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Examining cement-based materials by laser scanning confocal microscopy

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Abstract

While laser scanning confocal microscopy (LSCM) is widely used in a variety of fields, LSCM has not been broadly applied for the characterization of cement-based materials, despite the potential advantages of this technique. It is believed that the use of confocal microscopy for characterizing cement-based materials would be expanded by the further development of sample preparation and examination protocols. Three imaging methodologies: (1) "through-aggregate" examination, (2) wet-chemistry studies, and (3) surface characterization; and their potential applications to cement-based materials are described.

Keywords: Cement; Laser scanning; Confocal microscopy

1. Introduction

Laser scanning confocal microscopy (LSCM) is widely used in many fields including materials science, textile engineering, and biology, but the use of this technique to characterize cement-based materials remains relatively unexplored. LSCM does offer many unique capabilities that make this technique well suited for examining hydrated and roughly textured cement-based materials. In addition to good resolution (which is higher than with ordinary optical microscopy) and a broad magnification range, confocal imaging can be performed at standard temperatures and pressures (i.e., samples do not have to be subjected to drying during examination) and imaging and quantification of rough surfaces is possible. From the confocal images, volumetric representations may be generated which may yield additional information not apparent in thin sections or by surface characterization.

With confocal microscopy, three-dimensional images are formed by acquiring a series of images of the same object at consecutive focal planes. The basic principle of confocal microscopy is to illuminate only one location at a time on the sample, yielding enhanced axial resolution and the ability to perform non-invasive optical sectioning such that three-dimensional image data can be acquired [1,2]. This is achieved by a series of diaphragms that focus the light supplied by a laser onto the sample. The reflected and fluorescent light passes though a point detector which discards rays that are reflected or fluoresced by planes which are not in focus, improving resolution. A schematic of the laser scanning confocal microscope (Fig. 1) describes how the detector pinhole receives light from only the focal plane of the sample. The resulting images are essentially slices of the sample taken sequentially deeper (or shallower) through the sample. A three-dimensional representation can be assembled using computerized image analysis to reconstruct the sample from the image series [2].

Despite the potential advantages of confocal microscopy for examining cement-based materials (i.e., in situ, through-depth observation of hydrated samples over time), literature review reveals only limited application of confocal microscopy to examine cement-based materials. Most of these studies involve surface state analysis, including the quantification of surface roughness in fractured samples and the measurement of air void distribution and volume on a surface. Results obtained by Lange et al. [3,4], Zampini et al. [5], and Abell and Lange [6] demonstrate the utility of the confocal microscopy technique, particularly for examining rough

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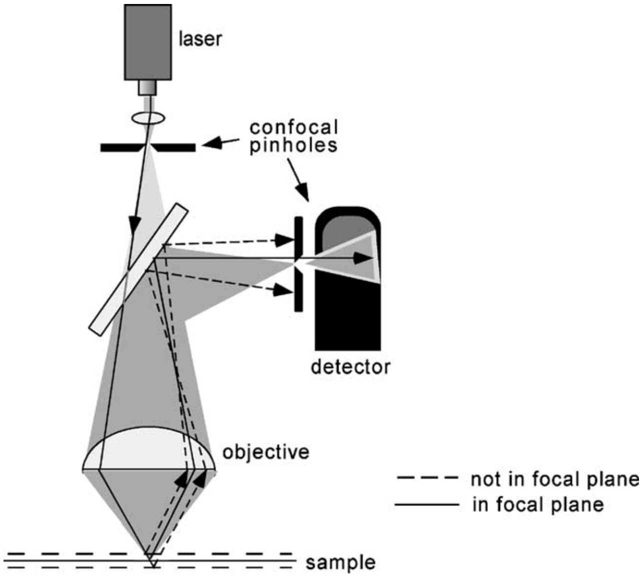

Fig. 1. Schematic describing the confocal principle. Adapted from http://www.llt.de/conprin.html.

