



Inference of the phase-to-mechanical property link via coupled X-ray spectrometry and indentation analysis: Application to cement-based materials



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ABSTRACT

A novel approach for the chemo-mechanical characterization of cement-based materials is presented, which combines the classical grid indentation technique with elemental mapping by scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS). It is illustrated through application to an oil-well cement system with siliceous filler. The characteristic X-rays of major elements (silicon, calcium and aluminum) are measured over the indentation region and mapped back on the indentation points. Measured intensities together with indentation hardness and modulus are considered in a clustering analysis within the framework of Finite Mixture Models with Gaussian component density function. The method is able to successfully isolate the calcium-silica-hydrate gel at the indentation scale from its mixtures with other products of cement hydration and anhydrous phases; thus providing a convenient means to link mechanical response to the calcium-to-silicon ratio quantified independently via X-ray wavelength dispersive spectroscopy. A discussion of uncertainty quantification of the estimated chemo-mechanical properties and phase volume fractions, as well as the effect of chemical observables on phase assessment is also included.

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1. Introduction

The grid indentation technique allows access to the characterization of cementitious microstructures at different length and time scales [1–5]. In the method's framework, a large set of measurements carries ample information concerning each mechanical phase of the bulk, which may be inferred via statistical deconvolution [4,6]. This allows for examination of cement systems beyond laboratory conditions, such as those where hydration products are created in a unique local environment. Because the inference is based solely on mechanical response, the direct correlation of measured properties to the local chemistry is only possible by the use of a reference material. It should be noted that phases of different stoichiometry but similar mechanical response, as well as their mixtures, may manifest as a single microstructural component and could therefore bias the analysis.

To address these issues, this work combines the indentation measurement with the elemental mapping by scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS), thereby linking mechanical response to in-situ chemistry. The applicability of the

proposed method is demonstrated for an oil-well cement system with a crystalline siliceous additive, cured at elevated temperature. The multivariate Gaussian Mixture Model is applied to analyze and cluster experimental data obtained in both measurements and to infer the phase distribution. The indentation response of the C-S-H solid is further linked to its stoichiometry via quantitative wavelength dispersive spectroscopy (WDS) microprobe analysis.

2. Materials

The cement-based system selected for this experimental study is based on the American Petroleum Institute (API) oil-well cement Class G (Dyckerhoff, Germany), and silica flour. The slurry was prepared at water-to-cement ratio of 0.44, slurry density 2030 kg/m³ and solid volume fraction (SVF) equal to 50%. Silica flour (α -quartz) with median particle size $d_m = 20 \mu\text{m}$ and specific surface $< 1 \text{ m}^2/\text{g}$ was used in the amount of 35% by weight of cement. The slurry was homogenized in a constant speed blender and hydrothermally cured for $\approx 144 \text{ h}$ at a temperature of 60 °C and pressure 20.7 MPa inside an ultrasonic cement analyzer (UCA). Such hydrothermal conditions could cause the pozzolanic reaction and impact the phase assemblage. However, the thermogravimetric analysis (TGA) showed a similar mass percentage of free

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portlandite, $\approx 15\%$, and only a slight difference, $\approx 1\%$, in the weight loss between 480 °C and 940 °C associated with the decomposition of CH and calcium carbonate, as compared to cement paste cured at ambient temperature and pressure. Additionally, the evolution of compressive strength over curing time, measured with UCA, shows no apparent signs of a silica reaction. Though, some interaction at the surface of the quartz grains cannot be excluded. Therefore, this sample can be considered as a close representation of phase assemblage of the ordinary cement paste. Furthermore, it can be used for the discussion of the characterization method proposed in this manuscript. Prior to experimental testing, the paste was stored in lime saturated water solution in a sealed container at room temperature.

3. Methods

3.1. Sample preparation

Samples for instrumented indentation, SEM imaging and X-ray spectrometry were prepared with a semi-automatic polishing procedure. In the first stage, cylindrical sub-samples, ≈ 1.0 cm in diameter and 0.5 cm in height, were cut from each bulk sample by the use of the diamond saw IsoMet, Buehler (Lake Bluff, USA). Each sample was then mounted with cyanoacrylate glue on the AFM disk (Ted Pella, USA), and automatically leveled and ground in a specially designed jig and post system [7]. A hard perforated cloth TexMetP (Buehler, USA) with a 9 μm oil-based diamond suspension MetaDi (Buehler, USA) was used for grinding. A typical grinding pass lasted around 20 min in total, with four stops for 3 min of ultrasonication in Isopropanol. Finally, the ground and cleaned samples were manually polished on the alumina abrasive disks FibrMet, Buehler (Lake Bluff, USA) of abrasive size 9, 3 and 1 μm . The exchange of each pad was accompanied by 1 min cleaning of the sample in the ultrasonic bath with Isopropanol.

