Influence of Water-binder Ratio on the Microstructure of Air-entrained Concrete

S S He¹, L M Wang², R R Zhang¹ and Z W Shi²

¹Jiangmen Polytechnic, Jiangmen City, Guangdong Province, 529090, PRC.
²Department of Civil Engineering, Northeast Forestry University, Harbin City, Heilongjiang, 150040, PRC.
songsonghe@hotmail.com

Abstract: The concrete’s microstructure affects its macroscopic properties such as the strength and the frost resistance. This research is to study the influences of different water-binder ratio on the microstructure characteristics of air-entrained concrete, which will be done by using both the mercury intrusion test and the optical lead test. The research aims to find out the influences of the change of water-binder ratio on the pore size distribution and pore structure of the air-entraining concrete and non air-entraining concrete. The research results showed that the water-binder ratio mainly influenced the pore gel pore volume in the non-entrained concrete, and the pore volume of capillary pores as well as excessive pores in air-entraining concrete increased along with the increasing of water-binder ratio. The most probable aperture and porosity also gradually increased, while the fractal dimension decreased, when the water-binder ratio increased. It was the increasing of entraining agent content in the air-entraining concrete that increased the pore fractal dimension. The lower average pore spacing factor was to get in the air-entraining, the higher water-binder ratio required more air content.

1. Introduction
Concrete is a kind of non-uniform and Porous materials. Previous studies have shown that the pore structure of concrete has an important influence on its mechanical properties and durability, thus the further researches on the concrete materials should be done from macroscopic aspects to microscopic ones. The quality and property of concrete raw materials as well as the different designs of concrete mix proportion will generate different microscopic pore structure forms. There are many factors affecting the mix proportion of cement concrete. The water-binder ratio is the most important parameter in the mix proportion design. The change of water-binder ratio will cause significant influences on the microscopic pore structure of concrete, which eventually changes the mechanical properties and durability of concrete. In this research, the mercury intrusion test and optical lead test were used to find out the influences of water-binder ratio on microscopic pore structure of air-entrained and non-air-entrained concrete.

2. Materials & Methodology
2.1. Raw materials & mix proportion design
The cement is P•O42.5R ordinary Portland cement. The coarse aggregate is continuous graded granites. The fine aggregate selects natural river sand with fineness modulus of 2.3, which is inside the range of Grade II. The lignin Sulfonate superplasticizer and rosin resin air-entraining agent are taken
as the admixture. The experiment changes the water-binder ratio within a wider range, thus in the case of restricting the cement dosages, a small amount of fly ash of Grade I is added to control the fluidity of cement concrete mixture. On the basis of basic mix proportion, the experimental mix proportion adjusts proportion to 0.35 and 0.45. In such a case, the air-entraining agents with the dosages of 0.1‰, 0.2‰ and 0.3‰ are respectively added to the mix proportion of 0.35, 0.40 and 0.45. The basic mix proportion of cement concrete is shown in Table 1, with the experimental mix proportion in Table 2.

Table 1. Basic mix proportion of concrete

| Water cement ratio | Water /kg·m$^{-3}$ | Cement /kg·m$^{-3}$ | Sand /kg·m$^{-3}$ | Stone /kg·m$^{-3}$ | Fly Ash /kg·m$^{-3}$ | Water reducer /% |
|--------------------|-------------------|--------------------|------------------|-------------------|---------------------|-----------------|
| 0.40               | 152               | 304                | 732              | 1194              | 76                  | 1               |

Table 2. Experimental mix proportion of concrete

| Number | Water-binder ratio | Water /kg·m$^{-3}$ | Air-Entraining Agent(AEA) /‰ |
|--------|--------------------|--------------------|-------------------------------|
| W/C-0.35 | 0.35              | 114                | 0–0.3‰                        |
| W/C-0.40 | 0.40              | 152                | 0–0.3‰                        |
| W/C-0.45 | 0.45              | 190                | 0–0.3‰                        |

2.2. Experimental methodology

2.2.1. Optical lead test. The average pore spacing of the cement concrete is measured by the optical lead test method in Technical Specifications for Construction of Highway Cement Pavement (JTG F30-2003). The continuous zoom microscope is used in the test, equipped with CCD HD camera and measurement software.

2.2.2. Mercury intrusion test. The AutoPore IV 9500 high-performance automatic mercury intrusion instrument is adopted to test the microscopic pore structure parameters and the distribution of cement concrete. At present, there are three ways to collect the test specimens to obtain them directly from the cement concrete, to make cement mortar and cement paste according to the same production ratio. In this research, the mercury intrusion test specimens are obtained directly from the cement concrete which has been maintained for 54 days.