surfaces characteristic of concrete. Lange et al. [3,4] characterized the roughness of fracture surfaces of cement pastes and mortars using confocal microscopy in the reflected light mode. Samples were fractured, gold-coated (to enhance reflectivity), and subsequently examined to provide data correlating surface roughness to fracture toughness using three-dimensional tomographic maps generated by the confocal microscopy and experimental fracture data. Using a similar technique, Zampini et al. [5] examined fracture surfaces at varying proximity to the aggregate/paste interface and correlated surface roughness data to the fracture parameters, K_{Ic} and δ_{ac}, from the two-parameter fracture model [7]. Abell and Lange [6] used measurements of surface roughness obtained through confocal microscopy to characterize the influence of aggregate size and gradation on fracture of mortar specimens in flexure. Recently, Becker et al. [8] demonstrated that the tandem scanning confocal microscope (TSM) could be used to estimate the volume and positions of air voids in concrete.

It is believed that the use of confocal microscopy for characterizing cement-based materials would be expanded by the further development of sample preparation and examination protocols. The goal of this paper, then, is to demonstrate the broad range of potential applications for this microscopy technique. The methodologies to be described herein are: through-aggregate examination, wet-chemistry studies, and surface roughness measurements.

2. Through-aggregate laser scanning confocal microscopy

A major obstacle to the in situ study of cement-based materials is that while interactions occurring at the cement paste–aggregate interface play a significant role in determining the physical and mechanical properties of the concrete, it is extremely challenging to examine this interface without introducing artifacts. LSCM offers several advantages because hydrated samples can be imaged over time as reactions progress, and through-depth characterization is possible through optically transparent media, such as glass aggregate, providing an observation ‘‘window’’ into concrete. Fig. 2 represents, conceptually, the imaging of aggregate and aggregate/paste interface in concrete by confocal microscopy. This methodology has been used to capture individual images at successive *z*-depths through glass aggregate. Currently, mortar and concrete samples are prepared using spherical borosilicate beads as aggregate. This has allowed the research team to develop the technique using samples with simple geometry, which is readily verifiable. However, crushed glass with a rough surface texture and single-crystal quartz, both of which are more similar to actual aggregates used in concrete, as well as flat glass slides, which offer an even more simplified geometry, could also be used. Here, the glass has been mixed into concrete and mortar samples as the coarse or fine aggregate or as partial replacement for aggregate; sections (up to 10 cm in thickness) are cut and polished prior to examination. Here, the sections examined were 2.5 cm wide by 2.5 cm in depth by 3.0 cm tall (or thick) and were polished on a Buehler ECOMET 4 grinder/polisher with grit sizes 120, 240, 320, and 600 and water as the lubricant. Due to imperfections generated during the initial polishing step, the sample surface was further polished with a cerium oxide (CeO_2) paste and a felt bob drill attachment.

In Fig. 3, three images, taken at successively greater depths through a spherical glass aggregate bead, show that LSCM can be used to image through-aggregate to the aggregate–cement interface. Stacks of such images can be assembled into a three-dimensional rotational video image, allowing volumetric characterization of the sample; ‘‘snap shots’’ from a rotational video generated from the complete stack of images of the region imaged in Fig. 3 is shown in Fig. 4. The images in Fig. 3 were acquired using a 5×/0.15 HC PL FLUOTAR objective on a Leica TCS NT LSCM through a sample prepared

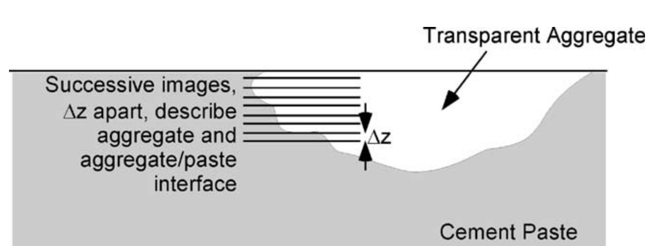

Fig. 2. Schematic demonstrating sample preparation to allow examination through transparent aggregate by LSCM.

