Characterisation of ‘Hadley’ Grains by Confocal Microscopy

M. K. Head*, H. S. Wong, and N. R. Buenfeld

Concrete Durability Group, Department of Civil and Environmental Engineering,
Imperial College London, SW7 2BU, UK

Abstract

This work forms part of an exploratory study to investigate the use of fluorescent laser scanning confocal microscopy (LSCM) for imaging pores and voids in hardened mortar and concrete. The study has revealed the suitability of the technique for the characterisation of hollow shell (Hadley) hydration grains (these are grains that contain a void within the original boundary of the cement grain). It was found that Hadley grains could be imaged using fluorescent light techniques, subsequent to their impregnation by epoxy resin doped with a fluorescent dye. Prior to this work, it was not clear whether hollow grains were impregnated due to connections with capillary pores, or if they had been impregnated due to connections with damage caused during surface preparation (i.e. micro-cracks or deep surface scratches). However using the 3D LSCM imaging technique it was observed that connections between Hadley grains and hardened cement paste (HCP) capillary pores did exist, in different forms, at depths well below the surface providing ‘conduits’ along which resin was able to flow and impregnate the hollow grains. Other aspects of imaging Hadley grains are also described, such as the sectioning of ‘tips’ of larger grains often taken as separate smaller pores or grains in 2D images, and internal shell hydration (inner) products.

Keywords: 3D Laser Scanning Confocal Microscopy (LSCM), Characterisation (B), Pore Size Distribution (B), Backscattered Electron Imaging (B)

1. Introduction

The hardened cement paste in concrete contains different types of pore, with sizes that cover six to seven orders of magnitude from the nanometre to the millimetre scale. Porosity is an important phase as it influences not only mechanical strength, but also shrinkage, creep and molecular transport. Pores are conventionally classified as, in the order of decreasing size: entrapped air, entrained air, capillary pores and gel pores. Cracks may also exist, and these are differentiated according to their size and origin. Another distinct type of pore is the hollow-shell hydration grain, also known as Hadley grain, after the discoverer [1].

Hollow-shells are hydrated cement grains that contain a void within the original boundary of the cement grain. In his Ph.D. thesis, Hadley [1] observed that a shell of hydration products form on hydrating cement grains at early ages. As hydration continues, a progressively larger void space develops within the shell. Most of the hydration shells eventually become completely hollow, while some contain remnants of anhydrous particles. This observation is not consistent with early hydration models [2] that predicted the deposition of hydration products both inside the original cement grain boundary (inner product) and outside in the original water-filled spaces between cement grains (outer-product). Later studies using backscattered electron imaging (BEI) confirmed that hollow-shells are indeed a characteristic feature of cement hydration [3-7].

According to Diamond [8], cement grains form a shell of hydration products around themselves during the first few hours of hydration. The shell is approximately 1μm thick, and is composed of calcium silicate hydrate (C-S-H) gel, with some calcium hydroxide (CH) and occasionally extensions of ettringite needles of thin calcium monosulphate plates [8]. During subsequent hydration, the shell may either deposit inner hydration products, forming what is known as a ‘Williamson grain’ [9], or, empty-out in a hollow-shell mode and precipitate hydration products in the capillary

* Corresponding author. Tel: +44 (0) 207 594 5956; Fax: +44 (0) 207 225 2716; E-mail: m.head@imperial.ac.uk
pores between adjacent shells. Diamond [8] suggested that whether a cement grain develops into a Williamson or a Hadley grain depends on the amount of pore-solution filled space in the vicinity. The hollow-shell mode appears to be favoured where pore-solution filled spaces are available, for example near the interfacial transition zone (ITZ), while the Williamson grain development appears to predominate in dense areas, for example in closely-packed cement grains.

Kjellsen et al. [5] observed that smaller cement grains will hydrate completely by one day, leaving complete hollow-shells. Larger cement grains may leave hollow-shells with a remnant anhydrous core. However, it is possible that some of the apparently completely hollow-shells are, in fact, corners of larger hollow-shells containing anhydrous cores.

Hadley grains are ubiquitous in hydrated cement paste, but their nature, process of formation and influence on bulk properties of cement-based materials is imperfectly understood. Part of the reason for this is that previous microscopical studies on Hadley grains have always been limited by the two-dimensional characteristic of electron microscopy. Therefore, this paper presents an attempt to explore the nature of Hadley grains, in three-dimensions, via fluorescent laser scanning confocal microscopy (LSCM). A particular focus of this study is the interconnection between hollow-shell voids and the surrounding capillary pores, which was first reported in a paper on the feasibility of using LSCM for imaging the pore structure of cement-based materials [10].

