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Pore Structure Characterization and Transport Performance Simulation of Cement Hydration Based on Irregular Particles

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ABSTRACT

Based on the CEMHYD3D hydration model, the irregular cement particles were introduced into the model, and three 3D micro structures under different water cement ratio (0.23, 0.35, 0.53) were obtained. Numerous physical models for calculating the characteristic parameters of pore structure are established and the characteristic parameters of pore structure obtained from the physical models. The characteristic parameters of pore structure include the total porosity (referred to as porosity), the porosity of continuous pore, isolated pore and dead-end pore, connectivity, pore size distribution and tortuosity. Finally, the transmission coefficient of each micro structure is calculated by the electric simulation method.

Keywords: Irregular cement particles; Pore structure characterization; Transport performance.

1.0 INTRODUCTION

In recent decades, with the rapid development of computer technology, it is possible to simulate hydration process and microstructure evolution process of cementitious material by means of computer. At present, some more advanced Hydration models such as the HymoStruc model (Breugel, 1992) , the μic model (Bishnoi and Scrivener, 2009) , and the CEMHYD3D model (Bentz, 2005) can be used to predict the hydration process and microstructure evolution of single mineral, cement and even cement based composites, and further predict the macroscopic properties of slurry. But both of them approximate the simulated objects into spherical particles, which restrict the hydration precision of the model itself and limit its application. In fact, cement based composites are made up of irregular shaped particles in accordance with a certain amount of behavior. The initial stacking behavior of these particles determines the hydration process of cement matrix composites and the microstructure evolution process of slurry, and further affects the macro-properties of the system, such as moisture and ion transport properties and mechanical properties of the system. Therefore, exploring the shape and stacking behavior of these particles is of great importance to the study of hydration process, microstructure evolution and macro-properties of cement-based composites.

As a porous material, the pore structure characteristics of cement based materials play an important role in the mechanical properties, transmission performance and durability of structural components (Matusinović *et al*., 2003; Zhang and Zhang, 2015). The pore distribution is complex, and the size of pore size is wide across the scale, which has a great influence on the strength of cement based materials (Kumar and Bhattacharjee, 2003a; Tang, 1986). Water filled with pores in the structure form an effective way of ion transport. Erosive harmful substances such as chloride and sulphate in the environment form corrosion through the medium to invade the material, resulting in structural damage. The evolution of pore structure is a part of the hydration process of cement-based materials. The characteristic parameters are often characterized by means of experimental methods, including small-angle X-ray scattering method (SAXS) (Jiang and Guan, 1999), mercury intrusion porosimetry (MIP) (Diamond, 2000; Kumar and Bhattacharjee, 2003b), method of synchrotron X-ray microCT (SX-microCT) (Gallucci *et al*., 2007) and nuclear magnetic resonance (NMR) (Justnes *et al*., 1990). There is no doubt that the test method has many advantages. But the existing test methods still have some limitations, such as the sample preparation process is difficult, and the test cost and time cost is high, and the test process cannot be monitored continuously and may cause some damage to the sample. At the same time, due to the restriction of the technical conditions, some parameters cannot be tested by experimental equipment (Guang, 2003), such as the porosity of isolated pore and dead-end pore. Because single pore parameter (such as porosity) is not sufficient to characterize the complex pore structure characteristics of microstructure (Aligizaki, 2005). In this paper, programs for characterizing the pore structure parameters of cement-based materials are established. All relevant parameters are systematically characterized in this study including porosity, specific surface area, pore size distribution, tortuosity and connectivity.

2.0 CONSTRUCTION OF IRREGULAR CEMENT PARTICLE AND MICROSTRUCTURE OF HYDRATION

Based on the cellular automata rules, a reconstruction method of irregular particles is developed in this study, which is named as central growth method or target growth method. Firstly a center cell specific is selected, then randomly activate any Moore neighbors in the neighborhoods, and turn them into the edge of particles. Then the Moore neighbors of the particle edge cell are activated randomly and transform them into the new edges of the particles. Finally particles continue to grow, until the growth meet certain conditions. The shape of the growth is controlled by the selected eigenvalue vectors. In the three-dimensional construction process, the Boolean operation is used to eliminate the voxel omission in the process of particle rotation. The method is then introduced into CEMHYD3D to establish three cement slurry hydration microstructures with different water cement ratio (0.23, 0.35, 0.53).

