

EXPERIMENTAL STUDY ON VOLUMETRIC CHANGE OF CEMENTITIOUS MATERIALS BASED ON LIQUID CHARACTERISTICS IN FINE PORES

Shingo ASAMOTO¹⁾, Kyosuke KATO¹⁾ and Kunio MATSUI²⁾

¹⁾ Structural Material Lab., Department of Civil and Environmental Engineering, Saitama University

²⁾ Construction Materials Lab., Asahi-KASEI Construction Materials Corporation

ABSTRACT

The objective of this study is to examine the drying shrinkage mechanism based on microscopic chemo-physical approach. The authors submerge the specimens of cement paste into various liquids after drying to focus on the recovery of drying shrinkage, in order to investigate each recoverable phenomenon causing the shrinkage depending on liquid characteristic in micro-pores. According to consistent experimental programs, the influences well-known capillary pressure, disjoining pressure and the increase of gel surface energy on the shrinkage are explicitly verified to be dependent on the liquid characteristics in pores. It is believed that such thermodynamic and interfacial approach focusing on the liquid characteristics could reveal the shrinkage mechanism of general porous media.

KEYWORDS: Cement paste, Shrinkage, Capillary tension, Disjoining pressure, Solid surface energy

1. INTRODUCTION

The mechanism of concrete shrinkage has been studied for decades because the shrinkage cracking is likely to deteriorate the performance of RC structures. There, however, has been no consistent theory to clarify the phenomenon clearly yet, since a number of factors in fine pores where are difficult to be directly observed affect the volumetric change. Such complicated mechanism could be comprehended if each phenomenon that engenders shrinkage is separately clarified based on microphysics. The objective of this study is to examine the drying shrinkage mechanism in terms of liquid characteristics in fine pores. The authors experimentally study the recovery of drying shrinkage by submerging specimens in various liquids, in order to investigate the role of liquid in fine pores in recoverable shrinkage.

2. OVERVIEW OF SHRINKAGE MECHANISM

Based on numerous researches, the acceptable explanations about the concrete shrinkage mechanism have been reported (Powers, T.C., 1968). They are dependent on the characteristics of moisture in fine pores of concrete. Some of them are summarized below.

2.1 Capillary tension

It is well known that the water in the capillary pore is under negative pressure due to the surface tension of water as shown in the schematic image of Figure 1(a). This is known as capillary tension. If the pores are assumed cylindrical in shape, the

capillary tension can be calculated as follows according to the Gibbs-Laplace equation.

$$P_c = \frac{2\pi r \cdot \gamma \cos \theta}{\pi r^2} = \frac{2\gamma \cos \theta}{r} \quad (1)$$

where, P_c : capillary tension, r : pore radius at the equilibrated interface between liquid and vapor, γ : liquid surface tension, θ : the contact angle between liquid and solid. When drying proceeds, the radius r where the meniscus forms decreases and leads to larger negative pressure calculated from Eq. (1). It has been widely supported that the capillary force causes the drying shrinkage of the concrete under the drying condition of moderate relative humidity.

2.2 Disjoining pressure

Disjoining pressure is the pressure in a thin adsorbed water film. The layers of adsorbed water on the surface of adjoining CSH gel particles create a repulsive force. As the relative humidity decreases, the adsorbed water is transported toward larger capillary pores and the water contained in areas of hindered adsorption moves to freely adsorbing zones. The movement of water reduces the disjoining pressure between the solid particles and causes shrinkage as shown in Figure 1 (b). On the other hand, when the relative humidity increases, more water can be adsorbed on the solid surfaces resulting in higher disjoining pressure in thin film.

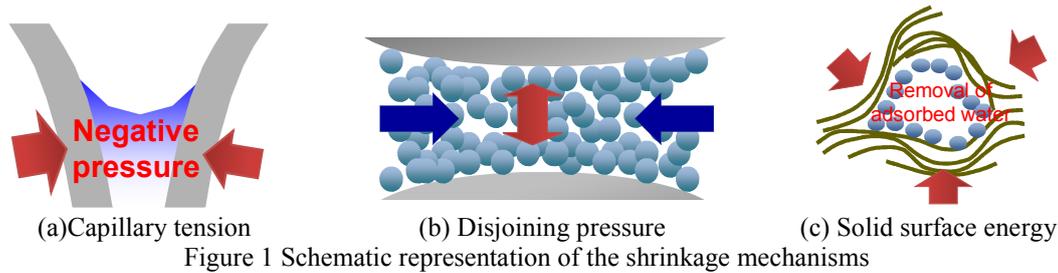


Figure 1 Schematic representation of the shrinkage mechanisms

Table 1 Liquids used in experiment

Liquid	Chemical formula	Density (g/cm ³)	Viscosity (10 ⁻³ Pa·s, 20 °C)	Surface energy (10 ⁻³ N/m, 20 °C)	Dipole moment (Debye)
Water	H ₂ O	1.00	1.00	72.7	1.85
Ethanol	C ₂ H ₅ OH	0.789	1.19	22.6	1.68
DMSO	(CH ₃) ₂ SO	1.10	1.98	43.5	3.96
Lubricating oil	-	0.832	2.11*	27.1*	-