2. Experimental: Technique

Recent advances in optical (visible) light microscopy have produced new techniques that allow imaging of structures in three dimensions, and at very high optical and spatial resolutions. Laser scanning confocal microscopy (LSCM) makes use of a very small pinhole aperture, which is placed directly in front of a light gathering sensor (photo multiplier tube), and blocks out-of-focus light from reaching the sensor (see Fig. 1). Light from immediately above and below the image plane is excluded from image formation resulting in a much higher resolved 2D image, with very little distortion from stray out-of-plane light. This kind of image is often referred to as an ‘optical slice’, because of the limiting effect of the aperture, and slices are routinely sub-micron in thickness. By focusing through the target specimen a series of slices can be acquired at sequentially deeper focal planes. The image ‘stack’ can then be reconstructed by specialist image software to produce a 3D projection of the specimen’s structure.
As with the SEM, confocal microscopes require optimising to obtain the best possible image resolution during image capture. This involves selection of an appropriate pinhole diameter, laser power and compensation for loss of signal with depth, pixel dwell time, scan method (e.g. averaging 4 scans per line), maximum imaging depth, optical slice thickness and spacing to give the number of slices required through the imaging depth. Also a digital zoom was selected to provide an appropriately sized image for approximate area matching with the SEM captured images. The confocal microscope used for this study was a Zeiss LSM 510 mounted on a Zeiss Axioplan2 upright microscope. The microscope is equipped with an argon laser emitting light of wavelength 488 nm, and oil-immersion objective lenses of magnifications ×40 (NA = 1.3) and ×100 (NA = 1.4).

Given that the technique is based on reflected fluorescent light, specimens can be either polished blocks or polished thin sections. If more detailed petrographic analysis of the material is required it may be appropriate to prepare thin-sections, whereas blocks are sufficient if only confocal work is required. Both types of specimen are also appropriate for BEI in a scanning electron microscope, as was done in the previous work, and in the present study. Given the prevalence of BEI for characterisation of cementitious materials, BEI forms a useful technique to employ to verify features imaged with the confocal microscope. Images familiar to most researchers are easily understood and related to the ‘reverse imaging’ type of confocal images. Reverse imaging of specimens merely refers to the nature of fluorescent light imaging, where it is the light emitted by the dye that is detected by the imaging sensor. Therefore, any feature imaged is in fact a pore or void of some kind that has been in-filled by the fluorescent resin during impregnation, and should not be interpreted as a solid structure. Solid structures in a fluorescent image normally appear black (unless they naturally fluoresce, which is not the case here).

Two concrete mixtures were studied. Specimens were manufactured with water/cement ratios of 0.4 and 0.6, comprising of ordinary Portland cement (OPC), medium graded siliceous sand and Thames Valley gravel. Mixture proportions for the 0.4 concrete were 1:2:3.14 (cement: sand: gravel), and 1:2.7:4 for the 0.6 concrete. To aid specimen identification each was given a designation as indicated in Table 1.

Table 1. Mix specimen designations for microscopy

<table>
<thead>
<tr>
<th>Mixture</th>
<th>w/c ratio</th>
<th>Curing age</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.4</td>
<td>3 days</td>
<td>0.4 – 3d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28 days</td>
<td>0.4 – 28d</td>
</tr>
<tr>
<td>B</td>
<td>0.6</td>
<td>3 days</td>
<td>0.6 – 3d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28 days</td>
<td>0.6 – 28d</td>
</tr>
</tbody>
</table>

Cylindrical specimens (100Ø × 250 mm) were cast and demoulded after 24 hours, sealed in cling film and cured at 20°C for 3 and 28 days. After each curing age, a 10mm thick disc was cut from each cylinder at approximately 100mm from the bottom cast face, from which a block specimen (40 × 20 × 10mm) was prepared for microscopy. The blocks were freeze-dried and vacuum-impregnated with a low viscosity epoxy resin doped with fluorescent dye. They were then ground using silicon carbide papers of successively finer grit size and finally polished with cloths embedded with successively finer diamond abrasives down to ¼ µm. Each grinding and polishing step was done at 70rpm and a 7N force was applied to the specimens. Polishing time was kept short (~5 minutes) to minimise relief. A non-aqueous solution was used as lubricant for cutting and polishing. Acetone was used as cleaning fluid.

Prior to confocal imaging, the specimens were mounted un-coated in a low vacuum SEM (JEOL 5410LV), and imaged in backscattered mode. Images were captured at various magnifications ranging from x100 to x1000. The
images were printed out to be used as an aid in re-locating the same areas with the confocal microscope. Unlike backscattered electron images, confocal images contrast only resin-filled voids against solid non-impregnated fractions of the material, therefore the BEI image shown in figure 2 a) was captured to help explain and correctly identify dark regions of a corresponding confocal image (Fig. 2 b)).

