

Natural fibre-enhanced CO₂ transport and uptake in cement pastes subjected to enforced carbonation

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ABSTRACT

Mineral carbonation is an effective CO₂ sequestration approach and can be applied to cement-based materials through enforced carbonation curing. To accelerate this process, this study investigated the use of natural fibres (hemp, jute, cotton, and wool) to enhance CO₂ transport in cement composites. Spun fibre yarns were added to cement pastes and subjected to enforced carbonation (20 vol% CO₂) at 25 °C and 1 atm for 24–168 hours. Carbonation profiles were evaluated using two methods: phenolphthalein indicator coupled with image analysis, and thermogravimetric analysis (TGA). A novel image analysis method, based on colour deconvolution of phenolphthalein-stained images, was developed. Results from this method were consistent with those from TGA, offering a reliable and rapid technique for quantitatively assessing carbonation profiles of cement-based materials. The results confirmed that the natural fibre yarns created preferential CO₂ transport pathways to facilitate CO₂ uptake. Hemp yarns led to the most significant acceleration of CO₂ transport, with carbonation fronts reaching 50 mm depths within 24 hours. Samples without fibres only showed superficial carbonation at the exposure surface. The findings of this study indicate the feasibility of using natural fibres to improve CO₂ sequestration in cement-based materials.

1. Introduction

Despite the low embodied energy and carbon footprint of concrete, its enormous application volume results in significant emissions. The International Energy Agency [1] reports that the cement industry accounts for approximately 7 % of global CO₂ emissions. To mitigate these emissions, CO₂ mineralisation of cement-based materials has emerged as a promising carbon capture, utilisation, and storage (CCUS) approach, attracting substantial attention in recent years. Mineral carbonation offers the potential to sequester a considerable fraction of emissions associated with cementitious materials, which has a permanent CO₂ uptake potential of up to 1.46 Gt per year [2–4].

Forced carbonation curing can artificially accelerate this natural process, positioning cement-based materials as significant global CO₂ sequestration sources [5,6]. Various approaches to mineral carbonation have been explored [7], such as treatment of recycled aggregates [8–11], wet-mixed cement composites [12–14], and carbonation of fresh and hardened cement-based materials [5,14,15]. Carbonation curing of concrete products is predominantly conducted by exposing

early-age samples to concentrated CO₂ gas in sealed or pressurized chambers [14,16]. For porous materials like cement paste, the carbonation process is initiated by gaseous diffusion of CO₂ through its porosity and dissolution in the pore solution. The dissolved CO₂ in pore solution subsequently reacts with aqueous calcium, destabilising hydrate phases and precipitating calcium carbonate and a silica-rich phase [17]. This precipitation of calcium carbonates gradually accumulates within the pores, ultimately restricting further CO₂ diffusion deeper into the material, while the moisture released during carbonation increases pore saturation, further impeding gaseous transport [18,19]. The efficiency of CO₂ diffusion during the curing process is governed by several factors, including the curing regime (CO₂ concentration, gas pressure, temperature, and humidity), the porosity, and mix design of the material [5,20,21]. While higher CO₂ concentrations and chamber pressures increase carbonation degree and rate [16], the associated energy-intensive separation and purification of CO₂ gas partly counteracts the emissions-reducing goal of carbonation curing, and increases cost [22]. Consequently, ambient pressure and temperature conditions are preferred to simplify the process and manufacturing costs. Flue gas

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carbonation, utilising CO₂ concentrations in such streams (approximately 20 vol%), has been demonstrated as a feasible approach [23,24]. However, under such conditions, CO₂ uptake in precast cement-based products is limited, and extended curing times (around two weeks) were argued as necessary for commercial concrete blocks [25]. The CO₂ uptake of Portland cement pastes (20 × 20 × 20 mm) cured for 24 hours under 20 vol% CO₂ was 8 wt% [26]. By cyclic closed circulation curing (20 vol% CO₂), 6.84 wt% CO₂ was absorbed in 12 hours (50 × 50 × 50 mm cement paste cubes) [24]. In dry-mix precast concrete (ϕ127 × 25 mm cylinders), the average CO₂ uptake achieved in 1 hour was 8.93 wt% with a flow-through reactor using 20 vol% CO₂ gas [27].

Current commercial applications of carbonation curing primarily focus on pre-cast, non-reinforced concrete products such as pipes, lightweight blocks, and pervious pavements [28–31]. Porous blocks and masonry are preferred due to their interconnected voids [32,33], which facilitate deeper CO₂ penetration and thereby more CO₂ sequestration. In contrast, there has been limited exploration of conventional concrete elements with steel reinforcements [14,34,35]; carbonation lowers the alkalinity of concrete, leading to steel depassivation and an increased risk of corrosion, which poses significant concerns for the structural integrity and longevity of the concrete elements [36,37]. These structural elements have a denser, less porous microstructure, which reduces CO₂ penetration and hinders the carbonation process [19,21]. As a result, the sequestration capacity of carbonation curing in dense cement-based products is reported to be only 20 %–50 % of the theoretical value [5], with CO₂ uptake ranging from 7 % to 20 wt% [38].

The discrepancy in CO₂ sequestration capacity is partly due to variations in quantification methods and their underlying assumptions [39], which poses challenges in comparing CO₂ uptake values across studies. Common methods, such as the mass change method [39–41], assumes a homogenous carbonation profile and reports CO₂ uptake as the average of the entire specimen, with little consideration given to the gradient in carbonation reaction degree from the exposed surface nor differences in sample size/surface area [14]. TGA uses small samples (< 100 mg) from different depths, so challenges arise in ensuring these samples are representative of the material at those depths and thus local CO₂ uptake. Other methods include gamma densitometry, infrared analysis and coulometric analysis, suffer from similar issues [39,42,43]. Indirect methods such as phenolphthalein spray has been extensively used to indicate carbonation depth, and when combined with image analysis [44,45], serves as an alternative approach to quantify indicative carbonation profiles using pH. Previous studies have proposed detecting the phenolphthalein stain by applying binary thresholding in the HSV (hue, saturation, value) colour space to identify purple-reddish hues [45], using intensity differences between blue and red channels in RGB space [46], or applying Otsu's thresholding on the green intensity image with convex hulls to outline carbonation fronts [44]. However, specimen heterogeneity, illumination variability, and differences in stain colour density necessitate manual threshold selection based on visual observation, introducing subjectivity and inconsistency into the image analysis. Hence, developing a standardised image analysis procedure for phenolphthalein-stained specimens would be beneficial for rapidly screening CO₂ uptake in cement-based materials.

Given the significant environmental benefits and potential for large-scale CO₂ sequestration in concrete products, further research is essential to enhance the rate and extent of CO₂ uptake in dense concrete through forced carbonation. The integration of natural fibres within concrete presents a potentially viable solution. This is analogous to their application in increasing water penetration [47,48]; when incorporated into the cement matrix as multifilament yarns, they permit rapid fluid transport along the fibres and through the pore spaces between them [48]. It is well-known that size effects influence the degree of carbonation. For example, it is very difficult to achieve complete and uniform carbonation in large-sized samples, as usually only the surface region can be fully carbonated [17,49]. Therefore, the integration of natural fibres provides a new strategy to address the challenge of carbonating

dense concrete by providing additional transport paths and increasing the surface area to CO₂ exposure.

Natural fibres have been used in concrete, either as discontinuous, randomly distributed elements in fibre-reinforced concrete [50,51], or as layers of woven or non-woven fabrics in textile reinforced mortars [52,53]. The cement matrix, being inorganic and hydrophilic, demonstrates greater compatibility with cellulose fibres, which are also hydrophilic, as opposed to hydrophobic fibres such as polyethylene, polypropylene, and other synthetic types [51]. However, the chemical compositions of natural fibres make them prone to dissolution in the highly alkaline environment of the cementitious matrix [54,55], resulting in a reduction in the tensile strength and a compromised integrity of the fibre-matrix interface [56,57]. Enforced carbonation of early-age natural fibre cement composites is a promising method for preserving natural fibres and densifying the interfacial transition zones in early-age engineered cementitious composites (ECC) [51,54,58–62]. Past research has also demonstrated the effect of carbonation curing on enhancing mechanical properties of ECC in terms of tensile, flexural, and fatigue behaviour [21,63,64].

Despite these advancements, research into utilising natural fibres to enhance CO₂ uptake is limited. Multiple studies have demonstrated the feasibility of enhancing CO₂ sequestration using dispersed fibre reinforcements [64,65]. An addition of 1 vol% sisal fibre in ECC with waste polyethylene fibre resulted in a 16 % increase in CO₂ uptake (99.8 vol% CO₂, 5 bar, 24-h carbonation curing), with CO₂ observed to migrate through the tubular channels of sisal [64]. In magnesium oxide binder, 0.25 vol% cellulose fibres moderately increased CO₂ uptake by 5.88 % with 7 days of enforced carbonation (20 vol% CO₂). These studies suggested that calcium carbonates primarily formed around near-surface fibres, with fibres in the inner regions having minimal effect on carbonation [64].

Spun natural fibre yarns can be used to address the limited effect of short dispersed fibres in promoting CO₂ transport into cement-based materials. Different from short-dispersed fibres, where one does not have control on connectivity of pore channels, these yarns can function as bulk interconnected channels for controlled CO₂ transport in specific orientations. The porosity of natural fibres yarns introduces additional pathways within the cement matrix, thus increasing the surface area accessible for carbonation reactions and facilitating deeper CO₂ penetration.

In light of these considerations, the aim of this study is to explore the integration of various natural fibres in spun yarns to enhance the targeted transport of CO₂ in cement pastes during enforced carbonation. A second objective is the development and application of novel image analysis methodology to rapidly and reliably quantify the carbonation profile of these samples. This method involves assessing the carbonated area fraction of cross-sections stained with a phenolphthalein indicator. Images of the stained discs are captured and analysed using colour deconvolution combined with an overflow segmentation technique [66, 67]. To ensure the accuracy and reliability of this new methodology, thermogravimetric analysis (TGA) is employed to validate the image analysis results by quantifying the CO₂ uptake and degree of carbonation. The results are discussed to establish the potential of natural fibre yarns in accelerating the carbonation curing process of cement pastes.

