed until 56 day immersion and became small after 270 day immersion in case of CASE9 and CASE11 whereas high effective ettringite distributed from surface to inner area constantly in case of CASE7. Therefore, the expansion pressure diminished and smaller cracks distributed at near the surface in the case of CASE9 and CASE11 in comparison with CASE7. For the distribution of sulfate ion, it can be confirmed that sulfate ion did not diffuse to deeper area where expansion crack is present such as in CASE9 and CASE11. Whereas, sulfate ion uniformly distributed from surface regardless the existence of expansion crack in case of CASE7. This is because sulfate ion could penetrate into expansion crack and the transfer of sulfate ion inward was delayed. Therefore, it can be interpreted that as sulfate ion transferred inward drop by drop through the expansion crack, increment of ettringite is reduced, and proportionally, the expansion pressure also decreased.

For the cases with high sulfate ion in outer solution, the amount of effective ettringite was found to be higher due to high sulfate ion concentration penetrated into a system and the expansion pressure also became higher in comparison with low sulfate ion in outer solution cases. Therefore, it can be observed that a significant amount of expansion crack distributed over the whole cross-sectional area in early stage. The effect of efflux and influx of sulfate ion through crack was similar to that of low sulfur ion in outer solution cases. In addi-

![Fig. 13 Change in distributions of crack, effective ettringite and sulfate ion at cross section area in case of CASE7-12. Left shows sulfate ion concentration of outer solution = 4g/L after 28, 56 and 270 days immersion and right shows sulfate ion concentration of outer solution = 44g/L after 7, 14 and 56 days immersion.](image-url)
tion, it was believed that crack propagated at the inner area due to the high expansion pressure at surface area as manifested by the precipitation of ettringite. In fact, the cross-section area of the subject specimen was very thin and internal constraint, therefore, seems to diminish so these cracks at the inner area were generated due to the expansion stress at the surface. That is to say, it seems to be difficult to clarify the expansion cracking behavior. Many researchers (see for instance Cheng et al. 2013) have observed the size effect of expansion cracking behavior due to sulfate attack.

In the presented results, it was confirmed that the transformation process of solid phase, and manifestation and propagation process of expansion crack is influenced by sulfate ion transfer through crack, and its diffusion to deeper area was delayed. It is necessary to discuss the relationships between expansion crack propagation and transformation of solid phase in order to evaluate the buffer effect of sulfate ion transfer through crack.

5.4 The evaluation of influence of ion transfer through expansion crack

In this section, the concept that sulfate ion transfer model can affect the process of sulfate ion transfer, expansion crack, and transformation of solid phase of target elements in case of low sulfate ion in outer solution cases (i.e., CASE7, 9, and 11) is discussed. The specific information is shown in Fig. 14. The target elements selected are those near the surface and near the bottom of the simulation model and are labeled as surface element and inner element, respectively. A surface element is in contact with the outer solution while the inner element is adjacent to the surface element. The target crack is obtained between surface element and inner element. In addition, to validate the interrelationship between crack, sulfate ion, and solid phase, the information from the three pyramids labeled as a, b, and c were extracted. Pyramid “a” is in contact with outer solution in the surface element while Pyramid “b” and “c” are part of the inner element. Pyramid Triangle-b is in contact with the target crack and pyramid-c is located in deeper in the inner element.

The change in sulfate ion concentration of target elements in case of CASE7, 9, and 11 are shown in Fig. 15. According to Fig. 15(a), sulfate ion concentration increased with time and its increment gradient tends to decrease as shown for CASE7. On the other hand, for CASE9 and 11, the tendency of sulfate ion concentration is same with that of CASE7 until 25 days immersion and, after that, it decreased once and somewhat increased again until 50 days immersion. After 50 days immersion, sulfate ion concentration of CASE9 still increased and remained constant. The sulfate ion concentration of CASE11, however, decreased again with a time. These tendencies were also observed for the inner element as shown in Fig. 15(b).

