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# **Mortar-Diatom Composites**

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ABSTRACT: To address the challenge of appropriate cementitious materials that can support future optical fibre sensors with reduced strains for smart city infrastructure, a series of samples made up of commercial grade instant mortar and increasing percentage of diatomous earth are fabricated and characterised. Hardness properties are measured using Mohs scratch test and portable field durometers, the latter shown to be effective in post-plasticity assessment of these cement composites. Structural colour is introduced by the diatoms and novel characterisation using a smartphone and polymer lens proposed and demonstrated. The implications for  $CO<sub>2</sub>$  trapping and intelligent structural health monitoring (ISHM) for internet-of-things (IoT) in smart city infrastructure are discussed.

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# **1. Introduction**

Smart city infrastructure  $\begin{bmatrix} 1 \end{bmatrix}$  will continue to need cement and cement related materials indefinitely although their environmental impact demands change. Further, whilst optical fibre sensors directly embedded in concrete have yet to take off commercially because of concerns about cost and lifetime in concrete, their potency as extreme sensors demonstrated in 2007 when they were successfully embedded in concrete and subject to temperatures up to 150  $^{\circ}$ C to interrogate and monitor concrete degradation [2] means they remain key elements to enabling genuine smart city infrastructure. The construction industry consumed nearly 4.1 Gt of cement in 2019 [3], a figure expected to rise to 5.8 Gt in 2027 [4], despite having slowed by the Covid-19 pandemic. At face value this appears to be a highly intractable problem and a substantive environmental challenge that originates largely in the manufacture of cement through heating of limestone with other materials. The resulting chemical reactions produce significant CO<sub>2</sub> emissions adding to that produced by the very high temperature kilns that process cement. Interestingly the products involved with generating  $CO<sub>2</sub>$  through calcination are unstable over time meaning that CO<sup>2</sup> recapture, through carbonation, is possible. This recapture has recently been estimated to be as high as 43% of total  $CO_2$  emission between 1930 and 2013 [5]. Unfortunately, the lengthy recapture time scales over decades means this is not usually considered in sustainable climate change goals [6]. These scales are long because the interaction with air is determined by surface area coverage, diffusion and access. It is no coincidence that mortar, which only uses  $\sim$  30% of the world's cement over that period, has captured 60% of the total  $CO<sub>2</sub>$  estimated across the board over this period  $[5]$ . Mortar is used as a filling element with high exposure to air in contrast to most applications of thicker layers of pure concrete where the volume to surface area is estimated to be significantly lower. Another neglected factor is relevant: due to faster setting times and approximate mixture components, mortar is typically less dense and more porous than cement which, through higher diffusivity rates, also accounts for reduced strength or hardness and higher carbon capture rate capacity. By optimising diffusivity whilst retaining suitable properties, there is a prospect that highly energy intensive cementitious materials can act as carbon capture elements in their own right to meet the sought after  $0.8\%$  annual decline in  $CO<sub>2</sub>$  emission

by 2030 [3]. Current approaches involve either reductions of the cement used by using supplementary materials such as waste glass, or creating porous concrete to adsorb  $CO<sub>2</sub>$  [3,7]. The latter uses relatively complex, and perhaps questionable from an energy and cost perspective, processes such as direct carbonation with coal powered station-generated  $CO<sub>2</sub>$  and calcium hydroxide mix that hardens with  $CO<sub>2</sub>$ to create a novel concrete <sup>[7]</sup>. Alternatively, we suggest the addition of porous glassy media in this respect to not only displace the amount of cement product but enhance direct loading in a controlled way. To this end, using safe amorphous diatoms, either low-cost diatomous earth which is readily available or their increasingly popular alternative obtained by direct algae breeding  $[8]$ , is considered – their uniformity coupled with small size gives added, unique benefits. For example, the expected improvement in structural homogeneity will be important for streamlining and controlling carbon capture rates. Perhaps more important, improvements in homogeneity lead to uniform strain loads critical for effective longterm embedding of optical fibres and sensors needed to ensure the future of smart buildings where sensors – these technologies have been developed for 20+ lifetimes in the telecommunications sector but have yet to integrate directly into smart buildings primarily because current sensor approaches rely on external adhesives neither pragmatic nor aesthetically satisfying. We have previously described the utilization of diatoms in 3D printing ceramics for sensor applications  $[9]$ . Given that these smart systems will form the edge backbone of massively scaled smart city IoT infrastructure network, their integration into cement and mortars critically depends on improved cementitious materials.