2. Materials and methods

2.1. Materials

To assess the performance of commercially available yarns in cement composites, spun natural fibre yarns of various sizes (0.96 – 4.38 mm diameter) and ply counts (i.e. number of strands twisted together) were sourced from Tenn well, Eco, and MacCulloch & Wallis. The fibre materials selected were jute, hemp, cotton, and wool, each in distinct colours to differentiate them during image analysis from the unstained cement paste and phenolphthalein stain. These spun yarns underwent

industrial pre-treatment to remove impurities—such as pectin, waxes, hemicellulose (for jute, hemp, and cotton), and lanolin (for wool). Some cotton yarns (CSS and CS in Table 1) were also mercerised. The pre-treatments provided consistent surface quality, allowing the fibres to be used as received without further processing.

Jute and hemp, representative of bast plant-based fibres, contain cellulose contents of 61–71 % and 70–74 %, respectively [68]. The porous structure of jute is conducive to moisture regulation [69], while the distinctive cellular structure of hemp [70] may facilitate CO₂ transport within the cement matrix. The yarns were produced using conventional methods, which generally include steps such as retting, softening, bleaching, and spinning for jute [71], and retting, scutching, and spinning for hemp, with additional softening for its coarser nature [72]. The jute and hemp yarns used in this study were bleached to beige.

Cotton, with a higher cellulose content (95 %) than jute or hemp [73], features a similar hollow central core (i.e., lumen); Cotton fibres were processed through a series of steps, including blowing, carding, combing, roving, and spinning, and were dyed orange [74]. Wool fibres are distinguished by their hygroscopic nature and their crimped morphology contributes to improved mechanical interlocking in cementitious composites [75,76]. Wool yarns were produced from scoured sheep's wool, spun into yarns, and dyed brownish-yellow [77]. All the selected natural fibres are hydrophilic and lightweight, with varying surface roughness, thickness and extensibility.

The properties and appearance of the fibres are shown in Table 1 and Fig. 1. Water absorption tests were carried out on cleaned and dried fibre yarns following a protocol adapted from BS EN ISO 62:1999 (detailed in Supporting Information S1, Section S1). The compactness of fibres, which denotes the density of fibre packing within the yarns, is quantified by the ratio of total fibre area (sum of the cross-sectional areas of individual fibres) to the total convex area of fibre bundle (Supporting Information S1, Fig. S1). Resin-impregnated fibre yarn samples and image analysis, as elaborated in the Supporting Information S1 (Section S2), was utilised to measure the areas.

CEM I 52.5 N Portland cement from Breedon was used to produce cement paste. The chemical compositions of the cement, as analysed by X-ray fluorescence (XRF), are presented in Table 2. The initial CO₂ content in the Portland cement was determined using thermogravimetric analysis (1.52 ± 0.35 wt%). In the calculation of CO₂ uptake upon enforced carbonation, this initial carbon dioxide content was accounted for and subtracted. A constant water-to-cement mass ratio (w/c) of 0.4 was maintained for all samples.

2.2. Sample preparation

Cylindrical paste samples containing a single fibre yarn were prepared in 15 ml polyethylene centrifuge tube. Prior to casting, the yarn was positioned along the centre of the centrifuge tube by threading through pre-drilled holes at the top and bottom, and fastened in place using waterproof duct tape (Fig. 2a). During casting, the tube was filled with fresh cement paste, then capped and firmly sealed. Thereafter, the fibres were manually tightened in the longitudinal direction of the centrifuge tube. The induced tensile stress caused a reduction in average fibre diameter (Table 1). The samples were then subjected to vibration

until no bubbles were observed escaping from the side of the tubes (~45 seconds). Samples were cured in the centrifuge tubes for the first 24 hours. Then, the upper portions of the centrifuge tubes were removed as shown in Fig. 2(b) using a Buehler IsoMet 1000 precision cutter, with water as the cooling agent. Identical samples were prepared in three batches, enabling each test to be repeated three times for representative results.

2.3. Enforced carbonation curing

Upon removal of the top, an electric fan with a wind speed of 1.11 m/s was employed to facilitate removal of free water from the exposed sample surface. The samples were fan-dried at room temperature (21 ± 2 °C) and humidity (~55 %) for 30 minutes. Thereafter, the samples were placed on a centrifuge stand in a Panasonic MCO-230AIC CO₂ incubator, leaving only the top surfaces exposed to CO₂. The conditions in the carbonation chamber were selected to approximate the cement plant flue gas, with a temperature of 25 ± 0.5 °C, atmospheric pressure, and a CO₂ concentration of 19.9 ± 0.1 vol% (mixing air with carbon dioxide gas of 99.8 % purity from BOC Ltd). Saturated sodium nitrite solution (NaNO₂) was used to maintain a relative humidity of 64 ± 2 % in the carbonation chamber [78]. After enforced carbonation of 1, 3, 5, and 7 days, the samples were retrieved in batches and cut into discs using Buehler IsoMet 1000 with water as the cooling agent at the locations shown in Fig. 2c. In addition, to investigate the vertical carbonation profile, some reference samples without natural fibre yarns were sectioned parallel to the direction of CO₂ penetration for examination of the carbonation depth.

For assessing the cross-sectional carbonation profile, discs taken from depths of 0 mm to 50 mm below the CO₂ exposed surface were extracted in 10 mm intervals (Fig. 2c). Immediately after cutting, the discs were wiped with tissue paper and fan-dried for less than 10 minutes to minimise the impact of excess moisture prior to phenolphthalein indicator testing. Once complete, the first 1 mm of each disc was sliced off and ground to powder for TGA. The remaining (9 mm thick) portions from the top and the bottom discs were used for X-ray diffraction (XRD), and the remaining portions from 11 to 20 mm in depth were prepared for scanning electron microscopy (SEM). The discs collected for characterisation tests were immediately subjected to solvent exchange with isopropanol for hydration stoppage as per Snellings et. al. [79]. These powdered samples were preserved in a low vacuum environment (0.2 bar) over silica gel and soda lime to mitigate further carbonation.

In this study, samples are identified using 'X-DY-Z' notation. Herein, 'X' refers to the type of fibre yarn used, 'DY' represents the enforced carbonation duration in days, and 'Z' indicates the depth in millimetres from the CO₂-exposed surface where measurements were taken. For instance, a disc labelled 'H-D7-20' is a hemp yarn embedded specimen, carbonated for 7 days, with data collected at a depth of 20 mm from the exposed surface.

2.4. Phenolphthalein indicator test

As carbonation is a neutralisation process that reduces the pH of the

Table 1
Basic properties of selected natural fibre yarns.

Annotation	Fibre Type	Ply count	Average diameter – original (mm)	Average diameter – manually tightened (mm)	Water absorption (%) – 24 h	Compactness of fibres (%)
J	Jute	3	1.99	1.52	68.9 %	68.7 %
H	Hemp	3	2.51	1.65	64.8 %	90.4 %
CSS	Cotton	3	0.292	0.272	47.6 %	44.8 %
CS	Cotton	3	0.960	0.656	49.9 %	52.0 %
CT	Cotton	7	2.23	0.981	48.7 %	39.3 %
WS	Wool	2	2.18	0.528	28.3 %	49.0 %
WT	Wool	3	4.38	1.09	39.0 %	43.5 %



Fig. 1. Selection of natural fibre yarns; J- jute, H – hemp, CSS – cotton (super slim), CS – cotton (slim), CT – cotton (thick), WS – wool (slim), WT – wool (thick).

Table 2
Chemical composition of the CEM I 52.5 N Portland cement (wt%). Loss on ignition was 1.72 wt%.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	Na ₂ O	K ₂ O	Cl ⁻
19.4	5.64	2.75	64.8	3.96	0.881	0.210	0.599	0.077

pore solution from ~13 to ~8, the changes in alkalinity upon carbonation can be rapidly assessed by a pH indicator. Hence, carbonation fronts were observed by spraying a phenolphthalein solution (10 g phenolphthalein in 1 L of 50 % ethanol-water solution) evenly onto the cut discs, as per BS EN12390-12:2020 [80]. The phenolphthalein indicator turns reddish-purple where the pH value exceeds 9 (indicating uncarbonated zones) and remains colourless when the pH is less than 9

(indicating carbonated zones). Three replicates were tested for each carbonation duration (1, 3, 5, 7 days) and depth (0 –50 mm) to account for error.

2.4.1. Image acquisition

After the phenolphthalein stain had stabilised, a digital colour (RGB) image was captured for each slice using an Olympus SZX10 stereomicroscope equipped with an SC50 CMOS colour camera. To achieve optimal colour contrast, oblique illumination was provided by two fibre-optic light guides from the Olympus Highlight 3000 system. The samples were placed onto a black motorised XY scanning stage so that their edges could be easily identified and subtracted during image processing. The acquisition parameters (normal light intensity, brightness level 3.5, exposure time 199 ms) were kept constant to ensure repeatable and comparable results across samples imaged on different days. A ruler was

