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Application of microstructurally-designed mortars for studying early-age properties: Microstructure and mechanical properties

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A B S T R A C T

A recently-developed technique for stopping hydration without altering the microstructure by invasive methods is studied. This technique is based on the replacement at the mixing stage of cement/binder grains that would otherwise remain unhydrated in real systems at defined hydration stages with inert quartz particles. This technique allows studying hydration-dependent properties in a static equivalent system, where these processes can be decoupled from hydration.

A comprehensive comparison between real and equivalent systems, in terms of mechanical properties as well as physico-chemical ones is presented. Results of mechanical properties support the validity of the approach. Microstructural characterization by means of mercury intrusion porosimetry shows comparable results in terms of total porosity and breakthrough radii. Thermogravimetric analysis shows comparable amounts of hydration products formed. These results suggest that the method can constitute a useful tool for studying the behavior of cementitious materials at early ages, in particular transport phenomena and shrinkage.

1. Introduction

A fundamental understanding of the microstructure development during cement hydration and of the simultaneous development of early-age properties is of paramount importance for studying and predicting the development of concrete performance.

Concrete shrinkage and its cracking susceptibility depend on several intrinsic parameters such as free shrinkage, strength, stiffness, fracture toughness and creep/relaxation. At early age, the above-mentioned material properties, and in general the microstructure properties (such as porosity, pore size distribution and pore connectivity), are in continuous development due to the progress of the hydration reaction.

However, for characterizing the microstructure of cement-based materials at early-age, one often needs to stop cement hydration. An ideal method to stop hydration should preserve the microstructure as well as the chemical and physical properties at a given degree of hydration, thereby enabling relevant measurements of unaltered material properties. At the same time, to stop the hydration at a given desired age, the method itself should not require long procedures.

Different techniques are commonly used to stop the ongoing hydration. They are mainly divided into two categories: direct drying methods and solvent exchange methods. Both types of methods are based on the removal of free water from the hydrating microstructure: the former by evaporation or sublimation, the latter by replacing water with a solvent (such as isopropanol) that is then evaporated as well [1–3].

Oven-drying is one of the most widely used techniques. However, many drawbacks have been associated with this method. From MIP measurements, Gallè [4] showed that significant damage occurs, which mainly affects the capillary porosity domain. Microcracking induced by differential thermal expansion of aggregates and hardened cement paste as well as the buildup of high capillary pressure during oven-drying may alter the microstructure [3]. Further, temperatures above 100 °C may both lead to ettringite and AFm decomposition [5] and induce further hydration, microstructure changes and favor carbonation [2]. The *D-drying method* is believed to be an efficient method to completely remove the free water while preserving the microstructure [2,6]. However, the time for attaining a constant sample weight can take several days (depending on several variables such as vacuum level, sample size, etc.), resulting in an unsuitable method to stop the early

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hydration at a given time [3]. *Freeze-drying* represents a good technique to preserve the microstructure by avoiding high capillary stresses. However, the freezing process associated with this method can cause stresses due to volume change, hydraulic pressure and crystallization pressure [7] and cause considerable microcracking [1]. In addition, Zhang and Glasser [8] showed that this technique may induce monosulfate degradation. Nevertheless, this technique is considered to be effective in arresting hydration with a limited effect on the microstructure.

The *solvent exchange* method is a common technique used to stop hydration by the use of an organic solvent that replaces water. In the literature, contradictory arguments are reported concerning the chemical and physical interaction between the solvents and the cement hydrates [2,3,9]. For example Beaudoin [10] concluded that solvents such as methanol and benzene could chemically react with calcium hydroxide. Knapen et al. [2] reported that the remaining solvents may react with cement compounds or hydration products to form carbonate-like phases during further thermal analysis. Aligizaki [11] reported no chemical interaction between isopropanol and cement paste, concluding that isopropanol could be an acceptable fluid for solvent exchange. Another discussed topic is the long time necessary for the exchange liquid to diffuse through the sample (estimated as about 18 h for pieces of 1 mm size, see [3]). More recently, the *supercritical drying* method has been suggested as an alternative technique for stopping hydration while preserving the microstructure. However this method is technically very challenging, in particular when carbonation needs to be avoided (CO_2 is usually used as a fluid for exchange with pore water) [3].

All the different drying methods appear to affect the microstructures in different ways [9]. Desaturation, desorption, dehydration phenomena or possible reactions between hydration products and solvents may generate damage like microcracking, capillary porosity alteration, collapse of gel pores and mineralogical transformations [4].