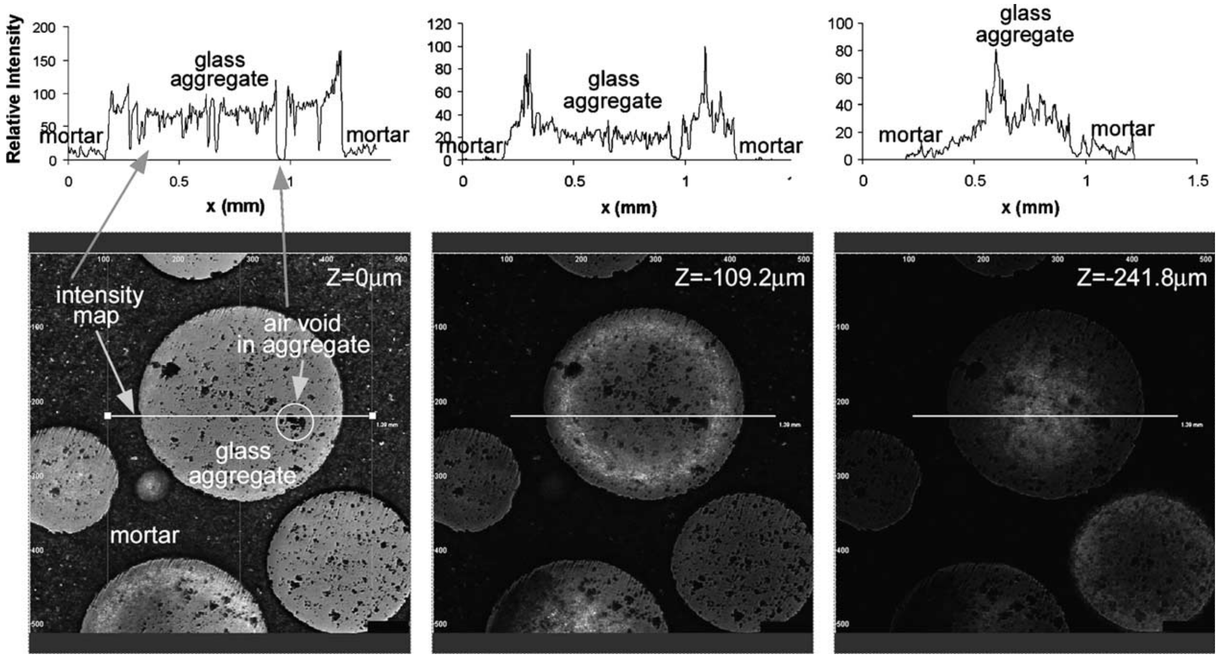

Fig. 3. Three LSCM images and corresponding intensity maps taken at three z-depths through a glass aggregate bead in a mortar sample. The intensity maps show that the microstructure is most varied at the aggregate/paste interface.

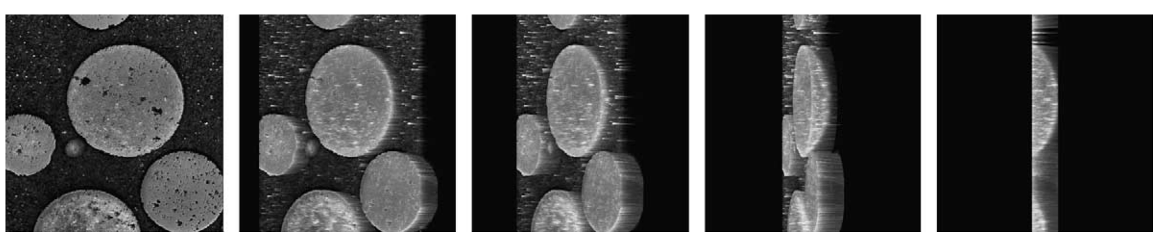

Fig. 4. Five snap shots from a rotational video showing the through-aggregate imaging technique. Images are of 1-, 2-, and 3-mm diameter spherical glass aggregates mixed in a mortar.

