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Durability of slag mortar reinforced with coconut fibre

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Abstract

A comparative study of the microstructure of both new and in-use aged blast-furnace slag cement coir reinforced composite was performed. Aged samples came from internal and external walls of a 12-year-old house, built in São Paulo. The panels of the house were produced using 1:1.5:0.504 (binder: sand: water, by mass) mortar reinforced with 2% of coir fibre by volume. The binder was blast-furnace slag activated by 2% of lime and 10% of gypsum.

Fibres were removed from the composite and subsequently cleaned with acid solution (chloridric acid, 10%) in an ultrasonic bath. Both aged and new fibres were studied under low pressure BSE SEM with EDS analysis. The lignin content of the fibre was measured by the acetyl bromide method and qualitatively evaluated by Weisner reaction using an optical microscope.

Cement transformations were studied by X-ray diffraction and TG. Its pore water composition was also determined. Carbonation was measured by phenolphthalein. Composites were studied under low vacuum SEM. Interfaces and deposition of inorganic species in the fibre lumen were also investigated. Methods are described.

After 12 years, the cement was fully carbonated. Fibres removed from the old samples seem to be undamaged when examined under SEM. Qualitative lignin content determination by Wiesner reaction suggests that old samples have lower content of guaiacyl lignin units. Nevertheless, the total lignin content of old fibres when measured by using the acetyl bromide method, is comparable to that reported in literature. No significant difference was found in the lignin content of fibres removed from external and those removed from internal walls.

Keywords: Cement composites; Vegetable fibres; Blast-furnace slag; Durability; Lignin; Coir fibres

1. Introduction

Vegetable fibres are complex natural composites with a cellular structure (Fig. 1). A single fibre is a composition of several cells. The cell has a very thin primary and secondary wall. The secondary wall is divided in to three different layers: (1) outer layer (S1), (2) middle layer (S2) and (3) inner layer (S3). In the middle of the cell, there is the lumen, a void space which influences on fibre's mechanical performance [1]. There are also transversal vessels or pits, which connect different fibres. Surface pits have been reported in coir fibres [2]. Different proportions of cellulose, hemicellulose and lignin, constitute the different layers. As can be schematically seen in Fig. 2, the middle lamella, that glues together the adjacent fibres, is almost pure lignin [3]. Additionally to lignin, cellulose and hemicellulose there are also extractives and a highly variable but usually small content of inorganic matter. Table 1 presents the different coir fibre compositions from selected references. The reported composition variability is partially a result of the differences in chemical analysis methodologies.

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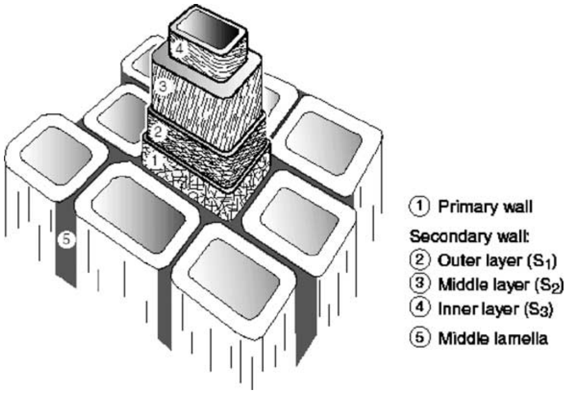

Fig. 1. Cellular structure of vegetable fibres, from Persson [1].

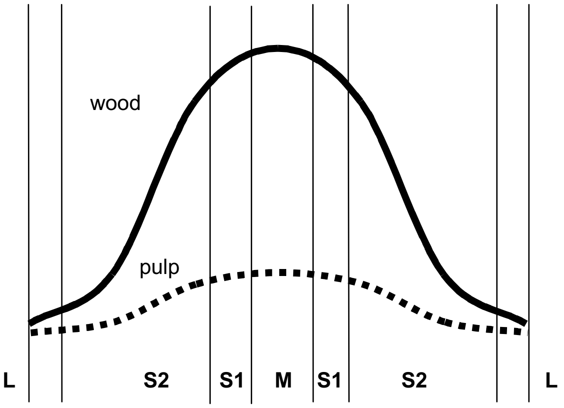

Fig. 2. Schematic representation of lignin concentration between the different cell layers (adapted from Rydholm [3]) for a fully lignified wood sample and in a pulp sample.