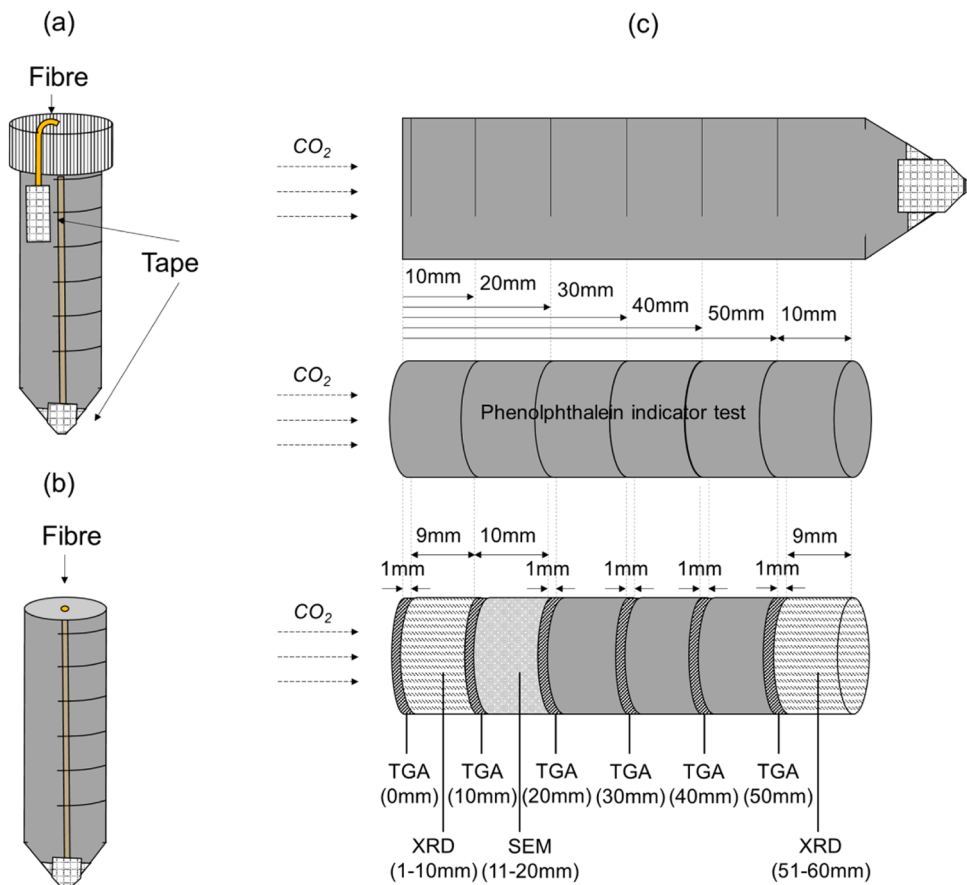


Fig. 2. Schematic diagram of sample preparation and tests; (a) mould assembly showing a centrally secured fibre yarn in centrifuge tube; (b) top removed after 24 hours; (c) enforced carbonation and disc extraction for subsequent characterisation tests.

placed on the sample focal plane to check for image scaling accuracy.

2.4.2. Image pre-processing

Images were processed using ImageJ (Version 1.54 h). Due to the presence of the plastic tube rim in the sliced sample, a region-of-interest (ROI) was carefully selected from the calibrated image (Fig. 3a), representing the material inside the tube only. Multiple existing image analysis methods were trialled but did not work well with the acquired images (Supporting Information, Section S3). Colour deconvolution was deemed suitable for this study [66], where the images were decomposed according to 2–3 sets of colour vectors. For phenolphthalein-sprayed samples, two distinctive colours can be identified: (1) yellowish-grey from the unstained (non-carbonated) areas ($\text{pH} < 9$) and (2) reddish-purple from the carbonated areas ($\text{pH} > 9$). To determine the values of these, the mean colour vectors pertaining to the uncarbonated and carbonated zones across all samples (504 discs) were measured and normalized from an RGB scale of 0–255 to a unitary scale of 0–1. These vectors were then applied in colour deconvolution to segment the original image into three separate 8-bit images, as shown in Fig. 3b–d. The first two monochrome images (Fig. 3b–c) represent the absorbance of RGB components of the calculated colour vectors in the original image. The third image (Fig. 3d) illustrates residual colours following the subtraction of the first two vectors, computed via the cross-product method [81], and this shows the residual colours of the original image after subtracting the first two vectors. A blank ROI in the third image indicates the high accuracy of the selected colour vectors in representing phenolphthalein-stained areas and unstained cement pastes.

2.4.3. Image processing

The overflow segmentation method [67], originally developed for

segmenting pores in backscattered electron images, was adapted to distinguish and measure the carbonated and uncarbonated areas. Upon visual assessment, the phenolphthalein stain image (Fig. 3b) generated from colour deconvolution matches better with the phenolphthalein indicator reaction. The unstained image (Fig. 3c), however, captures non-relevant artifacts surrounding the carbonated zones. Additionally, the histogram of the phenolphthalein stain image (Fig. 3b*) exhibits a unimodal, well-defined peak, providing effective contrast differentiation, whereas the histogram of the unstained image (Fig. 3c*) shows a broader spread of intensities, implying lower contrast. The colour-deconvoluted phenolphthalein stain images were therefore selected for overflow segmentation analysis (Fig. 3e).

To determine the threshold range of the carbonated zone, a cumulative histogram was first generated from the colour-deconvoluted phenolphthalein stain image by plotting the percentage segmented area (0–100 %) against colour intensity value (0–255). The inflection point was determined from the intersection of two linear segments on the cumulative histogram. The intensity value at this inflection point was set as the lower threshold bound, which is multiplied by a factor of 1.5 to compensate for the overestimation of carbonated areas by the overflow segmentation method. *With this correction, the overflow segmented area is nearly identical to that obtained from manual thresholding determined visually (Fig. 3e).* This excellent correlation was repeatable across the 504 samples analysed, thus validating the reliability of the proposed segmentation method. The determined threshold ranges were then applied to all phenolphthalein-stained images to obtain the areas of carbonated and uncarbonated zones. Notably, with careful selection of threshold ranges and correction factor, noise the unstained image (Fig. 3b) can also be accounted for, as detailed in the Supporting Information S1 (Fig. S5).

Due to the lighter colour of fibre yarns, the fibres were usually

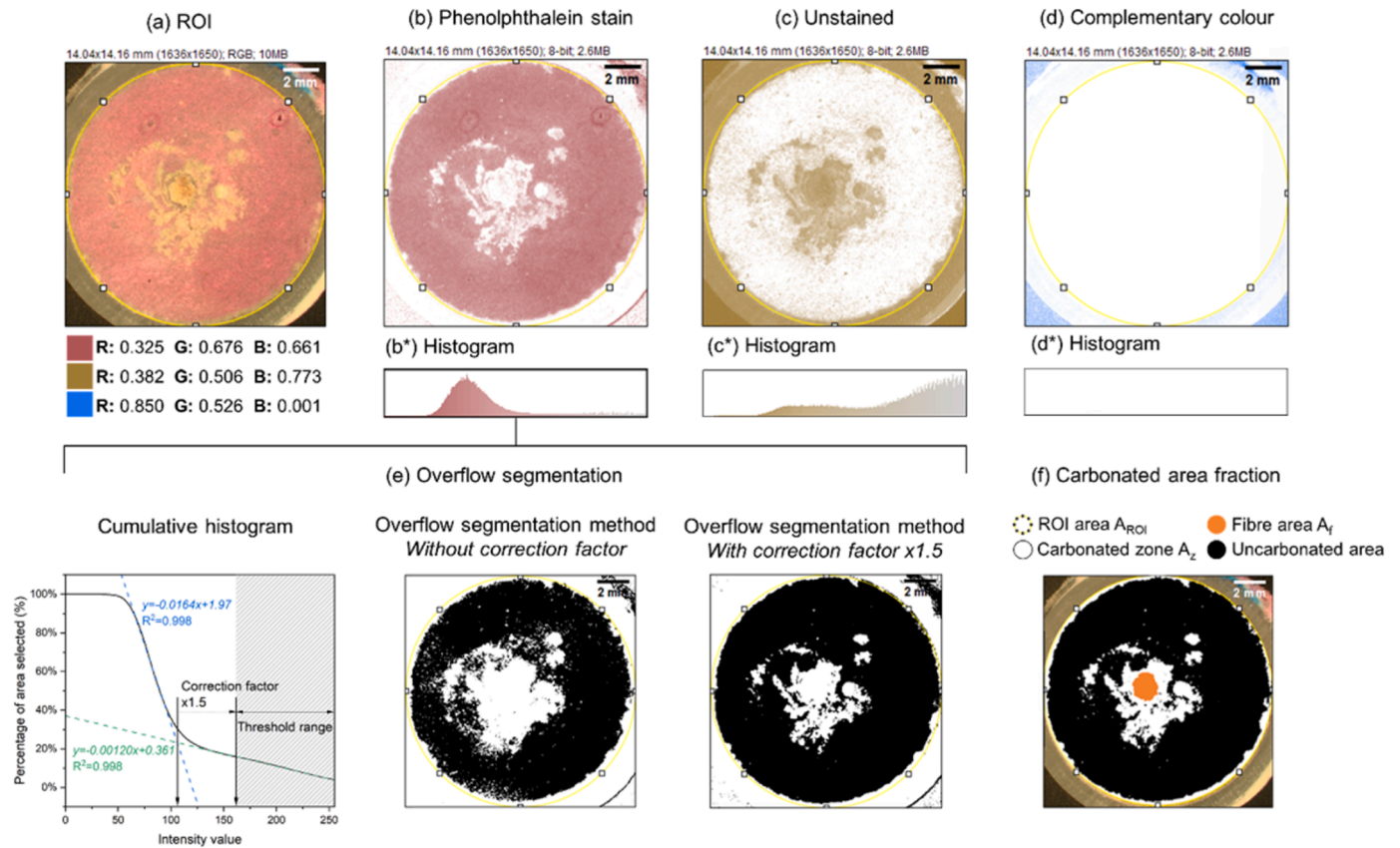


Fig. 3. (a) Selected region of interest of a carbonated jute yarn sample (J-D7–20); (b–d) colour deconvolution and the corresponding histograms in (b*–d*) using ImageJ; (e) overflow segmentation method to obtain the threshold range of carbonated zone [76]; (f) schematic illustration of carbonated area fraction based on image analysis.

included into the carbonated zone by the segmentation method described above. The convex areas of the fibre bundles were hence manually selected and excluded from calculation of the carbonated area fraction. Based on image analysis, the carbonation profile can be determined by calculating the carbonated area fraction (%) (Fig. 3f), using Eq. 1.

$$\text{Carbonated area fraction} = \frac{A_z - A_f}{A_{ROI} - A_f} \times 100 \quad (1)$$

Where, A_z = Area of the segmented carbonation zone (mm²), A_f = convex area of the fibre bundle (mm²), and A_{ROI} = Area of region of interest (mm²).

2.5. Scanning electron microscopy

A Zeiss Sigma 500VP field emission scanning electron microscope (FE-SEM) equipped with a 5-quadrant high definition backscattered electron detector was used to investigate the microstructure of natural fibre yarn composites after 7 days of enforced carbonation. Discs extracted at depths of 11–20 mm from the carbonated surface (Fig. 2c) were extracted and vacuum-impregnated with epoxy resin and placed in a high-pressure chamber at 2.5 bar for 24 hours. The impregnated samples were then carbon coated (15 nm) under 7×10^{-2} mbar using an Emitech K550X sputter coater. Back scattered electron (BSE) images (3072 × 2304 pixels) were acquired using an acceleration voltage of 12.5 kV at a working distance of 8.5 mm.

