Cement and Concrete Research 75 (2015) 42–52

Contents lists available at ScienceDirect

Cement and Concrete Research

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

Experimental chemo-mechanics of early-age fracture properties of cement paste

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ARTICLE INFO

Article history:
Received 11 November 2014
Accepted 17 April 2015
Available online 15 May 2015

Keywords:
Fracture toughness C
Material properties
Hydration A
Aging C

ABSTRACT

The risk of early-age fracture of cementitious materials in ever more challenging environments provides a unique opportunity to employ an experimental chemo-mechanical platform to develop functional relations between hydration degree, fracture and strength properties, assessed by isothermal calorimetry, micro-scratching, splitting and microindentation on white cement paste at various curing ages from 7 h to 28 days. We show that the modulus, tensile strength, fracture toughness and energy all evolve with a natural logarithmic dependence on the hydration degree. These trends are linked to the densification of the material during the hydration process, explained by compaction mechanics and free volume theory. We show that while the fracture process zone size is essentially constant during the hydration process, the ductility of the material, quantified by M/H, decreases, and is consistent with the evolution of K_c/H. Both quantities provide a convenient way to experimentally assess the fracture sensitivity of early-age cement-based materials.

1. Introduction

Fracture properties of cementitious materials are difficult to determine with classical experimental means as size effect tests require setups that are difficult to realize within normal laboratory settings [1–7]. It is thus not surprising that most engineering design methods, from materials to structures, are geared towards structural and/or materials strength; despite the fact that it is fracture, which ultimately limits serviceability and longevity of most concrete structures [8].

A typical and critical example is the property development of cementitious materials at early ages. As cement paste hardens, molecular bonds are formed between precipitating calcium-silicate-hydrate particles [9]; eventually reinforced by residual clinker grains. Since Powers [10], a great deal of research efforts have been dedicated to pinning down functional relations between strength and stiffness properties and intensive variables that capture the hydration process of cementitious materials, such as the hydration degree [11]. But the development of fracture properties, namely fracture energy and fracture toughness, have not – to the best of our knowledge – been addressed in the open literature. This is recognized as a serious limitation for engineers to design materials and structures against early-age concrete cracking [12,13], and provides enough motivation for this experimental chemo-mechanics investigation of early-age fracture properties of cement paste. Specifically, this investigation departs from the following points of inquiry:

- How does the early-age development of fracture energy ($\mathcal{G}_c = K_c^2/\mathrm{M}$) and fracture toughness (K_c) compare to that of tensile strength (f_t'), hardness (H), and stiffness (M)? What are the driving forces of the evolution?
- Does the material become more brittle or ductile with hydration progress, as captured e.g., by the fracture process zone size according to Dugdale's theory [14], $L_{FPZ} = (\pi/8)(K_c/f_t')^2$?

To answer these questions, we employ an original combination of micro-scratch, microindentation and Brazilian split cylinder testing together with isothermal calorimetry on white cement paste samples in which the hydration reaction was stopped by means of isopropanol alcohol at different curing ages, from 7 h to 28 days. Material, sample preparation and methods are first presented, before the results are shown and discussed in form of property–hydration degree functional relations.

2. Materials and methods

2.1. Casting and curing

A collection of samples cured at 7, 8, 12, 18, 24, 36, 48, 96, 168, 336, 504 and 672 h was cast in batches consisting of 100 g of White Ordinary Portland Cement (WOPC) at a 0.4 water-to-cement (w/c) ratio. The constituents were homogenized using a mixer and impeller from Heidolph

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http://dx.doi.org/10.1016/j.cemconres.2015.04.004
0008-8846/

at 730 rpm for 2 min, then cast into 20 mm × 55 mm cylindrical molds. The paste was tamped and vibrated to help work the paste into the molds and to expel air. Finally the molds were capped and stored in a sealed container.

Most specimens were de-molded after 8 h and stored in limewater. Just prior to the desired age, disk specimens were cut with an average thickness of about 8.5 mm from the parent samples using a drop saw with a diamond-coated blade. The hydration was stopped at the desired time by immersing the specimens into isopropanol alcohol and regularly stirring and replacing it over a 1-h period to replace the free water in the paste. Finally, the specimens were stored in isopropanol until the time of preparation. The 7 and 8-h-old specimens were extracted from their parent cylinders and treated with isopropanol right away, without being stored in limewater. At each curing time, at least 12 specimens were created, 4 were used for determining fracture toughness, 2 for microindentation and the rest for tensile strength tests.

2.2. Sample surface preparation

Sample surface preparation is essential for surface tests such as micro-scratching and microindentation. The surface to be tested should be as smooth as possible and parallel with the bottom surface of the sample. Following the procedure proposed in Ref. [15] the specimens were extracted with a drop saw held orthogonal to the samples. The specimens were ground using a jig and plunger to hold them in place and to ensure a uniformly distributed load by holding the specimen parallel to the grinding wheel. The specimens were then polished until the surface to be tested became reflective. The older specimens were ground using a 15 μm and 9 μm diamond/oil suspensions on a polishing table, using a jig to hold the specimen in place, then using 9, 3 and 1 μm alumina pads. The microstructure of the younger specimens was too fragile for the polishing table, so alumina pads were used for both grinding and polishing. In between each preparation step, the specimens were ultrasonicated in isopropanol to clean and remove debris. The surfaces of the Brazilian cylinders did not have to be polished; only the grinding procedure was used to help achieve a uniform specimen thickness.