This work describes the addition of high quality, micron-sized silica diatomous earth to dilute the cement mix within pre-prepared mortars commercially available for domestic and commercial spot use in Australia. In the spirit of in-the-field deployment of cement and mortar and the rising need for more crossdisciplinary expertise within the construction and real estate sectors more generally  $[10]$ , much of the work here is conducted outside the laboratory and assessed using low cost diagnostic tools. This also serves the purpose of demonstrating the potential for basic research combined with practical diagnostics into the field, including potentially on building sites where eventual deployment and routine maintenance of advanced, or smart, mortar and cement supported sensing networks that underpin the internet-of-things (IoT) within so-called smart cities needs to also consider integration with pragmatic maintenance and diagnostic capabilities.

#### **2. Sample Materials**

**Table 1** shows the composition of the commercial fast-setting mortar mix (Dingo Australia, Fast Set Mortar  $[11]$ ) which only requires water and is suitable for gaps, paving retaining walls, garden beds, BBQs, letterboxes and more. This flexibility and ease of use also makes it an interesting material to explore as potential component package material, with suitable adjustment, for in-fibre optical gratings, one-dimensional photonic bandgaps with either short or long period, within concrete infrastructure, for example. It is made primarily of crystalline silica, Portland cement and calcium hydroxide. The presence of crystalline silica probably helps reduce the percentage of cement but given the variations in the preparation it is far from optimized to begin with and not used for this purpose.

Component	<b>CAS No</b>	TWA (mg/m <sup>3</sup> )	
Portland cement	65997-15-1	10-30	10
Silica (Crystalline)	14808-60-7	>60	0.1
Calcium hydroxide	1305-62-0	10-30	5
non-hazardous Other ingredients	Secret	To 100	

**Table 1**. Composition of commercial prepared, fast-setting mortar (Supplier: Dingo Australia [11]). Some ambiguity around the exact composition keeps the exact formulation secret but in general it is unlikely to be optimized in terms of silica content. The added component studied in this work is diatomous earth (or diatomite) refined and sterilised for dietary ingestion  $([12])$  so is safe for handling and does not have the lung implications of crystalline sililca. Nevertheless, their small size warrants that a mask should be worn. As chemically grown silica, diatoms possess features that make them unique and much more interesting than conventional crushed glass used to strengthen cement  $[13]$ . More broadly, diatoms are the exoskeletons of organisms such as algae, amoebas, euglena, plasmodium, and slime molds – in diatomous earth form they are the fossilized

remains leaving behind silica and to a less extend other materials. In their living state diatoms play important ecological roles on a global scale including  $CO<sub>2</sub>$  capture - they are responsible for 20% of global natural carbon capture and 40% of marine primary productivity, making them overall an important CO<sup>2</sup> trap for the environment. For this reason alone, their introduction into cements can potentially lower the construction sector's carbon footprint – given recent studies pointing towards cements natural if slow trapping properties, we propose diatoms will play a critical role primarily through an increased rate of uptake as well as volume, reducing the timescale of cement  $CO<sub>2</sub>$  adsorption to much shorter periods. Diatomous earth is readily available but as an organically derived exoskeleton, instead of direct mining they can one day also be grown and scaled on algae farms  $\binom{8}{3}$ , further reducing climate impact. An advantage of such farming is the potential for precision selectivity in shape and size distribution ensuring both ultra-high quality for advanced functions and continuity of future supply.

**Figure 1** shows an SEM image of the typical fossilized freshwater cylindrical diatom within the sample used in this work. It is a cylinder composed of two parts and is hollow on the inside. These parts have sub-micron pores above and below the central region where one fits over the other – from the image the measured dimensions show a diameter  $\phi \sim 10 \,\mu m$  and length  $L \sim 25 \,\mu m$  with an overall periodic ( $\Lambda \sim 1 \,\mu m$ ) hole structure of sub-micron diameter ( $\phi \sim 0.85$  µm), all encasing a hollow interior. Whilst there is some variation, the overall periodicity and dimensions suggest diffractive optical effects should be present, accounting for the iridescence observed previously in diatom-ceramic mixes  $[9]$ . Consequently, this hollow interior along with silica's affinity with water, means additional water is usually needed when preparing the mortar mix. In the figure many of the diatoms are visibly crushed, so the amount increased is not as much as might otherwise be. This contributes to the reported size distribution.



**Figure 1.** Scanning electron microscope (SEM) image of a typical freshwater radial centered diatom, a silicate cylinder with dimeter  $\phi \sim$ 10 µm and length  $L \sim 25$  µm. The periodic hole structure is sub-micron approximately on average  $\phi \sim 0.85$  µm and the period on the order of  $\Lambda \sim 1$  µm. The corresponding duty cycle varies but is a little less than <100% in most places and the interior is hollow. The centre region shows where the two halves of the diatom meet.