*: Values at 25 °C

2.3 Solid surface energy

All materials, both liquids and solid, have surface free energy that minimizes the surface to achieve thermodynamically stable states. The surface energy is reduced by adsorption of vapor molecules and results in the swelling of the solid. On the contrary, if the adsorbed water is removed, a volume contraction of the C-S-H gel solid occurs as shown in Figure 1 (c).

3. EXPERIMENTAL PROGRAM

3.1 Objective

The above-mentioned phenomena causing the volumetric change of concrete are dependent on the moisture distribution in fine pores of cement paste. The different moisture distribution makes difference phenomena dominant at drying and leads to the different shrinkage behavior.

In this study, the specimens are dried under different conditions until a certain amount of shrinkage strain to intentionally produce the dried specimens with different water distribution in the pores but the same shrinkage strain. Then, the specimens are submerged in various liquids to focus on the recovery of the shrinkage. It is expected that the different shrinkage recoveries could be observed depending on the shrinkage driving forces and liquid characteristics and be useful information to reveal the shrinkage mechanism.

3.2 Specimens

The thin plate specimens with dimensions 10 x 40 x 160mm were used for experiment in order to accelerate the drying and soaking processes. The experimental material was cement paste to investigate the volumetric change mechanism clearly because the shrinkage of hardened cement paste matrix is dominant in the concrete shrinkage. The cement paste specimens with W/C 60% were

manufactured. The cement type was high-early-strength Portland cement. After removing the forms at 2days of age, the moist-curing was conducted for 5days before drying.

3.3 Test conditions

The specimens were dried under two conditions: a well-controlled chamber keeping 60% relative humidity and 20 °C and another one is drying condition of 15% relative humidity produced by LiCl as a bibulous material in the sealed desiccator at 20 °C. A longitudinal length change of 100 mm at the center of specimen was measured at drying by using a contact gauge with an accuracy of 0.001 mm. All of the results under each condition were obtained by the mean values of two specimens.

When the drying shrinkage of the specimen reached a certain strain, 1700 μ, under each condition, the dried specimens were submerged in various liquids such as water, ethanol, dimethyl sulfoxide (DMSO) and lubricating oil at a constant temperature of 20 °C. The characteristics of liquids used in the tests are shown in Table 1. The liquids were chosen from the viewpoints of variable characteristics such as surface tension, viscosity and dipolar moment. After soaking in liquids, the length change was continuously measured continuously as well as under drying.

4. RESULTS

Figure 2 shows the volumetric change variation of specimens exposed to relative humidity of 60 or 15 % at 20 and then submerged into various liquids. Even after subjecting to moderate and severe drying conditions, the tendency of the shrinkage recovery is similar. When the specimens were soaked in water after drying, the shrinkage appreciably recovered and exceeded original volume. It is attributed to the generation of micro-

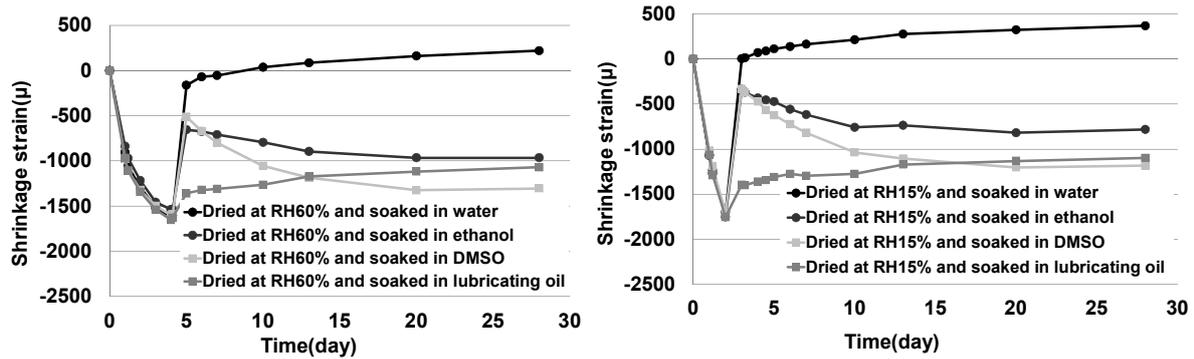


Figure 2 Shrinkage variations when specimens were dried and submerged into various liquids