Table 1
Composition of coir fibre published in literature

	Source					
	[4]	[5]	[6]	[7]	[8]	[9]
Cellulose			35–47	43		43–60
Hemicellulose			28–15	21		11.6–19[a]
Lignin	**33.5**	**48**	**20–31**	**31**	**31**	**27.7–45**
Ash	–					3.9–8.1
Extractives				4		

[a] Pentosans.

Cellulose is a linear polymer, containing glucose units and presents some crystalline regions. Hemicellulose is a branched polymer, made of various polysaccharides. Lignin chemistry is not yet completely understood but it is known to be an amorphous and heterogeneous mixture of condensed aromatic polymers and phenylpropane monomers [10]. Lignin is classified according to its main building blocks: guaiacyl, syringyl, and *p*-hydroxyphenyl groups, although other aromatic units also exist in many different types of plants [9]. The exact lignin composition is influenced not only by species but also by other factors, such as the plant's age.

The main aim of the pulping process, a strong alkaline attack, is to remove lignin from the wood. But there is some evidence that the process starts with removal of hemicellulose from the cell walls [10]. After this initial stage, the lignin from the middle lamella is progressively removed [10]. No data is available on the reduction of tensile strength resulting from delignification by cement alkali attack in coir fibre. The effect of delignification on wood tensile strength due to pulping process depends on the nature of the process (kraft, sulphite, etc.). For spruce wood submitted to pulping processes, a 8% reduction in lignin (from about 23% to 15%) will result in a 35–40% reduction in tensile strength, depending on the process [3]. Nevertheless, fibre liberation (cell separation) will only be achieved after removal of 75–80% of the total lignin and after removal of almost all the middle lamellae lignin [3]. Hafrén et al. [11] shows that lignin can be reduced from 28.4% to 1.3% without losing the integrity of *Pinus thunbergii* woodblock. TEM replica studies have shown that the delignification process causes an increase in the porosity of the middle lamella [11].

Sreenivasan et al. [12] exposed coir fibres to an 18% NaOH solution for 30 min at 30 °C and observed a 12% weight loss. The weight loss was attributed to delignification but probably included removal of fibre extractives. This treatment caused a small increase in the tensile strength. As there was no measurement of lignin content variation and the alkaline exposure caused the fibres to shrink in the length and swell in the diameter [11,13], it is difficult to draw a conclusion. Rout et al. [2] observed a significant reduction in tensile strength when previously de-waxed coir fibres were submitted to a 5% NaOH solution at 30 °C for 1 h. However, the exposure of fibres to a 10% NaOH solution resulted in an increase of tensile strength.

Non-alkali degradation mechanisms which have been reported are biodeterioration, photochemical (UV) degradation [14] and, in the case of vegetable fibre reinforced cement composites, fibre mineralization [15,16].

Gram [5] performed the first systematic and comprehensive investigation on the durability of vegetable sisal and coir fibre reinforced Portland cement. The degradation of fibres in alkaline environment was evaluated by exposing the fibres to alkaline solutions and measuring the variation in tensile strength. The investigation included natural aging of thin sheets in Dar El Salaam and Stockholm and different accelerated aging tests like CBI (cycles of one surface cycle wetting and drying), Finish Climate Box (immersion at 50 °C water followed by 3 h at 20 °C, 95% RH), wet and dry cycles at 20 °C for up to 40 months, continuous exposure to lab environment at 20 °C and continuous immersion in water at 50 °C. Exposure to dry environment did not cause significant degradation in coir fibre samples. Continuous exposure to hot water caused degradation. The CBI apparatus produced the highest degradation in accelerated tests. The author concluded wet-and-dry cycles increased the degradation speed because the water movement transports OH-ions, which dissolve the lignin and rinse out the decomposed lignin. Samples exposed in the hot climate of Dar El Salaam suffered more intense degradation than those exposed to the cold Stockholm climate. Carbonation of the matrix seemed to preserve the fibre strength. After these results, Gram concluded that the reduction of composite toughness was caused by fibre delignification due to the alkaline cement's pore water. Nevertheless, no direct measurement of lignin variation was performed.