3.2. X-ray powder diffraction

X-ray diffraction analysis was carried out on the representative powder samples of the investigated systems. For this purpose, the samples were prepared according to the following procedure: separation of a small piece weighing approximately 10 g of the mother sample, manual wet grinding in acetone, followed by drying in a vacuum-assisted oven set at 60 °C. Dried samples were gently re-grounded and homogenized just before loading onto the sample holder of the diffractometer. Powder diffraction patterns were collected on a Bruker D8 Advance multipurpose diffractometer with open Eulerian cradle and the Bragg-Brentano geometry, with the Cu-anode (Cu K-alpha $\lambda = 1.541$ Å). Scans were carried out from 5 to 90°/2 θ , with the step size of 0.009° and the speed of 0.5 s/step. Experimental diffraction patterns were analyzed with the HighScore Plus software and the Powder Diffraction Files (PDF) from International Centre for Diffraction Data (ICDD).

3.3. Wavelength dispersive X-ray spectrometry (WDS)

A quantitative analysis of the chemical composition was carried out with the JEOL JXA-8200 Superprobe electron probe micro-analyzer (EPMA). The polished specimens were analyzed by WDS under the following analytical conditions: accelerating voltage 15 keV, beam current 10 nA, beam diameter 1 μm and 10 s counting time per element with background correction applied at each spot. The mass fractions were calculated with the CITZAF package [8], using the $\phi(\rho z)$ -method (stopping power, back-scatter corrections and $\phi(0)$ from Love and Scott, mean ionization potential from Berger and Seltzer, Heinrich's tabulation of mass absorption coefficients, and Armstrong's modified equations for absorption and fluorescence corrections [9,10]). Table 1 lists the type of standards used and element-crystal association.

Table 1

List of measured elements with associated standard materials and diffracting crystals used in the WDS measurements.

Element	Standard	Crystal
Si	Synthetic diopside-jadeite	TAP
Ca		PET
Al		TAP
Mg		TAP
Na		TAP
Fe	Hematite	LiF
O		LDE1
K	Synthetic orthoclase	PET
Ti	Rutile	LiF
S	NiS	PET

The statistical treatment of the microprobe data and successive interpretation of the results were carried out with respect to the relative contents of elements expressed in their atomic fractions (at. %).

3.4. Elemental mapping with energy dispersive X-ray spectrometry (EDS)

Electron micrographs and EDS elemental maps were acquired with the JEOL 5910 general purpose scanning electron microscope equipped with Bruker EDX system for elemental analysis. The backscattered images of the region of interest (ROI) were obtained at a beam voltage of 15 kV and working distance of 10 mm, while 12 kV was used for the elemental maps. Major constituents were mapped, this includes: silicon (Si), calcium (Ca), aluminum (Al), iron (Fe) and sulfur (S) at the resolution of 2260 \times 1875 pixels.

3.5. Instrumented grid indentation

Instrumented indentation tests were carried out on the CSM Instruments standard nanoindentation tester equipped with an environmental control enclosure (18 ± 1 °C, $21 \pm 2\%$ RH) and a damping system. Force controlled tests were run to the prescribed maximum penetration depth $h_{\text{max}} = 250$ nm, with linear loading and unloading at a constant rate of 12 mN/min and a dwell time of 5 s. Constant value of the maximum displacement ensures comparable characteristic scale of the indenter–solid interaction volume, $d = 3-5h_{\text{max}}$ [4,11], for different phases incorporated in the bulk. Tip area function of the diamond indenter (Berkovich type) was calibrated on the standardized fused silica block ($E = 73.1 \pm 0.7$ GPa, $\nu = 0.16$), at 18 different loads ranging from 0.5 to 100 mN, and cross-validated on the natural α -quartz crystal [0001] sample as an auxiliary reference material. Indentation penetration–force curves were corrected with respect to point of contact as well as the frame compliance and then analyzed for indentation hardness, H , and indentation modulus, M , according to the Oliver and Pharr method [12–14]. For isotropic materials, M reduces to the plane-strain elastic modulus $E / (1 - \nu^2)$, independent of the shape of the indenter tip, where E and ν are the Young's modulus and Poisson's ratio, respectively. However, for general anisotropic materials M is a complicated function of elastic constants and, in general, is dependent on the shape of the indenter [15–18]. Indentation records associated with observed anomalies e.g. sudden compliance changes, which could result from the presence of local macro-voids, stratification of material, or fracture under the diamond probe, were filtered out prior to further statistical analysis.

A single indentation grid comprises of $N = 624$ measurement points minimum, arranged in the rectangular grid and spaced regularly around 10 μm apart in each direction. The test operated to the selected maximum indentation depth produced the residual imprint of approximately 1.5 μm . Such spacing ensures that successive measurements are independent of one another.

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