Component	<b>Percentage/Concentration</b>			
Silica (SiO2)	$\sim$ 85 % for superfine			
Calcium (Ca)	1.00%			
Magnesium (Mg)	0.60%			
Manganese (Mn)	0.50%			
Phosphorus (P)	0.01%			
Potassium (K)	0.20%			
Iron (Fe)	4.00%			
Cobalt (Co)	5 mg/kg			
Molybdenum (Mo)	5 mg/kg			
Sulphur (S)	$42 \,\mathrm{mg/kg}$			
Zinc(Zn)	$42$ mg/kg			

**Table 2**. Approximate composition of diatomous earth used in this work [12].

The diatomous earth used in this work is human food grade, providing very high-quality silica distributions and purities for little cost and do so with low energy consumption. The average size of most of the diatoms is  $\phi \sim 20$  µm, with a spread over  $\phi \sim 10$  to 200 µm - overall this remains considerably smaller than the coarser cement clinkers. In the present mortar the clinkers on the scale of mm. The grey/white diatomite powder used in this work feels like talc. Its main constituent is amorphous silica

freshwater diatoms ( $\sim 85\%$ ), much of which is soluble having a strong affinity for water and removing the surface reactivity that makes crystalline silica hazardous. It also has other components including substantive iron and calcium and a range of trace elements assumed beneficial for human health, summarised in **Table 2**.

Diatomous earth can, therefore, replace a substantial part of the silica crystalline component of cement or, alternatively, be an added ingredient to reduce the total amount of cement used in a range of products. Despite this potential, diatomous earth is not currently accepted for use in Australia and New Zealand and not covered in Australian Standards AS 3852.3 for added silica to cement  $[14,15]$ , although it is recognized specifically in American standard ASTM C618 [16]. This is surprising because, in addition to environmental benefits, diatomous earth of very fine quality of micron scale is readily available and relatively low cost.

# **3. Sample Fabrication, Characterisation and Analysis**

Focusing on small quantities of mortar prepared in the field for repairs or component device packaging, the *mortar* is set inside fold-assembled cardboard trays with small volumes  $\sim$  (5 x 7 x1) cm<sup>3</sup> (Figure 2). For ease of implementation, the amount of material used is measured in a metric plastic volumetric cylinder to be  $V \sim 30$  mL with about  $V \sim 7.5$  mL of added water. This smaller material volume tends to lead to faster drying (when the lowest moisture level reached was measured  $\sim 0.6\%$ ) – longer drying was qualitatively observed with increasing diatom concentration, consistent with water entering the diatoms interior. All the samples show reduced volumes relative to their starting volume, with reductions ranging from  $\sim$  15% for mortar only, signaling settling to a more packed state through reaction, to  $>50\%$  at the highest diatom quantities attributed to packing densities as they fill mortar free volume (summarised in Table 3). As well, the adsorption of water meant that the increasing addition of diatoms required additional water ( $> 25\%$ ) in the mix to ensure sufficient viscosity for flow in the tray comparable to the first sample without diatoms. This viscosity is described in terms of cement plasticity, differing in relation to final hardness when set – for example, Portland cement often requires additional water beyond that required for reaction to ensure flow and shaping of the cement in construction phases, whether building, architectural or sculpturing. Unfortunately, the addition of excess water produces a more porous structure that can threaten its hardness or integrity so efforts to improve plasticity by adding dopants, including organic [17], are a topic of research. Although mortar mixes are generally softer than Portland cement alone, the addition of diatoms also required an increase in water to retain some flow within the trays. However, since the water is retained within the diatoms, it is not expected to play a significant role in reducing hardness or increasing porosity. In any case that would be countered by a general decrease in volume arising from the smaller size and increased homogeneity. This novel feature could potentially be applied to other cement fillers for improving plasticity. Notably, the increase in water suggests that despite the presence of crushed diatoms and increased density, the silica material retains significant porosity and water affinity. **Table 3** summarises these measurements.



**Figure 2**: Six samples were produced in a controlled way within (a) a small origami cardboard package of dimensions  $x, y, z =$ 5, 7, 2 cm respectively; (b) shows the samples (b) prior to and after (c) 7 days to allow full drying. Sample 1 is with no diatom and the red clinker distribution contributes the apparent brown of the image. Addition of diatom made the samples greyer when wet and whiter when dry. Those with the highest diatom content took longest to dry corresponding with the notably larger change in colour, consistent with the additional stored water within the hollow diatoms. The images were taken with a Samsung Galaxy S10 smartphone camera.