In general, for the mere purpose of stopping hydration at early-age, freeze drying and solvent exchange with isopropanol have been identified as the most effective techniques to date [3]. Nevertheless, both techniques require the removal of water from the microstructure, precluding the possibility for further measurements involving water reintroduction into the sample, e.g., drying shrinkage, water transport, etc. If moisture is reintroduced into a sample with stopped hydration, unreacted cement grains may further react during the test, thereby altering the microstructure of the sample and affecting the results. Therefore, a method that creates a static microstructure after the hydration stops, even if the sample stays in contact with water, would be very useful.

In this paper, a recently-developed technique [12] based on the replacement of unhydrated cement grains is employed to stop hydration at defined hydration stages and obtain a representative early-age microstructure, while at the same time achieving a static system. Several types of measurements can be performed on the equivalent systems without being affected by ongoing hydration, even though water does not need to be removed from the samples. Therefore, it represents a powerful technique for studying phenomena that are both dependent on cement hydration and at the same time influence cement hydration, such as moisture transport (e.g., water transport and drying), along with time-dependent properties such as early-age shrinkage and creep, for which it is difficult to decouple the effects of hydration and transport or loading.

The aim of this paper is to validate this approach by a systematic comparison of mechanical properties and microstructural features between the real systems and the equivalent systems – both for OPC and cement blended with supplementary cementitious materials (SCM) – aided by the statistical analysis of variance (ANOVA). To this end, the similarity between the real and the equivalent microstructure was tested in terms of compressive strength, flexural strength and elastic moduli. Further, the microstructure is characterized by means of mercury intrusion porosimetry (MIP) and thermogravimetric analysis (TGA).

2. Equivalent systems

The concept of the equivalent microstructure relies on the substitution at the mixing stage (by volume) of the unreacted binder with quartz particles that simulate the unhydrated cement grains. This can be conceptually explained by means of Powers' model [13] in which the volume fractions of each constituent in a portland cement paste at a given hydration stage can be derived from a set of empirical equations. These empirical equations are based on a comprehensive study of water sorption isotherms and chemically bound water measurements in hydrated cement pastes [14–16]. It should be noted that the model by Powers is used here only to better explain the concept. The actual degree of hydration and the volumetric composition needed to determine the amount of inert filler replacement were determined based on the experimental investigations described at the end of this section.

According to Powers' model, approximately 0.23 g of water per gram of cement is chemically bound at complete hydration and becomes part of the gel structure; this water is defined as non-evaporable water. It should be noted that the chemically bound water coefficient can be slightly different for modern cements [15,16]. Approximately 0.19 g of water per gram of cement is further adsorbed on the surface of the gel. The remaining water occupies part of the capillary pores. Hydration stops according to the model when any of the three conditions takes place: 1) exhaustion of capillary water, 2) exhaustion of free space for hydrates to form (see also [17]), or 3) exhaustion of unreacted cement [13,14,17]. The studied method for creating the equivalent systems is based on reaching the third condition.

Finally, the cement paste undergoes a volume reduction called chemical shrinkage, due to the fact that the volume of the reaction products is smaller than the volume of the reactants (cement and water), corresponding approximately to 6.4 ml/100 g cement reacted [17]. Based on these three characteristics it is possible to estimate the fractional volumes of gel solid, gel water, capillary pores, chemical shrinkage and unhydrated cement in the physical structure of portland cement pastes at different hydration stages [14].

In Fig. 1a, the evolution of the phases by volume as a function of the degree of hydration is conceptually visualized in accordance with Powers' model. The specific diagram refers to a cement paste with water to cement ratio equal to 0.51 in sealed conditions. A water-to-cement ratio (w/c) > 0.42 theoretically allows for full hydration of the cement in sealed conditions [14]. Let us assume now that the hydration reaction must be stopped at a given hydration stage “A”, as shown in Fig. 1b. At this stage, a fraction of unhydrated cement is still present in the system. The replacement of this fraction with an inert material such as quartz particles with similar size distribution would allow for realizing an equivalent system at that given hydration stage (with equal porosity and equal volume fractions), but more importantly would also allow for “freezing” the microstructure also in the presence of water, since no additional cement is available for reaction.

Such approach allows obtaining static systems, i.e., whose microstructures do not change over time due to cement hydration because all the binder has reacted. Complete reaction is assumed to occur after at least 3 months of curing in moist conditions. An equivalent microstructure system relates to a predefined early-age hydration stage development of the system to be reproduced and it is built from the knowledge of the degree of hydration at a specified age of the real system. Specifically, knowing the volume fraction of unreacted binder in the system at a given hydration stage, a new mixture is formulated where the binder is replaced by an equal volume of inert quartz particles.

In this study, this approach is employed on three real mortar and cement paste mixtures with and without SCM: OPC, OPC + 45% Slag and OPC + 45% Fly ash (by volume). The three real systems were formulated in order to maintain the same water-to-binder ratios and paste-to-aggregate ratios by volume. For each real mixture, five different hydration stages were investigated, corresponding to five different