Theoretical consideration of ions transport for minor element in cement-based material

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Introduction

Recently, a minor element contained in cements such as hexavalent chromium (Cr^{6+}) has been significantly concerned because of its toxic effect to human and the environment. The important process relevant to that is the diffusion or the leaching of ion through a cement-based material. The multicomponent system of ion diffusion in the pore solution of a cement-based material should be mainly considered for reality. The purpose of this research is to apply the theories of ion transport in a multicomponent solution for calculating the mutual diffusion coefficients, i.e. D_{ij} of i_{th} species influenced by j_{th} species. The model is based on a generalized form of Fick's first law, which suggested by Onsager, combining to Onsager coefficient and the thermodynamic force between ions exerted by the gradient of electrochemical potential. Consequently, the concentration profile and the leaching amount of ion can be calculated.

Electrolyte diffusion by the thermodynamics law

In an electrolyte diffusion process, the movement of an species will occur by driving forces that created from the concentration gradient of that species itself and by those of other species. Moreover, another driving force is the gradient of electrical potential created by the difference between mobility of cation and anion in the solution. It can be illustrated schematically in **Fig.1**. Assuming that in an electrolyte solution composed of these ions and ME as the minor elements. Each pair of ion is constrained by the electrostatic force represented by electrical chains in **Fig.1**, to move at



re at **Fig.1** The interaction of ions in a multicomponent system

the same rate. The flux of one ion influenced by another ion can be characterized by D_{ij} as mentioned before.

The Calculation model of mutual diffusion coefficient

The generalized form of the Fick's first law suggested by Onsager, which can relate the flux of i_{th} species (J_i) to the concentration gradient of j_{th} species (dC_i/dx) by the mutual diffusion coefficient (D_{ij}) , is shown in Eq.1.

$$\mathbf{J}_{i} = -\sum_{j=1}^{n_{s}} \mathbf{D}_{ij} \frac{\partial \mathbf{C}_{j}}{\partial \mathbf{x}}$$
(1)

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By the definition of the Onsager coefficient and the thermodynamic force equations as shown in **Fig.1**, D_{ij} of i_{th} species that influenced by j_{th} species can be calculated from the following equation.

$$D_{ij} = \delta_{ij} D_i^0 (1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i}) - \left\{ \frac{z_i D_i^0 C_i}{\sum\limits_{k=1}^{n_s} z_k^2 D_k^0 C_k} z_j D_j^0 (1 + \frac{\partial \ln \gamma_j}{\partial \ln C_j}) \right\}$$
(2)

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By using above equations and the finite difference method, the transport of ions concerning to the interaction from all coexisting ions in the pore solution of a cement-based material can be determined.

Ion	C _i , Concentration in	α_i , Ion size	D ^o _i , Tracer diffusion
	pore solution (mol/l)	parameter (nm)	coefficient (m ² /s)
Ca ²⁺	0.001	0.60	7.92×10^{-10}
Na ⁺	0.271	0.40	1.33 x 10 ⁻⁹
K^+	0.629	0.30	1.96 x 10 ⁻⁹
SO4 ²⁻	0.033	0.40	1.07 x 10 ⁻⁹
Cl	0.0	0.30	2.03 x 10 ⁻⁹
OH	0.836	0.35	5.26 x 10 ⁻⁹
CrO ₄ ²⁻	2.58 x 10 ^{-5 [1]} [∞]	0.40	1.13 x 10 ⁻⁹

Table 1. The parameters for calculation of D_{ij} matrix

*Calculated by water soluble Cr⁶⁺ content.



Fig.2 Calculation results of the leaching of some ions



Fig.3 Leached amount of Cr⁶⁺ from mortar specimen

Calculation results of the leached amount of ions from the mortar specimen

The application of the calculation model for D_{ij} is performed by calculating the leached amount of some ions in the pore solution of mortar. In the simulation, mortar specimen is assumed to contact with water for exposure time 800 days. The porosity and tortuosity of the mortar is assumed as the physical parameters of the transport. In addition to the major ions contained in the pore solution of mortar, the minor element of chromate ion (CrO_4^{2-})

is introduced. The initial concentration in the pore solution shown in **Table 1** of $\text{CrO}_4^{2^-}$ is determined from the experimental result [1]. It is considered that some chromate salts in the cement composition can be dissolved to Cr^{6^+} . The calculated accumulative leached amounts of some major ions, e.g. K⁺, Na⁺, SO₄²⁻ etc. are shown in **Fig.2**. The calculated results of the leached amount of minor element comparing with the experimental ones are shown in **Fig.3**. Although calculated amount of leached Cr^{6^+} is lower than experimental result, it can be due to the difference of $\text{CrO}_4^{2^-}$ content in pore solution, which is controlled by a chemical equilibrium with cement hydration. The change of pH, which controlled by concentrations of NaOH and/or CH₃COOH in the leachant, also exhibits a certain effect to the calculated results.

Conclusion

Proposed calculation model provides a better understanding of the leachability of Cr^{6+} . Future research is necessary to clarify the content of Cr^{6+} in pore solution of a cement-based material.

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