**Figure 2 Sample 1** shows the set mortar (100 %) demonstrating some of its characteristics. Cracking around the edges is consistent with rapid drying and contraction of a heterogeneous sample within a small volume, a problem that is often observed in small domestic jobs as a gap filler, depending on the water added for a given volume of material and the drying time. Superficially, all the samples with diatom added to them subsequently showed an immediate improvement in this respect. These images before and after drying are all taken under identical lighting conditions and settings on a Samsung Galaxy S10 smartphone camera and subsequently sent to computer where the images are identically edited on Adobe photoshop. What is noticeable is the drying times – these increase substantially with added diatoms and can be seen in a distinct lightness change. Sample 6 for example, goes from deep grey to grey white, characteristic of Rayleigh scattering off the diatoms. Confirmation of dryness is confirmed after seven days using a conductivity meter. This time delay reflects the reduced pore sizes relative to cement only sample 1, silica affinity to water both van der Waals forces  $[18]$  and defect state attraction, and the outdiffusion of water from within whole diatoms through the  $85$  or so  $\mu$ m pores. With the exception of the SEM measurements, various parameters were measured using a range of field-portable equipment shown in **Figure 3**. All parameters and measurements are summarised in **Table 3**.



**Figure 3:** Being able to undertake diagnostic measurements in the field is important for future smart material assessments. The field kit includes: (a) USB high magnification microscope (x1000); (b) customised polymer lens to be placed on the smartphone for structural colour studies (Smartphone being used to take this image); (c) Shore C & D durometers; (d) Moh's Hardness Pick set; (e) thickness measurement gauge; (f) conductivity meter and (g) Portable carry box.

#	<b>Mortar</b> (mL)	<b>Diatom</b> (mL)	% ratio	<b>Water</b> (mL)	<b>Mohs</b> test	Shore D <b>Hardness</b>	Shore C <b>Hardness</b>	Layer thickness, $t$ (mm)	$Vol_{av}$ (cm <sup>3</sup> )	<b>Moisture level</b> (after drying) (%)
$\mathbf{1}$	30	$\mathbf 0$	100:0	7.5	$3 - 5$	$35 \pm 5$	$\overline{\phantom{a}}$	$8.5 - 6.0$	$25 \pm 4$	$0.6 \pm 0.2$
$\overline{2}$	25	5	82.5:17.5	10	$4 - 5$	$43 \pm 5$	$\overline{\phantom{a}}$	$7.5 - 6.0$	$24 \pm 3$	$0.6 \pm 0.2$
$\overline{3}$	22.5	7.5	75:25	10	$2 - 4$	$50 \pm 5$	$\overline{\phantom{a}}$	$7.5 - 5.5$	$23 \pm 4$	$0.6 \pm 0.2$
$\overline{4}$	20	10	66:34	10	$\leq$ 2	$40 \pm 5$	$\overline{\phantom{a}}$	$7.0 - 5.5$	$21 \pm 4$	$0.6 \pm 0.2$
5	15	15	50:50	10	$2$	$37 \pm 5$	$\overline{\phantom{a}}$	$6.0 - 3.5$	$17 \pm 4$	$0.6 \pm 0.2$
6	10	20	34:66	12	$\langle$ 2	$\overline{\phantom{a}}$	$20 \pm 2$	$5.5 - 3.5$	$16 \pm 4$	$0.6 \pm 0.2$

**Table 3**. A summary of the six prepared samples. Relative volumes of mortar, diatomous earth and water are shown. Mohs scratch test is measured at multiple points and an average with error estimated. The Shore hardness  $D \& C$  is also measured multiple times across each sample and an average with error recorded. Layer height and estimated volume are also similarly estimated. Given the potential for water retention, the moisture level is determined from conductance measurements to ensure all samples are dry. All measurements were conducted in the field using portable instruments.

To examine the sample surfaces more closely, optical micrographs were taken, using a field portable, usb powered microscope (x100 magnification). **Figure 3** summarises all the field-portable equipment used in this work. The optical images are shown in **Figure 4**. The optical illumination was from white light emitting diodes (LEDs) in a ring surrounding the imaging lens and striking to the sample from above. The starting cement exhibits a slight brownish colour with red spots consistent with its iron and copper oxide content. These are diluted with diatom additions and the samples with higher diatom concentrations tend to become whiter after drying, consistent with broader band, Rayleigh scattering of the surface of smaller features. Some of the samples when examined closely under microscopy show weak iridescence as the period internal structure of the diatoms scatters light incident at a particular angle. There is a change in surface features as the mortar component reduces and the diatom component increases. In addition to visual changes, the diatoms level the surfaces reducing local roughness by filling in gaps and effectively acting like a levelling medium because of their much smaller and uniform size relative to the cement. This leads to a decreased volume, measured by a drop in sample height upon drying and superficially the samples with the highest diatom concentrations show the smoothest surfaces. The measurements of height, across the dried samples to consider variations in preparation, and calculated reductions in volume are recorded in **Table 3**.