with portland cement ($w/c = 0.37$) and 1-, 2-, and 3-mm diameter glass beads as aggregate. Image intensity maps, such as shown in Fig. 3, can be generated at specific z-depths to show variations in light intensity at different locations through the sample. The map, drawn across an aggregate and through two interfaces, shows distinct differences in light intensity between the aggregate and the paste and wider deviations in intensity nearest the interfaces. The aggregate contour can also be observed in the stack of intensity maps. At greater depths (depths of $\sim$2 mm through the glass can be attained), the interfacial zone at the bottom of the aggregate particle can be imaged. More extreme variations in intensity, seen in Fig. 3 at both edges of the aggregate at $z = 0$ and $z = -109.2$ μm and at the bottom of the aggregate at $z = -241.8$ μm, seem to generally occur at the interfacial zone. The sudden variations in the intensity at the interface between the spherical aggregate and the surrounding paste appear to be indicative of the microstructure in that region, which is characteristically less dense and is more heterogeneous than aggregate and the bulk paste. In addition, at $x = 0.95$ mm, a defect in the aggregate is also observed to produce variations in intensity in each of the three images in Fig. 3.

Potential applications for this imaging methodology include study of reactions that occur at aggregate/cement paste interface or in the aggregate in cement-based materials. For instance, changes in microstructural features (e.g., solid-to-void ratio) in response to changes in mixture design, time, and loading could be imaged in this way. Also reaction products which form around the aggregate, such as alkali–silica reaction (ASR) gel or ettringite by delayed ettringite formation (DEF) could be imaged. In addition, the formation and progression of cracks in the glass aggregate during ASR or freeze/thaw cycling could be monitored over time.

3. Wet-chemistry laser scanning confocal microscopy

In dense samples, such as concrete, it is more difficult to distinguish morphologically between the various products of cement hydration. By focused examination of more dilute wet-chemistry systems contrast between solids and voids or solution is enhanced. In such samples, the water-to-solid ratio can be adjusted to allow for improved imaging of solids. With LSCM, an additional advantage is the generation of volumetric representations of reactants and products. In this way, the earliest stages of a reaction may be imaged, providing information regarding the kinetics of the reaction, the mechanisms of product formation, and the product morphology. Potential applications include examination of the hydration of the principal mineral components of portland cement, calcium aluminate cement, or specialty cements as well as the examination of the pozzolanic reaction or the interaction between supplementary cementitious materials and cements.

To demonstrate the value of this characterization method, LSCM images of a pozzolanic reaction product, specifically the product of a silicate gel in saturated calcium hydroxide solution, have been obtained using a 100× water-immersion objective on an Ar/Kr/He/Ne-laser Leica TCS SP spectral confocal microscope. The resolution of the instrument is 0.18 μm in the *x*–*y* directions and 0.30 μm in the *z*-direction or focal direction. The reaction product was imaged over a depth of 18.2 μm at 0.3 μm steps for a total of 61 images; using a small step size maximizes resolution. Twelve of those images, organized sequentially at greater depths through the sample, are reproduced in Fig. 5. A three-dimensional model of the reaction product, generated using Leica 3D reconstruction software, is available at http://www.ce.gatech.edu/~kkurtis/semitrans.avi. The images and the