3.0 PORE STRUCTURE CHARACTERIZATION AND CALCULATION METHOD OF DIFFUSION COEFFICIENT

In order to explain the idea of algorithm used in the study more clearly, the representation process in this paper is illustrated by a two-dimensional schematic diagram (Fig. 1).

3.1 Classification of Pore Types

According to connection between each pore and microstructure surface, the pores within the system are divided into three types, that is, the continuous pore having two connected surfaces on the surface

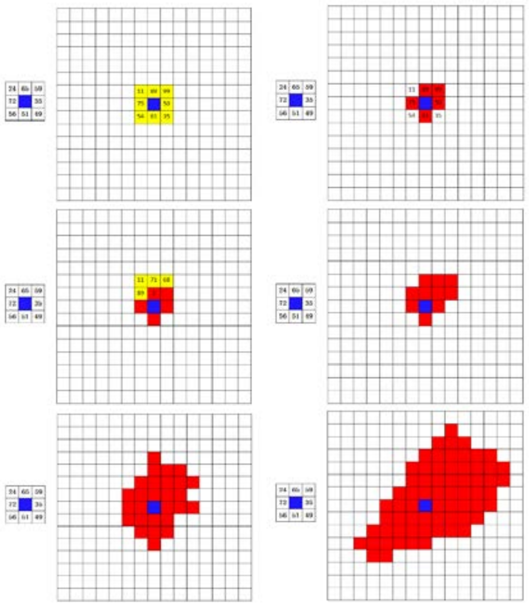

Fig. 1. 2D schematic diagram of central growth law (Red pixels are activated cells)

of microstructure, the dead-end pore having only one and the isolated pore having no connected surface (Guang, 2003). Taking into account the existence of "ink bottle pore", three kinds of pores diagram shown in Fig. 2.

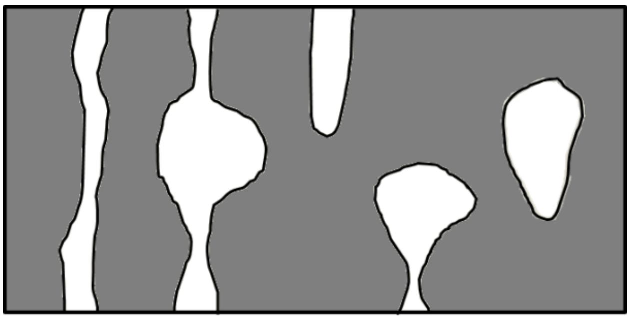

Fig. 2. Schematic diagram of various types of pores

3.2 The Calculation Model of each Parameter

Based on the CEMHYD3D hydration model, the parameters such as porosity, connectivity, pore size distribution, specific surface area and tortuosity were studied by "combustion algorithm", "mercury intrusion method-like algorithm" and "random walk algorithm" in this study.

3.3 The Calculation Method of Diffusion Coefficient

The electric simulation method (Garboczi, 1998) is suggested by Garboczi and converts the digital image of materials into the corresponding conductor network, according to the Nernst Einstein equation shows the relative conductivity equals the relative diffusion coefficient, so the solution of the relative diffusion coefficient is transformed into solving the corresponding conductivity of a conductor grid.

Since the relative conductivity is equal to the relative diffusion coefficient, the method can be used to calculate the relative diffusion coefficient of the system.

4.0 RESULTS and DISCUSSION

4.1 Pore Structure Characterization

Porosity of three types pores

The statistical results of porosity in each microstructure are shown in Fig. 3. The total porosity decreases gradually during the evolution of microstructures, and the total porosity decreases with the decrease of water-cement ratio at the same hydration degree. For instance when the degree of hydration increase from 0.2 to 0.5, the porosity decreases from 42.02% to 25.79% with water-to-cement ratio (w/c) of 0.35. At degree of hydration 0.35, the porosity are 19.77%, 33.88% and 47.76% with w/c 0.23, 0.35 and 0.53, respectively.