Mineralization is defined as the impregnation of the fibre cell walls and lumen by minerals species like Ca, Mg, Al and Si [15,16]. The reduction of the degree of fibre crystalinity measured by X-ray is considered a evidence of this degradation mechanism [14] but the same result can be seen in coir fibres delignification process [12]. Fibre mineralization is also evident by SEM. Toledo et al. [16] presented images of both sisal and coir cement composites with the cell's lumens partially filled with calcium and other mineral species after 25 wetting and drying cycles. Sarja [15] and Toledo et al. [16] presented EDS confirmation of fibre wall impregnation.

The opinion that mineralization is a very important degradation factor is supported by the fact that fibres with significantly lower tensile strength, when examined under SEM, prove to be impregnated by calcium and silicon and appear to be integer [15]. Nevertheless, as mentioned earlier, fibres can appear integer despite removal of most of the lignin [3,10]. Therefore, there is no direct evidence that fibre impregnation by mineral species can cause loss of mechanical properties in fibres. It is possible that the absorbed species do not cause any reduction in the mechanical performance but merely fill the empty spaces inside the cell lumen and wall.

Biodeterioration of cement-bonded wood particleboard has been investigated by Souza et al. [17]. These products contain a much higher fibre content than cement composites. Even though there was fungi growth in the sample, no mechanical degradation was observed. Also, the particleboard was immune to termite attack, and the insects had died of starvation by the end of the test. Biodeterioration is also part of the process of liberating fibres from the coconut husk [8], since the coconuts remain aging in a pile for some months before industrial processing. So any biodeterioration eventually found in fibres removed from composites can be a result of the coconut aging.

Transformations on the cement matrix, particularly at the fibre–matrix interface can also degrade composite performance. Fibre–cement interface densification has been identified as one of the mechanisms of degradation of glass fibre reinforced composites [18]. Savastano and Agopyan [19] had observed by SEM a reduction in the transition zone's porosity during aging of vegetable fibre composites between 28 and 180 days of standard wet curing. But they also observed a gap between fibre and the matrix, attributed to the higher drying shrinkage of the vegetable fibres. However this gap can be at least partially a result of the strong de-hydration process in preparation of the samples for the SEM observation. So when exposed to in-use conditions, the fibres have higher humidity content and the gap is probably reduced. The simple fact that the fibres actually do improve the post-cracking performance shows some degree of bonding between the fibre and the matrix. If there is a bonding between fibres and the matrix under normal environmental conditions, it is possible that some degradation is a result of interface degradation, due to swelling and contraction of the fibres, as suggested by John et al. [20].

To control composite degradation by alkaline attack, some alternatives have been suggested by Gram [5]: low alkaline binder, fibre protection against water and accelerated carbonation. This work aims to assess degradation on a wall panel composite made with a low alkaline, clinker free, activated slag cement reinforced with coir fibres that has been in use in a small house for 12 years.

2. Methodology

2.1. Composite samples

Composite core samples with 50 mm of diameter and about 20 mm thick has been taken from the walls of a 12-year-old house, erected in Rua João dos Santos Abreu, 607 Vila Nova Cachoeirinha, São Paulo, Brazil (approximately 23°33′S; 46°44′W). Two cores were removed from dry, indoor walls and two from the external face of the walls. In São Paulo between 1961 and 1990, the average minimum temperature during winter was 11.7 °C (July); the maximum average for February was 27.9 °C. The yearly average rainfall was 1477 mm. The lowest monthly average relative humidity was 74% for August and the highest 80%, observed during January, March, April and December (summer).