2.6. Thermogravimetric analysis

Thermogravimetric analysis was used to quantify the extent of carbonation and the results were compared against those from image analysis. As shown in Figs. 2c, 1-mm-thick discs were sampled at 10 mm intervals, then crushed and ground homogeneously to particles smaller than 125 µm. TGA measurements were conducted using a Netzsch STA 449 F5 thermal analyser. The powdered sample (55 ± 0.2 mg), was heated from 30 °C to 1050 °C at a heating rate of 10 °C per minute under a constant nitrogen flow rate of 50 ml/min. To accurately identify and quantify portlandite and calcium carbonate, TGA was integrated with mass spectrometry (TGA-MS) on representative samples. A QMS 403 Aëolos Quadro mass spectrometer was connected via a heated (300 °C) quartz glass capillary to detect the release of H₂O ($m/z = 18$) and CO₂ ($m/z = 44$) gases, which signify the decomposition temperature range of hydration products and carbonates. The mass loss due to decomposition of portlandite and calcium carbonate were determined using the tangential method at 420–520 °C and 550–850 °C respectively [82] (Supporting Information, Section S5, Fig. S8).

The CO₂ uptake (CO_{2 uptake}, wt%) represents the percentage of CO₂ absorbed during enforced carbonation relative to the initial mass of cement (M_{cement} , g). To account for amorphous calcium carbonates, which could decompose before 600 °C, M_{cement} is calculated by adding the mass loss from decomposition of CaCO₃ in the initial cement and the residual mass of the sample after heating to 1050 °C, i.e., the anhydrous and CO₂-free mass of cement (M_{1050} , g) (Eq. 2), assuming that the initial cement is dry.

$$M_{\text{cement}} = \frac{M_{1050}}{1 - \frac{CO_{2 \text{ initial}}}{100}} \quad (2)$$

Where CO_{2 initial} (%) is the percentage of CO₂ initially present in the cement (i.e., CEM I powder), and is determined via TGA. Based on the initial mass of cement, CO₂ sequestration during enforced carbonation of a sample can be derived from the total mass lost due to CaCO₃ decomposition excluding the mass of CO₂ initially in the sample. The CO₂ uptake can hence be quantified as follows [5,39] (Eq. 3).

$$CO_{2 \text{ uptake}} = \frac{WL_{CaCO_3} - CO_{2 \text{ initial}} \times M_{\text{cement}}}{M_{\text{cement}}} \times 100 \quad (3)$$

Where, WL_{CaCO_3} (g) represents the mass loss attributed to the decomposition of CaCO₃.

All of the yarns studied here were tested by thermogravimetric analysis (Supporting Information S1, Fig. S9) over the temperature range 30 °C to 1050 °C. The thermal decomposition trend of phenolphthalein was not observed. This is mainly due to the low concentration of phenolphthalein in the indicator solution. It was also found that bast fibres (jute and hemp) decompose between 240 °C and 380 °C, cotton fibres between 280 °C and 380 °C, and wool fibres from 200 °C to 480 °C. Given the small mass of fibres present in each disc, the DTG peaks indicating fibre decomposition were minimally visible in samples containing fibres and are therefore not elaborated upon.

To allow comparisons with the carbonated area fraction (%) from image analysis (Eq. 1), the TGA results were used to quantify the degree of carbonation (DoC) in each disc. The DoC (%) is defined as the ratio between the measured CO₂ uptake by TGA and the theoretical maximum CO₂ uptake (CO_{2 theoretical}) of the cement (Eq. 4). Here, the theoretical maximum CO₂ uptake value is defined as the amount of CO₂ that can react with CaO in cement paste samples (forming CaCO₃), excluding the amount of CaO in calcium sulphate phases (Eq. 5) [83]:

$$DoC = \frac{CO_{2 \text{ uptake}}}{CO_{2 \text{ theoretical}}} \times 100 \quad (4)$$

$$CO_{2 \text{ theoretical}} = \%CaO \times \frac{m_{CO_2}}{m_{CaO}} - \%SO_3 \times \frac{m_{CO_2}}{m_{SO_3}} \quad (5)$$

The contents of CaO and SO₃ in CEM I Portland cement were determined using XRF (Table 2) and the w/c used (0.4). The theoretical maximum CO₂ uptake for cement paste in this study is 48.6 wt%.

X-ray diffraction (Bruker AXS D8 Advance with Cu Kα radiation, 45 kV and 40 mA) was used to determine the CaCO₃ contents in carbonated samples, complementing the CO₂ uptake quantified through TGA. Disks from varying depths (0–1 mm, 1–10 mm, 50–60 mm) were homogeneously ground and sieved under 63 µm (Fig. 2b). The phase percentages were quantified through Rietveld analysis using a 20 wt% corundum internal standard, with data processed by HighScore Plus software incorporating the ICDD database (PDF-4+/Web 2023). Results can be found in Supporting Information S1, Section S5.

3. Results and analysis

3.1. Image analysis

In image analysis, the carbonated area fractions for fibre-embedded samples were consistently higher than their non-fibre reference counterparts (dotted black line, Fig. 4), confirming that the presence of fibres enhances the transport of CO₂ into the samples. This was also evidenced in the vertical profile carbonation depth tests, where reference samples (VP-REF) exhibited minimal carbonation, with depths of 0.18 mm, 0.63 mm, 0.80 mm and 0.94 mm respectively.

In the first 24 hours of enforced carbonation (Fig. 4a), all samples containing natural fibres exhibited minimal enhancement in carbonation depth. Significant carbonation was localised in the top disc but limited CO₂ penetration beyond 10 mm in depth. The most substantial carbonation occurred between 1 and 3 days (Fig. 4b), particularly in bast cellulose-based fibres such as hemp and jute, which displayed a marked increase in carbonated area. Carbonation progressed more slowly beyond 3 days of curing. After 5 days of enforced carbonation, the increase in carbonated area fraction at depth of 10 mm was less pronounced than that from 1 to 3 days. A reduced rate of carbonation was also observed between 5 and 7 days of enforced carbonation curing. The results reflected the influence of fibre type and the thickness of fibre yarns on enhancing CO₂ transport into the cement matrix.

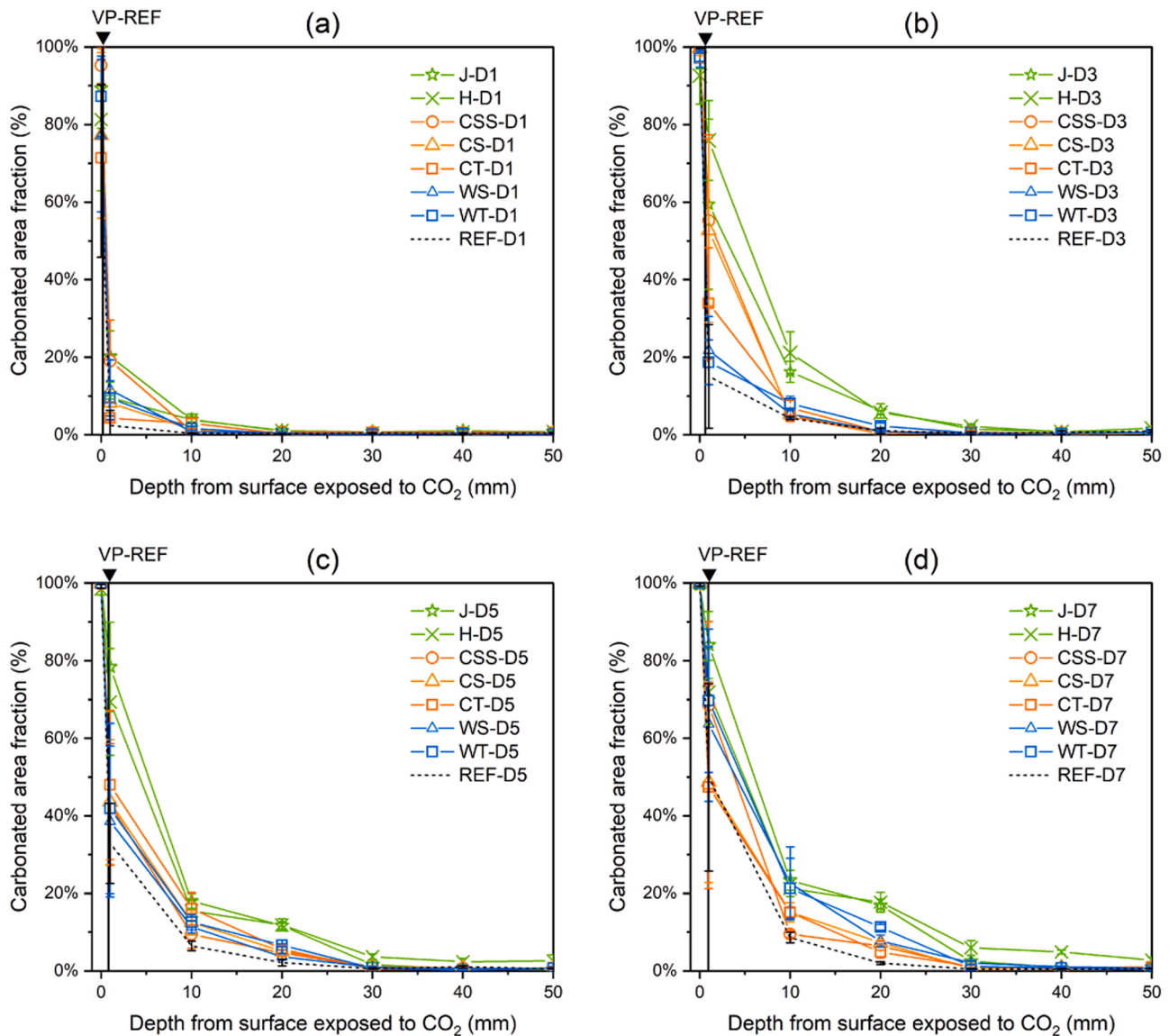


Fig. 4. Carbonated area fraction in specimens exposed to CO₂ curing; (a) 1-day carbonation curing; (b) 3-day carbonation curing; (c) 5-day carbonation curing; (d) 7-day carbonation curing. VP-REF: vertical carbonation depth of reference samples.

