

Study on shrinkage mechanism of cementitious materials based on liquid characteristics

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Cracking in concrete structures accelerates the deterioration process and decreases long term durability. Shrinkage is one of the major causes of cracks. In this study, the mechanism that causes shrinkage of cementitious materials is investigated experimentally. A cement based material, Autoclaved Aerated Concrete (AAC), was selected for the experiment, due its distinct pore size distribution compared to other cementitious materials. Firstly, ultimate shrinkage of AAC under equilibrium state was measured at various temperature and relative humidity. Secondly, shrinkage recovery behavior of AAC when immersed in various liquids(water, DMSO, ethanol, mineral oil and soap water) were tested. Finally, heat of immersion was measured. It was confirmed that various shrinkage behaviors were dependent on combined effect of capillary tension, surface energy and disjoining pressure.

1. INTRODUCTION

The major parameters that affect drying shrinkage of cementitious material are mix proportion, age, admixtures and surrounding environmental conditions. On the other hand, from microscale viewpoint, shrinkage is closely related to pore structure and internal water. Currently, three classical theories are broadly accepted to describe shrinkage and the role of pore water: Capillary pressure, Disjoining pressure and Solid surface energy (Fig. 1).

The capillary pressure in pores creates meniscus surface and negative pressure which can induce shrinkage strain. This force can exist only in partially saturated pores which have relatively large size.

The disjoining pressure theory states that the liquid molecule inside the pore tends to exert pressure to disjoin the adjacent surface of C-S-H gel particles. The change in pressure causes shrinkage or swelling.

Solid surface energy is unbalanced energy at the surface of material due to unbalance molecular force. This energy can be dominant as shrinkage driving force at low relative humidity condition i.e. when the condensed water inside the pore is negligible, generally below 33% RH (F.H. Whittmann, 1983).

2. OBJECTIVES

The study was carried out using AAC because of its characteristic pore distribution compared to other cementitious materials, which allows experiments to be carried out in short time (up to 80% of drying shrinkage can be attained in 24 hours).

The objectives of the study are as follows:

- To quantify the hysteresis of ultimate shrinkage of AAC at various temperature and relative humidity.
- To study shrinkage recovery behavior by immersing

AAC in various liquids.

- To measure heat of immersion of AAC samples under various liquids.

Capillary pressure

$$RH > 60\%$$

$$P = \frac{2\gamma}{r} \cos\theta$$

Disjoining pressure

$$RH = \text{all range}$$

$$\left(\frac{dV}{V}\right)_d = \beta f(w_a) \left[\frac{RT}{M_v V_w}\right] \ln(h)$$

Solid surface energy

$$RH < 30\%$$

$$\Delta\gamma = \frac{RT}{M_v} \int_{h_1}^{h_2} \frac{W_a}{V_s} d(\ln h)$$

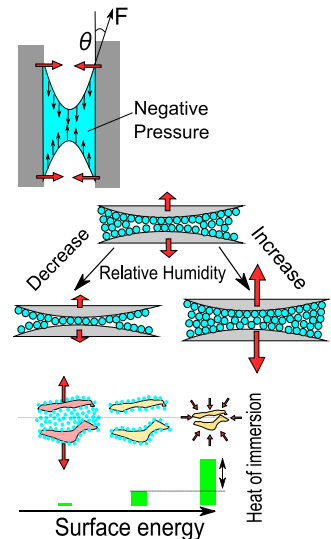


Fig.1 Schematic representation of shrinkage mechanism

3. Methodology

a) To measure ultimate shrinkage, AAC specimen with dimension of 60mm×40mm×10mm were prepared and strain gauge (WFLA-30-8, TML type) was attached on the surface using adhesive(EP304). Another specimen with the same dimension was prepared for weight measurement. The saturated specimens were then put in a climate control chamber and dried at specified temperature (20°C,40°C and 60°C) and relative humidity (40%, 60%, 80%)until strain and weight reach constant values (equilibrium state). The data of strain and weight were recorded at an interval of five minute.

b) Using same dimension and measuring method, AAC specimens after 24-hour drying (at 40%, 60% and 80%RH) were immersed in various liquids for 24 hours, and

shrinkage recovery were measured. Water, DMSO, ethanol, soap solution (1%) and mineral oil were used as immersing liquids. Table 1 shows property of each liquid.