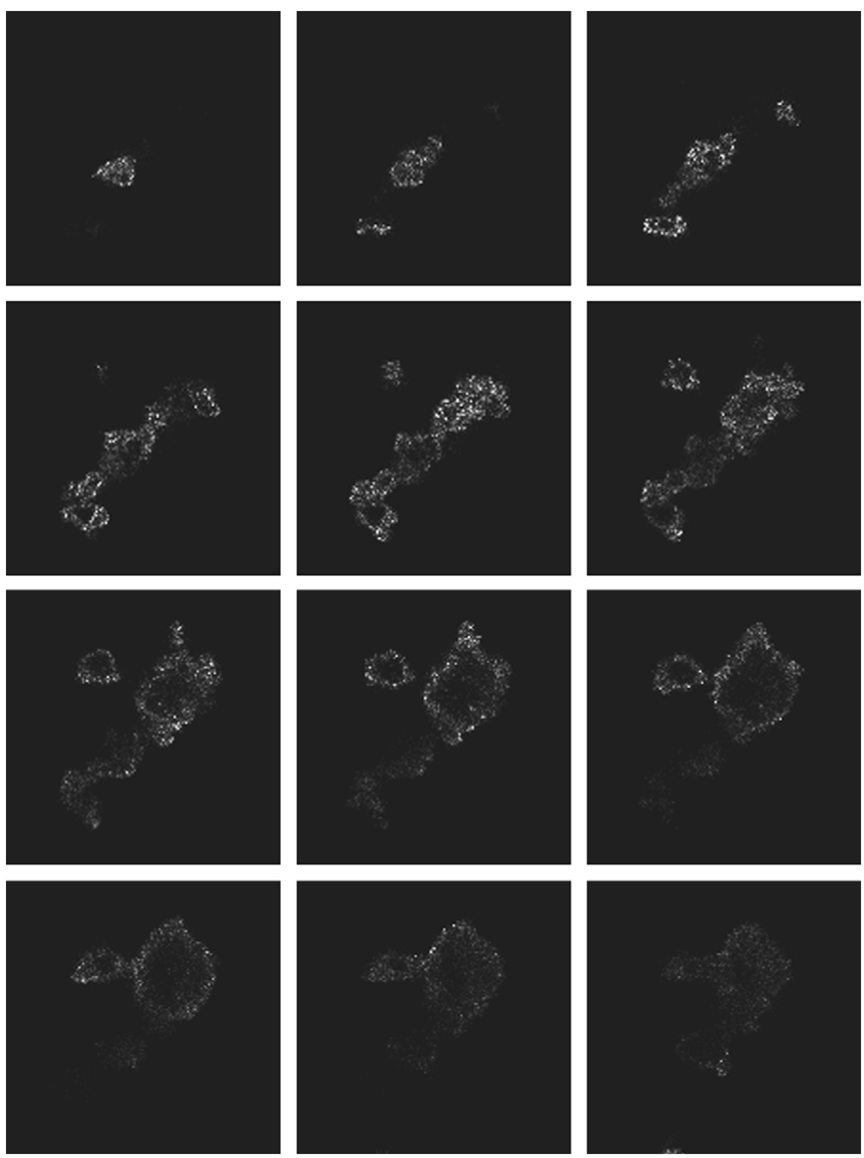

Fig. 5. LSCM images obtained at sequentially greater depths through wet-chemistry sample prepared to examine the pozzolanic reaction product. These images were used to construct a three-dimensional video model available online.

corresponding rotational model show the characteristic "sheaf of wheat" morphology, described in the literature as C–S–H or a C–S–H precursor. Microstructures of this morphology are typically composed of lathlike structure in a near-spherulitic arrangement, as shown previously by SEM [9,10] and soft X-ray microscopy [11–13]. The three-dimensional model obtained by LSCM provides additional information about the sheaf of wheat microstructure, in that the microstructure can be observed volumetrically. In general, three-dimensional characterization affords some advantages over traditional two-dimension characterization, including the opportunity to assess whether growth occurs "in the round" or in plane and to determine, in thin samples where light transmission is possible, if the structure varies through the depth of the sample (i.e., Is it hollow?). By examining this model, the sheaf of wheat structure is found to be composed consistently throughout its volume of lathe-like structures (i.e., the interior portion of the structure is not hollow). This information provides additional understanding about the mechanisms of the structure's formation and supports the model described by Gartner [14] for C–S–H growth during C_3S hydration and by Gartner et al. [13] for C–S–H growth in the sheaf of wheat morphology.