Figure 4: Optical microscope images of the six samples. The images were taken in the field with a portable microscope (x 100). The scale bar is 1 mm. What is observed is the reduced mix of cement as the diatom reduces and the diatom content, mainly the white, increases.



**Figure 5.** Combined plots of geological scratch hardness test (Moh's hardness) and mechanical durometer indentation test (Shore Hardness) against the relative percentage of diatom by volume (V).

#### *3.1 Mortar Hardness*

The effect on properties by adding diatoms to the mortar was assessed in several ways. Simply adding the diatoms creates a volume decrease, measured through a decreased sample thickness in the trays and explained by the higher packing density possible with the smaller-sized diatoms - these fill the gaps between the coarser clinker material. What is the impact on a key property such as plasticity and hardness, crucial for assessing the potential usefulness of this composite mix as a mortar replacement? In keeping with in-the-field diagnostics, the standard geological Moh's scratch test was carried out along with an equivalent indentation test using Shore C and D durometers to assess hardness. Shore durometers are not typically used for measuring cement as they are usually not considered plastic and may be expected to be highly heterogenous across a cement sample. From the data in **Figure 5**, a trend is observed: for the first two samples,  $(1 \& 2)$ , the scratch tests on their own indicate little if any difference within error by adding  $\sim$  17% diatoms – there appears to be a slight increase. This quantity of diatoms is a relatively substantial amount having displayed a similar amount of mortar, which can be translated into a likewise similar net  $CO<sub>2</sub>$  reduction required at the point of manufacture. As expected, the mortar itself, between 4 and 5, is approaching the gemstone apatite in aridness, below that of quartz silica (Moh's hardness 7). At higher diatom percentages, consistent with increased softening, the scratch hardness starts to reduce significantly more and above 30% the value falls at or below that of gypsum. Given there should be an upper limit to additional binding with the diatoms, the scratch measure should reduce as the composite softens and overall chemical binding reduces. The possible initial rise at lower concentrations suggests natural mortar is slightly plastic because of the porous heterogeneity and filling this with diatoms increases the composite hardness. For comparison, there is an increase in average hardness between these samples when measured by indentation with the Shore durometers. By measuring the resistance to penetration by a tip, Shore values typically reflect the elastic modulus of the composite system – whilst the pure cement value might be expected to be highest, in fact the samples with diatom volumes up to 50 % all appear to be have higher values, notwithstanding some uncertainty due to error. This is similarly explained by the increased density associated with a decreased volume as the diatoms primarily fill in the gaps of the cement mix, removing

compressibility of the heterogenous cement. At higher percentages (notably measured with a Shore C durometer), the values drop off as may be expected. Qualitatively there are some similarities between the two tests but the differences are significant. This is most readily accounted for by noting that the overall hardness translates to increased brittleness when there is a finite additional chemical bonding possible and consequently running along the surface is likely to be more sensitive to this bonding than the indentation. A further detailed study at lower volume percentages can help illuminate optimal parameters.

Fine tuning quantities can therefore be used with some precision to adjust the stiffness, or hardness, of the mix as required. Whilst, alternatively, this can be rephrased as composite plasticity, a degree of brittleness also appears to increase with the addition of diatoms - this is evidenced by fine line cracking when mishandling the samples containing higher concentrations of added diatoms. In particular, sample (6) was not able to be measured using a Shore D durometer, cracking into small pieces with immediate contact and could not be taken out of its tray readily. With a volume percentage as high as 66%, the sample is noticeably softer but not powdery and varies drastically to the other samples, enough that an indentation measurement could only work with a rounder press from a Shore C Durometer typically otherwise used for soft rubbers. This illustrated how dramatic a change in hardness is possible.

