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Investigation of pore structure and mechanical property of cement paste subjected to the coupled action of freezing/thawing and calcium leaching

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ABSTRACT

In order to comprehensively understand the degradation of cementitious materials when subjected to the coupled action of calcium leaching and freezing/thawing, changes of the pore structure and the Vickers hardness of cement paste are investigated. In this study, the coupled action are designed as Case I (first leaching then freezing/thawing) and Case II (first freezing/thawing then leaching). The effects of Case I on the mechanical degradation are greater than Case II. This is further clarified by changes of the pore structure. For freezing/thawing, the level of deterioration qualified by hardness decrease is sensitive to the proportion of big pores (i.e., > 100 nm). For calcium leaching, it is determined by the amount of CH and C-S-H. In addition, the hardness-porosity relationship is discussed. A quantitative prediction model from theoretical deviations considering influences of pore size is established.

1. Introduction

In cold regions, hydraulic concrete structures submerged, or partially submerged in water, such as dams, harbors, canals and bridge foundations may have high risk of calcium leaching and frost damage [1,2]. No matter calcium leaching due to soft water erosion or frost damage due to freezing/thawing cycles, detrimental effects will be produced, such as decreases in the strength, stiffness and elastic modulus of the material, and increases in the permeability and diffusivity [3–12]. In practical engineering, progressive damage to the concrete surface of hydraulic concrete structures under the coupled factors of calcium leaching and freezing/thawing cycles have been observed, and the deterioration rates can be dramatically fast [1]. At present, many researchers have focused on either calcium leaching or freezing/thawing, however, rare research has been reported about the coupled effects of calcium leaching and freezing/thawing.

1.1. Calcium leaching

Calcium leaching is a combined diffusion-dissolution driven process [13–15]. The concentration gradients between the pore solution and soft water environment cause the diffusion of calcium ions from the pore solution to the surrounding water. According to Mainguy et al. [16], the dissolution process can be divided into three stages: At initial stage, in which the calcium ion concentration in pore solution is approximately 21 mol/m^3, the dissolution of portlandite (CH) buffers the solution with respect to calcium and hydroxyl ions; At intermediate stage, which commences as soon as all CH has dissolved, now, the calcium ion concentration in pore solution is about 2 mol/m^3, and initiates the progressive decalcification of C-S-H gel; At final stage, in which most of the calcium content of C-S-H has been lost, leaving behind a high-silica amorphous phase. Calcium leaching of cement-based materials by soft water in nature is a slow process. To accelerate the calcium dissolution process, ammonium nitrate solution (NH_4NO_3) was usually used in research. Studies have indicated that NH_4NO_3 solution can greatly shorten the dissolution time of solid calcium, because the equilibrium concentration of calcium was increased from 22 mol/m^3 to 2900 mol/m^3 [3]. Comparing with other acceleration methods, it not only accelerates the calcium dissolution, but has the same effect on mechanical and physical properties as the long term soft water erosion

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[4].

Many studies about the influences of calcium leaching on the mechanical properties of cementitious materials have evaluated compressive strength [3–6]. It was measured on cubic or cylindrical samples cut or drilled from different depth of leached specimen, which gives the mechanical behavior on average. In order to understand the mechanical changes of leached area with different leaching degree, micro-hardness test was introduced [6,7]. Based on applying a static load for a known period of time and measuring the response in terms of size of indentation, the local mechanical behavior of material in question can be evaluated [12]. Yang et al. compared the compressive strength and the average Vickers hardness of the same leached specimen, and found that the linear correlation between these two parameters was very predominant [6].

The intrinsic reason for concrete degradation is that calcium leaching changes the microstructure of cementitious materials [3,5,8], including alteration of the pore structure and change of the chemical composition of calcium-silicate-hydrate (C-S-H). Research from Phung et al. [8] has shown that the accelerated leaching significantly altered the microstructure of the cement paste to a material with a higher specific surface area, increased total porosity and a shift to larger pore sizes. By using mercury intrusion porosimetry (MIP) test, Choi and Yang [5] have indicated that volume of pores with diameters ranging from 50 nm to 500 nm is greatly increased by leaching, and that pores larger than 200 nm in size rapidly increase in number during the initial leaching time. Generally speaking, the pore structure is coarsened by leaching. However, according to the calcium dissolution process, the characteristics of pore structure change attributed to CH dissolution and C-S-H decalcification may be different.