2.3. Results & Discussion

2.3.1. Influences of water-binder ratio on concrete pore size distribution. The durability and strength of concrete not only depend on the characteristics of the pore structure, but the differences in the macroscopic properties of concrete are also resulted from the range of the pore size distribution and the variation of pore volume [7,8,9]. There are many kinds of concrete aperture classification methods. The most widely-used one is to divide the pore sizes into four kinds of sizes, according to the pore size distribution: gel pore (<10nm), excessive pore (10–100nm), capillary pores (100–1000 nm), macropores (>1000 nm). The diagram of curves shown in Figure 1-4 are the results of mercury intrusion test.
As shown in Fig.1, the change of water-binder ratio in non air-entraining concrete resulted in a significant change in the gel pore of concrete. With the increase of water-binder ratio, the volume of gel pores gradually increased, while the influences of water-binder ratio on excessive pore, capillary pores and macropores were insignificant. Figure 2-4 shows that with the rising water-binder ratio increasing the pore volume, the change of water-binder ratio in air-entraining concrete exerted an insignificant influence on the gel pores and macropores, while it mainly affected the excessive pores and capillary pores in the pore structure of concrete. The more air-entraining agents were added, the more significant the water-binder ratio became for the volume of excessive pores and capillary pores. Compare with the non air-entrained concrete, the mix of air-entraining agent greatly increased the pore-size volume of concrete.

2.3.2. Influence of water-binder ratio on porosity and most probable aperture of concrete.

The pore diameter corresponding to the peak numerical in the concrete pore size distribution curve is the most probable aperture, which is the most widely distributed pore size in the pore structure of concrete. The most probable aperture and porosity are important indicators to analyse the permeability of concrete. The relationship between water-binder ratio and porosity is reflected in Fig.5. With the increase of water-binder ratio, the porosity gradually increased. The relationship between the water-binder ratio and the most probable aperture of concrete can be found in Fig.6. As the water-binder ratio increased, the most probable aperture of concrete gradually increased. The reason may be that the increase of water-binder ratio resulted in an increase of free water content in concrete. The evaporation of free water would enlarge the pore-size structure of concrete.
2.3.3. Influence of water-binder ratio on fractal dimension of concrete. The microcosmic pore structure, pore volume and pore specific surface of concrete showed the irregularities of pore when observed by electron microscope scanning and it is hard to describe its irregularities quantitatively. Fractal theory is able to describe the complexity and irregularity of the matter. Thus, the complexity of pore-size structure of concrete can be described by using the fractal dimension \([9]\). At present, to describe the pore structure of cement concrete based on the Fractal theory is still in the research stage and many domestic and foreign experts have also established various models. The dimension is to draw the differential curve of pore size distribution of concrete, and its relational expression and correlation coefficient are obtained by linear regression. The slope of the linear expression is the fractal dimension \(D_\text{f}[10,11]\). Based on the Menger sponge model, this research analyses the relationship between the water-binder ration and fractal dimension, which can be found in Fig 7-8. The pore fractal dimension of concrete with different air entrainments decreased with the increasing water-binder ratio.

2.3.4. Influence of water-binder ratio on average pore spacing of concrete. The average pore spacing factor is an important index to evaluate the frost resistance of cement concrete. The larger the average pore spacing factor coefficient, the greater the distance is between the two adjacent bubbles and the greater the hydrostatic pressure and the infiltration pressure the concrete is under during the freeze-thaw cycle when the concrete water is saturated, which then leads the concrete frost resistance to decrease.
As shown in Fig. 9, with the increase of water-binder ratio in air-entrained concrete, the average pore spacing factor coefficient of concrete becomes larger. When the water-binder ratio is 0.45, it is necessary to add 0.3‰ or more air-entraining agent to keep the average pore spacing coefficient of concrete less than 220 μm, while the water-binder ratio of 0.35 just requires 0.1‰. That is, to get the concrete with lower average pore spacing Coefficient, the higher water-binder ratio requires more air content. The Fig. 10 shows that the water-binder ratio has an insignificant influence on the average air bubble spacing coefficient of non-air-entrained concrete. As the water-binder ratio increases, the average air bubble spacing coefficient fluctuates between 400 and 450 μm. The reason may be that few microscopic air bubbles in the non-air-entraining concrete are mainly brought in by the cement’s hydration reaction in the process of mixing. In comparison with non-air-entraining concrete, the water-binder ratio in air-entraining concrete exerts greater influences in the average pore spacing coefficient.

2.3.5. Influence of water-binder ratio on BET surface area and average pore size of concrete. The average pore size and BET surface area of cement concrete are important indexes to evaluate microscopic bubble structure. As can be seen from Fig. 11 and Fig. 12, the water-binder ratio has a greater influence on the average pore size and BET surface area. When the water-binder ratio gradually increases, the average pore size also increases, while the BET surface area decreases. Different from air-entrained concrete, an insignificant influence is exerted from the water-binder ratio on the average pore diameter and BET surface area of the non-air-entrained concrete. The average pore diameter basically maintains between 22 and 24 nm and the BET surface area is about 200 m²/g.