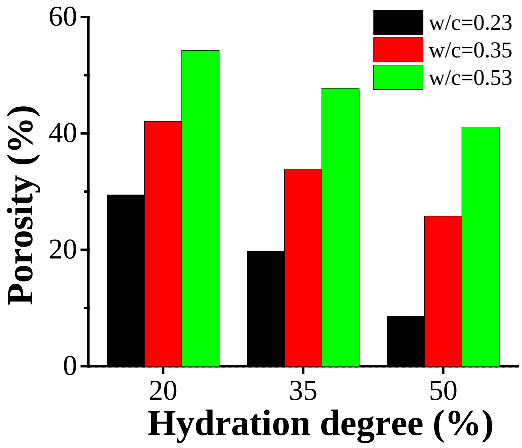

Fig. 3. The total porosity of the three water-to-cement ratio in the microstructure with the degree of hydration

The porosity of three types of pores are presented in Fig. 4. When the water-cement ratio is low, the pores will become discontinuous as the cement paste mature with the hydration progress. But when the w/c is relatively high, the pores will remain connected despite the cement hydration degree is very high. The continuous pores gradually decrease from 26.64% to 0 with water-to-cement ratio (w/c) 0.23. However when the water-to-cement ratio (w/c) is 0.53, continuous pores are still maintained at a high rate. The percolation threshold is that value of p, usually denoted pc, at which there is no longer an unbroken path from one side of the system to the other. Bentz *et al*. (Bentz and Garboczi, 1991) found the percolation threshold of approximately 18%. This theory can be verified in this study. When the water-to-cement ratio (w/c) 0.23 at degree of hydration 0.35 and 0.5, the porosity are 19.77% and 8.59% which are close to the percolation threshold and there are no continuous pores in pore structure. Due to the relatively large water-to-cement ratio in other microstructures, the porosity after hydration is still above the threshold. So the continuous pores still account for a large proportion. By comparing the pore structure with different water-to-cement ratio, the pore evolution process can be divided into two sections. When the pores are still connected, the continuous pores gradually decrease, and the dead-end pores and the isolated pores gradually increase until the continuous pores are completely blocked. When the pores are completely blocked in the later stage of hydration, the dead-end pores and the isolated pores begin to decrease. When the water-to-cement ratio (w/c) is 0.23 from degree of hydration 0.35 to 0.5, the porosity of the dead-end

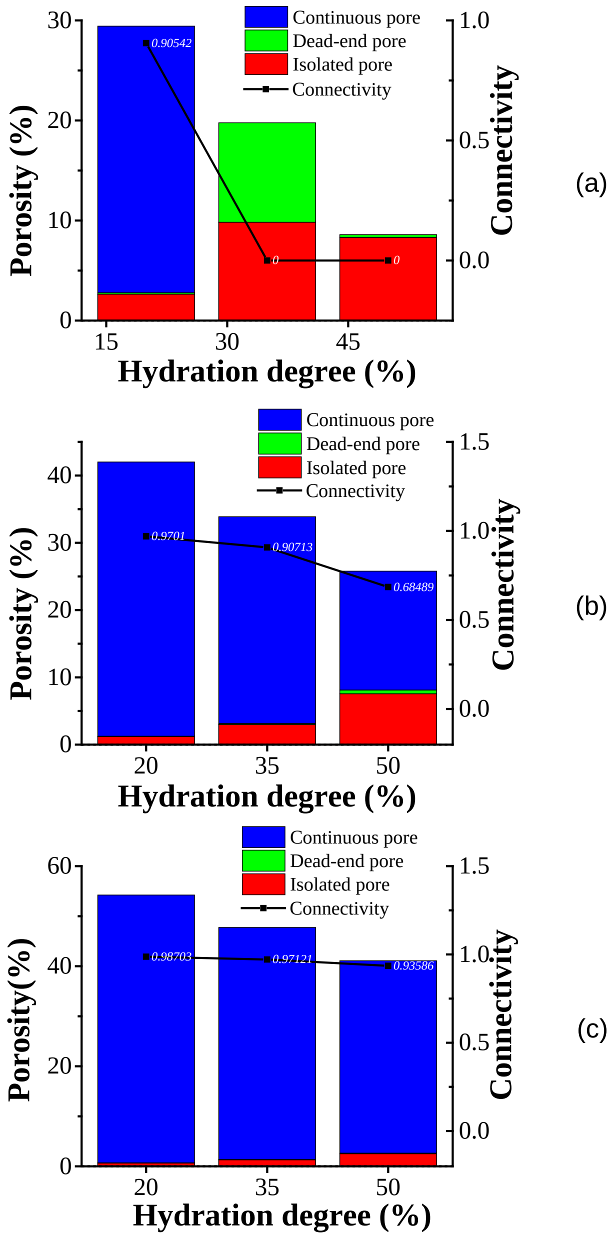

Fig. 4. The porosity of various types of pores in the three water - cement ratio of microstructure