Ground, granulated blast-furnace slag activated with 2% hydrated lime and 10% natural gypsum was used as a low alkaline binder. The matrix with mix proportion of 1:1.5:0.509 (binder:quartz sand:water, w/w) was reinforced with 2% volume of coir fibres. The hollowed panels, 10 cm thick, were wet cured during at least 28 days before wall assembling. All walls were painted at least twice during the 12 years using a water-based PVA paint. The panels were fully carbonated in less than one year. More details about the composite and prototype production can be found at [21–23].

2.2. Experimental methods

The degradation of the composite was assessed comparing samples from the internal wall, protected from rain, with those from the external walls. Fibre degradation was evaluated by the (a) lignin content measurement, (b) qualitative lignin distribution by Wiesner reaction method and (c) SEM and EDS analysis of fibres removed from the matrix. SEM/EDS analysis was used to analyse composites. Matrix transformations were analysed by DR-X and TG as well as by pore water analysis.

Lignin content in coir fibres was determined using UV spectrometer (Hitachi U1100) at 280 nm, accordingly to the acetyl bromide method [24]. Fibres were hand removed from the matrix after it has been crushed with a steel hammer. Before the lignin content determination, the fibres were repeatedly washed in deionised water at ambient temperature for at least 24 h to remove inorganic impregnated species. Since the fibre's diameter lies between the specified particle size ranges, it was not necessary to grind the samples and the samples were fully dissolved.

Qualitative lignin distribution in the fibres were evaluated by Weisner reaction method, performed following Yoshizawa et al. [25]: (a) cross-sectioning epoxy impregnated fibres using microtome, (b) pouring a few drops of 1% phologloucinol ethanol solution on the section mounted on a glass slide, (c) adding one drop of 37% hydrochloric acid, (d) covering the section with a cover slip and (e) taking micrographs using an optical microscope equipped with a high resolution video camera in less than 5 min. This dye reacts with the guaiacyl units in the lignin, turning them red or purple.

Fibres were observed using a Hitachi SM3000 SEM at low vacuum (BSE images). In order to remove the mineral species that covered the surface, they were submitted to an ultrasound agitated 1:30 hydrochloride acid solution, at room temperature for 15 minutes. Composite samples were vacuum impregnated with epoxy resin (Epofix) and air cured for 24 h before grinding and polishing with diamond paste (10 μm). Subsequently, they were observed in low-vacuum (40 mPa), with 20 kV acceleration and 100 μA current.

In order to measure pore water composition samples produced with similar chemical composition, wet cured for 28 days and carbonated at 100% CO_2 concentration for 28 days. The samples were then submersed in deionised distilled water (pH = 6) inside an evacuated desiccator. The solid/water concentration was 1 g/50 ml for all four samples. The samples were considered to be in equilibrium with the water when the pH of the water remained constant during a one-week period of time. The concentration of Ca^{2+}, Na^+ and K^+ were estimated by atomic absorption. The pH was measured by titration with 0.02 M HCl using phenolphthalein as an indicator.

XRD, TG and DTG tests were performed on samples ground to pass through a 75 μm sieve. TG and DTG were made with a NETZSCH STA 409C flushed with 20 ml/min of Argon. XRD was made using a Philips MDP 1880, radiation Cuα, 0.02 (2θ) step and 1 s counting time.

3. Results and discussion

Fig. 3 presents the X-ray diffraction pattern of samples from internal and external walls. External wall samples have a higher content of gypsum than the external ones. Additionally, all the most common hydrated cement phases of this kind of cement, except aluminium hydroxide, were identified in the samples: calcium silicate hydrate (C–S–H), etringitte ($C_3A\cdot 3CaSO_4\cdot 32H_2O$) [26,23]. Additionally to those, thaumasite, gypsite, vaterite, calcite and calcium monocarboaluminate. Quartz is from the sand aggregate.