4. Surface characterization by laser scanning confocal microscopy

As described in Section 1, much of the existing research using confocal microscopy to examine cement-based materials has focussed on surface characterization. Lange and coworkers have explored the correlation between fracture surface roughness and fracture energy [3–6]. A roughness number (RN) is a quantification of the roughness of a surface; RN can be generated from surface topographies acquired by confocal microscopy. As shown in Fig. 6, RN is the area of a triangulated surface (A_i) compared to the corresponding nominal area (A_{pi}):

$$\mathrm{RN} = \frac{\sum A_i}{\sum A_{pi}}$$

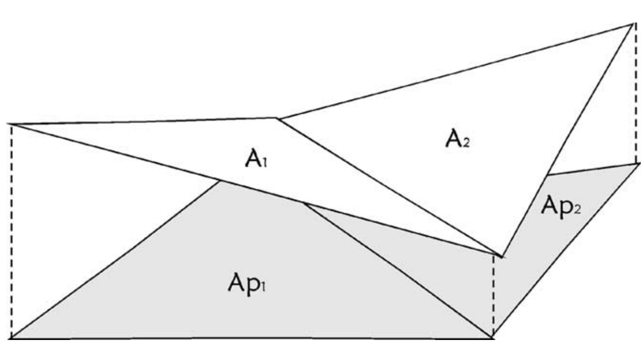

Fig. 6. Illustration describing the concept of the RN.

It follows, then, that a planar surface has RN equal to one. Also, RN will generally increase as surface scanning intervals or resolution decrease.

To demonstrate this methodology, fracture surfaces of fiber-reinforced mortars were examined and their roughness quantified. Unlike earlier examinations of fracture surfaces of cement-based materials [3,4], these fracture surfaces were not prepared in any way (e.g. gold coating) prior to examination by LSCM. Flexure tests were performed on fiber-reinforced $2.5 \times 2.5 \times 10.1$ cm ($1 \times 1 \times 4$ in.) mortar beams prepared with fiber volume fractions of 0%, 0.6%, and 1.2% and constant sand-to-cement ratio of 1 and w/c of 0.50. Softwood kraft pulp fibers were used as reinforcement. The span-to-depth ratio was 3, which complies with ASTM C 348-97 "Flexure Strength of Hydraulic Cement Mortars". The fractured surfaces of the specimens were then observed with a Leica TCS NT confocal microscope using an HC PL FL 5×/0.15 objective. For each fracture surface, a total of eight images were acquired. Each was then analyzed by measuring the true area of the fracture surface and the projected area. The true area was measured using Leica image analysis software that can generate surface topographies (such as in Fig. 7) and quantify the true surface area from the reconstructed three-dimensional digital image. The projected area is constant. In this case, the projected area was 4 mm^2 as the scanned area for the confocal microscope using the 5× objective was 2×2 mm. In addition, the resolution for all the digital imaging was kept at 512×512 pixels. The RN, then, is the relationship between the true and projected areas. Fig. 8 shows that a good correlation can be made between RN, toughness, and fiber volume fraction in *these* pulp-fiber reinforced mortar samples. Thus, this