Table 1 Properties of liquids

Properties	Water	DMSO	Ethanol	Oil	Soap
Dipole Moment, (Debye)	1.85	3.96	1.68	-	-
Surface tension (10^{-3} N/m)[25C]	72.7	43.5	22.6	27.1	25
Molecular diameter (nm)	~ 0.28	~ 0.50	~ 0.44	-	4.5

c) For heat of immersion, samples were prepared by crushing AAC into 0.5-1.0mm granules and filled in a glass ampule. The sample was vacuum dried (0.1MPa) at 105°C for 24 hours. Then, the ampule was sealed by melting the glass. The heat of immersion was measured by immersing it in water, methanol, ethanol and soap solution.

4. Result and discussion

a) AAC showed hysteresis of moisture content and drying shrinkage during desorption-adsorption cycle (Fig. 2). At 20°C slight recovery of strain was seen at 70-90% RH which could be a result of diminishing capillary tension force (Maruyama et al). At higher temperature, strain hysteresis is reduced. The reason may be that higher thermal energy of vapor, due to high temperature, prevents water condensation and meniscus formation.

Similarly, the water content curve shows distinct hysteresis starting near 65% relative humidity, which is due to ink-bottle effect. The moisture can dissipate from larger saturated pores, however, it cannot be refilled during absorption due to insufficient capillary suction or reduced contact angle.

b) In shrinkage recovery experiments, **DMSO and Ethanol**, although highly soluble in water, recovered only about 80% of shrinkage (Fig. 3). The recovery increased with the moisture content, which suggests two possibilities. The first possibility is that DMSO and ethanol either eliminate capillary forces as it can mix with water. The second possibility is that DMSO and ethanol serves as bridge to transport pore water towards water deficient region and reduce solid surface energy. At low moisture content, molecules of DMSO/Ethanol, due to their large size, are restricted to enter smaller pores, and thus cannot penetrate into pore water. A slight recovery by **mineral oil** was observed when the moisture content in the sample was about 14-18%. At lower and higher moisture content, the recovery was negligible. The reason for such partial recovery can be attributed to the reduction of surface tension or increase in contact angle. The **soap water** solution showed expansive behaviour. The soap reduces the capillary tension in smaller pores and allows wetting of the surface. The saturation exceeded 100% for soap. This indicates that extra water entered and wetted additional surface. Alternatively, it is possible that hydrogen bond of

water and soap is strong enough to pull the soap molecule inside the pore raising the disjoining pressure and resulting in expansion.

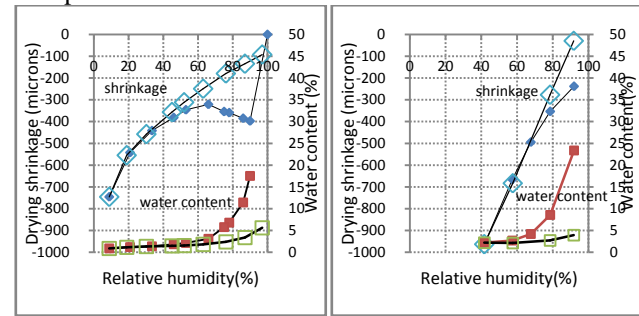


Fig 2. Ultimate drying shrinkage and moisture content a)20°C; b)40°C

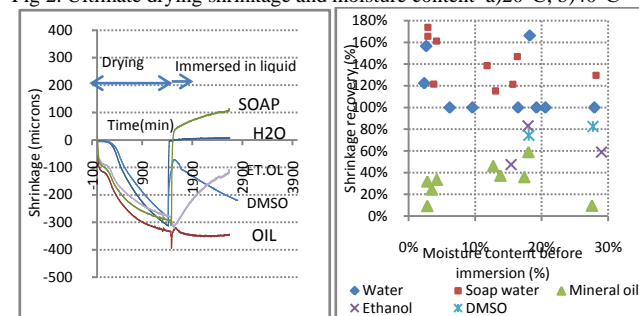


Fig 3. a) Recovery of shrinkage at 20°C; b) Shrinkage recovery versus moisture content

c) In heat of immersion experiment, water was found to release the highest amount of energy whereas ethanol generates the least amount (Table 2). For small molecules, the quantity of accessible surface area is much higher than large molecule. Therefore, large energy could be generated for small molecule.

Table 2 Heat released by various liquids

Liquid	Water	MtOH	EtOL	Soap
Molecule section area (nm^2)	0.1	0.22	0.28	-
Heat of immersion (J/g)	87	50	0	90

5. Conclusion

(a) In AAC, shrinkage occurs due to interaction of pore and liquid. Moisture and strain hysteresis occurs due to ink bottle pores. (b) Solid surface energy and capillary tension are the dominant shrinkage mechanism. (c) Smaller molecule can release more heat than larger molecules.

6. References

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