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Supercritical drying of cementitious materials

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ABSTRACT

Techniques to characterize the microstructure of hydrated cement require dried materials. However, the microstructure of hydrated products is significantly altered by high capillary forces during drying when using the conventional drying methods. To avoid drying stresses when preparing samples, we have employed supercritical drying (SCD) which has been used for decades to prepare aerogels that undergo no shrinkage during drying, but has rarely been used for cementitious materials. The pore solution is first replaced with isopropanol, and then with trifluoromethane (R23). The temperature and pressure are raised above the critical point, where no menisci or capillary pressure can exist; therefore, the dried samples are free of artifacts created by stresses. Images from scanning electron microscope show less compact morphology for supercritically dried samples than that dried by conventional methods, while BET surface areas of SCD samples are very close to samples dried by the isopropanol replacement method. This can be explained by the fact that isopropanol and supercritical fluid enter the micropores and block them. The nature of the chemical interactions of isopropanol and R23 with cement pastes are still not clear, but no reaction products were identified in the present study.

1. Introduction

Pore structure of cementitious materials is a decisive factor that can be used to determine materials properties, such as permeability, and also can help us to understand the process of nucleation and growth of hydration products. To characterize the pore structure and the morphology of calcium silicate hydrate (C-S-H), various techniques have been used, such as scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and gas (nitrogen or water vapor) adsorption. These techniques require dried samples, and unfortunately the pore structure is significantly affected by drying.

Drying can remove water, classified as evaporable water, from two types of pores. Capillary pores are larger and hold water in saturated conditions but lose water on exposure to air (at ambient relative humidity). Gel pores are nanometer-size pores (< 10 nm) [1] and water present in gel pores is more strongly bound than capillary water, so that ambient relative humidity (RH) may not be able to remove it; reduced pressure or elevated temperature is required. No matter what drying method is used, the ideal condition is that no water is left in capillary and gel pores after drying. The residual evaporable water in the material interferes with the characterization of the pore structure. However, in most drying methods, the interface between liquid water and air creates capillary pressure. According to the Laplace equation, capillary pressure increases with the decrease of pore size ($P_c \propto 1/r$). This means that the removal of gel-pore water can cause high capillary pressure so the damage to gel pores is more significant than that to capillary pores. The damage is mainly from the shrinkage of pores and rearrangement of particles. Various drying methods used to minimize the influence of drying on the pore structure have been extensively reviewed in the literature [2,3].

The process of taking water out the porous media can be achieved in three ways according to the phases of water (Fig. 1). Direct drying (e.g., flowing N_2 drying, oven drying and vacuum drying) lets liquid water directly evaporate to the vapor phase. The vapor pressure of water is at the saturation level at the surface of the body, and the rate of evaporation is controlled by diffusion through a boundary layer [4,5]. The flowing N_2 creates the zero-humidity environment to force liquid water to evaporate, and the higher the velocity of the nitrogen, the thinner the boundary layer, which accelerates the kinetics of drying. Oven drying, either at 60 °C or 105 °C, speeds up the evaporation by raising the vapor pressure and diffusivity of the water vapor, but usually does not permit strong convection. Oven-drying above 40 °C may lead to dehydration and rearrangement of hydration products [6], and consequently more coarsening of pore structure than other methods. Vacuum drying is also an acceleration process which decreases the surrounding vapor pressure, but it is slow because the absence of convection results in a thick boundary layer. Direct drying methods do not eliminate or reduce capillary pressure (except for the small effect of temperature on surface tension), so materials still suffer high capillary forces.

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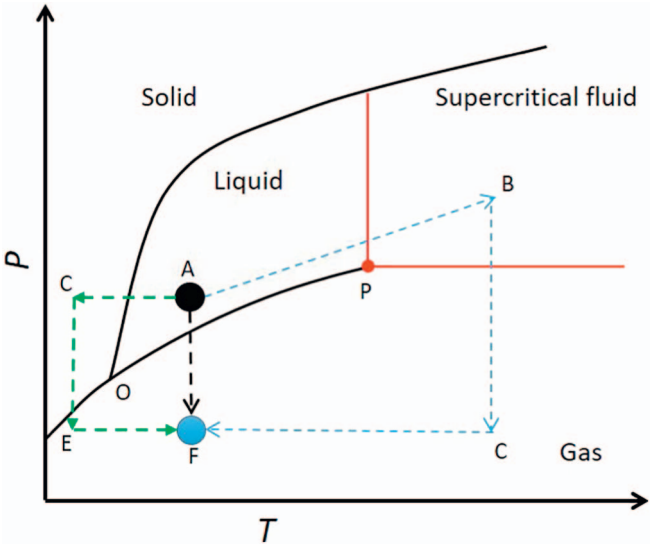

Fig. 1. Schematic single-phase phase diagram.