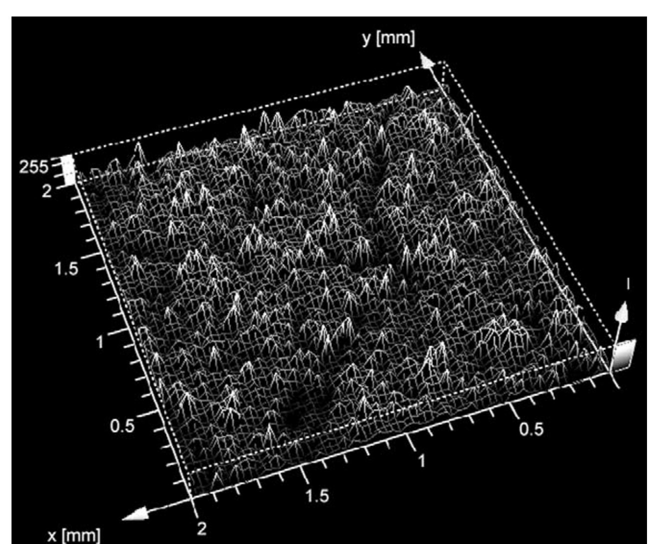

Fig. 7. Computer-generated mesh showing the fracture surface topography of a mortar sample containing 0.6% softwood pulp fibers by volume.

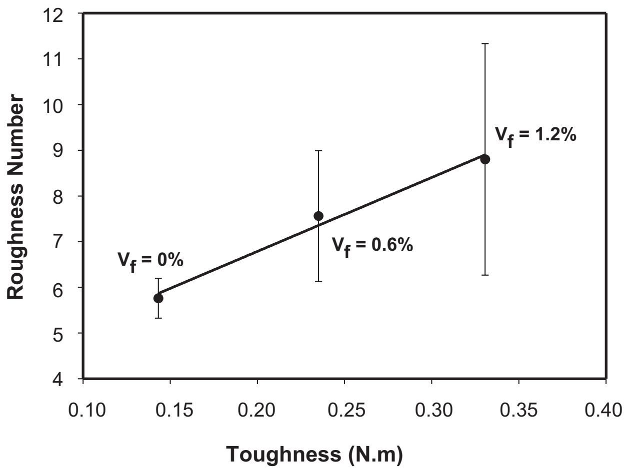

Fig. 8. A relationship is found to exist between the volume fraction of fiber reinforcement in mortar samples, their toughness, and their RN as measured by LSCM.

method may be useful for providing an important link between mixture design and mechanical behavior, but further research is required.

In addition to quantifying the roughness of surfaces, LSCM can also be used to generate high-resolution images of rough surfaces. LSCM affords improved resolution with depth, in particular, as compared to ordinary optical microscopy. In addition to allowing imaging of rough surfaces (as demonstrated previously in Fig. 7), this capability can make LSCM useful for examination of voids and cracks at the surface. Fig. 9b is a projection image showing an air void at the surface of a concrete section. The image was generated from 32 individual images taken 32.2 m apart. These images, shown in Fig. 9a, demonstrate the confocal principle whereby a series of images are acquired of the same object at focal planes consecutively deeper into the sample. This technique can be used to measure void size volumetrically, as described by Becker et al. [8]. Fig. 10 is a projection image assembled from individual images of the cracked surface of a cement paste sample prepared from Type I cement with a $w/c = 0.60$. After exposure to a sodium sulfate solution with 10,000 mg/l sulfate ion concentration for 50 days, surface cracking and spalling were noticed. Fig. 10 is an image of one of these surface cracks. It is noticed that within the crack, several needlelike and apparently crystalline products, perhaps ettringite, are present. The images in both Figs. 9 and 10 were acquired on a Leica TCS NT system using

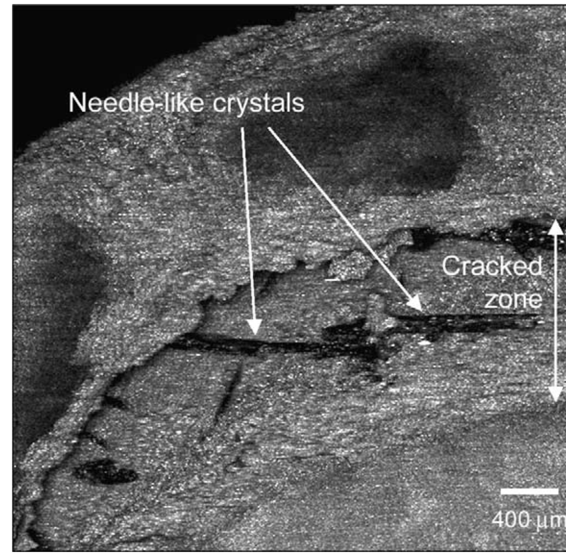

Fig. 10. LSCM image of the cracked surface of a cement paste sample subjected to sulfate attack. Reaction products, apparently crystalline and likely to be ettringite, are visible within the crack.