Gypsum ($CaSO_4\cdot 2H_2O$) is most probably originated by the carbonation of ettringite, since XRD from non-carbonated samples reveal no peaks related to this mineral. The PVA paint is not effective against carbonation. Manns and Wesche [27] suggested the following carbonation reaction:

$$C_3A\cdot 3CaSO_4\cdot 32H_2O + 3CO_2 \rightarrow 3CaCO_3 + 2Al(OH)_3 + 3CaSO_4\cdot 2H_2O + 23H_2O$$

This carbonation process causes significant lost of water and an increase in the matrix porosity. It also explains the presence of some phases. Calcite and vaterite, are mineral forms of calcium carbonate. Thaumasite, a variety of hydrated calcium silicon carbonate sulphate, is a result of carbonation, as well as the calcium monocarboaluminate. Not all ettringite formed was carbonated.

External walls seem to have a slightly higher content of gypsum and calcite than the internal ones. The internal wall shows a higher content of vaterite. There are no other significant differences between the two X-rays patterns.

DTG results (Fig. 4) of the internal wall sample show an endothermic peak just above 100 °C which can be attributed to the humidity and possibly to decomposition or a chemical reaction of an unknown phase. This peak is superimposed on the next one, common to both samples, related to C–S–H and gypsum dehydration. At 800 °C there is a peak from the decomposition of calcium carbonate. Assuming that the decomposition of these phases will go from 560 up to 1000 °C [28], weight losses of 9.08% and 9.26% were obtained respectively for internal and external samples. No peak related to the decomposition of the wood fibre was detected around

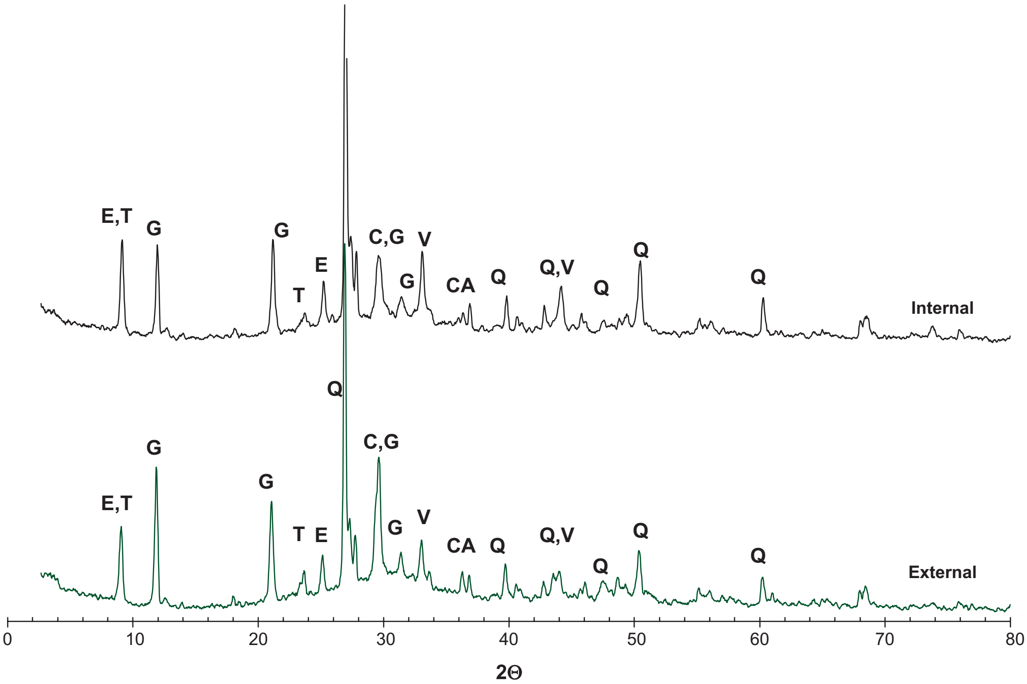

Fig. 3. X-ray diffraction patterns of internal and external samples. E represents ettringite; T, thaumasite; G, gypsum, Q, quartz, V, vaterite, CA calcium monocarboaluminate and C, calcite.

