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COMMENTARY - 75 YEARS OF RILEM: MATERIALS & STRUCTURES

M&S highlight: Constantinides et al. (2003), On the use of nanoindentation for cementitious materials

John L. Provis

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The 2003 paper of Constantinides et al. [1] on the application of nanoindentation to probe cementitious phases and microstructures has achieved a significant citation impact since its publication, being the paper which introduced the application of statistical nanoindentation to hydrated cements. The paper provides a brief introduction to the theory and practice of nanoindentation, which had previously been applied under that name (i.e. distinct from "microindentation" on a larger length scale) to clinker phases [2]. This work represents the first published description of its use in a statistical manner (i.e. applied to a pre-defined large grid of points to gain additional information about constituent phases and their volume fractions) to characterise cement hydration products and how they come together to form hydrated microstructures. A 2015 review of the application of nanoindentation to cementitious materials cited and critically assessed over 100 publications which had applied the technique up to that point in time [3], and this number has grown to well over 500 by mid-2021 according to a Scopus keyword search, the majority of which are now applying multi-point statistical approaches. It is therefore evident that the techniques and ideas introduced in this 2003 paper [1] have become widely integrated into the available toolkit of analytical approaches to cementitious materials science, which is the core reason for its selection as a highlighted paper in this collection of highly impactful contributions published in *Materials & Structures*.

In addition to introducing nanoindentation as an analytical technique for hardened cements, the paper of Constantinides et al. [1] also focuses on formalising the dual-density conceptual model for different types of C-S-H: low-density and high-density C-S-H regions were distinguished on the basis of differing nanoindentation responses, deconvoluted from histograms of nanoindentation data collected at a large number of points on a grid. The conceptual model of C-S-H consisting of distinct regions of similar chemistry but different densities was formalised several years prior to the publication of the paper of Constantinides et al. [1], as a means of interpreting results obtained by neutron scattering [4] and by nitrogen porosimetry [5], but lacked more direct experimental validation. In the Constantinides et al. study, the identification of the two distinct C-S-H types in bimodal stiffness (elastic

This commentary is part of our celebration of 75 years of RILEM, highlighting Materials and Structures most highly influential and cited publications.

Highlighted paper: Constantinides, G. et al. On the use of nanoindentation for cementitious materials. 2003 Materials and Structures. 36(3), pp. 191–196.

J. L. Provis (✉)
Department of Materials Science & Engineering, University of Sheffield, Sheffield S1 3JD, UK
e-mail: j.provis@sheffield.ac.uk

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modulus) histograms was argued in part based on analysis of decalcified (leached) specimens, in which the apparent prevalences of the two populations of stiffness measurements was preserved despite the chemical degradation of the samples [1]. This was further developed in a 2004 publication by Constantinides and Ulm [6], which expanded upon their 2003 results and used the information obtained by nanoindentation in modelling of macroscopic elastic properties.

Since the publication of these results in 2003 there has been much discussion regarding the exact identification of C-S-H phases from statistical nanoindentation data. An "ultra-high-density C-S-H" phase was described in some studies, but was later identified as a "nanocomposite" mixture of C-S-H and CH phases rather than a purely C-S-H structure [7]. There have also been arguments raised in favour of a continuous distribution of C-S-H densities rather than two discrete populations, with the breadth of the distribution controlled in significant part by the inclusion of different pore volumes within different regions of a "hydrate foam" [8]. This conceptual model is also broadly supported by a study in which a continuous distribution of elastic property measurements from nanoindentation was matched very closely by the greyscale distribution of voxels obtained from an X-ray microtomographic scan of the sample [9], and from coupled nanoindentation-electron microscopic analysis [10]. It is not the purpose of this article to enter into the debate around classification or deconvolution of C-S-H signals in nanoindentation histograms – a topic which continues to generate high-quality analysis, including a more recent paper that was identified as one of the Best Papers of 2019 in *Materials & Structures* [11]. Rather, the fact that the highlighted article introduced an experimental tool which continues to be used, developed and debated is notable in and of itself when considering contributions to scientific advancement.

There has also been rather a robust discussion of the importance (or absence thereof) of microstructural influences on the distribution of mechanical properties reported for C-S-H, and the deconvolution procedures that are applied to histograms of nanoindentation results to extract material properties [12–14]. This is challenging because there are such wide differences in the elastic properties of the anhydrous and hydrous phases present in hardened Portland cement; remnant clinker phases and some supplementary cementitious materials (e.g. fly ash, blast furnace slag) have elastic moduli in the range 100–150 GPa [2, 15], while the hydrate phases mostly have elastic moduli below 50 GPa – e.g. Constantinides et al. [1] distinguished LD C-S-H at approx. 20 GPa from HD C-S-H at approx. 30 GPa. Key questions that are still under discussion relate to the identification of the relevant probe-sample interaction volume, and how this influences the determination of individual phase characteristics within a composite material of complex microstructure [16]. The importance of achieving a small interaction volume has led to other important developments such as the implementation of nanoindentation-based techniques within atomic force microscopes [17]. The characteristic size of the interaction volume in cementitious pastes has been determined to be more than 100 times the contact indentation depth under some circumstances [15], due to the presence of very hard particulate inclusions within a much less hard gel microstructure, and the importance and implications of this relationship remain subject of ongoing discussion.

The results obtained through application of nanoindentation to cementitious materials have been applied extensively in the development of discussion of the poromechanics of cements, including in another highly-cited 2004 *Materials & Structures* paper from Ulm et al. [18], and subsequent work from the same and other groups. The NICOM (*Nanotechnology in Construction*) conference series launched from the work of RILEM TC 197-NCM in the early 2000s and has now seen six successful events, in which statistical nanoindentation has featured as a core analytical technique across a wide range of materials and applications.

Nanoindentation has been used in particular to probe and analyse creep phenomena [19, 20], and to develop an improved understanding of the interfacial transition zone in cementitious composites [8, 21]. Through advances in instrumentation and theory, the nanoindentation technique itself has been accelerated [22, 23], implemented (or approximated) in scanning probe and atomic force microscopes [24, 25], and complemented by various other nanomechanical techniques [26]. Nanoindentation has also been hyphenated with electron microscopy and X-ray spectroscopy [10, 27], and coupled with techniques including focused ion beam nanotomography [12] and

Raman spectroscopy [28], to now form a key part of the available analytical toolkit by which the complex and important material characteristics of cementitious materials can be probed at the micro- and nano-scale. The fact that this technique was introduced to the core cementitious materials research community through the 2003 Constantinides et al. paper [1], and has now grown to such widespread utilisation and evident technical value, marks this highlighted paper as a truly important contribution published in *Materials & Structures* for this commemorative collection.

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