In the same water-binder ratio, when the air entraining dosages increase, the average pore diameter of air-entraining concrete will first decrease and then increase, while the BET surface area does in reverse. As for macro-frost resistance, the frost resistance of the same water-binder ratio presents a trend of from increasing to decreasing with the increasing of air content. Again, it can be explained from the microscopic point of view that only the introduction of uniform and tiny pores can make the...
concrete have a good durability, on the condition of controlling the air content within an appropriate range. Therefore, the water-binder ratio serves as the main factor influencing the average pore diameter and BET surface area of the air-entraining concrete, so does the air content when water-binder is at the same ratio.

3. Conclusion
The water-binder ratio in the non air-entrained concrete mainly influenced the pore volume of gel pores, which increased as the water-binder ratio increased. However, the water-binder ratio in the air-entrained concrete had significant influences on the pore volume of capillary pores and excessive pores, which increased as the water-binder ratio increased. Moreover, as the air-entraining agent increased, the increasing of pore volume of capillary pores and excessive pores became more significant. Besides, when the water-binder ratio increased, the most probable concrete pore size and porosity gradually increased.

With the increasing of water-binder ratio, the pore fractal dimension gradually decreased and the pore structure became less complex, which were more significant in the air-entraining concrete. When the water-binder ratio in air entraining concrete is same, the increasing of air content would increase the fractal dimension and enhanced the complexity of pore structure. Thus, to increase the pore fractal dimension in the concrete structure of civil engineering, water-binder ratio should be decreased as well as the air content being increased.

As the water-binder ratio increased, the average pore spacing factor coefficient also gradually increased. Under the same water-binder ratio, the average pore spacing coefficient significantly decreased with the air content increasing. Furthermore, to get the concrete with lower pore spacing coefficient, more air content was required when the water-binder ratio was higher. The water-binder ratio in non air-entrained concrete influenced the pore spacing coefficient insignificantly. Due to the lower pore spacing coefficient would enhance the durability of concrete, thus to add a small amount of air content in the lower water-binder ratio to the concrete was suggested, which satisfied the requirements of the frost resistance and impermeability in the pore structure of civil engineering.

Following the decreasing of water-binder ratio, the average pore size of air-entrained concrete significantly decreased, while the BET surface area increased. When the water-binder is at the same ratio, with the air content increasing, the average pore size decreased first and then increased, while the BET surface area had a reverse reaction. The water-binder ratio in the non air-entrained concrete had an insignificant influence on the average pore diameter and BET surface area. Therefore, to ensure the durability of concrete structure in civil engineering, the water-binder ratio should be controlled more or less in the 0.40 and the appropriate air content was suggested.

References
[1] Powers T C and Brownyard T L 1970 Studies of the physical properties of hardened Portland cement paste Journal of the American Concrete Institute.53 53–59.
[2] Shanshan Jin, Jinxi Zhang and Song Han 2018 Fractal analysis of relation between strength and pore structure of hardened mortar Construction and Building Materials.135 1–7
[3] Rakesh Kumar and B Bhattacharjee 2003 Porosity, pore size distribution and in situ strength of concrete Cement and Concrete Research.32 155–164.
[4] Care S. 2008 Effect of temperature on porosity and on chloride diffusion in cement pastes Construction and building Materials.22 1560–1573.
[5] Wu Zhongwei 1988 Concrete Science of Technology and Cement Products. 12 4–5.
[6] Ester Venhodová, Radek Janovský and Rostislav Drochytka2014Influence of Material Properties of Input Raw Materials on Microstructure of Aerated Concrete Advanced Materials Research.3353 73–76.
[7] Cousy O and Monteiro P J M 2008 poroelastic model for concrete exposed to freezing temperayures Cement and Concrete Research.38 40–48.
[8] Manmohan D and Mehta P K 1981 Study on blended Portland cements containing santorini
earth Coement and Concrete Research.11 575–579.

[9] Ayda S. Agar-Ozbek, Jaap Weerheijm, Erik Schlangen and Klaas van Breugel 2013 Investigating porous concrete with improved strength: Testing at different scales Construction and Building Materials.41 480–490.

[10] Tang ming and Li xiao 2004 Status and Progress of fractal characteristics of concrete points Journal of concrete.12 8–11.

[11] Tang ming and Li xiao 2005 Influence of various factors on the concrete pore structure fractal characteristics Journal of Shenyang Jianzhu University (Natural Science Edition).21 232–237.