![BeI image](image1.png) ![Confocal image](image2.png)

a) BEI of specimen surface captured at x1000 and cropped to area-match with confocal image set. Voids are black.  
b) Top image in z-stack file. Note that voids in confocal images are areas of brightness.

**Figure 2.** Approximate area match between BEI and confocal images, specimen 0.6 – 28d, (FOV ~ 66 x 66 µm). Note: Confocal image has been contrast enhanced to improve clarity for viewing. Hollow shell grains marked 1 – 6.

Also indicated in figure 2 (a and b) are some of the many hollow shell grains present in the images (marked 1 – 6). These are some of the larger grains. Smaller apparently fully hydrated grains can be observed in all parts of the images, most noticeably in the top half and lower right of both images.

**3. Experimental: Images and Hollow Grain Features**

One of the most important observations made thus far with the confocal technique is the existence of channels, which connect Hadley grains to areas of capillary pores located within HCP. These channels or connections were observed at depths below the specimen surface with no links to the surface, and were not therefore specimen damage caused during surface preparation. The channels were observed to have varying morphology, with some appearing as large open, poorly defined features, and others appearing as very fine hair-like structures only extending for short distances away from reacted grains. Examples of both structure types are given in figures 3 and 4 below.
Figure 3. ‘Large’ connecting channels (circled) between Hadley grains (dotted lines) and capillary pores, (a - e & f - j = specimen 0.6 – 3d; k - o = specimen 0.4 – 28d). All scale bars = 10 µm.

Figure 3 comprises of a series of optical slices extracted from confocal image stacks of two specimens. Each series show how large pore channels connect reacted cement grains (outlined by dotted lines, breaks in lines indicate where channels exist) to capillary pores, at depth in the specimen. Series a - e demonstrate how a large grain exhibits full rectilinear outer-shell morphology at a depth of approximately 0.88 µm below the top of the stack (approximate position of the specimen surface), with no breaks visible in the shell. At a depth of ~ 3.5 µm however, the grain has grown in size and a large section of the outer shell has ‘opened up’ (circled in c)) connecting the grain directly to surrounding capillary pores. Below this the shell reappears and is evidently continuing at deeper levels, but the lower boundary of the grain is not seen. Series f - j show how a grain, which is sectioned through by the specimen surface, connects to a large area of capillary pores at a depth of about 1.3 µm (circled in g)). Below this the grain reduces in size (indicating the lower extents of the grain), and has disappeared by the time the last slice in the stack is reached. Both series a - e and f - j are from specimen 0.6 – 3d. The last series (k - o) are taken from the 0.4 – 28d specimen. The top optical slice (k) is just cutting through the top of a large, partly reacted grain. This grain exhibits ‘large’ connecting channels more than 2 µm across, at approximately 2 – 4 µm of depth (circled in n)). The lower extent of this grain is not seen.

It was noticed that although large connecting channels were evident in both w/c ratio specimens, they mainly occurred in the higher 0.6 w/c specimen and at an early age. Also, these channels linked directly into large areas of capillary pores. In contrast, the image data from figure 4 illustrate pore channels of a very fine morphology, and seem to occur in both specimens at both ages. Figure’s 4 a - d are from specimen 0.4 – 3d, and series e - i are from specimen 0.6 – 28d.
In figure 4, series a - d illustrate a large cement grain that is partly reacted. The grain has a well developed shell of dense inner product C-S-H, and lower density inner product can be observed as shadowy inclusions within the grain. There is also a small area of relic anhydrous material present as a small rounded black area. In a) no visible connection to outer capillary porosity can be observed. However in b), which is approximately 0.4 µm deeper into the specimen, the presence of a very small (< 1 µm) connecting channel has been circled in the top right region of the grain as viewed. Another similar structure can be seen in the lower right area of the grain, but is in fact located entirely within the shell of the grain (marked with an arrow). c) is a magnified image of the region circled in b) and the connection can be clearly observed, but is not forming a complete bridge between the grain and the capillary pores, but in d), the depth is 2.19 µm below the surface and the channel is now complete. At this depth, the fully connected channel measures approximately 1 µm long, by ~ 0.4 µm wide at the narrowest point. Series e - i illustrate identical structures present in specimen 0.6 – 28d. Several connection channels (labelled ‘cc’ on images) can be observed between different grains and capillary pores. The areas concerned are circled in the top image- ‘e’ (where no sign of the deeper channels can be observed). In f), a large capillary pore ‘p’ is located in the centre of the image, with small links to two separate cement grains. The form of this connecting structure is very similar in g), h) and i), again forming links between Hadley grains and capillary pores.