Whilst all fibres were effective in enhancing CO₂ transport into greater depth during enforced carbonation, hemp and jute outperformed other type of fibres regardless of thickness or ply count. Jute and hemp-embedded samples showed detectable carbonated area fractions at 50 mm depth after 3 days of curing (0.692 % and 1.69 %, respectively), whereas cotton and wool demonstrated little to no carbonation beyond 20 mm. Thicker yarns demonstrated slightly increased CO₂ sequestration around the fibres, as implied by the slight increase in unstained areas by the phenolphthalein indicator. Fibre type had a significantly greater effect on carbonated area fraction than yarn thickness.

The geometry of carbonated area also varied among different type of yarns (Supporting Information S1, Figs. S6–7). Hemp and jute embedded samples (Fig. 5a–b) displayed an irregular and spread out carbonation front, demonstrating a more extensive CO₂ transport throughout the matrix. Apart from the colourless carbonation rings around the fibre yarns, patches of carbonated area could also be observed in the uncarbonated region. Cotton and wool (Fig. 5c,d), on the other hand, exhibited a more defined and concentrated carbonation front around the yarns, with a clear demarcation between the carbonated and uncarbonated area. The irregular carbonation fronts can be ascribed to the presence of stray fibres, i.e., fibres that diverge from the main yarn

bundle. The fibrillation of fibres form separate CO₂ transport channels and extended carbonated strips from the centre yarn.

3.2. Scanning electron microscopy

SEM-BSE imaging (Fig. 5e–n) further elucidate the interface between natural fibre yarns and the cement matrix, revealing variances in the structural and spatial arrangements of fibres within different yarns.

The bast fibre yarns (Fig. 5e–f) jute and hemp have larger and more internally porous fibre filaments with irregular cross-sections, with hemp fibres (average fibre spacing <10 μm) more compactly arranged than jute (average fibre spacing <15 μm). Bast fibre yarns demonstrate a clearly defined boundary between the yarn bundles and the cement matrix. Hydration products, carbonation products, and unreacted cement grains only rarely penetrated into the bast fibre yarn convex areas. The edges of individual hemp and jute fibres were surrounded by bright and discrete patches of carbonated hydration products, aligning with previous research that the surfaces of cellulose-based natural fibres are not inert in early interactions with cement-based materials [84].

Cotton fibres, in contrast, possess a distinctive twisted ribbon-like shape (i.e. convolutions) [85]. Due to the smaller size of cotton fibres,

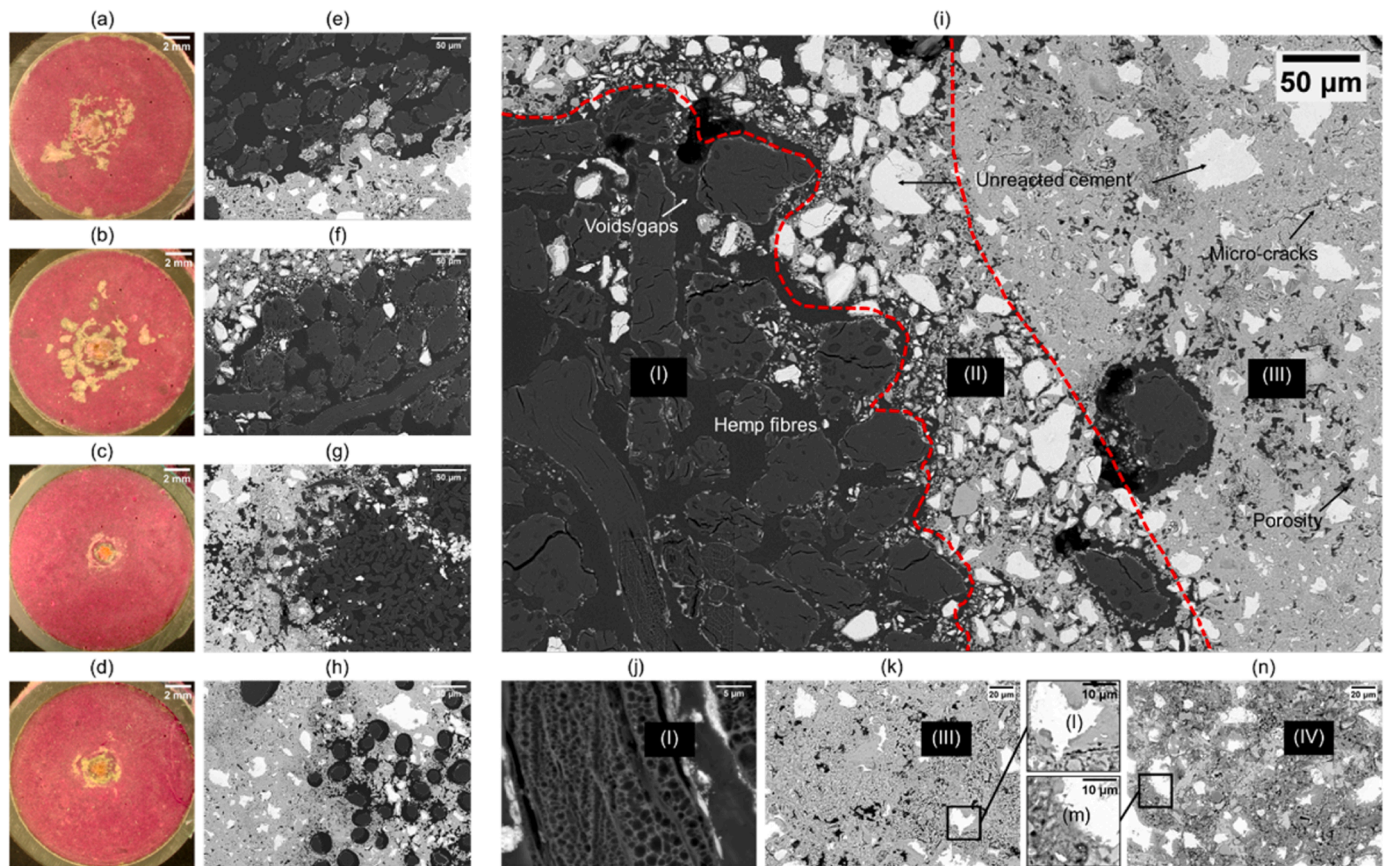


Fig. 5. Microstructure of carbonated natural fibre cementitious composites. Panels (a-d) show the carbonated areas in samples containing (a) jute (J-D7-20), (b) hemp (H-D7-20), (c) cotton (CT-D7-20), and (d) wool (WT-D7-20) yarns. SEM-BSE images (e-h) detailing the paste-fibre interface for (e) jute (J-D7-11), (f) hemp (H-D7-11), (g) cotton (CT-D7-11), and (h) wool yarns (WT-D7-11). Images (i-k) further illustrate the microstructural variations in (i) the transition zone featuring the porous hemp yarns adjacent to carbonated cement pastes, (j) internal structure of hemp fibre, (k) a dense calcium-rich carbonated area, and (n) an uncarbonated reference zone. (l) 2-tone inner C-S-H with residual alite observed in carbonated area, (m) inner and outer C-S-H surrounding alite in uncarbonated area. Annotations: (I) natural fibre yarn, (II) porous interfacial transition zone, (III) carbonate-rich zone, (IV) uncarbonated reference zone.

the cotton yarn was made from several threads twisted together. Despite the higher local compactness (average fibre spacing $< 5 \mu\text{m}$), the multi-thread composition of cotton yarns leads to a relatively lower overall compactness as gaps exist between the threads. Cement paste seeped into the voids in between cotton threads (Fig. 5g).

Jute, hemp, and cotton embedded samples showed a gradational interface pattern in transition from the yarn to the cement paste. This pattern is particularly evident in hemp yarn samples (Fig. 5i), where there are three distinct regions: the yarn bundle (I), a porous and carbonated transition zone in the cement paste (II) with higher concentration of unreacted cement grains, and a densified, carbonate-rich region in the cement paste (III). Among the different natural fibres selected in this study, bast fibres have the highest internal porosity (i.e. pores within fibres). Detailed examination of hemp fibres reveals numerous vessels and pores (Fig. 5j). The SEM data show that CO₂ is able to penetrate through the porous transition zone (II) to carbonate more internal regions of the cement paste (III), within which micro carbonation cracks and voids around fibres were observed. There was no clear indication of internal curing effects brought by the yarns (I) [86], as the transition zones (II) did not exhibit increase in hydration products but appeared largely carbonated.

Wool fibres have elliptical or ovate shapes, larger average fibre spacing ($> 20 \mu\text{m}$), and do not form distinctive boundaries between the main fibre bundle and the cement matrix. Partial dissolution of individual wool fibres is observed [87], creating voids around the fibres (Fig. 5h). The SEM images for wool containing samples show fewer interactions between fibres and a more homogenous integration in the

cement matrix. Carbonated cement paste is present amid the wool fibres.

Carbonated cement paste adjacent to the centre yarn show a more refined and less porous microstructure than the uncarbonated counterpart, with significant transformation of calcium hydroxide, C-S-H, and unreacted cement into calcium carbonates. The densification of cement matrix, associated with the formation and volumetric expansion of calcium carbonates, likely caused local stress concentrations, resulting in some microcracks, as observed in SEM-BSE images taken near the fibres (Region III). The size of cement grains and hydration products were reduced in the carbonated cement paste (Fig. 5k), and portlandite was absent in the carbonated region (III) but present in the uncarbonated cement paste (Fig. 5l). The low-density outer C-S-H, which was evident in uncarbonated regions (Fig. 5n), transformed into a densified matrix following extensive carbonation. This transformation substantially reduced the porosity of the outer C-S-H. Scattered darker grey areas within this region indicated silica gel formation from enforced carbonation reactions [88].