pores and the isolated pores decrease from 9.95%, 9.82% to 0.29%, 8.31%. As can be seen from Fig. 4(b) and Fig. 4(c), the isolated pores grow more slowly than the dead-end pores. The reason is that the throat diameter of the “ink bottle” pores in the microstructure is most likely to be blocked by hydration products to form a isolated pore.

Pore size distribution

The cumulative porosity curve and differential curve obtained by MIP simulation and the algorithm of “Continuous PSD” are shown in Fig.5. With the decrease of the pore size, the cumulative porosity curve obtained by MIP simulation is lagging behind the continuous pore size. This is especially noticeable at a w/c of 0.23.

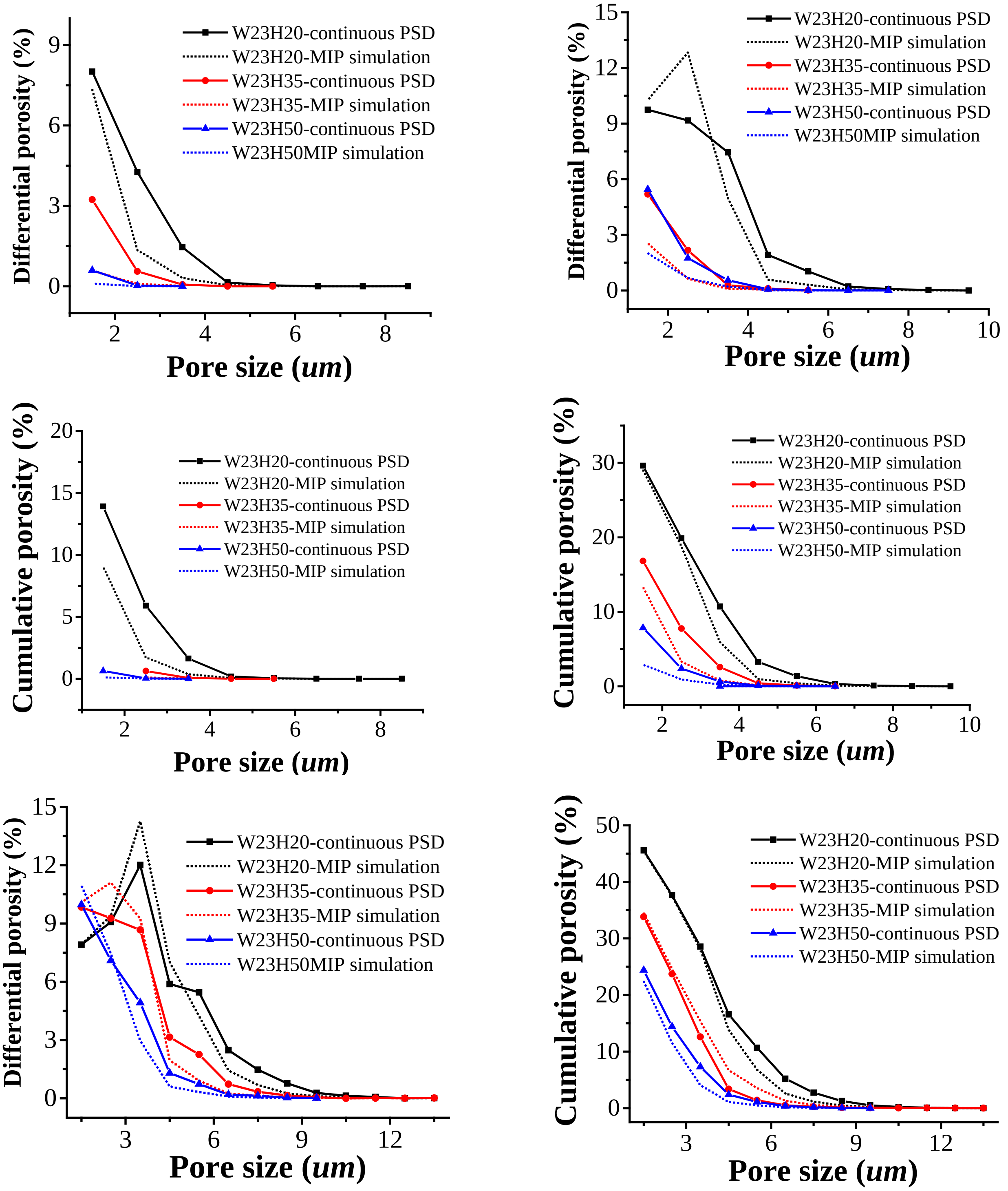

Fig. 5. The pore size distribution in each microstructure by MIP Simulation, and the algorithm of “Continuous PSD” (W23H35 reprasents the water cement ratio is 0.23 and hydration degree is 35%; MIP Simulation and Continuous PSD represent the results obtained by MIP Simulation, and the algorithm of “Continuous PSD”, respectively).

The reason for this phenomenon is that many isolated pores and "ink bottle" pores in pore structure result in underestimation of the total pore volume by MIP simulation. For a clear illustration, the differential porosity of the pores is obtained. Compared with the pore size distribution obtained by continuous statistics (actual results), the porosity of some large pores by MIP simulation is reduced, and the porosity of some smaller pores is improved. Such as when the water-cement ratio is 0.35 at hydration degree 20% and pore size is 2.5 μm, the porosity increases from 9.17% to 12.83% in MIP simulation statistics. But when pore sizes are 3.5 μm and 4.5 μm, the porosity decreases from 7.45% and 1.92% to 4.97% and 0.58%. This is because that there exists a smaller pore 'neck' in samples, through which the mercury can access the inner parts of the samples. In other words, the existence of 'ink-bottle' pores and 'throat' pores underestimates the porosity of larger pores and increases the volume of small pores (corresponding to 'neck' diameter.