The change in target crack width in case of CASE7, 9 and 11 were shown in Fig. 16. The tendencies of target crack were similar to each other. The expansion crack occurred at 25 day immersion and it propagated until about 50 days immersion and, after that, its gradient significantly decreased and seemingly remained constant. These inflection points in case of CASE9 and 11 were similar to the change in sulfate ion concentration in the target elements. Figure 17 shows the relationships between crack width and sulfate ion in the target crack for CASE9 and 11. The relationships show that sulfate ion concentration increased corresponding to crack width but these tendencies were different from CASE9 and CASE11. For CASE9, the tendency is nonlinear and the increment of sulfate ion is smaller than that of CASE11. On the other hand, for CASE11, sulfate
ion showed a linear relationship with crack width. These differences can be interpreted by transfer model. Sulfate ion, for CASE9, transfers as diffusion phenomena from adjacent element and crack. For CASE11, sulfate ion in crack is always held in equilibrium with the two adjacent pyramids of target elements and sulfate ion concentration is, therefore, largely influenced by crack propagation. In the present circumstance, we cannot say that which transfer model can demonstrate the actual phenomena. It can be said, however, that diffusivity of sulfate ion was strongly influenced by sulfate ion transfer through expansion crack.

Next, the difference of transformation of solid phase due to transfer model is discussed. The change in phase assemblage of pyramid-a, b and c in all cases were shown in Figs. 18 ~ 20. Phase assemblage after 28 days curing calculated by CCBM (Fig. 6) was set to initial state for 0 day immersion. In addition, un-hydrated cement cannot interfere with the reaction of sulfate attack in this model, those phases did not change during sulfate ingress, so C3S, C2S, C3A, and C4AF was collectively named un-hydrated and, then, portlandite, monosulfate, ettringite and gypsum were only involved by sulfate attack. According to Fig. 18, it can be confirmed that ettringite precipitated corresponding to the consumption of monosulfate and subsequently, gypsum precipitated after completely consuming monosulfate. Essentially, the precipitation of gypsum is strongly influenced by pH value and sulfate ion concentration in a system, gypsum does not precipitate immediately even when monosulfate is completely consumed by precipitation of ettringite. Note that this analytical model is a simplification and does not consider the influence of pH and sulfate ion concentration. The phase assemblage at pyramid-a, which are in contact with outer solution in all cases, has almost the same tendency and this precipitation rate was somewhat higher in comparison to those of CASE7, 9 and 11. At this location, gypsum can be largely observed even in the early immersion time. As can be observed in Fig. 19, the tendency of phase assemblage at pyramid-b in contact with target crack is similar to that of pyramid "a" cases although the transformation speed was somewhat slower. In addition, the difference between CASE9 and CASE11 can be observed with the precipitation speed of gypsum as more gypsum precipitated in CASE9 than CASE11 because sulfate ion in element of CASE11 was reduced due to efflux of sulfate ion to crack. In Fig. 20, the difference of phase assemblage for pyramid-c, located in deeper in the inner element due to transfer model, was indicated. For CASE7, the tendency of phase assemblage was similar to pyramid-a and b cases. The transformation of solid phase in case of CASE9 and 11 is, however, slower, especially because gypsum was not observed after 300 day immersion in case of CASE11. Therefore, it can be said that the effect of sulfate ion transfer through expansion crack can delay sulfate ion diffusion inward and the transformation of solid phase.

5. Discussion

In this analysis, the transformation process from proposed diffusion-reaction model considering ion transfer into crack indicated the same tendency as those observed in the experiment. That is to say, without considering the efflux and influx of sulfate ion through crack, the mass balance of sulfate ion concentration which diffuse inward, is not consistent with actual phenomena and the transformation of solid in deeper area might be estimated earlier than in reality.

Based on analytical results, especially from Figs. 18 ~ 20, the relationships between transformation process of solid phase and expansion crack can be described as shown in Fig. 21. Generally, it was observed that expansion crack was locally distributed in cross-section area (for instance, El-Hachem et al. 2012). Expansion crack locally generates at inner area and its crack width increases. At the same time, the crack—which is probably caused by expansion pressure at inner area—was also observed at the surface. The crack at the surface was filled by high concentration of sulfate ion from outer solution and the sulfate ion can be transferred to inner area from its cracking surface. In addition, at the surface area, the precipitation of gypsum should be dominant because monosulfate was already consumed and the pH

![Fig. 16 Change in target crack width.](image1)

![Fig. 17 Relationships between crack width and sulfate ion in target crack in case of CASE9 and CASE11.](image2)
value of pore solution should be low. At inner area where the observed expansion crack is due to ettringite, sulfate ion penetrated into the crack from pore solution as diffusion phenomena. Then, the sulfate ion can be stored in the crack and the diffusion of sulfate ion inward should be retarded. Furthermore, these diffusion phenomena influenced by expansion crack could propagate continuously with equilibrium condition between sulfate ion in liquid phase of adjacent paste and crack. This buffer effect of sulfate ion was indicated by proposed model. Moreover, sulfate ion in crack is supposed to react with solid phase of cracking surface and, gypsum and ettringite could precipitate or could be consumed by crystal growth of ettringite in the crack. At relatively near the surface, there are co-existence area of gypsum and ettringite depending on pH value and sul-