Inner C-S-H was not extensively formed due to the early age of the samples. After a prolonged enforced carbonation period (i.e., 7 days), the inner C-S-H remained visible, exhibiting a two-tone appearance (Fig. 5m), suggestive of changes in the Ca/Si ratio due to carbonation reactions [89]. The observations show that while outer C-S-H was more susceptible to carbonation, inner C-S-H remained relatively resistant [15,90,91]. Additionally, volume shrinkage, characterised by shell-like boundaries, was observed around some inner C-S-H rims after carbonation (Fig. 5m). SEM-BSE imaging thus indicates reaction of C-S-H with CO₂ and localised decalcification of C-S-H in regions adjacent to the

natural fibre yarns. Fourier-transform infrared spectroscopy (FTIR) results (Supporting Information S1, Section 6) report significant decalcification of the C-S-H only in the surface disc, with little signs of decalcification in discs extracted from deeper layers of the samples. This also suggests that the decalcification of inner C-S-H was a localised phenomenon occurring in cement paste in proximity to the natural fibre yarns.

In addition, SEM results suggested that hydrated cement paste might have penetrated the yarns, hence, the convex area measured likely contained a fraction of carbonated cement paste, which leads to potential underestimation of the carbonated area fraction in Fig. 4.

3.3. Thermogravimetric analysis

Fig. 6a-b shows TGA-MS analysis of representative discs extracted from the surface and deeper sections of the samples. The TGA results showed three main features [17,58,92]: (1) the early dehydration of C-S-H gels and ettringite (30–200 °C), dehydroxylation of Ca(OH)₂ (420–520 °C), and decarbonation of calcium carbonate (550–850 °C). In TGA-MS, two major water releases were observed: the initial release between 50 °C and 200 °C, attributed to incomplete dehydration of C-S-H gels and ettringite, and a later release between 420 °C and 520 °C, corresponding to Ca(OH)₂ (CH) dehydroxylation. The results are consistent with literature asserting that C-S-H gradually decomposes

until 600 °C [93,94]. The reduced mass loss between 30 °C and 200 °C for the surface disc compared to the other deeper discs (Fig. 6d) is caused by smaller amounts of ettringite (AFt) and/or C-S-H due to their decomposition upon reacting with CO₂.

In mostly carbonated discs (Fig. 6a), two types of calcium carbonates (CC) peaks were identified: a broad and relatively flat DTG peak spanning from 450 °C to 740 °C, and a subsequent more pronounced decomposition extending from 740 °C to 850 °C. This suggests the coexistence of amorphous/poorly crystalline calcium carbonates (which decomposes at lower temperature) and well-crystallised carbonates (i.e. calcite polymorph) [17,42,95,96]. In partially carbonated samples (Fig. 6b), CC decomposition initiated at higher temperatures, typically 550 °C to 850 °C. Amorphous or poorly crystalline calcium carbonates decomposed before 740 °C, in alignment with literature findings [21, 97–99].

Fig. 6c-d presents the TG-DTG curves from 0 to 50 mm of both reference and hemp-embedded samples subjected to 5 days of CO₂ curing. Irrespective of fibre inclusion, the topmost discs (0–1 mm) were mostly carbonated and had very little remaining hydration products, as identified by their lower chemically bound water. Portlandite is preferentially carbonated over other cement hydrates here, which is consistent with literature [14,15,17,21], followed by the consumption of calcium silicate hydrate (C-S-H) gel and ettringite. The content of chemically bound water was similar in discs extracted from deeper

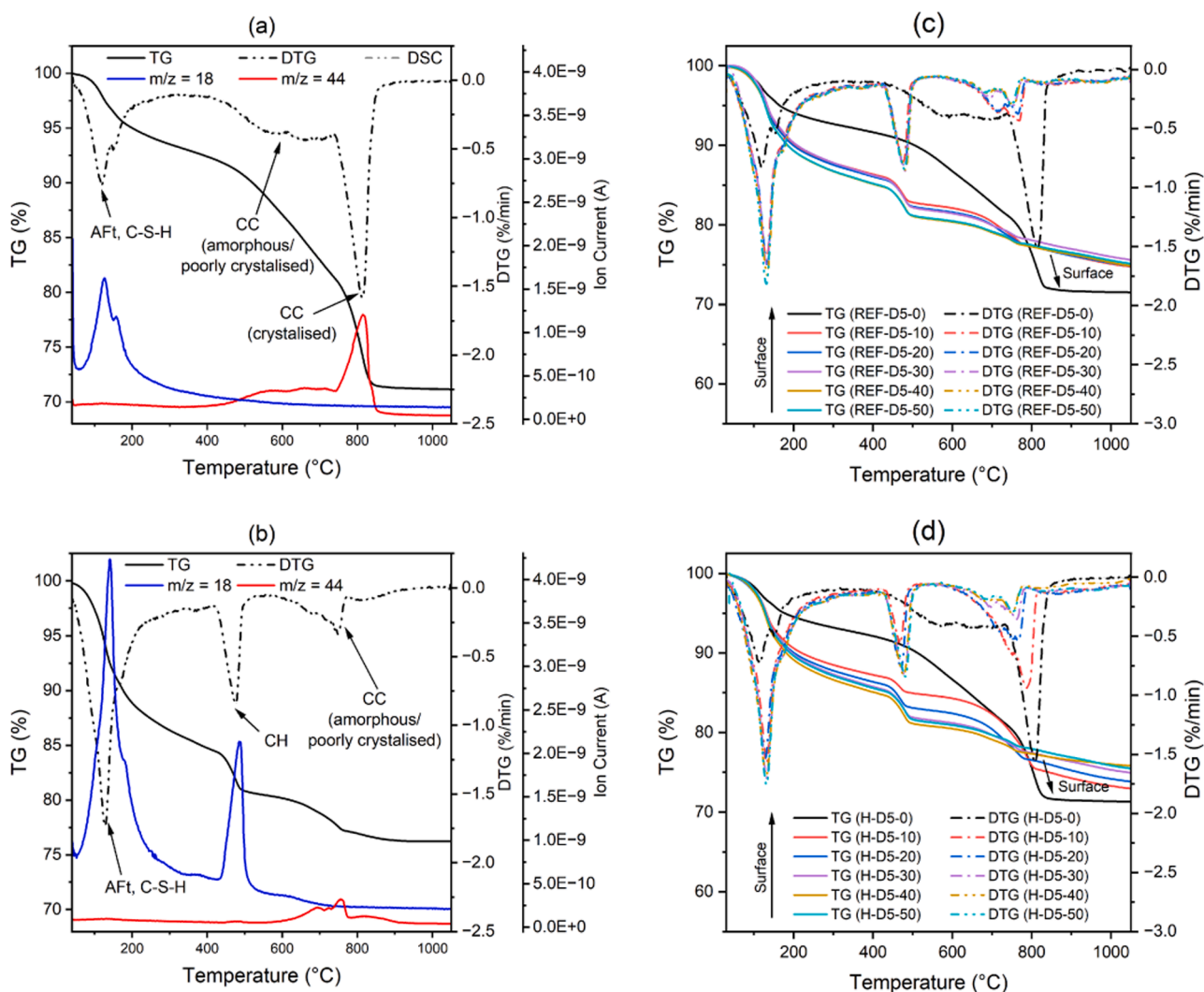


Fig. 6. TGA-MS analysis of selected (a) mostly carbonated disc (H-D7-0) at surface and (b) partially carbonated disc (H-D7-50) at bottom. TGA-DTG curves of (c) reference and (d) hemp-embedded samples at different depths after 5-day enforced carbonation.

sections (10–50 mm), regardless of fibre addition. FTIR showed a depletion of portlandite in the topmost disc (Supporting information S1, Section S6), alongside decalcification of C-S-H gel. At deeper sample depths no signs of significant C-S-H decalcification and the presence of calcium hydroxide were observed. TGA, FTIR and XRD (Supporting information S1, Section S5) analysis all suggested that the major polymorph of calcium carbonate formed was calcite.

The incorporation of hemp yarn greatly enhanced the mass loss between 550 °C and 850 °C, as shown by the size of DTG peaks across the depth range for samples subjected to enforced carbonation (Fig. 6d). Similar enhancement of mass loss between 550 °C and 850 °C was observed for hemp fibre samples cured using enforced carbonation for 1, 3, and 7 days (Supporting Information S1, Fig. S10). In contrast, the TG-DTG curves largely overlapped (10 – 40 mm) for reference samples; other than the top discs, the remaining discs demonstrated similar level of mass loss between 550 °C and 850 °C (Fig. 6c), which can be ascribed to the decomposition of limestone originally present in the cement.

The quantitative assessment of CO₂ uptake in the samples derived from TGA results indicate a distinct enhancement in CO₂ uptake for the hemp samples across all measured depths and time intervals, as evidenced by the increased calcium carbonate content across various depths and curing duration (Fig. 7a, S11). This corroborates the image analysis findings presented in Fig. 4.

For hemp-embedded samples subjected to 1, 3, 5, and 7 days of carbonation curing, the average CO₂ uptake from 0 to 50 mm depth was 4.92 wt%, 6.40 wt%, 7.23 wt%, and 8.19 wt%, marking 23.4 %, 37.7 %, 36.6 %, and 45.1 % increases compared to the respective reference samples. The CO₂ uptake decreased exponentially across the 50 mm profile from the exposure surface, with the highest absorption in the top 10 mm. CO₂ uptake in the top discs of each sample was relatively consistent. Initially, for reference and hemp-embedded discs, the 1-day CO₂ uptake at 0–1 mm was between 21 wt% to 23 wt%, which then increased to between 26 wt% and 28 wt% from days 3–7. The sample depth where there was the greatest increase in CO₂ uptake from the addition of hemp fibres was observed at the 10 mm depth and after 3 days of carbonation curing, with CO₂ uptake rising from 0.969 wt% to 6.98 wt%. At deeper depths from 20 mm to 50 mm, even with 7 days of

enforced carbonation, the reference discs showed minimal CO₂ uptake ranging from 1.21 wt% to 0.594 wt%, whereas the addition of hemp yarns increased the variance in carbonation profile from 4.49 wt% to 1.81 wt%.