400 °C [29], probably because the content of fibre was lower than 1% of the total weight. It is necessary to point out that there are very few published data about this kind of cement to support a more definitive interpretation of these DTG results.

The internal wall also shows a significantly higher total volatiles content—defined as total weight loss from 105 to 1000 °C, expressed as percentage of the anhydrous cement content—compared to the external wall (Table 2). Since this sample is the one protected from rainwater for the 12 years, most probably this difference did not result from a higher degree of hydration. Nevertheless, carbonation of this kind of cement is rather complex and not fully understood and different environments can result at the formation of different phases as shown in the XRD results. Formation of different phases imply different mass balances due to the differences in the rates of released water and combined carbon dioxide. Carbonation also results in a soluble gypsum phase that can be leached from the external wall by rainwater, but the insoluble residue (Table 2) suggests that there is no significant difference among the samples in terms of insoluble residue, relative to aggregate content.

Fig. 5 presents typical SEM backscattered electron images of polished epoxy impregnated samples from external (a) and internal (b) samples. The cellular structure of the coir fibres looked preserved. In some areas lignin appeared to have been removed, probably due to biodeterioration (center of Fig. 5b). However, new commercial fibres not in contact with cement can also present the same degradation. Some deposition of mineral species covering the cell walls and even inside the walls and lamellae tissue were also observed (see Fig. 6, arrows in Fig. 5a and the bright area at the centre of Fig 5b). EDS analysis shows calcium is the main mineral component, but silicon, aluminium and even sulphur could also be detected at lower contents (Fig. 6), as previously reported by Savastano and Agopyan [19] and Toledo et al. [16]. Extensive impregnation of the lumen by minerals species like those observed by Toledo et al. [16] was not observed.

It was not possible to detect any concentration of Portlandite in the transition zone, including the cementitious covering of the external walls of the fibres (Fig. 5a and b), as reported by Agopyan and co-workers [21] for Portland cement matrix. That had been expected because the cement had a very low content of free CaO [23]. The pore water analysis (Table 4) revealed that calcium ions (Ca^{2+}) are by far the most common specie in solution. This is coherent with the predominance of Ca species inside the fibre tissue. Oliveira [30] reported a significant content of SO_4^{2-} as well as the presence of SO_3^{2-} in pore water of cement with a similar composition but containing only 6% of gypsum.

A gap between most of the fibres and the matrix was observed (Fig. 5a and b), confirming previous results. This gap was between 0 and 25 μm.

The analysis of the surface of coir fibres previously washed in acid solution (Fig. 6) revealed the external