Specific surface area

The specific surface area of the microstructure pore under different hydration degrees is shown in Fig. 6. Water-cement ratio and hydration degree have a significant effect on the surface area. The higher hydration degree and the smaller the water-cement ratio show the greater the specific surface area. This is consistent with the decrease of water-cement ratio, the decrease of large pores and the decrease of small pores. The increase of specific surface area indicates the refinement of the internal pores. It is generally known that the interior of pores is very rough. The larger pore surface area reflects the complex nested structure of pore structure with larger fractal dimension.

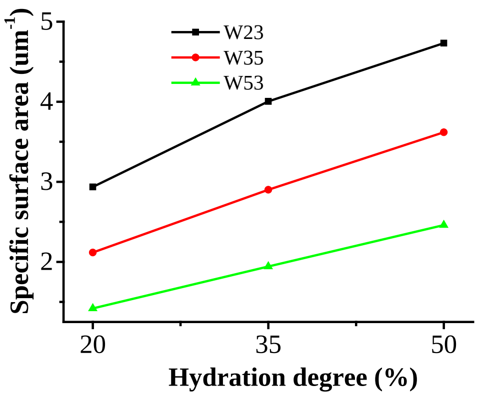

Fig. 6. The change of specific surface area with the various hydration degree

Tortuosity of pore structure in cement paste

In this study, the mean square displacement of the microstructure during random walk process has been counted, and then getting the tortuosity by linear fitting, the statistical results as shown in Fig. 7. Overall, with the increase of hydration degree, the tortuosity of the pore structure increased gradually. Further, the tortuosity decreases with the increase of water-cement ratio at the same hydration degree. The cause of this situation is that the pore structure is filled with hydration products in the progress of hydration which forms a relatively complex pore structure. When the water-cement is small, there are more fillers inside the microstructure under the same hydration degree, which hinders particle movement.