Fig. 7b shows that there is a positive linear relationship between the carbonated area fraction determined by image analysis and degree of carbonation determined by TGA. The calculated carbonated area fraction went as high as up to ~100 % for the topmost discs, while the highest degree of carbonation obtained was 56.8 %. These results show that the carbonated area fraction based on phenolphthalein indicator determined was approximately 1.78 times the degree of carbonation determined from TGA. Hence this study contrasts statements reported in the literature that phenolphthalein underestimates carbonation depths in concrete materials [42,43,100].

4. Discussion

4.1. Natural-fibre induced modifications in carbonation mechanisms

This study elucidates the influence of natural fibres on carbonation rate and extent in cement paste samples. The phenolphthalein indicator test revealed two types of carbonation profiles. (1) in the reference cement paste without fibre addition, carbonation was slower and was largely confined to the sample surface. This was evidenced in the vertical profile carbonation depth tests, where reference samples were carbonated to depths of <1 mm after 7 days. (2) Accelerated carbonation was observed in all samples embedded with natural fibres, where CO₂ was transported along the channels made by the yarns to deeper sections of the cement paste, significantly surpassing the carbonated area fraction and CO₂ uptake recorded by the reference samples. The TGA results indicated that the CO₂ penetration was deeper and faster than that indicated by image analysis, and within 24 hours of enforced carbonation they showed that the CO₂ uptake at 50 mm depth was increased from 0.010 wt% to 0.423 wt% with hemp yarns. Fig. 8a provides a schematic illustration of how natural fibre affects carbonation of cement paste.

Our results demonstrated the feasibility of embedding natural fibre

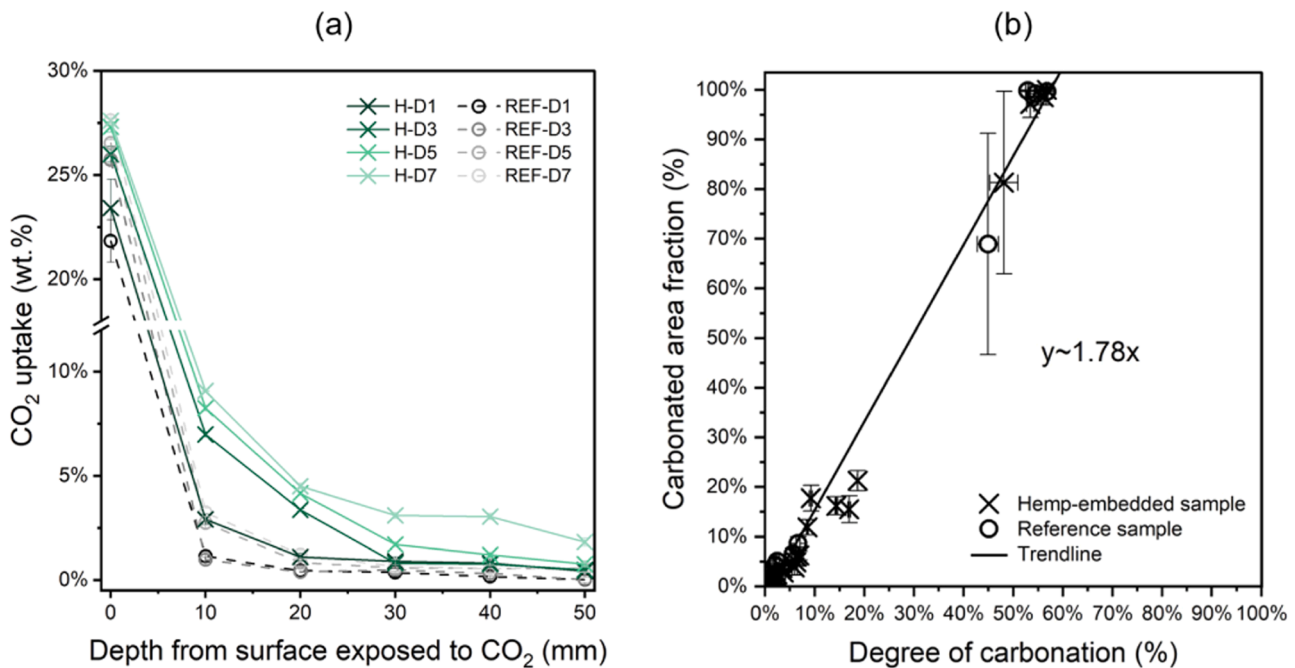


Fig. 7. (a) CO₂ uptake by wt% for reference (REF-D1, REF-D3, REF-D5, REF-D7) and hemp-embedded (H-D1, H-D3, H-D5, H-D7) samples subjected to carbonation curing of 1, 3, 5, and 7 days, determined by Eq.(3). (b) Comparison between the carbonated area fraction obtained by image analysis against the degree of carbonation measured by TGA.

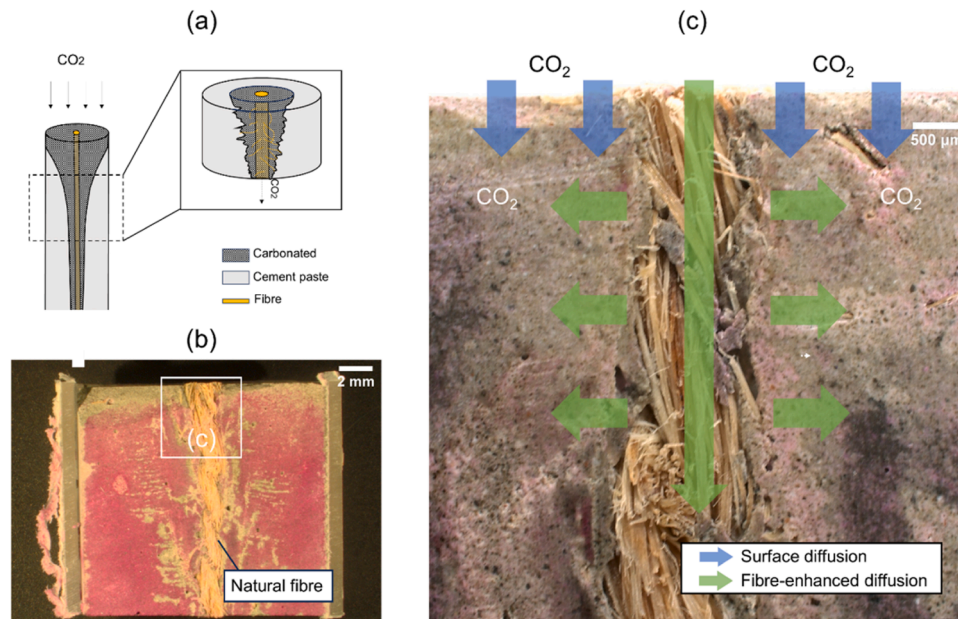


Fig. 8. (a) Schematic illustration of fibre-enhanced carbonation mechanism; (b) Vertical carbonation profile (0–15 mm) of a hemp-embedded sample subjected to 5 days of enforced carbonation (c) CO₂ transport pathways in natural fibre (hemp) embedded cement paste (5× magnification, darkfield, light intensity 50.2 %).

yarns in cement pastes to direct CO₂ transport along designated paths, resulting in funnel-shaped carbonated areas. The phenolphthalein-indicated carbonated areas are concentric around the yarns (Fig. 8b), showing that the natural fibres act as bulk channels from which carbonation propagates into the cement paste samples. Overall, the geometries of the fibre-modified carbonation fronts observed here are similar to that caused by short dispersed natural fibres [63], where thread-like uncarbonated areas were observed along the fibre/cement interface. Hence carbonation initiates at the exposed cement paste surface, CO₂ transports through the bulk channels caused by the natural fibres, and its uptake in the cement paste radically narrows with increasing distance from the surface. The carbonation observed in these samples represents a combination of surface-diffused carbonation and transport-enhanced carbonation along the bulk channels created by the natural fibres (Fig. 8c).

The properties of different fibres also impacted the carbonation rate due to variations in internal porosity and water absorption. By creating CO₂ pathways, the natural fibres also influenced moisture distribution in the surrounding cement matrix. As fibres released absorbed water, they altered local moisture conditions, which may have facilitated CO₂ dissolution and enhanced carbonation near the fibre-matrix interface. This could have led to increased calcium carbonate formation, densifying the microstructure around the fibres. SEM observations (Fig. 5) suggested densified zones and indicated carbonated areas around the natural fibre yarns.

A notable gradient in CO₂ uptake of the cement pastes was observed, with a higher degree of carbonation near the yarns and little to no degree of carbonation further away from the yarn channels. This gradient likely results from the natural fibres acting as conduits, concentrating CO₂ transport through the yarns and leading to accelerated carbonation in their immediate vicinity. The higher degree of carbonation near the fibres can result in denser precipitation of calcium carbonate, which could enhance the bond between the fibre and the matrix. However, the areas further from the yarns, where little to no carbonation occurs, experience fewer benefits in terms of densification or mechanical improvements. This spatial variation highlights the importance of fibre selection and placement in composite design, to maximise carbonation without compromising the composite's overall integrity. Moreover, wool and cotton yarns, which exhibit better fibre-cement bonding, resulted in shallower CO₂ penetration. In contrast, jute and hemp yarns, which

created larger gaps and more porous interfacial transition zones, enabled deeper carbonation but may adversely affect mechanical performance. Therefore, we expect that selecting and placing the appropriate natural fibre type requires balancing CO₂ sequestration benefits with the mechanical and durability requirements of the intended application.

Overall, the natural fibre properties and the CO₂ transport pathways created by the natural fibre yarns actively modify carbonation mechanisms by altering the spatial distribution and precipitation of carbonation products within the cement pastes. These modifications significantly affect CO₂ transport, microstructure, and CO₂ uptake, which we explore further in the following sections.

4.2. Effect of natural fibre properties on CO₂ transport and carbonation rate

The diffusion of CO₂ into cement pastes, modified by the addition of natural fibre yarns, is primarily governed by the internal porosity of fibres, the porosity of yarns (i.e. the spatial arrangement of fibres within yarns), and the interconnected pores throughout the system.

