Microstructural and bulk property changes in hardened cement paste during the first drying process

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ABSTRACT

This paper reports the microstructural changes and resultant bulk physical property changes in hardened cement paste (hcp) during the first desorption process. The microstructural changes and solid-phase changes were evaluated by water vapor sorption, nitrogen sorption, ultrasonic velocity, and ^{29}Si and ^{27}Al nuclear magnetic resonance. Strength, Young's modulus, and drying shrinkage were also examined. The first drying process increased the volume of macropores and decreased the volume of mesopores and interlayer spaces. Furthermore, in the first drying process globule clusters were interconnected. During the first desorption, the strength increased for samples cured at 100% to 90% RH, decreased for 90% to 40% RH, and increased again for 40% to 11% RH. This behavior is explained by both microstructural changes in hcp and C–S–H globule densification. The drying shrinkage strains during rapid drying and slow drying were compared and the effects of the microstructural changes and evaporation were separated.

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1. Introduction

Among cement hydrates, calcium silicate hydrate (C–S–H) plays an important role in the physical properties of concrete and cement paste, because it forms the matrix. Experimental studies of sorption properties, drying shrinkage, strength, and Young's modulus of hardened cement paste (hcp) confirm that C–S–H is a gel-like or colloidal system, and the behavior of the system depends strongly on its surrounding water molecules [1–6]. Concrete is usually made with a water-to-binder ratio of 0.50–0.60, and begins its service life with relatively high water content. Over time, concrete releases water into the atmosphere, causing shrinkage and changes in physical properties. The performance of concrete is strongly affected by the first desorption process that the hcp undergoes. Therefore, studies of C–S–H and cement paste during the first desorption process are crucial for concrete engineering.

1.1. Microstructural changes

1.1.1. Mesoscale microstructural changes

N_2 sorption is widely used for characterizing hcp. The Brunauer–Emmett–Teller (BET) surface area of N_2 (S_{N2}) corresponds to the surface of the C–S–H gel particles in hcp. Hereafter, "globule" is used according

to the definition in ref [3]. N_2 can penetrate into only the mesopores and can be adsorbed on only the outer surface of globules; it does not reach the interlayers of the lamellar C–S–H structure [7].

Hunt et al. reported the difference in S_{N2} of hcp samples cured under different drying conditions [8]. A local minimum value of S_{N2} was reached for curing conditions of around 50% RH under drying conditions from 80% to 5% RH. The decrease in S_{N2} from saturated curing conditions to around 40% RH has also been reported by Parrott [9], and Litvan and Myers [10]. Parrott concluded that the development of capillary tension stress in hcp is related to the closure of nitrogen-accessible pores.

Small-angle X-ray scattering, which assumes that the globules are spherical, also shows a decrease in the estimated surface area from saturated curing conditions to around 40% RH [11–13]. Small-angle neutron scattering (SANS) can also detect mesoscale microstructural changes in hcp. Thomas et al. used SANS to study cement paste cured under different RHs and resaturation conditions [14]. They found that the number of interparticle spaces (gel pores) decreased and the bulk density of the C–S–H gel increased for curing conditions of 100% to 54% RH. Below 54% RH, a gas/C–S–H gel interface was formed and the C–S–H gel lost the water adsorbed on the surface.

Environmental scanning electron microscopy gives a comprehensive view of the morphological changes in C–S–H during drying. Fonseca and Jennings experimentally confirmed that fibrillar and amorphous morphologies of the outer product C–S–H (Op C–S–H) are present under wet conditions, and the amorphous phase is dominant. This is consistent with the reported microstructural changes mentioned above [15].

1.1.2. Interlayer spaces in C–S–H

Feldman and Sereda reported that the water adsorption process under low pressure is interlayer rehydration [7]. Thus, the surface area derived from the water vapor isotherm (S_{H2O}) corresponds to the interlayer spaces in C–S–H globules. In addition, the decrease in S_{H2O} caused by prolonged drying can be explained by the difficulty in breaking the solid–solid contact in the interlayer space, due to its large connecting force.

Powers and Brownyard reported a linear relationship between chemically bound water and S_{H2O} [16,17]. However, Tomes et al. found that the S_{H2O} of hcp decreases with repeated drying and wetting cycles, and that the total volume of adsorbed nitrogen decreases [18]. Chiang et al. used SANS to determine the behavior of synthesized C–S–H globules during drying. The globules were modeled as disks containing a lamellar structure. They experimentally confirmed that the interlayer distance and the number of C–S–H layers in the globules decreased during drying [19].

1.1.3. Solid-phase changes

Parrott and Young carried out quantitative gel permeation chromatography of trimethylsilyl silicate derivatives and found that the effect of prolonged drying on the silicate chain length was small [20]. However, Bentur et al. observed polymerization in pure calcium silicate paste during the drying process [21]. Cong and Kirkpatrick used nuclear magnetic resonance (NMR) to observe the polymerization of silicate chains in C–S–H. The polymerization did not occur during drying at room temperature, whereas it did occur at elevated temperatures [22]. Aono et al. also reported silicate polymerization in Portland cement paste during drying at 50 °C [23].