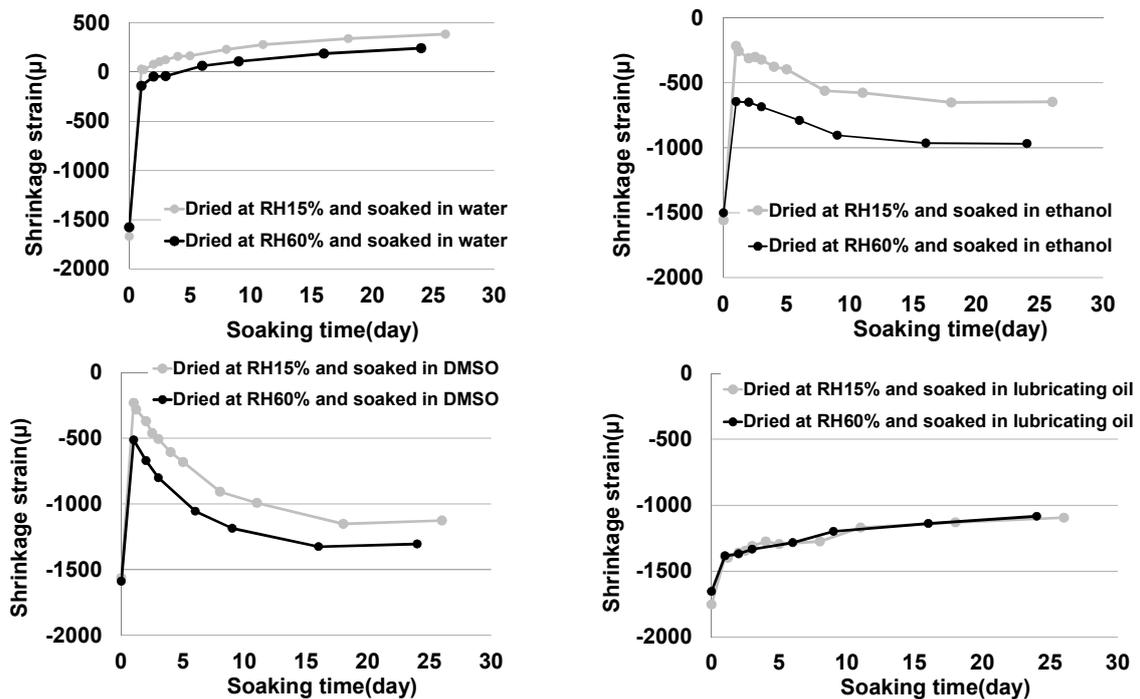


Figure 3 Recovery of shrinkage after submerging into various liquids

cracks on the surface during drying. In the case of lubricating oil, the shrinkage recovered about 30%. When the ethanol and DMSO infiltrated into dried cement paste, once the shrinkage was recovered about 80% and the specimens gradually shrunk again. As shown in Fig3, the degree of saturation was recovered around 100% in spite of different liquid characteristics.

The comparison of the recovery of the shrinkage among different liquids is given in Figure 3. According to the Figure 3, the difference of shrinkage recovery between drying conditions at low relative humidity and moderate humidity was not observed when the specimens were soaked in water and lubricating oil. On the other hand, ethanol and DMSO caused larger shrinkage recovery after exposed to 15 % relative humidity than that in the case of 60 % relative humidity drying.

Based on these test results, the reason for causing the different shrinkage recovery results when soaked various liquids is discussed next chapter based on each shrinkage mechanism.

5. DISCUSSION OF VOLUMETRIC CHANGE BASED ON EACH SHRINKAGE MECHANISMS

5.1 Capillary tension

When the specimens were soaked in ethanol and DMSO, it is deduced that the organic solvents are dissolved into water in the pores of cement paste and eliminated the meniscus as shown in Figure 4(a); capillary tension disappears. Thus, the shrinkage was greatly recovered soon after the immersion of the organic solvents. The difference in the recovery of shrinkage exposed to moderate and severe drying conditions could be ascribed to the disappearance of different shrinkage forces arising from the capillary tension. It is speculated

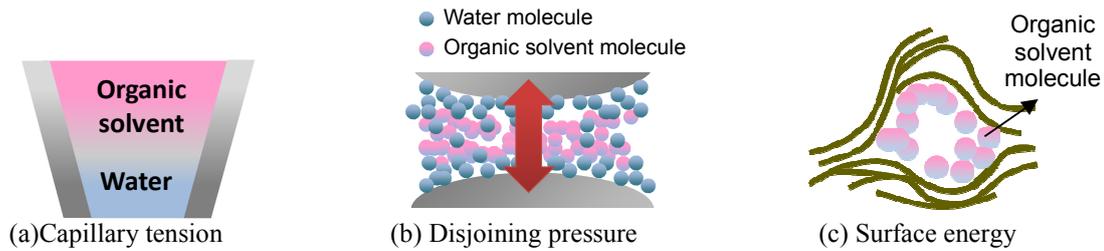


Figure 4 Schematic representation of each phenomenon when dried specimens are submerged in organic solvent