# *3.2 Structural Colour*

Given the finer, periodic micro and sub-microscopic structure of the diatoms themselves, the possibility of structural colour arising from Bragg scattering was considered. In addition to the observation in ceramic mixes [9], such colour has been reported directly for diatoms and it is highly likely a functional property that scatters UV light, perhaps filtered out to protect organic components, as well as scatter and diffract visible light presumably to optimize photosynthesis  $[19-21]$ . Sample 6, made up of 60% diatoms by volume, would be expected to show some. It was not observed in the portable microscope images in part because of averaging of the illuminating light from all sides where significant Rayleigh scattering occurs, makes the dried samples overwhelmingly white. To explore this further a simple imaging equivalent instrument using a smartphone (Samsung Galaxy S10) camera and lens was used to examine sample 6. Enhanced imaging was obtained using a small (diameter  $\phi = 5$  mm) polymer hemispherical macro lenses (x10) with long focal length  $(L_f = 20 \text{ mm})$  placed over the camera lens. This did not overlap the white light flash LED which was to one side – **Figure 4 (a)** shows a schematic of the setup. Whilst the magnification is comparatively poor, the point of difference with the portable field microscope is the source of illumination. At the relatively long focal plane, the sample is being illuminated from the edge of the white light source at a similar distance away as the focal length, so can be approximated as a beam of light in the first instance. With triangulation the angle of incidence is  $\theta \sim 45^{\circ}$  to the orthogonal. From the SEM images, the approximate period of the holes ( $\phi \sim 0.85$  µm) in the centre of each diatom valve is on the order of  $\Lambda \sim 1$  µm. This condition should allow some visible observation of colour dispersion from the periodic structure within the diatoms mitigated in part but not completely by their random orientation. To reasonable approximation the received light at the detector can be considered a one-dimensional scattering problem describing an effective 1D Bragg grating scattering light from the transmitters in the plane of alignment. The white Rayleigh scattering from the diatoms compared to the relatively weak colour observed, is indicative of a largely surface effect. This then translates to a direct inference that spectral variations largely arise from tilt of the sample surface relative to the incident normal used as a reference point (in this case as measured with green). To improve quantification and spectral resolution, a more thorough analysis via 2D and even 3D scattering of the structure can be undertaken but this presently would limit in-the field analysis. Thus, for the first order Bragg equation ( $n\lambda = 2\Lambda\sin\theta$ ) to be satisfied, and assuming the light incident on the camera is orthogonal, then the collected light is from an average tilt of the diatom grating structure where  $\theta = 45/2 = 22.5^{\circ}$ . The approximate effective index can be assumed to be  $n_{\text{eff}} = (n_{\text{SiO2}} + n_{\text{air}})/2 \sim 1.23$  (where  $n_{\text{SiO2}} \sim 1.45$ , treating the diatom silica as conventional silica glass). An estimated wavelength reaching the camera is therefore  $\lambda \sim 560$  nm, agreeing with the green that is generally observed in **Figure 4(b).** When the colour detected by the smartphone camera is enhanced, and zooming, other colours are observed (inset) – these are consistent with different local tilts providing a novel approach to potentially estimating the degree of surface flatness, or roughness, of the sample (mapping tilt could potentially offer a novel figure of merit for roughness). For a blue wavelength of  $\lambda \sim 450$  nm the tilt relative to the green is calculated to be  $\Delta \theta \sim -4.7^{\circ}$  whilst for a red wavelength of  $\lambda$ ~ 650 nm it is  $\Delta\theta$  ~ +3.5°, where the sign indicates a relative tilt away from the normal in Figure 4 (i.e. for the blue to reach the detector, the local surface tilt must be leaning away from the incoming source relative to the green incidence whereas the red must be leaning towards). Whilst much more precise measurements are feasible in a better controlled laboratory setting, these results demonstrate the potential of portable smartphone field instrumentation for sophisticated diagnosis of niche materials, including a potentially novel approach to measuring surface roughness.



**Figure 4.** The offset white LED of a smartphone (a) offers a simple approach to undertake off-incidence illumination of a sample. The sample is imaged through a customised polymer hemispherical lens placed over the existing camera lens to both selectively collect light at approximately normal incidence and increase magnification. Using this approach reveals structural colour, largely a green iridescence, from Sample 6. The inset images show a zoomed section of an apparently highly flat region together with enhancement, revealing a patchwork of other colours that mirror the surface deflection tilt relative to the incident light. This kaleidoscope betrays the underlying surface roughness or variability.