Both forms of channels shown in figures 3 and 4 connect hollow cement grains with capillary pores, facilitating the transportation of fluids and ions. It was felt however, that further proof for the penetrability of hollow grains independent of other structures such as micro-cracks would support this observation. Accordingly, further investigations of the image data were performed. It was soon realised that hollow shell cement grains could be observed below specimen surfaces, due to the semi-transparency of C-S-H and other reaction products. The laser probe has
sufficient power to penetrate several micrometers of overlying material, and to excite fluorescent dye-filled voids lying below. Several grains were identified that were not observed to lie in the vicinity of micro-cracks and/or air voids.

Figure 5 is an image gallery captured from specimen 0.4 – 28d. The first image in the sequence is actually the third in an original sequence, which has been cropped laterally to give a 41 x 41 µm field of view, as well as being cropped horizontally by 0.88 µm from the original surface. The gallery images are labelled sequentially and indicate actual depths below the specimen surface.

![Figure 5. Image gallery from a confocal image stack that has been cropped to a selected region, and shows the presence of hollow shell grains below the surface. A larger grain has been sectioned through at a ‘tip’ (circled in image 1), which can be seen to grow in size through the rest of the image stack, as the focal plane of the microscope is moved deeper below the specimen surface (specimen 0.4 – 28d: FOV ~ 41 x 41 µm).](image)

The images show two different features of the porous microstructure. A large porous region has been circled in image 1, which can be interpreted as a section through a hollow cement grain. In the following images this region is seen to increase in size, indicating that the cement grain was sectioned through at a ‘tip’, as predicted in section 1. This is a demonstration of the limitations imposed by 2D imaging (i.e. BEI) as was pointed out recently by Scrivener [11], where the true nature of 3D objects cannot be observed. The confocal technique however, is able to reveal the grain in three dimensions, which is seen to possess internal anhydrous relics (observed in the second half of the data set).

Other features marked by arrows in figure 5, are small hollow shell grains that only appear well below the specimen surface, and are further evidence of connecting conduits between hollow grains and outer product C-S-H capillary porosity. The arrows mark the first instances on the z-axis where the grains can be identified as autonomous objects and, from the relatively even distribution of arrows across the data set, it can be noted that the grains are appearing regularly at nearly all levels throughout the imaging depth. However some of these may be the tips of larger
grains originally extending below the lower specimen surface but lost when sectioning the specimen, similar to the region marked in figure 5-image 1. In total, eleven grains have been marked in this way.

The following images (Fig. 6) show evidence of a hollow grain apparently underlying a region of dense C-S-H (marked by a white square on Fig. 6 a)). It is possible that this area of C-S-H is actually inner product forming a shell (given the appearance and shape of the feature), which has been sectioned during specimen preparation. Neither the BEI, nor the uppermost confocal image slice of this feature (Fig’s. 6 a) and b)) reveal the presence of porosity within this feature, and are not conjoined by cracks. There is therefore no artificial or damage-formed conduit present, which would have allowed resin to penetrate into the hollow shell fraction of the grain. This implies that resin was able to enter via naturally existing links with external capillary pores.

Another partly reacted grain is present in the centre of the backscattered image (indicated by arrow in Fig. 6 a)). Given the relatively uniform thickness of dense inner product C-S-H surrounding the partly reacted core, it is assumed that this grain has been sectioned in a place that passes through, or close to a centre plane. The inner product C-S-H was measured to be approximately 3 µm thick using the centre of the total-grain region as the centre of gravity for measurement vectors (measurement lines radiating out from a central point here on a 2D plane). When the confocal image stack was subsequently measured in the z-axis, the difference in height from the top of the stack to the approximate appearance of the sub-surface hollow grain was also about 3 µm, supporting the view that a shell had in fact been sectioned in the vicinity of its uppermost extent.
a) BEI of specimen with hollow grain shell (marked by square, see text for description of arrow).

b) Feature cropped from confocal data set (a) showing transition from outer shell C-S-H to hollow grain through 6.58 µm of depth. FOV for each frame = 27 µm.

c) Orthogonal sectioning of image stack (from image slice 11, highlighted in b)). Shows outline of grain below C-S-H layer (see text for annotations).

