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Modeling of diffusive mass transport in micropores in cement based materials ☆

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ABSTRACT

In order to predict long-term leaching behavior of cement constituents for safety assessments of radioactive waste disposal, we modeled diffusive mass transport in micropores in cement based materials. Based on available knowledge on the pore structure, we developed a transport porosity model that enables us to estimate effective porosity available for diffusion (transport porosity) in cement based materials. We microscopically examined the pore structure of hardened cement pastes to partially verify the model. Effective diffusivities of tritiated water in hardened cement pastes were also obtained experimentally, and were shown to be proportional to the estimated transport porosity.

1. Introduction

High-level radioactive waste generated from reprocessing of spent nuclear fuel in Japan is vitrified, encapsulated in a metal container called overpack, surrounded by engineered buffer material, and emplaced in a deep geological repository. Cement based materials will be used as structural materials to support the disposal tunnels, and bentonite clay will be used as the engineered buffer material to reduce permeation of groundwater and migration of radionuclides. Over a long time period, cement based materials will be altered by contact with groundwater. Highly alkaline pore water will be leached from the cement based materials, and is likely to cause the physical properties such as hydraulic conductivity and/or chemical properties such as sorptivity of the buffer materials to deteriorate. In order to evaluate the alteration of bentonite, the leaching behavior of cement constituents should be modeled mathematically. Diffusion of solutes in cement based materials is the important factor that will determine the process of leaching of cement constituents. Therefore, we focus on modeling of diffusion of solutes in cement based materials in order to predict the long-term leaching behavior of cement constituents. Diffusion of dissolved chemical species in cement based materials is a combined process of physical transport and chemical interactions. The objective of this study is to model the physical transport in cement based materials.

In previous studies, the diffusivity of solutes in cement based materials has been of interest and modeled as a function of porosity. Numata et al. [1] reported the diffusivity of tritiated water in cement based materials as a function of the porosity obtained by mercury intrusion porosimetry:

$$D_e = 3.55 \times 10^{-11} \phi^{0.947}, \qquad (1)$$

where D_e is the effective diffusivity of tritiated water in cement based materials, and ϕ is the porosity of cement based materials. Mihara et al. [2] proposed the diffusivity of tritiated water in cement based materials as the third power of the porosity:

$$D_e = D_v \phi^{3.05}, \qquad (2)$$

where D_v is the diffusivity in free water. The two equations yield quite different estimates on the porosity value, which seems to attribute to a lack of information on the pore structure. Garboczi and Bentz [3] modeled the microstructure of hardened cement pastes by applying percolation theory and quantitatively explained the dependence of diffusivity of chloride ion in plain Portland cement paste with the following expression:

$$\frac{D_e}{D_v} = 0.001 + 0.07\phi_{cp}^2 + H\left(\phi_{cp} - 0.18\right) \times 1.8 \times \left(\phi_{cp} - 0.18\right)^2, \qquad (3)$$

where ϕ_{cp} is the capillary porosity of cement based materials, H the Heaviside's step function of $H(x) = 0$ for $x \leq 0$, and 1 for $x > 0$. Modeling the diffusivity in cement based materials needs scientific soundness, therefore should be based on reliable information on the pore structure.

In this study, based on available knowledge on the structure of micropores in cement based materials, we developed a transport porosity model that enables us to estimate effective porosity available for diffusion. We analyzed the micropores of hardened cement pastes

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by image analysis to partially verify the transport porosity model. We used non-sorbing tritiated water in order to investigate the physical transport process independently of the chemical interactions. We also determined the effective diffusivity of tritiated water in the hardened cement pastes to establish the correlation between the transport porosity and the effective diffusivity and discussed validity of the correlation.

2. Development of a transport porosity model

2.1. Basic concepts

The pore spaces of various size are known to be present in cement based materials [4]. The pore spaces in hardened cement paste, mortar, and concrete consist of air and water voids. The air void includes the entrapped air rolled up during the mixing process and the entrained air with air-entraining agents. The water voids are comprised of the gel pore space corresponding to the space between the C–S–H interlayer and capillary pore space unfilled with the hydrated minerals in hardened specimens [4]. Part of the pore space is not effective for the diffusive transport. Goto et al.[5] reported that the diffusivity in hardened cement is not correlated with the total porosity but negatively correlated with the partial porosity of the pores with the diameter below 2 nm. They presumed that the diffusivity was dominated by the connected pores of relatively large size, which decreased with the increase in the smaller pores. Atkinson and Nickerson [6] measured diffusion-related parameters for several ions in cement pastes to identify mechanisms of the diffusion. They concluded that the results could not be rationalized by the simple pore-diffusion model and that each ion had more than one diffusion processes in the cement, which were characterized as fast and slow diffusivity networks in the cement pore space. These studies did not identify the pore space dominating the diffusive transport although empirically discussed the correlations between the diffusivity and the pore structure. It is necessary to identify and quantify the pore space dominating the diffusive transport.