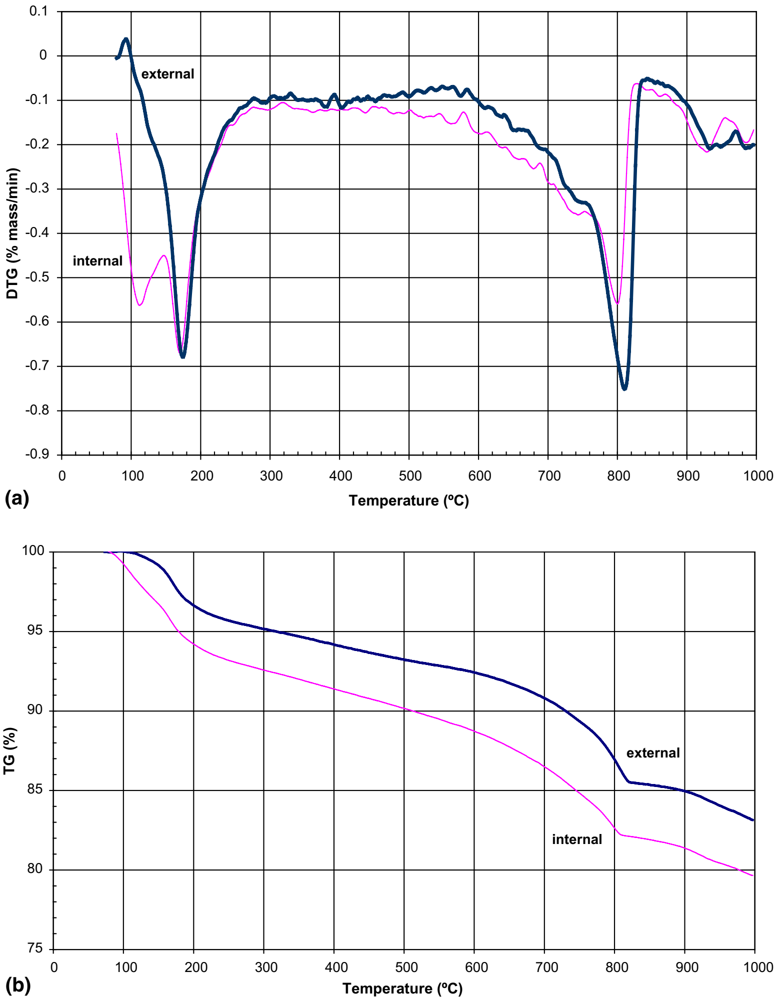

Fig. 4. TG and DTG curves of external and internal walls samples.

Table 2
Insoluble residue and loss on ignition of samples

Sample	Size (g)	Humidity (%)	LOI (%)	Insoluble (%)	Volatiles (%)[a]
External	14	1.48	7.77	57.7	18.4
Internal	34	2.22	9.63	58.0	22.9

[a] Of the anhydrous binder content.

surface to be morphologically integer. Surface pits, as reported by Rout et al. [2], are clearly visible, both in new (Fig. 7c) and old (Fig. 7a and b) fibres. But in disagreement with the observations of these authors, many of the pits, in both old and new fibres, present silicon occlusions instead of being fill with fatty materials (see white dots in Fig. 7). Some of the old fibres did present surface cracks (see Fig. 7b) or other damage probably due to a mechanical origin. However, same kind of damage is also detected in new fibres, such as the cracks visible in Fig. 7c.

Table 3 shows the lignin content in the fibres. The high dispersion of the values can be explained by the variability of the natural product combined with the small size of the sample (~10 mg) and the fact that the sample fibres were not ground to prevent further sample weight loss. Differences in the degradation speeds among different individual fibres can also play a significant role in the lignin content. These results are slightly above the average of those published (Table 1). Comparing the results with maximum lignin content in the published data, it is possible to have a delignification of as high as 14%, which could cause a significant loss in strength.

In terms of lignin content, there are no significant difference between external and internal samples. Since