In terms of internal fibre porosity, both SEM-BSE imaging and the resin-impregnated sample analysis (Supporting Information S1, Fig. S2) reveals that hemp and jute possess the most internal porosity among the fibres examined, including hollow centres (i.e., lumens) (Fig. 5e-f) that offer additional channels for CO₂ transport. Cotton and wool fibre bundles have less internal porosity (Fig. 5g-h). The different internal pore characteristics of the natural fibre yarns (hemp, jute, cotton, wool) contribute to variations in moisture absorption and water retention capabilities, which in turn created different gaps between the fibres and matrix. SEM observations showed that some natural fibre yarns contracted as they released moisture into the matrix, particularly hemp and jute (Fig. 5d-g), forming larger gaps at the fibre-matrix interface. This observation is consistent with the high water absorption values of jute and hemp in the first 24 hours (Table 1), while cotton absorbed less water. Wool fibres, being protein-based, experienced partial dissolution in the alkaline cement paste. These variations in internal porosity influence the CO₂ transport pathways available within the fibres, and also at the interface with the cement matrix. The more porous the natural fibres, the faster the carbonation rate.

The spatial arrangement of fibres within the yarns was quantified as

the compactness of fibres and visually analysed by SEM-BSE imaging. Table 1 shows that hemp yarns were the most compact (90.4 %), followed by jute (68.7 %), cotton (39.3–52.0 %) and wool (43.5–49.0 %). Wool yarns had the largest spacing between fibres (typically > 20 µm) which resulted in filling of the spaces with cement paste, obstructing CO₂ transport deeper into the samples. On the other hand, the smaller size of individual cotton fibres resulted in greater local compactness, which narrows the bulk channel for CO₂ transport. Therefore, a balance could be made to achieve an optimum spatial arrangement of fibres within the yarn.

While the bulk yarn bundle is the major network for CO₂ diffusion, the pore distribution within the cement paste is also affected by the morphology of the natural fibres. This is because ‘fluffy’ yarn surfaces, especially bast fibres, can stretch out horizontally into the cement paste, creating additional pathways for CO₂ diffusion and thus enhancing the carbonation rate. Cotton and wool yarns, with their smoother surfaces, offer fewer connected pores for CO₂ transport, resulting in more concentrated carbonation patterns as observed in Fig. 5c–d.

Therefore, our results indicate that natural fibre yarns with higher internal fibre porosity and intermediate spacing within yarns create more interconnected pores within the cement pastes, resulting in deeper CO₂ diffusion and faster carbonation rate.

4.3. Natural fibre yarn composites under enforced carbonation conditions

While fibre properties significantly influenced early-stage carbonation, their impact diminished over prolonged curing durations, as evidenced by the plateau in both carbonated area fraction and CO₂ uptake at 7 days of enforced carbonation with 20 vol% CO₂ at ambient pressure and temperature. This could be due to limitations in CO₂ transport into the carbonated cement paste or within the fibre structure, e.g., by pore space filling by carbonation products.

In past experiments under similar carbonation curing conditions (20 vol% CO₂ and 8 hours of in-mould curing), the 1 day CO₂ uptake for 20 mm cement paste cubes (w/c = 0.35) was found to be 7.98 wt% [26], with CO₂ diffusing from around the samples. This value closely aligns with the average 1 day CO₂ uptake of 7.80 wt% found here in the first 20 mm of reference samples. The inclusion of hemp yarn enhanced this uptake by 15 %, to achieve a CO₂ uptake of 9.14 wt%. Comparatively, after 1 day of curing under 99.8 vol% CO₂ at 5 bar pressure, dispersed short-sisal-fibre engineered cementitious composites showed an average CO₂ uptake of 8.99 wt% along a 50-mm depth [63], surpassing the uptake in hemp-embedded samples (4.92 wt%) which were carbonated at ambient pressure. Therefore, we expect the carbonation extent of fibre embedded samples to be enhanced at elevated pressure. We note that despite the higher overall CO₂ uptake in carbonated dispersed natural fibre samples, there was no carbonation at sample depths greater than 30–35 mm, while the hemp samples presented a gradual, yet consistent carbonation from the surface to 50 mm depth.

Our study indicates that CO₂ transport and uptake can be increased through the use of natural fibre yarns, although the full potential of fibre-enhanced CO₂ transport and uptake is yet to be uncovered. SEM-BSE and XRD (Supporting Information S1, Section S5) results showed unreacted cement clinkers and incomplete hydration across the samples that indicates the need for optimisation of the curing regime. Factors to be optimised include considering the in-mould curing period, pre-curing conditions (i.e. controlled water removal prior to carbonation), CO₂ exposure conditions, and post-curing conditions to enable further hydration of unreacted cement grains (i.e. water baths).

This study provides a basis for employing more complex natural fibre yarn arrangements in future research. Unlike conventional ECC, which involves the random distribution of fibres, the concept proposed in this study can be utilised as organised placement of fibre yarns in cement-based materials, akin to textile-reinforced mortars [51,96], where fibres are systematically organised into woven or stitched meshes across at least two orthogonal directions. Our results confirm the practicality of

creating natural textile-reinforced mortars under enforced carbonation conditions, and established a fundamental understanding for controlled CO₂ transport and uptake within these composites.

To implement this concept, natural fibre yarns can be arranged in layers of meshes (i.e., nets) as reinforcements in cement composites, forming interconnected pathways for bulk CO₂ transport. The density and spacing of these meshes can be optimised to facilitate enhanced CO₂ ingress. As the phenolphthalein-stained carbonation fronts observed around each yarn form distinct zones with measurable diameters, the proposed image analysis can also be used to compute the effective thickness of the carbonated region (i.e., the carbonated rim around the yarns). These measurements can inform the optimal spacing between fibre yarns to maximise carbonation coverage throughout the composite. Properly spaced fibres would promote more uniform carbonation, which helps maintain the benefits of fibre-enhanced CO₂ transport while reducing microstructural density differences from uneven carbonation, thus preserving the composite’s mechanical properties under enforced carbonation.

With carbonation processes already prevalent in non-reinforced and pervious concrete [19,101], these natural fibre yarn composites could be utilised as precast structural and semi-structural components. When designed as functionally graded materials combined with steel-reinforced structures, this concept can also help achieve desired carbonation depths without compromising the integrity of the reinforcing steel. These composites can be integrated into existing structures as thin external layers, similar to the use of textile-reinforced mortars in reinforcing and retrofitting existing structures, such as pedestrian bridges, and in precast textile-reinforced façade panels [52,102]. Moreover, with two or three-dimensional natural fibre yarns/textiles, we anticipate that structural elements with diverse shapes can be created [103,104], serving dual purposes of structural support and CO₂ sequestration. The approach demonstrated in this study is also applicable to various construction components such as structural bricks [105], concrete blocks and concrete canvas [106–108].

4.4. Carbonation profile assessments

We identified a strong linear relationship between the carbonated area fraction determined by image analysis and degree of carbonation determined by TGA (Fig. 7b). The data points were clustered at both the lower and higher ends of the carbonation spectrum, with a uniform scatter along the trendline. However, variability increases slightly with higher degrees of carbonation, largely due to limitations in the image analysis method. As three sets of replicas were produced to enable error calculation and comparison across phenolphthalein-stained discs, the larger error bars in the measured carbonated area fractions are largely caused by the errors induced by the cutting process, where discs were obtained by slicing the samples at certain depths. These include inaccuracies in marking the precise cutting locations, and material loss induced by the thickness of the saw blade. The precision of disc preparation is thus susceptible to both machine and human errors, highlighting the need for careful handling during sample preparation to maintain the accuracy of the image analysis method.

In addition, as the proposed image analysis protocol relies on the strong colour contrast between the carbonated and non-carbonated area; other pH indicators with weaker colour transition, such as thymolphthalein, are not recommended since the blue stain cannot be easily distinguished from the greyish colour of the cement paste. Nevertheless, comparing with time-consuming characterisation techniques that rely on specific instruments such as TGA and QXRD [7,13, 23], this image analysis method provides a rapid and reliable alternative to quantify carbonation profiles in cementitious materials.

5. Conclusion

Under enforced carbonation (20 vol% CO₂) at ambient temperature

and pressure, it was found that all types of natural fibres, but especially bast fibres (i.e. jute and hemp), increased CO₂ uptake. Distinct carbonation fronts were observed around different natural fibres. Bast yarns exhibited irregular and wider carbonation fronts, whereas cotton and wool yarns showed concentrated patterns.

The controlled diffusion of CO₂ is influenced by the internal porosity of fibres, the spatial arrangement within yarns, and the interconnected pores within the system. Porous natural fibres yarns create additional CO₂ diffusion pathways into the cement paste, as evidenced here by the continuous increase in carbonated area fraction and CO₂ uptake along the yarns relative to the bulk material. This indicates effective CO₂ transport through the interconnected pore networks formed by the yarns.

Hemp yarns were the most effective in enhancing CO₂ uptake of the natural fibres studied here. In the first day of carbonation, hemp-embedded samples achieved significant CO₂ uptake throughout the entire sample depth including at 50 mm (0.432 wt%). The most pronounced increase in CO₂ uptake occurred within three days of curing, with hemp-embedded samples showing a 37.7 % increase in average CO₂ uptake compared to non-fibre samples. Over a 7-day enforced carbonation period, hemp addition increased the CO₂ uptake from 5.64 wt% to 8.19 wt%.

A positive linear correlation was established between the carbonated area fraction from image analysis and the degree of carbonation from TGA. Despite the perceived pH-dependent limitations of the phenolphthalein indicator, a novel image analysis method based on colour deconvolution was found to be a quick and reliable methodology for carbonation quantification.

This study demonstrated the potential of natural fibre yarns to enhance CO₂ transport and uptake in cement paste, offering a new strategy to improve carbonation sequestration efficiency in cementitious materials.

CRedit authorship contribution statement

Rupert J. Myers: Writing – review & editing, Visualization, Supervision, Funding acquisition, Conceptualization. **Yixiu Zhuge:** Writing – original draft, Methodology, Investigation, Formal analysis. **Pei B. Ong:** Writing – review & editing, Investigation, Formal analysis. **Hong S. Wong:** Writing – review & editing, Visualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supporting information

A document presenting fibre property testing methods, additional image analysis, and TGA, XRD, and FTIR results is available as supplementary data.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2024.102983](https://doi.org/10.1016/j.jcou.2024.102983).

Data availability

No data was used for the research described in the article.

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