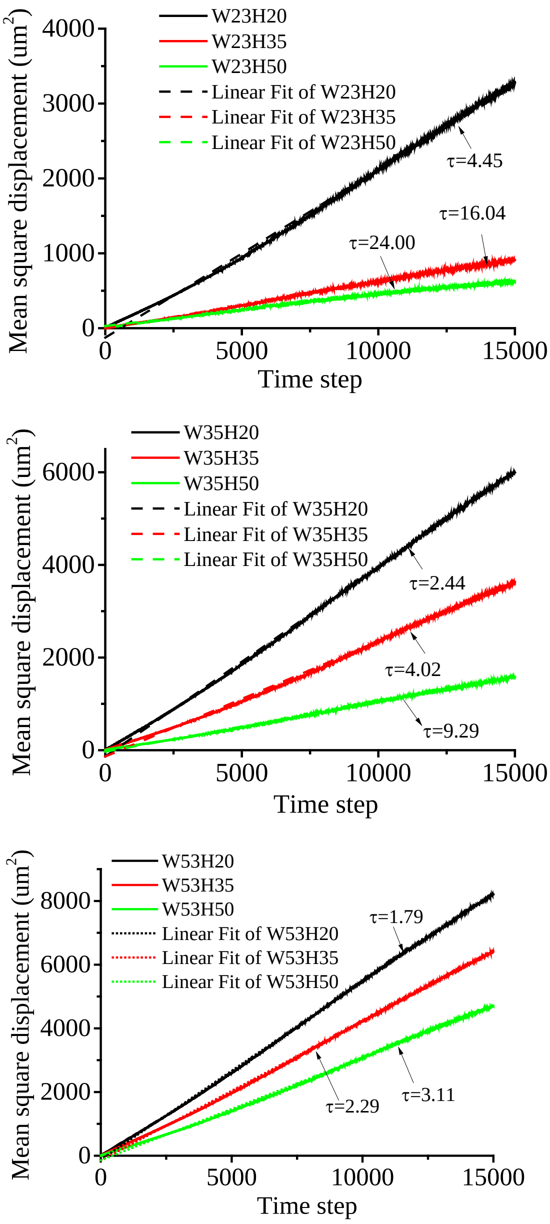

Fig. 7. Tortuosity of each microstructure

4.2 Diffusion Coefficient of Chloride Ion in Saturated State

It can be seen from Fig. 8 that in the microstructures with the same water-cement ratio chloride ion diffusivity decrease gradually with the hydration. The same hydration degree, the microstructure with a larger water-cement ratio has a larger diffusion coefficient. Combined with the structural characterization parameters obtained in Section 4.1, it can be seen that as the hydration progresses, the pores are gradually filled with hydration products, thereby interrupting the connectivity of the internal pores, resulting in a decrease in diffusion capacity. However, the larger pores in the microstructure of the larger water-cement ratio account for a larger volume of the structure and still have greater connectivity when the degree of hydration is 50%, resulting in a larger diffusion coefficient. At the same time, it can be seen that there is a certain relationship between the diffusion coefficient and the tortuosity of the pore structure. The smaller the tortuosity, the larger the diffusion coefficient of chloride ions in the microstructure.

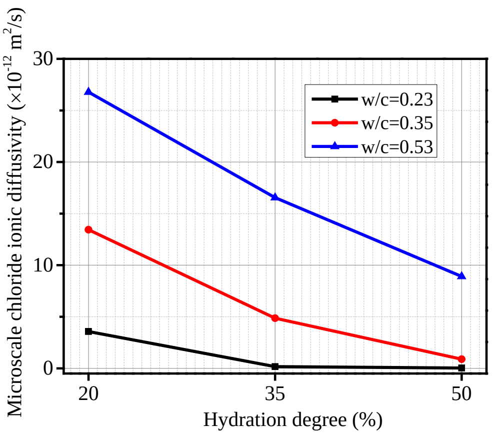

Fig. 8. The relationship between the diffusion coefficient of chloride ion and hydration degree at different w/c

5.0 CONCLUSIONS

Based on the central growth rule, the irregular cement particles are reconstructed, and the irregular particles are introduced into the CEMHYD3D model to obtain the microstructure model based on irregular particles. Then, a series of algorithms are used. The changes of pore structure and transport performance of microstructures with hydration are analyzed under different w/c. In this study, the reconstruction method makes the cement particles in CEMHYD3D closer to the real particles, and those methods present another methods for characterizing the three-dimensional pore structure of cement hydration with continuous monitoring, no damage and time-saving.

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