1.2. Physical properties of hcp during drying

The physical properties of dry hcp have been extensively studied by Feldman and Sereda [7,24,25]. Sereda et al. used hcp and compacts of bottle hydrated cement. The strength of the hcp increased when it was strongly dried, and then gradually decreased during the re-wetting process. Young's modulus increased from 50% to 100% RH during the rewetting process and exhibited a slight additional increase during the re-drying process with a maximum at around 30% RH. However, these values were obtained after strong drying, and there were no data for the first desorption process.

Wittmann studied the properties of hcp during the first desorption process [26]. Young's modulus decreased for drying at 90% to 40% RH, reached a local minimum around 40% RH, and then increased for 40% to 11% RH. He proposed that the increase in Young's modulus for 40% to 11% RH was caused by the surface free energy of the C–S–H gel and the decrease under 90% to 40% RH was caused by the disjoining pressure of the adsorbed water. The study did not include data on the strength of the hcp between 100% and 40% RH, although the strength increased below 40% RH. Wittman concluded that the surface free energy of the C–S–H gel also contributes to this behavior.

The behavior of the dynamic elastic modulus of hcp cured under different RHs is similar to that of Young's modulus [27]. Zech and Setzer reported a multicomponent model showing that the decrease in the dynamic elastic modulus under 100% to 40% RH can be explained by water content, although below 40% RH, the surface free energy should be taken into account. Pihlajavaara measured many physical properties of mortar under different curing conditions [28]. The behavior of the compressive strength is similar to that of Young's modulus [26] and the dynamic modulus [27].

Studies of the shrinkage behavior of hcp during the first desorption process are limited. Helmuth and Turk showed that irreversible shrinkage occurred at 100% to 47% RH and was strongly affected by the water-to-binder ratio. This shrinkage was irreversible because of the collapse of the small pores, although after the hcp was dried at 11% RH, the change in the hcp strain caused by changes in water content became

reversible [29]. Recently, Setzer developed an apparatus to measure the length-change isotherm. The length-change isotherms of the first desorption and the subsequent re-wetting and re-drying processes had identical curves when the strain data were plotted as a function of the evaporable water content [2]. Maruyama confirmed experimentally that the ratio of the amount of C–S–H to adsorbed water, which can be represented by a statistical adsorption thickness, determined the change in the length of hcp during both the first desorption process and the subsequent re-adsorption process [30].

1.3. C–S–H model and physical properties during the first drying

Feldman and Sereda proposed a model of hcp in which the layers or sheets in the C–S–H gel are rearranged during the first desorption process, where the main driving force is the capillary tension force or the surface free energy acting on the C–S–H gel. Consequently, the external surface area exposed to nitrogen decreases, producing irreversible shrinkage. They attributed the irreversible shrinkage to the rearrangement of layers in the C–S–H gel [7].

Jennings proposed a colloidal model based on existing cement paste data for water vapor adsorption, density, C–S–H stoichiometry, and specific surface area [1,3]. The data were unified using the basic D-drying conditions for C–S–H. In the colloidal model, the C–S–H system is composed of C–S–H flocculations with two different densities. The C–S–H system depends on time, temperature, RH, and the history of the C–S–H. The aging process consists of the polymerization of the silicates in the C–S–H, and the globules become more tightly packed as it ages. Thus creep and shrinkage are a function of the C–S–H aging [31]. In the refined CM-II model, C–S–H is mainly composed of 4-nm-thick C–S–H globules, 30–60 nm globule clusters, and water-filled spaces, which consist of interlayer spaces, inter-globule spaces, small gel pores, and large gel pores.

1.4. Objective

Our research focuses on the microstructural changes during the first desorption process and the resultant changes in the physical properties of hcp, such as the strength, Young's modulus, and drying shrinkage. The relationship between microstructural changes and the physical properties of hcp during the first desorption process has not been thoroughly investigated. The previous studies of microstructural changes were reported based on the measuring methods and did not focus on the changes in the physical properties of the material. The issues relating to changes in physical properties due to drying have been discussed in terms of thermodynamics in stable porous materials, even though there are many reports of microstructural changes occurring during the first desorption. In the present paper, microstructural change is explicitly treated as a key factor in the changes in the physical properties. Data are collected for providing mechanistic explanations for the changes in physical properties.

The microstructural changes are interpreted using the water vapor and nitrogen isotherms, and the changes in the interlayer spaces, mesopores, and macropores are determined quantitatively. The nitrogen sorption isotherm is also used to confirm the microstructural changes, and N_2 accessible and inaccessible mesopores are discussed. NMR techniques are used for the solid-phase transition during drying. In addition, ultrasonic measurement, particularly using shear waves, is used for detecting large solid-phase differences from saturated curing conditions to slightly drier conditions, such as 95% RH, which have not been thoroughly investigated. On the basis of these experimental results, we describe C–S–H globule cluster conditions, globule densification, and the resultant pore structures.

Changes in strength during the first drying process are explained by the microstructural changes. By comparing the shrinkage strain during long-term drying and short-term drying, the effects of microstructural changes and water evaporation on the shrinkage strain are