2.3. Fracture property assessment via micro-scratch technique

Scratching a weaker material with a tougher one is no doubt the most elemental conceptualization of a mechanics-of-material test ever conceived by mankind. In use as a tool to compare the relative hardness of two materials since ancient time, the first abstraction of scratch resistance into a quantitative metric of material classification is due to Carl Friedrich Christian Mohs (1773–1839), who in 1824 put the ability of one mineral sample to scratch another on an ordinal (rank-ordering) scale, the Mohs scale of mineral hardness [16,17]. Scratch force criteria as a basis for comparison of scratch resistance of materials emerged throughout the 20th century, leading to the development of instrumented scratch tests in the early 1970s, in which the applied forces and acoustic emissions generated by microcracks are measured simultaneously [18]. The scratch test is highly sought after as a means of classification of materials due to its simplicity (it is almost non-invasive) and ease of application to only a small amount of many different materials including metals [19], polymers [20–24], rocks [25–29], ceramics [30–32], coatings and adhesion of thin films [33–37], and hardened cement pastes and cement slurries [38–43].

This study presents a unique application of the instrumented micro-scratch test to early-age cement pastes, as a means to assess the evolution of fracture properties. The scratch test herein employed consists of pushing a hard probe of known geometry (a 200 μm spherical–conical Rockwell C diamond probe) at a controlled horizontal scratch speed, $V_{H,f}$, and vertical load rate $\dot{F}_V$, across the surface of a weaker material (Fig. 1a), while measuring the scratch depth, d, and the horizontal scratch force F_T [37].

2.3.1. Scratch test setup and scratch test parameters

A Micro Scratch Tester (MCT) from Anton Paar (formerly CSM, Neuchatel, Switzerland) [44] with a vertical load cell capacity up to 30 N was used for all scratch tests. The tests were performed by first probing the location of the reference surface by applying a 0.03 N load along the scratch length. Once the sample surface profile was mapped, the test began and the penetration depth d was determined from the surface profile. After the test was completed, some of the scratch grooves were then photographed (Fig. 1b). Just prior to testing, the specimen was glued to a 4 mm thick piece of steel with cyanoacrylate ("super glue"). The steel base was then tightly secured in the jaws of the MCT testing machine. The specimen was oriented inside the machine to ensure that if there was a small incline to the surface, the probe would scratch 'down-hill'.

In all our tests, the same scratch speed ($V = 6$ mm/min) and vertical loading rate ($\dot{F}_V = 60$ N/min) over a scratch length of 3 mm to a maximum vertical load of $F_V = 30$ N was employed. For each sample, a minimum of 7 and maximum of 17 scratches on 20 mm diameter specimens were performed, and scratch depth d and scratch force F_T were recorded. These measurements form the backbone for a fracture mechanics analysis of the scratch toughness.

2.3.2. Scratch toughness model

Based on Linear Elastic Fracture Mechanics (LEFM), the model here employed resolves the micro-scratch fracture toughness K_c from the measured scratch force history, F_T, and penetration depths d collected

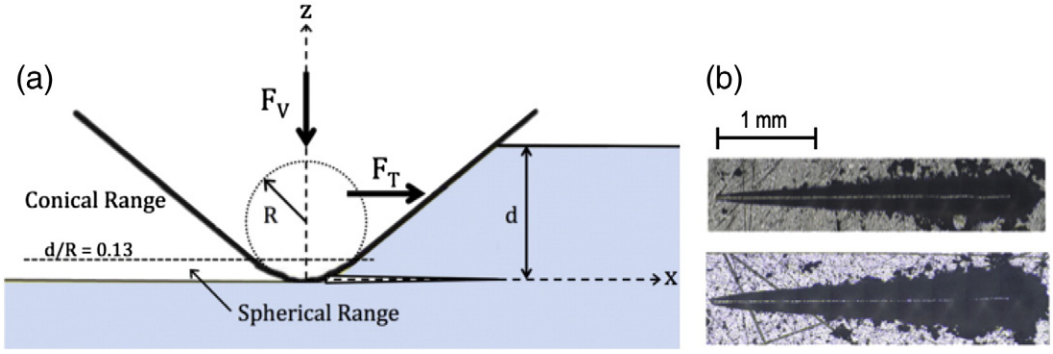

Fig. 1. (a) Schematic of the scratching process showing the applied normal F_V and measured tangential F_T forces. The spherical tip drives the fracture process for scratch depths less than 13% of the sphere radius R. (b) Scratch groove in a sample cured for (top) 2 weeks and (bottom) 1 day. The scratch cured for 1 day is wider because the probe penetrated deeper into the material.