Cement and Concrete Composites 94 (2018) 153–165

Contents lists available at ScienceDirect

Cement and Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Coupling statistical indentation and microscopy to evaluate micromechanical properties of materials: Application to viscoelastic behavior of irradiated mortars

Benoit Hilloulin[a,*], Maxime Robira[a,b,c], Ahmed Loukili[a]

[a] Institut de Recherche en Génie Civil et Mécanique (GeM), UMR-CNRS 6183, Ecole Centrale de Nantes, 1 rue de la Noë, 44321, Nantes, France
[b] SUBATECH, Unité Mixte de Recherche 6457, École des Mines de Nantes, CNRS/IN2P3, Université de Nantes, BP 20722, 44307, Nantes cedex 3, France
[c] Tractebel Engineering – Le Delage, 5 rue du 19 Mars 1962, 92622, Gennevilliers CEDEX, France

ARTICLE INFO

Keywords:
Indentation
Cement paste (D)
Mechanical properties (C)
Creep (C)
Radioactive waste (E)
Image analysis (B)

ABSTRACT

In this work, an original method coupling statistical indentation and 3D microscope image analysis for heterogenous materials characterization is developed. Statistical microindentation test results performed on γ-irradiated and pristine mortar specimens are presented and analyzed using a clustering data mining technique. The outputs are compared with the phase identification from 3D image analysis to effectively reduce uncertainties in the material properties of one of the phases (cement paste). With respect to the effects of irradiations on cementitious materials, a significant increase of cement paste creep modulus and hardness, and a significant decrease of creep characteristic time, are highlighted after an exposition of 257 kGy at 8.5 Gy/min. Young's modulus of the cement paste is not significantly affected. These results confirm macroscopic concrete creep observations presented in previous studies fitted with dose-dependent logarithmic laws.

1. Introduction

The macroscopic mechanical properties of concrete mainly depend on micro-mechanical properties of its binding phase (i.e., the cement paste) and more particularly on the calcium silicate hydrate (CSH) gel, which exhibits significant local variations. For some years, microindentation and nanoindentation have been widely investigated to characterize elasto-plastic and creep properties of cementitious materials [1–4]. Indentation elastic parameters can then be input in homogenization schemes to determine concrete elastic properties [5–7].

According to Oliver and Pharr theory [8], the initial elastic unloading part of indentation curves can be analyzed to determine the indentation modulus and the indentation hardness of homogenous materials. Because cement paste is highly heterogenous, even at very small length scales, statistical nanoindentation performed at loads leading to penetration depths of some hundreds of nanometers has been developed. Assuming several phases may be indented at the same time, statistical indentation's main objective is to collect enough data points to apply a deconvolution algorithm giving the individual phase properties [9,10]. However, two main critical aspects were identified regarding the application of statistical indentation technique to cementitious materials [11]: the size of the interaction volume may be larger than the size of the single phases at the risk of creating spurious peaks in the probability density function (PDF) [12,13] as well as micromechanical values depending on the applied load [14], and the deconvolution analysis based on Gaussian Mixture itself may converge to local minima [15]. Therefore, coupling indentation results to other techniques identifying the effective nature of the indents is of great interest at different scales: using atomic force microscope [16] or SEM [6,17,18]. Coupling nanoindentation and SEM-EDS to filter data points, Chen et al. highlighted the presence of ultra-high density CSH/$Ca(OH)_2$ nanocomposites in low water-to-cement ratio cement paste by correlating micromechanical properties, e.g. indentation hardness or indentation modulus, to the portlandite volume fraction measured in volumes with approximately the same size as the one investigated through nanoindentation. Localization of indents by imaging techniques can also be used to differentiate the properties of several inclusions [19,20] and eventually map a restricted area depending on the measured mechanical properties [19,21]. From the microscale to the macroscale, 3D image analysis of concrete or mortar surface appears to offer a promising field of research for purposes of generating geometric or topological data and supplementing other experimental techniques or providing input for numerical models [22–24].

Besides these developments concerning statistical indentation and

---

[*] Corresponding author.
E-mail addresses: benoit.hilloulin@ec-nantes.fr (B. Hilloulin), robira@subatech.in2p3.fr (M. Robira), ahmed.loukili@ec-nantes.fr (A. Loukili).

https://doi.org/10.1016/j.cemconcomp.2018.09.008
Received 22 February 2018; Received in revised form 10 September 2018; Accepted 10 September 2018

imaging, it has been found out that the long-term creep properties of concrete specimens are related to the creep properties measured during minute-long microindentation or nanoindentation experiments. Both creep behaviors can be described using logarithmic time-dependent functions with two main variables: creep modulus and creep characteristic time [7,25,26]. Creep modulus of cement paste is linearly correlated with indentation hardness which means that the lower the hardness, the greater the creep strains, though the slope of the regression depends on the material: creep modulus of pure CSH is greater than the one of cement paste and it decreases with Ca/Si ratio [27]. Like macroscopic creep, indentation creep depends on the relative humidity [28].