![Fig. 18 Change in phase assemblage of pyramid-a in case of CASE7, 9 and 11.](image1)

![Fig. 19 Change in phase assemblage of pyramid-b in case of CASE7, 9 and 11.](image2)

![Fig. 20 Change in phase assemblage of pyramid-c in case of CASE7, 9 and 11.](image3)
fate ion concentration. Therefore, there is a possibility that sulfate ion are consumed by precipitation/crystal growth of gypsum and ettringite in addition to the buffer effect of sulfate ion and this possibility can interfere sulfate ion diffusion inward. Considering this effect, ettringite locally precipitated at the same location for extended periods in comparison to those cases without ion transfer through crack, are expected to contribute to the manifestation of signature expansion crack which locally occurred at inner area.

It is therefore necessary to experimentally prove buffer effect of sulfate ion diffusion inward due to expansion crack and the consumption of sulfate ion by precipitation of ettringite and/or gypsum in expansion crack as described Fig. 21. Moreover, the expansion cracking process should be observed in more detail to indicate the possibility that this concept involves the manifestation and propagation of expansion crack.

6. Conclusion

In this paper, a coupled analysis which consist of CCBM for hydration model, diffusion-reaction model for sulfate attack, and RBSM for manifestation and propagation behavior of expansion crack was proposed. It was found that expansion crack can influence to the transformation of solid phase and expansion cracking behavior, as the sulfate ion concentration in element decreased corresponding to increment of sulfate ion in crack when sulfate ion transfer through crack was considered. With regard to the ion transfer through expansion crack, the calculated distribution of SO$_3$ in depth direction was found to agree with experimental result, and was not affected by immersion time and of sulfate ion concentration in outer solution. Using proposed model, it was observed that this phenomena comes from the inhibition of sulfate ion diffusion inward due to the penetration of sulfate ion into crack. Therefore, the analytical results show one possibility of the expansion mechanism, that is, the expansion crack acts as a buffer of sulfate ion, and have an influence to the propagation of expansion cracking behavior itself. Consequently, a relationship between transformation process of solid phase and expansion crack was proposed. This concept showed that expansion crack behaves as a buffer effect of sulfate ion, and that sulfate ion in crack is consumed by precipitation/crystal growth of gypsum and ettringite.

As for future work, it is necessary to experimentally prove the buffer effect of sulfate ion diffusion inward due to expansion crack and the consumption of sulfate ion by precipitation/crystal growth of ettringite and gypsum in expansion crack. Moreover, the expansion cracking process should be observed in more detail to indicate the possibility that this concept involves the manifestation and propagation of expansion crack.

Acknowledgment

Parts of this paper were funded by Grant-in Aid for Young scientists (B). The authors would like to thank the financial support.

References

Cheng, Y., Wei, S. and Scrivener, K., (2013). “Mechanism of expansion of mortars immersed in sodium sulfate solutions.” *Cement and Concrete Research*, 43, 105-111.

El-Hachem, R., Roziere, E., Grondin, F. and Loukili, A., (2012). “Multi-criteria analysis of mechanism of degradation of Portland cement based mortars exposed to external sulphate attack.” *Cement and Concrete Research*, 42, 1327-1335.

European Standard, (1994). “EN196-1, method of testing cement Part-1: Determination of strength.”

Flatt, R. J. and Scherer, G. W., (2008). “Thermodynamics of crystallization stresses in DEF.” *Cement and Concrete Research*, 38, 325-336.

Gabrisova, A. and Havlica, J., (1991). “Stability of calcium sulphaolamine hydrates in water solutions with various pH values.” *Cement and Concrete Research*, 21, 1023-1027.

Garboczi, E. Z. and Bentz, D. P., (1992). “Computer simulation of the diffusivity of cement-based materials.” *Journal of Materials Science*, 27, 2083-2092.

Glasser, F. P., Marchand, J. and Samson, E., (2008). “Durability of concrete-degradation phenomena involving detrimental chemical reactions.” *Cement and Concrete Research*, 38, 226-246.

Gerard, B. and Marchand, J., (2000). “Influence of cracking on the diffusion properties of cement-based

---

**Fig. 21 Concept of the effect of sulfate ion transfer into expansion crack and consumption of sulfate ion due to precipitation.**
materials, Part I: Influence of continuous cracks on the steady-state regime.” Cement and Concrete Research, 30, 37-43.