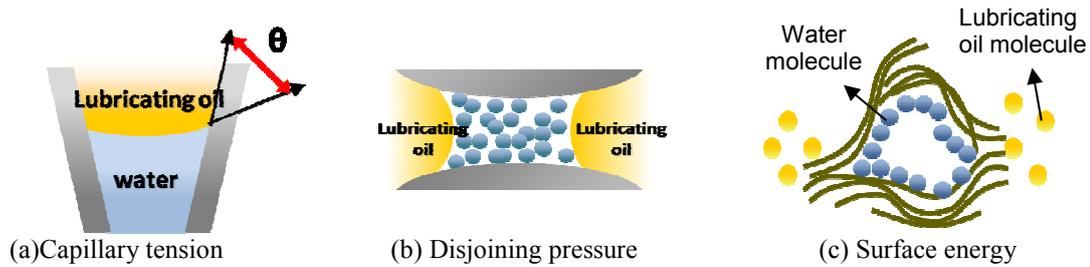


Figure 5 Schematic representation of each phenomenon when dried specimens are submerged in lubricating oil

that larger capillary tension under lower relative humidity as calculated in Eq.1 is eliminated and leads to greater recovery of the shrinkage after submerging into ethanol and DMSO, in the case of RH 15%.

On the other hand, lubricating oil is insoluble in water and the capillary tension is not able to be eliminated even after the infiltration of lubricating oil. The shrinkage of specimens soaked in the oil, however, was slightly recovered. One of the interpretations of the recovery is the increase of the contact angle between water and cement paste. It is suggested that the penetration of the oil into relatively larger capillary pores can reduce the surface energy of unsaturated cement paste wall and result in the increase of the contact angle. The small increase of the contact angle reduces the negative pressure as indicated in Eq. 1 and leads to the shrinkage recovery. Figure 4 (a) and Figure 5 (a) show the schematic representation of the above discussion.

5.2 Disjoining pressure

It is plausible that the organic solvents can gradually diffuse into the fine space of adjoining C-S-H particles and form the thin films of water and organic solvent between C-S-H gel grain walls. Thus, the disjoining pressure can increase for the sake of the organic solvent immersion and then shrinkage was recovered. In the case of lubricating oil, it is deemed that the oil cannot penetrate into water film in fine pores, because it cannot be dissolved in water.

In addition, the behavior of re-shrinking when the specimens soaked in organic solvent can be also explained by disjoining pressure. It is possible that organic solvent diffuse into the water saturated

fine space between adjoining C-S-H particles and replaced with water. The replacement decreases the disjoining pressure due to smaller surface tensions of ethanol and DMSO than that of water and results in the gradual shrinkage of specimens. Figure 4(b) and Figure 5(b) describe the schematic image of diffusion of organic solvent and lubricating oil into water film.

5.3 Solid surface energy

The organic solvent could gradually diffuse into very fine pores such as gel and interlayer pores and organic solvent can be replaced with the adsorbed water in the gel pores or interlayer water between C-S-H gel sheets or remove the water due to the concentration gradient. The replacement or removal of the water increases the surface energy of C-S-H gel grains, because the surface tensions of organic solvent are smaller than that of water. Hence, it is deduced that the increase of the solid surface energy of gel grains could cause the gradual shrinkage of specimens submerged into organic solvents after immediate shrinkage recovery. In contrast, lubricating oil cannot osmose into such fine pores and not cause re-shrinkage behavior. Figure 4(c) and Figure 5(c) show the schematic representation of the above discussion.

6. CONCLUSION

In this study, three typical theories supported as the possible shrinkage mechanism of cement paste were discussed based on liquid characteristics and the moisture distribution of cement paste pores. According to experimental results, the shrinkage recovery when specimens were soaked in organic solvents after drying could be explained by the

disappearance of capillary tension and disjoining pressure. However, it is deemed that the recovery when the dried specimens were soaked in lubricating oil could be caused only by the decrease of the capillary pressure. When the specimens were soaked in organic solvent, the gradual shrinkage was observed after immediate shrinkage recovery. It is attributed to the increase of the solid surface energy of C-S-H gel grains due to replacement or removal of the adsorbed water in fine gel by organic solvent. The experimental study verified that the above typical theories could be explainable for the shrinkage of cement paste. We believe that the various approaches based on thermodynamic and interfacial chemical theories could reveal the complicated mechanism of concrete shrinkage.

REFERENCES

Powers, T.C. (1968) "Mechanisms of shrinkage and reversible creep of hardened cement paste" *Proceedings of International Conference on the Structure of Concrete*, Cement and Concrete Association, London, pp.319-344