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Micro- and nano-scale characterization to study the thermal degradation of cement-based materials



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ABSTRACT

The degradation of hydration products of cement is known to cause changes in the micro- and nano-structure, which ultimately drive thermo-mechanical degradation of cement-based composite materials at elevated temperatures. However, a detailed characterization of these changes is still incomplete. This paper presents results of an extensive experimental study carried out to investigate micro- and nano-structural changes that occur due to exposure of cement paste to high temperatures. Following heat treatment of cement paste up to 1000 °C, damage states were studied by compressive strength test, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) atomic force microscopy (AFM) and AFM image analysis. Using experimental results and research from existing literature, new degradation processes that drive the loss of mechanical properties of cement paste are proposed. The development of micro-cracks at the interface between unhydrated cement particles and paste matrix, a change in C–S–H nano-structure and shrinkage of C–S–H, are considered as important factors that cause the thermal degradation of cement paste.

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1. Introduction

An exposure to high temperature causes cement-based composite to suffer significant degradation and loss of mechanical properties [1–7]. Although continuous attempts have been made to understand the complex mechanisms of thermal degradation, the micro- and nano-structural changes that drive the process and ultimately result in macroscopic damage are yet to be well characterized.

It is generally accepted that thermal degradation of hydration products in cement paste, such as calcium-silicate-hydrate (C–S–H) and calcium hydroxide (CH), which can induce micro-cracking and pore-coarsening [1–3], are the primary causative factors leading to high temperature degradation [8–10]. CH is dehydrated between 400 and 500 °C [2,11,12]. Decomposition of C–S–H, the phase responsible for most of the

engineering properties of cement paste, has been reported to occur in a wide temperature range due to its amorphous characteristics. The results of thermogravimetric analysis (TGA), nuclear magnetic resonance (NMR) and neutron diffraction (ND) show that the primary temperature range of C–S–H dehydration varies between 100 and 450 °C [8,12–14]. Another hydration product, ettringite, is also known to be thermally unstable in its crystalline form, losing its stability at temperatures below 120 °C [15].

Although temperature ranges for the degradation of each hydration product have been established, it is not well understood yet how these changes manifest in the micro- and nano-structure of cement paste. It is generally believed that micro- and nano-structural changes are ultimately responsible for the loss of macroscopic mechanical properties, though the lack of characterization at the micro- and nano-scale at

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elevated temperatures have made it difficult to establish a link between the two. Due to this research gap, several questions regarding the thermal degradation of cement-based composite remain unanswered. For example, the mechanism behind the increase in compressive strength of cement paste after exposure to 200 °C [1], even though this temperature is enough to initiate the dehydration of C–S–H. A loss of compressive strength and an increase in porosity are insignificant even after exposure to temperatures as high as 300 °C [1], which can result in shrinkage of C–S–H [16,17]. In spite of the degradation of C–S–H observed at lower temperatures, manifestation on the microscopic and macroscopic level does not occur until C–S–H is exposed at much higher temperatures [1]. Therefore, further research is necessary to understand the effects of exposure to high temperatures on the micro- and nano-structure of cement paste and how it governs macroscopic degradation of the system. In this paper, thermally degraded cement paste samples are prepared; the loss of macroscopic properties and the degradation of hydration products were confirmed using compressive strength measurement and thermal analysis, respectively. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) imaging techniques were used to characterize micro- and nano-scale damage due to thermal exposure. Image analysis was performed on images obtained from AFM for quantitative analysis of particle size distribution and particle connectivity. As per the author's knowledge, this paper reports for the first time evidence of changes in C–S–H nano-structure based on AFM characterization and its image analysis that can cause thermal shrinkage of C–S–H, a phenomenon indicated in the paste by other researchers [16,17]. By combining SEM and AFM characterization, this paper elucidates the degradation mechanism that initiates at the micro- and nano-scale and drives the loss of mechanical properties at the macro-scale.

2. Experimental Procedures and Sample Preparation

Cement paste samples with water to cement (w/c) ratios of 0.35 and 0.45 were prepared using Type I Portland Cement and de-ionized water. Chemical composition and physical properties of the cement provided by the manufacturer are given in Table 1. Cement paste was mixed in a Hobart mixer according to ASTM C305. Two different-sized samples, cylinders 2.5 cm in diameter \times 5 cm in length and prisms 2.5 \times 2.5 \times 10 cm, were prepared. As this paper focuses on understanding the changes that occur at the micro- and nano-scale due to the thermal degradation of hydration products, small sample sizes were

intentionally used in order to minimize the influence of thermal gradients during heat treatment.

After demolding for 24 h, samples were stored in an environmental chamber at 25 °C and 100% R.H. for the remaining 27 days of curing. Cured samples were then exposed to different cycles of heat treatment with maximum temperatures ranging from 105 to 1000 °C at an increment of 100 °C per cycle. Fig. 1 shows the 10 different heating and cooling cycles employed in this study. During each cycle, a heating rate of 1 °C/min was used to reach the target temperature. Samples were held at 105 °C for 2 h in order to ensure removal of free water. After reaching the target maximum temperature, T_m , it was held constant for 6 h to confirm uniform temperature throughout the samples. In the final step of the cycle, samples were allowed to cool down to room temperature at a cooling rate of 1 °C/min. Once cooled, samples were stored in vacuum desiccators filled with nitrogen gas to avoid further hydration or carbonation.

A compression test was performed on 6 paste cylinders before and after each heat treatment to examine whether the desired damage state (loss in macroscopic mechanical property) was achieved. Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were performed to identify the chemical changes the hydration products underwent due to high temperature exposure. The test samples for TGA and XRD were obtained from the inner core of cylindrical samples with w/c ratio of 0.35 after compression testing. A ground paste sample (approx. 30 mg) was subjected to TGA using an SDT Q600 thermal analyzer. The temperature was programmed to rise at a constant heating rate of 10 °C/min up to 1000 °C and was held constant at 105 °C for 2 h to ensure removal of free water. The test was performed under a nitrogen flow of 50 ml/min. XRD was carried out on paste samples after exposure to various temperatures (105, 300, 500, 700 and 900 °C) using a Siemens-Bruker D5000 XRD with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Scanned 2-theta angle from 4 to 80° was used with step size of 0.02° and scan rate of 1°/min. JADE software suit was used to characterize the mineralogical crystalline phases.

Samples for scanning electron microscopy (SEM) and atomic force microscopy (AFM) were obtained from the inner core of prism samples with w/c ratio of 0.35 after a three-point bending test to diminish additional damage to the sample during specimen collection (specifically, cracking, which can occur during breaking of samples). Freshly fractured surface samples were investigated using a JEOL 6060LV scanning electron microscope in secondary electron mode. Samples for AFM were vacuum-impregnated with epoxy resin to minimize damage during polishing. The epoxy impregnation was

Table 1 – Chemical composition and physical properties of cement.

Chemical composition (%)											
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
20.2	4.8	3.4	63.3	2.4	3.1	–	–	67.12	7.37	6.97	7.00
Physical properties											
Fineness (Blaine, m ² /kg)					Initial set (minutes)				Final set (minutes)		
379					119				263		

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