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Use of nanoindentation phase characterization and homogenization to estimate the elastic modulus of heterogeneously decalcified cement pastes

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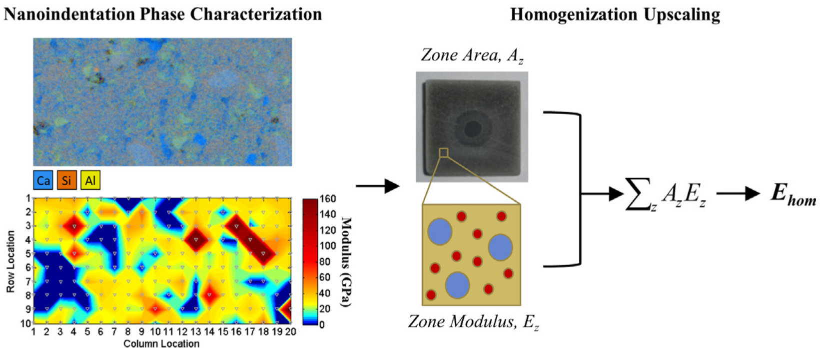
HIGHLIGHTS

- Macroscopic mechanical response of non-uniformly degraded cement pastes with large chemically-induced gradients were predicted from measured local microscale mechanical properties.
- Grid nanoindentation coupled with constitutive phase analysis captured progressive degradation of the material's mechanical properties during leaching-induced decalcification.
- Local mechanical properties of the material's constitutive phases were investigated as a function of induced decalcification under 3-dimensional exposure conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanoindentation phase characterization is used with a homogenization method to estimate the macroscopic response of heterogeneous, multiphase materials with large chemically-induced gradients from their measured micromechanical properties. The method was applied to predict the macroscopic response of a non-uniformly degraded cement paste from leaching-induced decalcification by ammonium nitrate under 3-dimensional exposure conditions. Coupled nanoindentation with scanning electron microscopy and energy dispersive x-ray spectroscopy constitutive phase elemental analysis was used to link the mechanical response at each nanoindentation location to chemical composition and relate the mechanical phases identified statistically by Gaussian deconvolution to the chemical phases present in the microstructure. The nanoindentation phase characterization-based micro-macroscale upscaling method provided quantitative characterization of the relationship between microstructure evolution and mechanical properties as a function of chemical changes. The calculated homogenized elastic moduli of the reference and decalcified cement pastes ranged from 24.2–31.2 GPa and 9.2–11.7 GPa, respectively, and were of similar magnitude to the dynamic elastic moduli measured experimentally (31.1 ± 0.9 GPa and 13.7 ± 1.7 GPa, respectively). Furthermore, the degradation of the cement paste macroscale elastic modulus was controlled by the decalcification of the calcium-silicate-hydrate phases and the mechanical properties of the most prominent zone of the material.

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1. Introduction

Traditional mechanical testing typically represents only the average constitutive macroscale behavior of the material and does not provide information on the mechanisms occurring at the nano- and microscales that control the overall response of the material [1,2]. This is especially true for degraded materials, which demonstrate high heterogeneity at the microscale and a gradient of mechanical properties throughout the material. For many multiphase materials, including fiber reinforced polymer composites, granular materials, and cement-based materials, chemical leaching promotes heterogeneous chemical conditions at the nano- and microscales and the formation of a series of successive fronts of different chemical compositions, mechanical properties, and porosity distributions. In addition to the inability of traditional macroscale mechanical testing to capture structural anisotropy resulting from local heterogeneity, computational prediction of the progressive degradation of material integrity during chemical leaching by modeling the material microstructure evolution remains a challenge [3,4]. The relationship between microstructure evolution and mechanical properties has been hindered by the lack of an effective method for quantitative characterization of the intrinsic mechanical properties of the material constitutive phases as a function of chemical changes and thus remains unresolved. An alternative approach to direct modeling of damage evolution is the use of grid nanoindentation coupled with phase elemental composition and a combination of homogenization and area-averaging techniques. Grid nanoindentation coupled with scanning electron microscopy (SEM) [5–13], energy dispersive x-ray spectroscopy (EDS) [5,9,10,12], and statistical methods [7,8,12,14–16] provides a unique opportunity to analyze the micromechanical properties of highly heterogeneous materials and synergistically inform computational approaches. This method is illustrated in this paper to determine the micromechanical properties of heterogeneously decalcified cement pastes and to link the local microscale behavior to the overall macroscopic mechanical response of the material. This paper extends the initial nanoindentation results presented by the authors in a conference proceeding paper [17] to the coupling of the nanoindentation data with constitutive phase elemental analysis linking the mechanical response to chemical composition and to the upscaling of the nanoindentation data to the macroscale.

