Evaluation of Pore Structure of Hardened Cement Paste Immersed in Sodium Sulfate Solution

Otsuka Sakata, H. Nicolas[1], Kennosuke Sato[2] and Shigehiko Saito[2]

[1] University of Yamanashi, Faculty of Engineering, Integrated Graduate School of Medicine, Engineering and Agricultural Sciences, 4-3-11, Takeda, Kofu, Yamanashi, 400-8511, Japan, g19tc003@yamanshi.ac.jp

[2] University of Yamanashi, Graduate School of Engineering, Department of Civil Engineering and Environmental Engineering, 4-3-11, Takeda, Kofu, Yamanashi, 400-8511, Japan, satok@yamanashi.ac.jp

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1 Introduction

Generally, in order to predict the deterioration phenomenon, it is necessary to grasp the ion transfer characteristics affecting the degradation of hardened cement paste. Furthermore, the ion transfer in the hardened cement paste is known to be greatly affected by the pore structure. Thus, in order to predict the progress of sulfate attack, it is necessary to grasp the pore structure as a transferring field of sulfate ions.

Therefore, we evaluated the oxygen transfer characteristics affected solely by pore structure to clarify the change in the pore structure of the hardened cement paste immersed in sodium sulfate solutions.

2 Specimens and Methods

Three types of cement paste specimens having water to cement ratio of 45%, 55% and 65% were prepared using ordinary portland cement. The size of the specimens was $3 \times 4 \times 0.5$ cm. It was demolded at 1 d, and it was wet-sealed curing until 28 d at 20 °C. The specimens were immersed in sodium sulfate solutions (0.5 and 5 mass%) and ion-exchanged with the liquid-to-solid ratio of 5.0 at 20 °C for 2 weeks.

The pore volume of each specimen was measured by Archimedes method. The pore size distribution was measured by mercury-intrusion-porosimeter. The oxygen diffusion test was carried out with reference to the method of Shirakawa *et al.* (1999) to grasp the pore structure of the specimens immersed in sodium sulfate solutions. Moreover, the phase composition of the sample was quantified by XRD / Rietveld analysis and by mass balance calculation (Maruyama *et al.*, 2010).

3 Results and Discussion

Figure 1 shows the oxygen diffusion coefficient of the sample immersed in sodium sulfate and ion-exchanged water. The oxygen diffusion coefficients of the specimens immersed in sodium sulfate were reduced regardless of the water-to-cement ratio as compared with the case of ion-exchanged water. However, the degree of decreasing in the oxygen diffusion coefficient
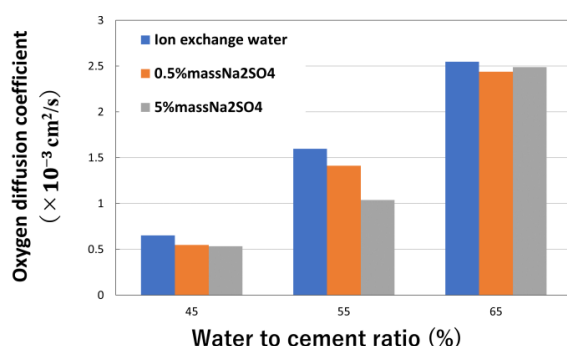
Figure 1. Oxygen diffusion coefficient of hardened cement pastes after immersion.
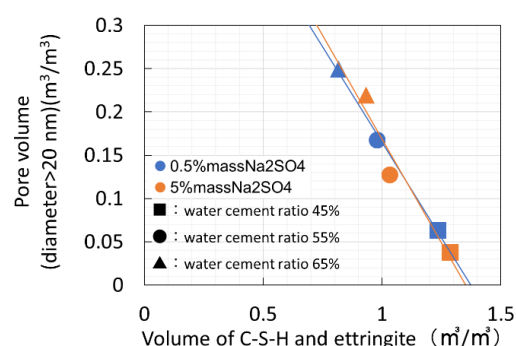
Figure 2. Relationship between pore volume (d > 20nm) and volume of C-S-H and ettringite.

varies from water-to-cement ratio.

The relationship between the decreasing in the oxygen diffusion coefficient affected by sodium sulfate and the change in the pore structure of the specimens was examined by quantify the effect of the change in the tortuosity. The oxygen diffusion coefficient is reduced with increasing of the tortuosity. These results suggest that the decreasing of the oxygen diffusion characteristics in the hardened cement paste affected sodium sulfate was caused by the increasing of the complexity of the pore structure due to sodium sulfate immersion.

Subsequently, in order to investigate the increasing of the pore structure complexity, we focused on changes in the pore size distribution. It was confirmed that the diameter of 20 nm is the boundary of the trend change. These results suggest that because the pore volume having a diameter > 20 nm in the specimen immersed in sodium sulfate decreased, the pore structure was complicated and the oxygen transfer was suppressed.

We examined the relationship between the pore volume having a diameter > 20 nm and the generation of C-S-H and ettringite. Figure 2 shows the relationship between the pore volume having a diameter > 20 nm and the volume of C-S-H and ettringite. The regression line drawn for each sodium sulfate solution concentration showed almost no error.

These results suggest that the decreasing of the oxygen diffusion coefficient of the specimens affected by sodium sulfate was caused by the formation of ettringite, which is filling the pores having a diameter > 20 nm and the complication of the pore structure.

ORCID

Herly Nicolas Otsuka Sakata: https://orcid.org/0000-0003-0434-9595
Kennosuke Sato: http://orcid.org/ 0000-0002-3456-4037
Shigehiko Saito: http://orcid.org/0000-0001-6789-3198

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