Figure 6. Image set showing C-S-H region overlying hollow shell grain (specimen 0.4 – 3d).
Figure 6 (b) is a confocal image stack gallery, and shows the transition of the grain from the C-S-H region that intersects the specimen surface (1st image), to the appearance of the hollow grain at approximately 3 µm below the surface (8th image). The grain appears to be rhombohedral in shape. Figure 6 c) demonstrates this feature through use of the microscope’s 3D software where the image stack is observed in ‘orthogonal’ display mode. The cross hairs in the centre of the grain indicate the position of the x and y planes for imaging through the z-axis. The smaller window to the top of the graphic represents an optical cross section parallel to the y-z axial plane of the image stack, and the window to the right illustrates the same aspect for the x-z plane. The main image in the centre of the graphic shows the 11th image in the stack (marked by the bold white frame in Fig. 6 b)) located at a depth of ~ 4.4 µm, and is marked in the y-z and x-z windows as the ‘Z position’.

The position of the z plane can be observed to lie below the upper parts of the grain characterised by formation of inner product C-S-H. In the y-z and x-z windows, the region of C-S-H has been marked. Points A - D indicate the corners of the hollow grain. Line 1 (in the y-z window) represents a plane between points B and C, and line 2 indicates a parallel plane between points A and D. Lines 3 and 4 (in the x-z window) represent planes AB and CD respectively. Interestingly, the C-S-H region seems to be more laterally extensive in the y-z plane, where the grain surfaces (planes 1 & 2) are almost normal to the specimen surface, compared to the x-z plane, where the grain surfaces (planes 3 & 4) are oriented at approximately 45° to the specimen surface. Indeed, plane 3 does not link into the C-S-H region at this point along the x axis. This could provide an explanation for access of resin into and out of the hollow part of the grain, as indicated by the double headed arrows in both the x-z window and the main window.

Products of reaction within the grain and non-reacted parts of original grains are also readily observed with the confocal technique. For example, figure 4 a) presented a Hadley grain displaying patchy inner morphology. Parts of the grain appeared ‘shadowy’, probably indicating areas of C-S-H that had been impregnated with resin to varying degrees. Figure 7 a) below is an enlarged version of the same image region, with an accompanying BEI (Fig. 7 b)). The BEI image shows that a particle of relic anhydrous material is still present as a small bright region ‘a’, and corresponds to the dark ‘spot’ located in the same position on the confocal image. It is highly likely however that not all black areas (of a confocal image) of a similar shape and located within porous regions are grain relics; some are probably air bubbles trapped in the hardened resin and can be recognised by their spherical appearance.

![Image](image.png)

**Figure 7.** Hadley grain with variable inner shell pore structure (FOV = 29.8 x 16.9 µm).

Also observed on the backscattered image (Fig. 7 b)), is an area of porosity marked ‘p’. The porosity is seen to be almost completely enclosing the anhydrous relic and is also located between areas of lower density inner product (IP) C-S-H developed around the interior of the outer shell. The confocal image (Fig. 7 a)) has been marked to show the...
same area of porosity, however, this image was captured at a depth of 2.63 µm below the specimen surface, and is actually optical slice number 7 in the confocal image stack. It is only at this depth that the area of porosity in the confocal image starts to resemble the area of porosity in the BEI. Above this level there is very little porosity evident in the confocal images. The implications for this are that detected electrons are coming from a depth approximately 2 µm below the surface plane, suggesting that softer overlying material (i.e. inner product C-S-H) has been lost from the interior of the grain during final polishing stages. Figure 8 shows the top 10 slices of the set corresponding to a depth of 3.95 µm below the specimen surface. The first 4 images were captured to a depth of 1.32 µm, and show the presence of pores at each depth. If the above conclusion regarding the removal of material is correct, then the images show remnants of resin filled pores that would originally have been located within the polished-out inner product C-S-H.

![Image of confocal stack images](image_url)

**Figure 8.** Sequence of confocal stack images of Hadley grain presented in figure 7, with depth below specimen surface marked.

4. **Conclusions**

1. Three-dimensional imaging of hollow shell cement grains is possible by LSCM. The resin impregnation and imaging of hollow shell cement grains well below the specimen surface, shows that hollow shells are connected to HCP capillary pores by channels supporting molecular transport.

2. As with bulk porosity, the dimensions and connectivity of these channels reduces with reducing w/c and increasing age.

3. 3D confocal imaging has confirmed sectioning of grain tips during specimen surface preparation. These ‘tips’ would normally be categorised as smaller hollow shell grains if only 2D surface imaging was performed.

This work is part of an exploratory study using fluorescent laser scanning confocal microscopy. Future work will aim to improve image clarity at capture and by processing with image filters, develop methods for thresholding 3D structures, investigate the 3D geometry and connectivity of capillary pores, and develop models for quantification of 3D pore connectivity.
References


