Cement and Concrete Research 71 (2015) 66–77

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Microstructurally-designed cement pastes: A mimic strategy to determine the relationships between microstructure and properties at any hydration degree

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ARTICLE INFO

Article history:
Received 23 October 2014
Accepted 20 January 2015
Available online 11 February 2015

Keywords:
Hydration
Compressive strength
Pore size distribution
Microstructure
Mimic cement paste

ABSTRACT

This paper proposes a new strategy to study the relationships between cement paste microstructure and its properties. In this perspective, microstructurally-designed cement pastes are produced by replacing a specific part of the actual binder by inert particles of similar fineness. This strategy is referred to as 'mimic' in this paper. It is shown that, after complete hydration of the reactive part, the microstructure obtained, in which the inert particles play the role of unhydrated binder particles, exhibits similar properties as a cement paste at a lower hydration degree. The concept is tested and validated on pore profile measured by mercury intrusion porosimetry and compressive strength. The same concept could be applied to other properties. In particular, the obtained materials are fully hydrated, which allows performing time-consuming testing (such as e.g. creep and drying-shrinkage tests) on microstructures equivalent to low degrees of hydration, which would not be possible on the hydrating material counterparts.

1. Introduction

In order to develop innovative binders and concretes, it is essential to master the link between their composition and the performance they can develop.

The following two types of concrete properties can be considered:

- On the one side, some properties are time-dependent (for instance rheology and compressive strength) but can be easily characterized with simple and rapid tests.
- On the other side, some properties cannot be characterized rapidly compared to the rate of hydration (for instance transport or creep properties), and it becomes difficult, if not impossible, to estimate how hydration modifies these properties.

Moreover, many phenomena can occur simultaneously, making it even more difficult to estimate the role of each individually. For instance, measuring drying shrinkage on a fully reacted concrete sample is obvious, but interpreting the results of a drying shrinkage experiment in which the binder is still hydrating is not an easy task. However, this is closer to real conditions, in which concrete is cured for less than one day before being exposed to drying conditions when the formworks are removed.

In order to explore how hydration modifies these properties that need long experiments to be evaluated, one could think of stopping hydration (for example by freeze-drying). This method is commonly used to measure the hydration degree at given times, but cannot be considered for properties such as shrinkage, creep or transport properties which are closely linked to the water saturation of the porous medium.

A novel strategy is proposed in the present paper, with which it should be possible to study properties that need long experiments to be evaluated, depending on the hydration degree, and by such offer new possibilities to better understand coupled phenomena. This strategy is referred to as 'mimic' in this paper. Rather than trying to stop hydration, the idea is to design a mix so that once fully reacted, its microstructure is equivalent to the microstructure of interest. Since this sample does not evolve anymore, it is easy to evaluate its properties such as shrinkage, creep, transport properties and others.

The novel concept of microstructurally-designed cement pastes or mimic microstructure is described, and the equivalence of microstructure (porosity and distribution) and properties (compressive strength) is presented. The strategy is first applied on Portland cement, and then extended to blended cements.

2. Description of the mimic strategy

2.1. Defining mimic strategy for Ordinary Portland Cement (OPC)

The assumption behind the mimic cement paste concept is to consider that two materials having the same volume fractions of hydrates,

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http://dx.doi.org/10.1016/j.cemconres.2015.01.020

porosity and unreacted products would demonstrate similar properties. We assume that, as it has been shown for compressive strength [1–3], the impact of properties of the unreacted products is of second order, so that OPC could be indifferently replaced by an equivalent volume of inert mineral, as shown in Fig. 1.

The hydration degree of OPC is defined as the volume fraction of reacted OPC over the initial volume fraction of OPC. One can also define the *average* hydration degree as the volume fraction of reacted OPC over the initial volume fraction of cement, where OPC and fine inert material will be considered as cement Fig. 2 illustration of the evolution of the OPC hydration degree and the average hydration degree for a mimic cement paste as a function of time. In this study, the amounts of replacements of fine quartz were chosen so that the average hydration degree of the fully hydrated mimic paste can mimic the hydration degree of interest for the pure OPC system.

2.2. Defining mimic strategy for blended cements

As for OPC, mimic cement pastes can be useful to study the relationships between cement paste microstructure and its properties when the binder is not just OPC but a blend of OPC and a supplementary cementitious material (SCM) such as fly ash or slag. The main difference originates from the fact that SCMs react with different (usually slower) kinetics than OPC.

In order to capture the effects of SCMs on microstructure and related properties, the volume fractions of the phases in a fully hydrated mimic cement paste with SCMs should be representative of the state of hydration of the blended system of interest at a given state of hydration.

For the sake of simplicity, it is easier to decouple the kinetics of OPC and SCM, a first stage before SCM has started to dissolve (Fig. 3), and then a second stage when SCM is partially hydrated (Fig. 4). In both cases, similarly to what was proposed for unhydrated OPC, the volume of unhydrated SCM is replaced by the same volume of inert material.