#### **3. Discussion**

From an applications perspective, the selected volume of diatoms is heavily dependent on the nature of applied loads and intended application – for example, packaging of components may preferably lean towards higher diatom concentrations to improve homogeneity whereas structural considerations may require lower concentrations that improve hardness. For sensing, this depends on the necessary transduction or coupling efficiency required. In the case of temperature measurements, decoupling of optical fibre strain suggested the softness obtained at higher diatom concentrations are preferable whilst for strain measurements, lower concentrations are needed to maximize coupling of surrounding strain. The integration of optical fibres in walls and in mortar requires consideration, through routine diagnostics, about these strains because any heterogeneity in principle can restrict bare fibre implementation as sensors since over time these will be points at which breaking occur. In this situation the traditional surface scratch test is less relevant than the use of Shore durometer – importantly, Shore meters can also be applied in the field with spot mortar preparation and drying but also routine diagnostics. Porous mortar, or indeed cements, made with diatoms will breathe and potentially remove humidity, offering a simple way to monitor humidity through changes in mechanical properties. Any changes in this breathability can provide information on degradation or indeed changes in the environment, a new approach to smart cement buildings. The value of Shore and other field portable measurements for routine diagnostics will therefore increase as the move towards smarter intelligent buildings and infrastructure increases.

The use of structural colour also leads to exciting possibilities and requires application-specific considerations. In decorative areas, for example, higher concentrations of select diatoms may instead be more important to maximise aesthetic iridescence but as well the ability to add colorants could see potential in an alternative gemstone space. Interestingly, any changes in structural colour at a given angle can in principle be utilised as a novel sensing surface – for example, the detection of mortar or cement swelling over time with water ingress can be monitored as a colour and intensity shift because the refractive index of water changes both the effective diatom period and fringe contrast. In this work we also proposed a novel surface mapping tool that can gauge roughness by angular colour scattering (this could be in the near IR if discretion is required for the purposes of monitoring degradation over time). Amongst various applications, potentially, by controlling the type of diatom, this could also be translated into a form of optical signature for construction tracking purposes. As well as humidity monitoring, chemical detection or release,  $CO<sub>2</sub>$  capture and other gas capture or sensing may also be optimized and monitored using these approaches. Further, this sub-micron and micron porosity along with diatom water affinity may reduce surface virility when droplets strike the surface by drying them out. This forms a basis for working smarter buildings better optimized and maintained with integrated structural health monitoring (ISHM). This approach potentially provides future opportunities such as the further integration of anti-virals to reduce fomite lifetimes on surfaces so that future construction technology is not only smarter but healthier  $[10]$ .

#### **4. Conclusions**

The role of diatoms as a valuable co-dopant in mortar has been explored. Overall, the properties of the combined mixed systems are highly tunable and hardness can be both increased or decreased depending on concentrations. Shore measurements have been shown to work well in characterizing properties in the field. Along with simple microscopy methods, the potential for packaging cables, optical fibres, components and devices along with routine diagnostics in future IoT cities depends on key building materials becoming smarter and more tunable in properties. Here, the focus on mortar-diatom composites has shown that this both plausible and pragmatic. In addition, a new tool that exploits structural properties of diatoms that give rise to iridescence has been demonstrated – as an optical probe it has considerable potential in characterizing structurally periodic materials not only for physical properties but chemical, particularly through changes in signal attenuation and refractive index in porous systems that impact spectral dependence of angular diffraction. Confining the analysis to one dimension has produced reasonable agreement with experiment and simultaneously permitted a simple implementation in the field. This material tunability through the addition of a porous silica structure with strong affinity for water and gas loading, inevitably impacts the potential of these materials as  $CO<sub>2</sub>$  traps and chemical agent hosts that may benefit living conditions for future generations. Importantly, we establish a reasonable basis for portable measurements and assessment outside the laboratory in assessing the fabricated materials, consistent with a growing need for customization and routine diagnostics as new technologies demonstrate the potential to modernize the construction and real estate sectors that plan to underpin smart cities. Overall, this forms a basis for working, intelligent buildings and other infrastructure better optimized and maintained with true integrated structural health monitoring (ISHM).

# **Acknowledgements**

This work was supported by private funding. The coronavirus pandemic is gratefully acknowledged for providing time off on weekends to undertake the field work reported here.