Idiart, A. E., Carlos, M. L. and Carol, I., (2011). “Chemo-mechanical analysis of concrete cracking and degradation due to external sulfate attack.” Cement and Concrete Research, 33, 411-423.

Ikumi, T., Cavalaro, S. H. P., Segura, I. and Aguado, A., (2014). “Alternative methodology to consider damage and expansions in external sulfate attack modeling.” Cement and Concrete Research, 63, 105-116.

JSCE, (2012). "Standard specifications for concrete structures-Design.”

Kawai, T., (1978). “New discrete models and their application to seismic response analysis of structure.” Nuclear Engineering and Design, 48, 207-229.

Krajcinovic, D., Basista, M., Mallick, K. and Sumarac, D., (1992). “Chemo-micromechanics of brittle solids.” J. Mech. Phys. Solids, 40 (5), 965-990.

Lothenbach, B., Bary, B., Bescop, P. L., Schmidt, T. and Leterrier, N., (2010). “Sulfate ingress in Portland cement.” Cement and Concrete Research, 40, 1211-1225.

Maltais, Y., Samson, E. and Marchand, J., (2004). “Predicting the durability of Portland cement systems in aggressive environments—laboratory validation.” Cement and Concrete Research, 34, 1579-1589.

Maruyama, I. and Igarashi, G., (2015). “Numerical approach towards aging management of concrete structures: Material strength evaluation in a massive concrete structure under one-sided heating.” Journal of Advanced Concrete Technology, 13, 500-527.

Mehta, P. K., (1973). “Mechanism of expansion associated with ettringite formation.” Cement and Concrete Research, 3, 1-6.

Miura, T., Yamamoto, Y. and Nakamura, H., (2016). “Fundamental study of crack propagation of external sulfate attack with mesoscale analysis system for coupled chemo-mechanical behaviors.” 9th International Conference on Fracture Mechanics of Concrete and Concrete Structures, (DOI 10.21012/FC9.085).

Multon, S., Sellier, A. and Martin, C., (2009). “Chemo-mechanical modeling for prediction of alkali silica reaction (ASR) expansion.” Cement and Concrete Research, 39, 490-500.

Nakamura, H., Srisoros, W., Yashiro, R. and Kunieda, M., (2006). “Time-dependent structural analysis considering mass transfer to evaluate deterioration process of RC structures.” Journal of Advanced Concrete Technology, 4(1), 147-158.

Odler, I. and Colan-Subauste, J., (1999). “Investigations on cement expansion associated with ettringite formation.” Cement and Concrete Research, 29, 731-735.

Powers, T. C., (1960). “Physical properties of cement paste.” Proceedings of 4th international symposium on the chemistry of cement, 577-613.

Schmidt-Dohl, F. and Ferdinand, S. R., (1999a). “A model for the calculation of combined chemical reactions and transport processes-Part I. Simulation model.” Cement and Concrete Research, 29, 1039-1045.

Schmidt-Dohl, F. and Ferdinand, S. R., (1999b). “A model for the calculation of combined chemical reactions and transport processes-Part II. Experimental verification.” Cement and Concrete Research, 29, 1047-1053.

Skalny, J., Marchand, J. and Odler, I., (2002). “Sulfate attack on concrete.” Modern Concrete Technology 10. Taylor, H. F. W., (1997). “Cement chemistry.” 2nd ed., Thomas Telford.

Tixier, R. and Mobasher, B., (2003a). “Modeling of damage in cement-based materials subjected to external sulfate attack. I: Formulation.” J. Mater. Civ. Eng., 15 (4), 305-313.

Tixier, R. and Mobasher, B., (2003b). “Modeling of damage in cement-based materials subjected to external sulfate attack. II: Comparison with experiments.” J. Mater. Civ. Eng., 15 (4), 314-322.

Tosun, K. and Baradan, B., (2010). “Effect of ettringite morphology on DEF-related expansion.” Cement and Concrete Composites, 32, 271-280.

Wellman, H. W. and Wilson, A. T., (1965). “Salt weathering a neglected geological erosive agent in coastal and arid environments.” Nature, 205, 1097-1098.

Yamamoto, Y., Nakamura, H. and Miura, T., (2014). “Numerical analyses of seismic response of a reinforced concrete building using discrete model with random geometry.” WORKSHOP SMART2013.