The first stage is similar to the pure OPC case, for which the dilution of OPC with inert material allows controlling the final average hydration degree. The second stage is more complex due to the fact that the hydrates in the system to be mimicked come from both OPC and SCM. It is thus necessary to introduce SCM in the mimic paste, or at least a reactant that will produce similar hydrates. Moreover, in order to achieve rapidly a fully hydrated mimic paste (typically in about 3 months), it was decided to use ultrafine ground slag to mimic slag blends and silica fume to mimic fly-ash blends.

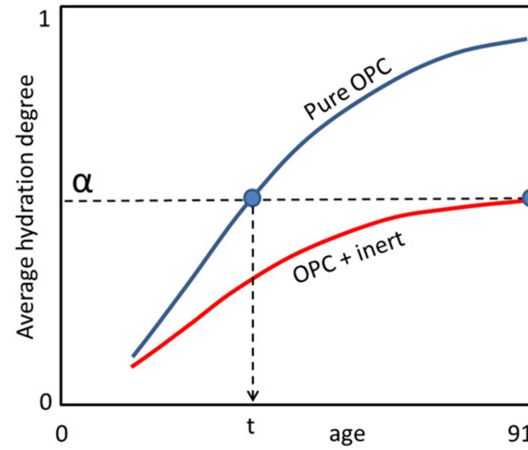

Fig. 2. Illustration of the evolution of the OPC hydration degree and the average hydration degree for a mimic cement paste as a function of time.

3. Experimental methods

3.1. Cement pastes

For cement paste, all materials and apparatuses were pre-conditioned at 20 °C. Water, OPC and fine quartz were mixed with a Waring blender for 60 s at 3000 rpm. Paste spread on the mixer bowl was put back in the mix. Then cement paste was further mixed for 60 s at 3000 rpm. The fresh cement paste was poured into 7.4 mm diameter and 22.7 mm height waterproof molds. To prevent segregation, the molds were continuously rotated at about 5 rpm for 24 h at 20 °C. After that, the samples were demolded. The specimens were cured under water at 20 °C until the required age. To stop hydration of cement paste, the samples were broken at a given age in pieces of maximum 5 mm and were put in acetone for 15 min. Then the specimens were removed from acetone and vacuum-dried by a pump with a pressure of

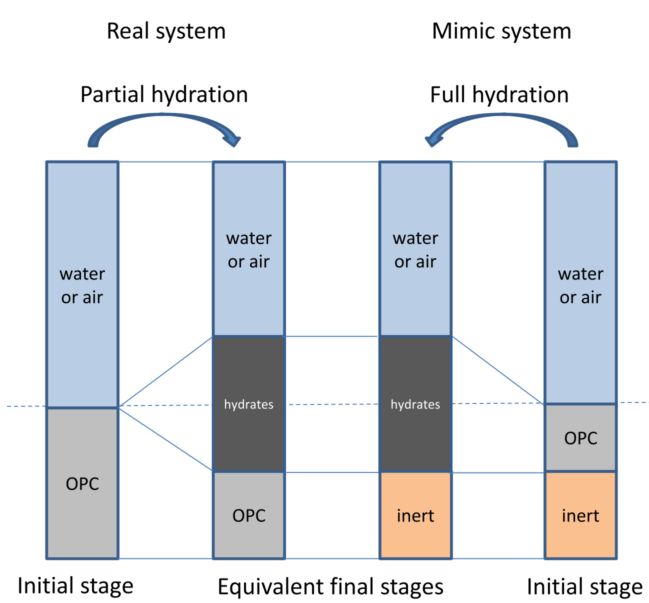

Fig. 1. Mimic cement paste concept for OPC system.

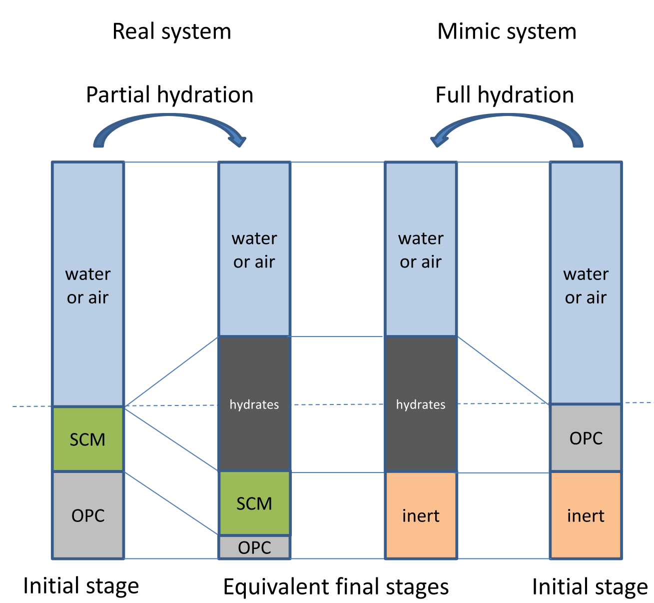

Fig. 3. Mimic cement paste concept for blended cement with supplementary cementitious materials, before SCM starts to hydrate.