1.2. Freezing/thawing

The freezing behavior of concrete is a complex physical phenomenon, and mechanisms governing the frost damage of cementitious materials have been studied for decades. Researchers consistently found that harmful stresses could result from hydraulic pressure, ice crystallization pressure and the mismatch of thermal effects between ice and solid phases [17–23]. As temperature decreases, ice is formed in the capillaries of cement paste, and in order to accommodate the 9% volume increase associated with ice formation, excess water is expelled from the freezing sites which will cause a hydraulic pressure, this is the well-known hydraulic pressure model proposed by Powers [20]. Experiments from Beaudoin and MacInnis [22] gave the evidence for the importance of crystallization pressure. In order to maintain the equilibrium of chemical potentials between crystals of ice and liquid water, stresses may be exerted on pore walls due to the ice crystallization pressure. Scherer and Valenza [23] indicated that a tensile hoop stress exerted by ice crystals on the pore wall could approach the tensile strength of concrete at low temperatures. As to the formation of ice, the well-known Gibbs-Thomson equation gives the relation between pore size and its freezing temperature [17–19]. By considering the stresses resulting from hydraulic pressure, ice crystallization pressure and mismatch of thermal effects, Liu et al. have simulated the internal damage development in terms of creation of microcrack in cement paste during freezing [18].

Reduction in mechanical resistance [9–11] and the microstructural changes [17–19,24,25] in hardened cement-based systems after freeze-thaw cycles have also been intensively studied. In order to evaluate the progressive degradation of cementitious materials subjected to F-T cycles, compressive strength and dynamic modulus of elasticity of specimens were usually measured after repeated F-T cycles [9–11]. In order to obtain changes in the microstructure due to frost damage, a variety of experimental techniques were employed [19–25]. By measuring the pore structure of concrete before and after F-T cycles through mercury intrusion porosimetry (MIP), Wang et al. [24] found that the frost damage altered the pore structure. The proportion of larger pores (diameter > 100 nm) increased, while that of smaller pores (diameter < 100 nm) decreased after cyclic F-T testing. By using X-ray image analysis techniques, Yuan et al. [25] have investigated the variation of concrete pores under the action of F-T cycles, and have confirmed that big pores are more sensitive to freezing/thawing.

1.3. Quantitative relationship between mechanical property and pore structure

Pore structure influences the physical and mechanical properties of cementitious materials (e.g., strength, fracture energy, toughness, elastic properties, permeability, and effective diffusivity) [26]. In order to understand the relationship between properties of cement paste and its corresponding pore structure, many studies has been conducted [26–28]. The macroscopic property of cement-based material can be predicted from its representative volume element (RVE) as a function of the microscopic phase properties and phase volume fractions by homogenization methods [28–33]. Property-porosity relationship is the most popular. Consider the influence of pore structure by a parameter in terms of total porosity or effective porosity, quantitative relationships between the porosity and the mechanical properties of porous cement-based materials have been established [27,29]. Further, by taking gel pore, small pore and large pore into account, multiscale mechanical model of porous cement-based material has been proposed [28,30]. It has been well acknowledged that pores of different sizes have different impact intensity on the mechanical properties of the material. Nevertheless, an explicit agreement on pore size division according to its influence on the mechanical properties has not been reported. In order to explicitly reveal this, systematic comparison between the mechanical properties and the pore structure and a quantitative prediction model considering influence of pore size are in need.

1.4. Work objectives

Field observation on hydraulic concrete structures has indicated that the damage to the concrete surface becomes more serious due to the alternating action of freezing/thawing and leaching, and interactions between multiple degradation mechanisms accelerate deterioration [2]. So far, many studies focus on changes of the mechanical properties or changes of the microstructure of the material due to either calcium leaching or freezing/thawing. However, rare studies discuss influences of the coupled action of freezing/thawing and calcium leaching, especially on the pore structure and the mechanical property of cementitious materials.

It is common that the concrete in service was first damaged due to freezing/thawing then subjected to calcium leaching, or it was first leached to a certain degree then subjected to freezing/thawing, or it subjected to the two alternating factors. In order to acknowledge the interaction between leaching and freezing/thawing, two experimental procedures are designed as Case I (first leaching then freezing/thawing) and Case II (first freezing/thawing then leaching). Case I answers influences of freezing/thawing on the specimens at different degree of decalcification (with mass loss of 5%, 10% and 15% where CH dissolves, CH totally dissolved and C-S-H decalcifies, respectively). Case II answers influences of calcium leaching on the specimens at different degree of frost damage (i.e., 4, 8 and 12 F-T cycles).

Previous studies have indicated that both freezing/thawing and calcium leaching can coarsen the pore structure. Freezing/thawing especially enlarges big pores attributed to hydraulic pressure and crystallization pressure [24,25]. While calcium leaching changes the pore structure from two aspects: CH dissolution and the decalcification of C-S-H, which may demonstrate different patterns. Since the pore structure undergoes different alteration experiences due to the action of calcium leaching or freezing/thawing, the final pore structure may be different because of the coupled actions. Therefore, further