#### **References**

- [1] <https://cities-today.com/industry/smart-concrete-bridges-highways-public-infrastructure/>
- [2] J.C. Cardozo da Silva, C. Martelli, H.J. Kalinowski, E. Penner, J. Canning, N. Groothoff, "Dynamic analysis and temperature measurements of concrete cantilever beam using fibre Bragg gratings", Opt. & Las. in Eng., **45** (1), 88-92 (2007).
- [3] Cement, International Energy Association IEA, (2020)<https://www.iea.org/reports/cement>
- [4] Global Cement Industry, Reportlinker, New York (2020) [https://www.globenewswire.com/news](https://www.globenewswire.com/news-release/2020/07/08/2059633/0/en/Global-Cement-Industry.html)[release/2020/07/08/2059633/0/en/Global-Cement-Industry.html](https://www.globenewswire.com/news-release/2020/07/08/2059633/0/en/Global-Cement-Industry.html)
- [5] F. Xi, S. J. Davis, P. Ciais, D. Crawford-Brown, D. Guan, C. Pade, T. Shi, M. Syddal, J. Lv, L. ji, L. Bing, J. Wang, W. Wei, K-H. Yang, B. Lagerblad, I. Galan, C. Andrade, Y. Zhang, Z. Liu, "Substantial global carbon uptake by cement carbonation", Nature Geoscience, **9** 880-883, (2016)
- [6] <https://www.un.org/sustainabledevelopment/climate-change/>
- [7] M. Galluci, "Capture carbon in concrete made with CO<sub>2</sub>" IEEE Spectrum, (Feb 2020)
- [8] J. Quinn, L. de Winter, T. Bradley, "Microalgae bulk growth model with application to industrial scale systems", Bioresource Technology, **102** (8), 5083-5092, (2011).
- [9] T. Saxod, M. Combrouse, K. Cook, J. Canning, "Low cost 3D-printing of budget glassy ceramic/polymer composites for contech sensor host applications", 8<sup>th</sup> Asia Pacific Opt. Sensors Conf. (APOS 2019), Auckland, New Zealand (2019).
- [10] J. Canning, "Livability in a time of Corona: the need for intelligent buildings and real estate", Pulse Jun (2020), [https://www.linkedin.com/pulse/livability-time-corona-need-intelligent-buildings-real](https://www.linkedin.com/pulse/livability-time-corona-need-intelligent-buildings-real-john-canning/)[john-canning/](https://www.linkedin.com/pulse/livability-time-corona-need-intelligent-buildings-real-john-canning/)
- [11[\]https://dingocement.com.au/product/fast-set-mortar/](https://dingocement.com.au/product/fast-set-mortar/)
- [12[\]https://diatomaceousearth.net.au/buying-diatomaceous-earth-in-australia/](https://diatomaceousearth.net.au/buying-diatomaceous-earth-in-australia/)
- [13] B. Lothenbach, K. Scrivener, R.D. Hooton, "Supplementary cementitious materials", Cement and Concrete, **41**, 1244-1256, (2011)
- [14] "Amorphous Silica: Properties, characterisation and uses", Cement Concretes & Aggregates Australia (CCAA) [https://www.ccaa.com.au/imis\\_prod/documents/TECH\\_NOTE\\_79\\_-](https://www.ccaa.com.au/imis_prod/documents/TECH_NOTE_79_-_Amorphous_Silica.pdf) [\\_Amorphous\\_Silica.pdf](https://www.ccaa.com.au/imis_prod/documents/TECH_NOTE_79_-_Amorphous_Silica.pdf)
- [15] Standards Australia, Australian Standard 3582.3 (2002), "Supplementary cementitious materials for use with Portland and blended cement, Part 3: Amorphous silica", SAI Global, ISBN 0 7337 4929 1
- [16]ASTM C 618 (2017), "Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete", ASTM International, West Conshohocken, PA United States, [www.astm.org](http://www.astm.org/)
- [17]P. J. Sandberg and F. Doncaster, "On the mechanism of strength enhancement of cement paste and mortar with tri-isopropanolamine," Cement & Concrete Res., **34** (6), 973–976, (2004).
- [18] J. Canning, H. Weil, M. Naqshbandi, K. Cook, and M. Lancry, "Laser tailoring surface interactions, contact angles, drop topologies and the self-assembly of optical microwires", Opt. Mat. Express, **3** (2), 284-294, (2013).
- [19]T. Fuhrmann, S. Landwehr, M. El. Rharbi-Kucki, M. Sumper, "Diatoms as living photonic crystals. Appl. Phys. B. Lasers Opt. **78**, 257–260, (2004).
- [20] M. Ellegaard, T. Lenau, N. Lundholm, C. Maibohm, S. Michael, M. Friis, K. Rottwitt, Y. Su, "The fascinating diatom frustule – can it play a role for attenuation of UV radiation?", J. Appl. Phycol. **28**, 3295–3306, (2016)
- [21]J. W. Goessling, S. Frankenbach, L. Ribeiro, J. Serôdio, M. Kühl. "Modulation of the light field related to valve optical properties of raphid diatoms: Implications for niche differentiation in the microphytobenthos." Marine Ecology Prog. Ser. **588,** 29-42 (2017).