Non-decalcified (reference cement paste) and decalcified cement pastes were subjected to a grid nanoindentation and phase identification technique to determine the influence of non-uniform decalcification on the change in the micromechanical properties. The focus was on identifying the primary cementitious phases and using changes in the primary phases to distinguish the characteristics in non-decalcified and decalcified zones. A statistical Gaussian fitting method was used to segment the nanoindentation data into mechanically distinct phases, and SEM-EDS analysis was used to correlate the mechanically distinct phases with chemically distinct phases at each indent. A homogenization approach based on the Mori-Tanaka scheme and an area-averaging method then were applied to upscale the local micromechanical properties derived from grid nanoindentation and phase identification to the overall macroscale elastic modulus of the decalcified material. The homogenized modulus was then compared with macroscopic experimental measurements of the dynamic elastic modulus from ultrasonic pulse velocity. To the best of the authors' knowledge, this is one of the first times that the micromechanical properties of a heterogeneously degraded cement paste with high chemical and mechanical gradients and distinct zones of decalcification were linked to the macroscopic mechanical response using grid nanoindentation with phase identification. The presented method further paves the way for improved estimation of the macroscopic behavior of various heterogeneous multiphase materials with evolving microstructure from their measurable microstructural features. Furthermore, the paper addresses the relationship between material structure evolution and mechanical behavior, which plays a significant role in the design requirements of infrastructure materials.

2. Materials and methods

2.1. Cement paste preparation

Type I/II Portland cement (Lafarge, Nashville, Tennessee, USA) and Glenium® 7500 (BASF, Ludwigshafen, Germany), a polycarboxylate-based, high range water reducer (HRWR) were used to prepare the cement paste. A water to cement (w/c) ratio of 0.28 and a loading of 1% HRWR per mass of cement were used. After mixing, the paste was poured into 2.54 cm × 2.54 cm × 69 cm (H × W × L) beam molds and compacted by hand. After 24 h, the beams were de-molded and cured at room temperature under 100% relative humidity for a minimum of 28 days. Prior to decalcification, the beams were sectioned into shorter beams with a length of 11.5 cm.

2.2. Accelerated decalcification

After curing, some of the beams were exposed to ammonium nitrate (NH_4NO_3) solution for 125 days to promote the leaching of calcium and accelerate the kinetics of the decalcification process. Each beam was placed in a sealable plastic container with 1 L of 6 M NH_4NO_3 solution, and periodic monitoring of the pH was performed to ensure that the infinite bath condition was maintained. A total of five replicates were used. Accelerated decalcification of cement pastes by NH_4NO_3 has been shown to be similar to decalcification by water [18,19] with preferential dissolution of calcium hydroxide (CH) followed by progressive decalcification of the calcium-silicate-hydrate (C-S-H) phases [18], the main products of the hydration process of cement. After exposure, the samples were cut perpendicular to the centerline axis to expose the cross-section of the region where progressive decalcification occurred and the non-decalcified core (Fig. 1a).

2.3. Characterization

2.3.1. Grid nanoindentation

Reference (non-decalcified) and decalcified cement paste samples were prepared for nanoindentation by epoxy-mounting and polishing (details on the polishing procedure can be found in the supplementary material, Section S1.0). The decalcified cement paste samples demonstrated strong chemical gradients, resulting in zone formation. Changes in the calcium depth profile within the cement paste samples and visible color changes (Fig. 1a and c) were used to divide the gradient into 3 main zones for nanoindentation. Grid nanoindentation was performed using an Agilent Nanoindenter G200 Testing System (Agilent Technologies, Santa Clara, California, USA) and a diamond Berkovich tip. The tip was calibrated using a fused silica standard with known mechanical properties and a second-order area function [20]. A load-based approach was chosen to allow for examining the shift in indentation displacement at peak load and changes in the deformation and stiffness of the primary cementitious phases as a function of decalcification. A maximum force of 2mN was applied during testing, with a targeted strain rate of 0.050 s^{-1}. This maximum load was held for 15 s, followed by a 10 s unloading period. These loading conditions led to average maximum penetration depths ranging from 150 to 450 nm in the decalcified cement paste depending on the hardness of the indented cement phase. Fiducial indents were used to mark the beginning, middle, and end of the grid in order to locate the grid for subsequent SEM-EDS analysis. Spacing between indents was fixed at 10 μm on center in both the X and Y directions to prevent any adjacent indents from influencing the next indentation result. A spacing between indents of 10 μm has been shown in the literature to be sufficient for nanoindentation of cementitious materials [7,21–27]. Three grids of 200 indents, each covering an area of 200 μm × 100 μm, were collected on the reference cement paste as well as in each of the 3 main identified degraded zones of the decalcified cement paste (Fig. 1). This number of indents allowed for identification of the primary cementitious phases and