Capillary pressure can be reduced by replacing water with low-surface-tension solvents. Solvent replacement drying is considered as the best technique with respect to preservation of the pore structure [3,7]. Commonly used solvents, such as acetone, ethanol, isopropanol, methanol, tetrahydrofuran and dimethyl sulfoxide, are miscible with water. When samples are immersed in the solvent, the interdiffusion of water and solvent reduces water content with time. Hydration can be arrested in a short time by reducing the water activity in the cement matrix [8] while it may take a long time to completely replace water, depending on solvent diffusion coefficient, sample size, etc. After solvent replacement, samples can be subjected to normal drying methods, either low vapor pressure drying or oven drying or vacuum drying. Due to the low surface tension, drying of solvent creates much smaller capillary pressure, so that solvent exchange presumably causes less damage to the microstructure than water. The main risk from this method is that some solvents can react with cementitious materials. For instance, thermogravimetric analysis (TGA) results from both cement paste and calcium hydroxide showed that methanol alters sample composition by reacting to form a carbonate-like product [9]. Various techniques, such as X-ray diffraction (XRD), infrared spectroscopy, thermal analysis and conduction calorimetry, further show that when methanol is mixed with calcium hydroxide, methylated complex or calcium methoxide is formed [10]. The reaction of acetone with calcium hydroxide was also found to affect TGA results because of aldol condensation [11]. Dimensional changes are observed for the samples immersed in acetone, ethanol and isopropanol. Beaudoin [10] argued that this is the sign of chemical interaction between solvent and calcium hydroxide, although no reaction products were identified. Zhang and Scherer compared solvent exchange by using isopropanol, tetrahydrofuran, ethanol and acetone. The TGA curve for isopropanol (IPA) had less weight loss between 600 °C and 1000 °C than other solvents. Weight loss within this temperature range may indicate chemical reaction or strong absorption between solvents and hydration products. They concluded that solvent exchange with isopropanol can best preserve the microstructure.

If one wants to eliminate capillary pressure during drying, freeze-drying is one of the choices. When samples are directly immersed in liquid nitrogen, pore water is instantaneously frozen, so hydration stops simultaneously. Then, ice is sublimated under vacuum without going through the liquid state. Freeze-drying is considered as the best way to chemically preserve each component in cementitious materials. However, the freezing of water in the pore network generates crystallization pressure that can damage the microstructure of hydration products [12]. The volume increase of 10% during freezing can also damage the sample, because freezing proceeds inward from the surface, so expansion of the interior occurs within a frozen shell [13,14]. Another drawback is that freeze-drying needs a long time for sublimation and removes less water compared to other methods [13].

The question still remains as to which one is the best drying method in terms of preserving the microstructure of hydration products. Various techniques have been used by researchers in the literature to quantify different drying methods. By using MIP, Galle [13] recommended freeze-drying as the best method to investigate the pore structure of cement based materials. This recommendation was supported by Korpa and Trettin [15] who concluded that freeze-drying gives the most accurate picture for the microstructure based on data measured by nitrogen adsorption (NAD), TGA and Nuclear Magnetic Resonance spectroscopy (NMR). Using the same techniques, Feldman and Beaudoin [16] concluded that isopropanol exchange was less destructive than vacuum drying and drying at low RH. Konecny and Naqvi [7] concluded that solvent replacement with isopropanol was preferable for MIP samples. By analyzing the water vapor sorption isotherms measured by Dynamic Vapor Sorption (DVS), Snoeck et al. [17] reported that vacuum-drying and the solvent exchange with isopropanol can minimize the effect on the microstructure during drying the cementitious samples. Clearly, the results are contradictory, but a thorough review of the literature concluded that solvent exchange with isopropanol is the best method to preserve the microstructure [3].

The purpose of solvent exchange is to reduce surface tension and thereby reduce the capillary pressure. There is one method that can eliminate capillary pressure entirely. It is known as supercritical drying (SCD) or critical point drying, which has been mentioned in the literature but rarely used to dry cementitious materials [2,3]. In this method, the temperature and pressure are raised above the critical point of the pore liquid (see Fig. 1), following a path such that the liquid becomes a supercritical fluid without creating a liquid-gas interface, so no capillary pressure develops in the pores [18]. Supercritical fluid can be removed by depressurization while the temperature remains above the critical temperature. This technique has been widely used to make aerogels that have high porosity (typically $> 95\%$) and fragile pore structure [19]. To avoid the high critical temperature of water, it is common to exchange the pore liquid with a fluid that has a lower critical point, most commonly carbon dioxide (CO_2, critical point at 31.03 °C and 7.38 MPa).

The most challenging problem for supercritical drying of cementitious materials is to find a suitable supercritical fluid. In the study by Litvan [20], samples were first washed with methanol, followed by exchange with pentane (critical point 196.7 °C, 3.36 MPa). The final step was to evaporate pentane above the critical pressure and temperature (which was done at 205 °C). There are two obvious risks that can potentially alter microstructure in his study. First, the critical temperature for pentane is high enough to dehydrate C-S-H and ettringite. Second, methanol can react with calcium hydroxide as stated above. Using carbon dioxide would solve the first risk, but also carbonate the C-S-H, as well as calcium hydroxide. The ideal fluid should have minimal chemical reaction with cement and hydration products, and have a critical point below 40 °C.

Freon® R23 (trifluoromethane, CHF_3) has been suggested for supercritical drying of cementitious materials because it has a low critical point (25.7 °C and 4.82 MPa) and is expected to be inert to cement [3]. This paper is devoted to examining the use of R23 as a supercritical fluid to dry cementitious materials. We focus on drying of pastes hydrated for24 h or less, to investigate the microstructure when it is most fragile.

2. Overview of supercritical drying

Because R23 is nonpolar, it is immiscible with water, so an intermediate solvent is needed that is miscible with both water and R23. As concluded in the literature, isopropanol is the best solvent for