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Cement and Concrete Research

Comparison of methods for arresting hydration of cement

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ABSTRACT

Arresting of cement hydration, followed by drying, is necessary to prepare samples for many techniques of microstructural analysis. This paper reviews the effects on microstructure and composition of cement paste caused by the most common drying techniques, including direct drying (oven, microwave, D-drying, P-drying, and freeze drying) and solvent exchange methods. Supercritical drying is proposed as a method that could effectively preserve the cement microstructure, but which has not been applied to cementitious materials. Experiments are reported that systematically quantify the effects of drying from several solvents, freeze drying, and direct drying of young paste. Freeze drying is an effective drying method to prepare samples for chemical analysis, but it might change the microstructure. Isopropanol exchange followed by ambient drying is the best known method for preserving the microstructure with minimal effect on the composition of cement.

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1. Introduction

A wide variety of techniques has been used to characterize the composition and structure of calcium silicate hydrate (C–S–H), the early nucleation and growth of hydration products, and the pore structure of cement-based materials, due to our need to understand the hydration process of cement [1], and to develop models that describe and predict the properties of cementitious materials [2]. Most materials characterization techniques, such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), nitrogen adsorption/desorption (NAD), mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), can only test dry samples. To obtain cement specimens at a defined degree of hydration (DOH), they must be subjected to a treatment that arrests the hydration reaction; then the sample can be crushed or cut, dried, and put under vacuum for examination. Preserving the microstructure is especially challenging for very fresh cement pastes that contain a lot of free water, but are mechanically weak and highly reactive. The purpose of this paper is to review the methods that have been used for sample preparation, and to identify those that are most satisfactory for preserving the chemical and/or physical state of the sample, particularly for young pastes.

Water in hydrated cement is present in many forms, often classified as structural water, gel water, and capillary water. Structural water includes water of crystallization and chemically bound, non-evaporable water that can only be extracted through hydrate

decomposition. Gel water is held by capillary tension and strong hydrogen bonding on to the surface of the main cement hydration product, C–S–H gel. This water, which is in nanometer-scale pores, can be removed by evaporation at ambient or reduced pressure, at ambient or elevated temperature. Capillary water is the unbound water inside the pores that is available for reaction during hydration. When arresting hydration and drying cement paste, capillary water must be removed, while removal of the first two types of water may be undesirable, because the composition and microstructure of many of the cement hydrates could be altered, so that the dried sample would provide incorrect information about the microstructure and phases present in the cement paste. This is certainly true when structural water is removed. Water in the smallest gel pores is difficult to remove or replace, because those pores have the highest relative surface area, so the stresses related to surface tension of the receding water menisci generate temporary capillary pressure that may cause shrinkage of the sample and alter the fine pore structure of the cement paste [3–5]. The capillary pressure, P_{cap}, is related to the liquid/vapor surface tension, γ_{LV}, the contact angle between liquid and solid, θ, the specific surface area, S, the bulk density, ρ_B, and the porosity, ϕ, by [6]:

$$P_{cap} = \frac{\gamma_{LV} \, \cos(\theta) S \rho_B}{\phi}. \tag{1}$$

For water, $\gamma_{LV} = 0.072$ J/m^2, and for cement paste we can estimate $S \approx 50$ m^2/g, $\rho_B \approx 2000$ kg/m^3, and $\phi \approx 0.3$, so if $\theta \approx 0$, the capillary pressure during drying of cement paste is about $P_{cap} \approx 24$ MPa. Clearly, such a large pressure could alter the microstructure, particularly in small pores and/or young pastes.

The drying of hardened Portland cement paste has been the subject of considerable study since the 1960's, not only due to its

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