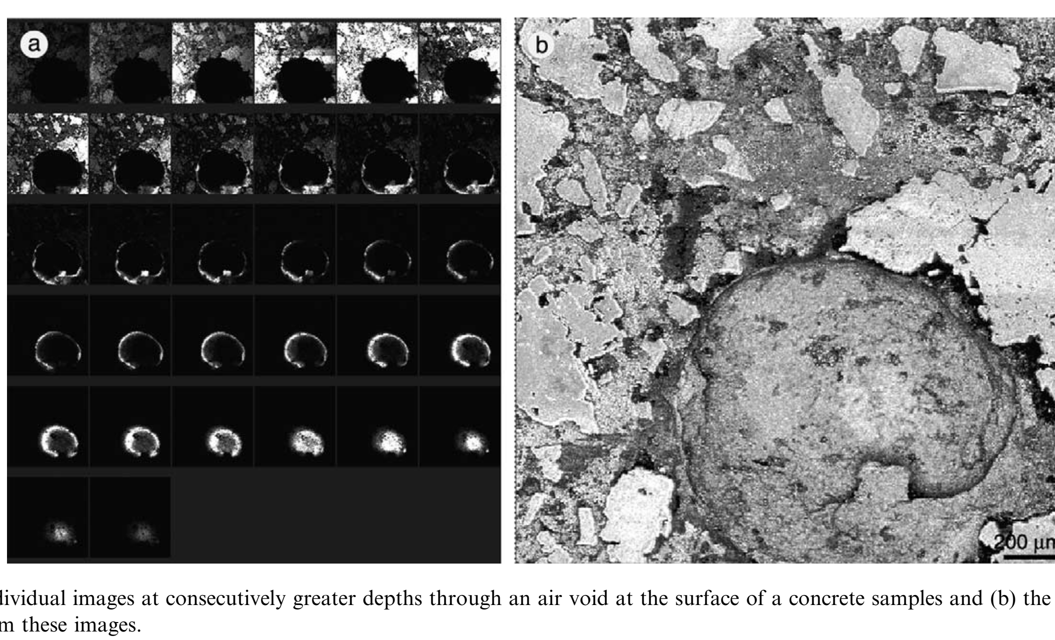

Fig. 9. (a) Individual images at consecutively greater depths through an air void at the surface of a concrete samples and (b) the projection image assembled from these images.

an HC PL FL 5×/0.15 objective and a 2.5 × 0.7 NA dry NPLAN objective, respectively. Such images can give useful insights into the changes occurring to the microstructure while the sample is undergoing environmental degradation.

While such images are challenging to acquire using conventional optical microscopy, good quality images of rough surfaces can be acquired by LSCM. The range of potential applications for this methodology is quite broad and includes: quantification of fracture surface roughness and correlation of the measured RN to mechanical properties and/or mixture design, examination of void spacing and volume, and characterization of cracks and products within cracks, among others.

5. Concluding remarks

Three methodologies for examining cement-based materials by LSCM have been presented. These are through-aggregate LSCM, wet-chemistry LSCM, and surface characterization. Of course, additional imaging methods are possible—for instance, fluorescence LSCM is used widely to examine biological materials and could be used advantageously to examine cement-based materials. The flexible sample preparation requirements for LSCM make it well suited for studying the textured, hydrated systems that exist in concrete. In addition, LSCM can be used to generate data (e.g. RN, volumetric representations) that is not available through other characterization methods. Further development of sample preparation and examination protocols should lead to increased application of confocal microscopy for characterizing cement-based materials.

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