Nishiyama et al. [7] studied the correlation between effective diffusivity of iodide anion (I^-) and the porosity in rocks. They classified the pores into transport and storage pores according to diameters of the pores. They successfully correlated the effective diffusivity of I^- in rocks to the transport porosity and explained quantitatively the effective diffusivity in accordance with the pore-diffusion model. Our model intends to categorize the pores in cement based materials by the transport properties and to quantify the porosity which effectively acts as diffusive transport paths.

The air voids are dispersed in the cement based materials and do not form effective transport paths by being interconnected each other. Therefore, we assume that the air voids act as storage pores, not the transport pores ignoring moisture transport. The gel pores are also assumed not to act as the transport paths, because almost all the water filling the gel pore space is confined in the C–S–H interlayer [8]. These assumptions may be valid only for pastes with high *w*/*c* ratio; gel pores are in charge of slow transport process for pastes with *w*/*c* ratio lower than 0.38. The capillary pores are the residual space unfilled with hydrated cement minerals after the hydration process as shown schematically in Fig. 1. It is inferred from the formation process that the capillary pores have large variety in size and those with relatively large size are connected via those with smaller size. We assume that a part of capillary pores with small sizes are self-connected pores and can be act as transport pore. This is called capillary transport pore. The other part of the capillary pores with larger size is assumed to act as storage pore space and is called capillary storage pore.

Transport porosity which counts the capillary transport pores forming diffusion paths in cement based materials is expressed as

$$\phi_{tra} = V_{cp-tra} / V_{tot}, \tag{4}$$

where $V_{\text{cp-tra}}$ is the volume of capillary transport pores and V_{tot} the total volume of the hardened cement based materials. It is necessary to determine $V_{\text{cp-tra}}$ and V_{tot} to estimate the transport porosity.

2.2. Model for evaluating porosities in cement based materials

(1) Total volume of the hardened cement based materials
The volume distribution of the minerals and pores is calculated based on the model of Powers and Brownyard [9]. The total volume of a cement based material is calculated by summing up volumes of the original cement, water, aggregates and air void as

$$V_{\text{tot}} = V_{\text{w}} + V_{\text{c}} + V_{\text{fa}} + V_{\text{ca}} + V_{\text{a}}, \tag{5}$$

where V_{w} is the volume of original water, V_{c} the volume of original cement, V_{fa} the volume of fine aggregates, V_{ca} the volume of coarse aggregate and V_{a} the volume of air void. The volume of original water is supplemented with volume of absorbed water during the curing process which is approximately 6% [10] of the original cement in weight. This value is assumed based on the knowledge on the hydration of ordinary Portland cement with *w*/*c* ratio between 0.38 and 0.8 [10].

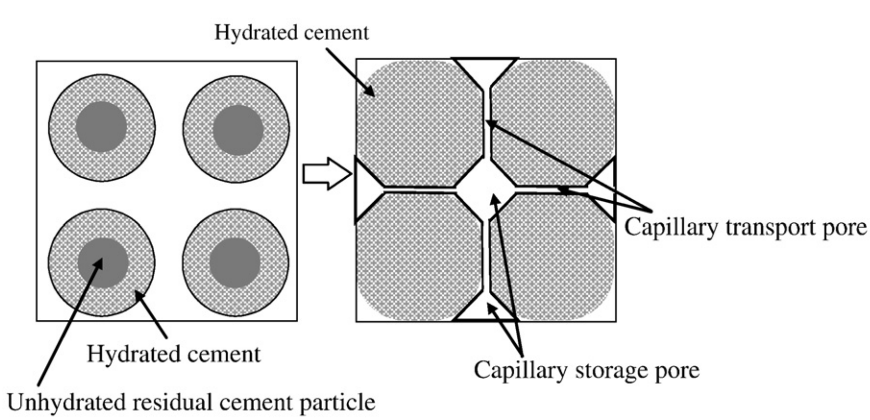

Fig. 1. Schematics of formation of capillary storage pore and capillary transport pore accompanied by hydration of cement particles. Capillary pore is the residual space unfilled with the hydrated cement after the hydration process. The capillary pores with relatively larger sizes (capillary storage pores) are connected through the smaller ones (capillary transport pores).