In the context of nuclear waste disposals and, more generally, in the scope of nuclear safety structures characterization, the assessment of mechanical properties of irradiated concrete is of great interest to speculate over long term behavior of concrete under irradiations. Concrete properties evolutions with radiations have recently been summarized [29]. An extensive literature review ensures that irradiations lead to a decrease of the macroscopic strength of concrete under several types of radiations (α, γ and neutrons). The main mechanism behind concrete degradation under α-radiation is radiation-induced volumetric expansion (RIVE) of siliceous aggregates [30,31] at doses greater than a reference dose of around 1×10^{20} n/cm^2 [32]. But under pure γ-radiation (exposition condition of structural concrete element of disposals [33]), degradation mechanisms are not understood yet and there is still a debate whether a reference level of 2×10^5 kGy introduced some decades ago is relevant or not as some recent studies showed degradations after the exposure to lower doses [34,35]. Water radiolysis triggered by γ-radiation is supposed to be the main phenomenon responsible of possible degradations located in the cement paste [36,37] and phase alterations occurs only at very high doses of some dozens or even hundreds of MGy [38]. Concrete creep under low dose irradiation (< 1 Gy/h [33]) is one of the major preoccupations concerning long-term behavior of waste disposal infrastructures. To our knowledge, only one study reported the smaller extent of creep of γ-irradiated concrete under compression, though measurements were carried out over a relatively short period of one year without any repetition [39].

The growing use of various data mining techniques in civil engineering and materials science applications is changing the way scientists and engineers are facing issues and creating promising paths of investigation at the same time. Larger datasets can be obtained and the challenge is to find useful and innovative information out of them [40]. Data mining techniques are being developed to identify materials properties [41] and even leading to the creation of novel materials. In civil engineering [42], data mining has mainly been used for large scale transportation problems for some years [43].

A main objective of the present work is to demonstrate the potential of data mining techniques for material properties identification in civil engineering at a microscale and mesoscale, at the crossroads of materials science and civil engineering. For this purpose, two complementary methods, namely statistical microindentation and microscopy, were performed on mortar specimens and combined to detect hidden data trends. Used together with adequate data mining techniques, microindentation data analysis and optical microscopy image analysis are shown to reduce the uncertainties associated with cement paste mechanical properties identification. An application to the determination of mechanical properties of γ-irradiated mortars is then proposed. The first micro mechanical dataset of this type is reported and compared with the only, because tedious, measurement performed on concrete some decades ago [39]. Hundreds of measurement points obtained from 3 irradiated and 3 pristine control specimens are compared to highlight hidden trends due to radiation exposure.

Table 1
Mortar compositions.

Cement (kg/m^3)	Calcareous Sand 0/4 (kg/m^3)	Water (kg/m^3)	W/C	Paste volume (%)
566	1344	270	0.43	45

2. Materials and methods

2.1. Specimens preparation and irradiation conditions

Mortar was prepared with CEM I 52.5 and 0/4 mm calcareous sand (to avoid the activation of alkali-silica reaction by irradiation) with the proportions detailed in Table 1. Any use of organic additives like superplasticizer or demolding oil was avoided to not induce a possible premature degradation by the irradiations. This mortar formulation was determined to be as representative as possible of a high-performance concrete used in nuclear waste storage facility galleries.

Six mortar prisms with dimensions of $4 \times 4 \times 16$ cm^3 were cast in polypropylene molds to avoid any presence of metallic compounds from the molds. After 1 day of curing under sealed conditions in an air-conditioned room at a temperature of 20 °C and 90% RH, the specimens were demolded. The specimens were further cured in lime-saturated water until the age of 28 days. Mortar prisms were then dried during 14 days in an oven at 45 °C (a constant mass was measured at 10 days).

Half of the mortar prisms (MD-257kGy-I1 to MD-257kGy-I3) were then introduced in an irradiator at ARRONAX (^{137}Cs source, 661 keV, 123.4 TBq) at the age of 42 days. Specimens were exposed as close to the source as possible to guarantee a spatially homogenous dosage during 3 weeks. The total γ dose received by the specimens was calculated to be around 257 kGy based on a map of the γ fluxes in the irradiator realized by Fricke dosimetry measurement. The other half of the specimens (MD-257kGy-S1 to MD-257kGy-S3), e.g. the control specimens, were kept in an air-conditioned room at relative humidity of around 65% close to the ones measured in the irradiator at the end of the irradiation period.

Several mechanical and chemo-physical tests were performed on these mortars and on other series as well. The results will be presented in future communications but, in the sake of clarity, some results may be evocated in regards to micromechanical results presented herein. No evident carbonation, pore size evolution or hydrated phases transformations were measured. Thus micromechanical properties evolutions may not be attributed to calcite formation in contrast with [44].

2.2. Indentation setup and theory

Microindentation tests were performed during the week following the irradiation period with the main objective of comparing the properties of irradiated and control specimens. Thus, a volume of $2 \times 2 \times 1.5$ cm^3 was sawn from the middle part of a half of the $4 \times 4 \times 16$ cm^3 broken by three-point bending test. This location was selected to avoid damage due to the three-point bending test. The 2×2 cm^2 section was polished with Si—C paper with decreasing particle size (500, 1200, 2000, 4000) using ethanol as polishing liquid. Polishing times were selected around some minutes per paper to limit the risk of aggregate cracking. These times are much shorter than the ones used for nanoindentation on cement pastes [45] but were sufficient to obtain a surface roughness R_q of around 0.5–1 µm which is acceptable for micro-indentation with penetration depth of some microns.

A typical cement paste area with a typical indent is presented in Fig. 1. As it can be observed, the scale of the indent is larger than the characteristic scale of the microstructure of the cement paste (residual anhydrous clinker size): thus, the performed microindentation tests provided the mechanical properties of the cement paste or the sand, or