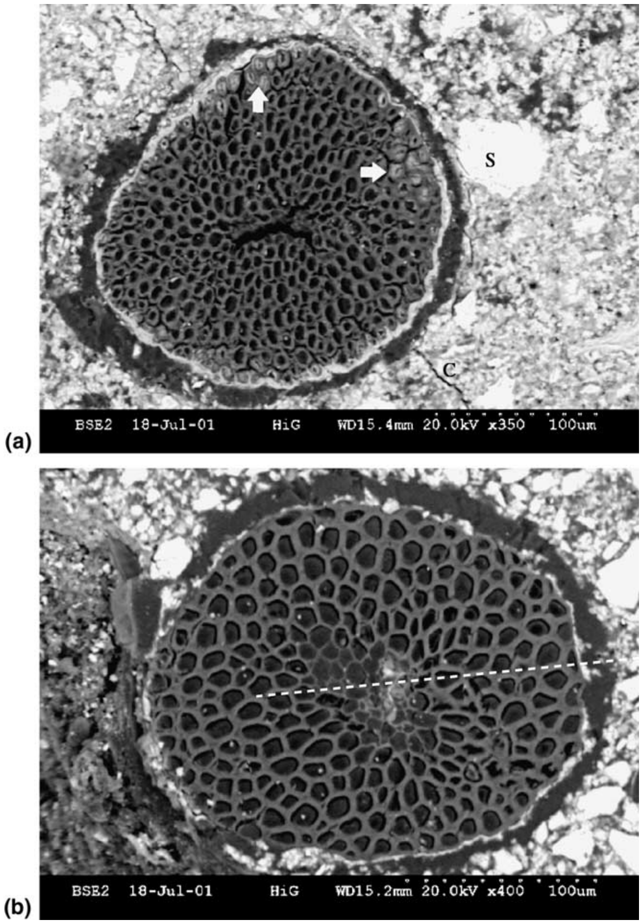

Fig. 5. Back-scatter electron images from epoxy impregnated external (a) and internal (b) 12-year-old samples. The arrows show cells with higher lumen impregnation. "S" identifies unreacted slag grains. The dashed line represents the position of the line scan in Fig. 6.

water is essential to delignification and if the cement pore water was aggressive enough to decompose lignin, the sample exposed to rainwater would present a lower lignin content. This observation seems to support the conclusion that no significant lignin has been leached out.

Fig. 8 presents optical microscope micrographs from samples submitted to the Weisner reaction, which dyed the guaiacyl lignin groups red or purple. As can be seen in Fig. 8 the new fibre has a much higher red/purple intensity than the other samples removed from the walls. Also, the external wall samples presented a red intensity a lower than those from internal walls. It is possible to conclude that guaiacyl groups had been removed from the samples. The availability of rainwater seems to speed up the process. Also the pore water of cement stored in an ambient with a relative humidity above 74% was enough to cause some degradation after 12 years.

Table 3
Lignin content by acetyl bromide method

Sample	Wall	
	External	Internal
1	34.6	34.1
2	35.6	34.2
3	38.8	36.5
4	34.8	nd
Average	35.9	34.9

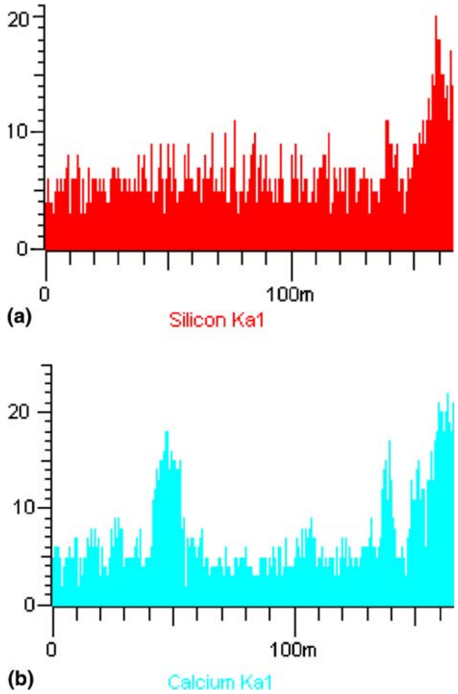

Fig. 6. EDS line-scan from the line presented in Fig. 5b.

Table 4
Pore water composition of the sample

Sample	Na^+(mmol/l)	K^+ (mmol/l)	Ca^{2+} (mmol/l)	pH
A	1.40	0.94	15.03	10.33
B	1.57	0.95	15.33	10.33
C	1.46	0.81	15.50	10.31
D	1.58	0.88	12.71	10.36
Average	1.50	0.89	14.64	10.33

4. Conclusions

Twelve-year-old coir fibre reinforced low alkaline cement was studied.

The cement, ground granulated blast-furnace slag activated by 2% of calcium hydroxide and 10% of gypsum, was fully carbonated. Additionally to C–S–H, vaterite, calcite, ettringite, thaumasite, calcium monocarboaluminate and gypsum were detected by XRD. Even after cement carbonation, ettringite was detected in the samples. Small differences in the amount of vaterite,

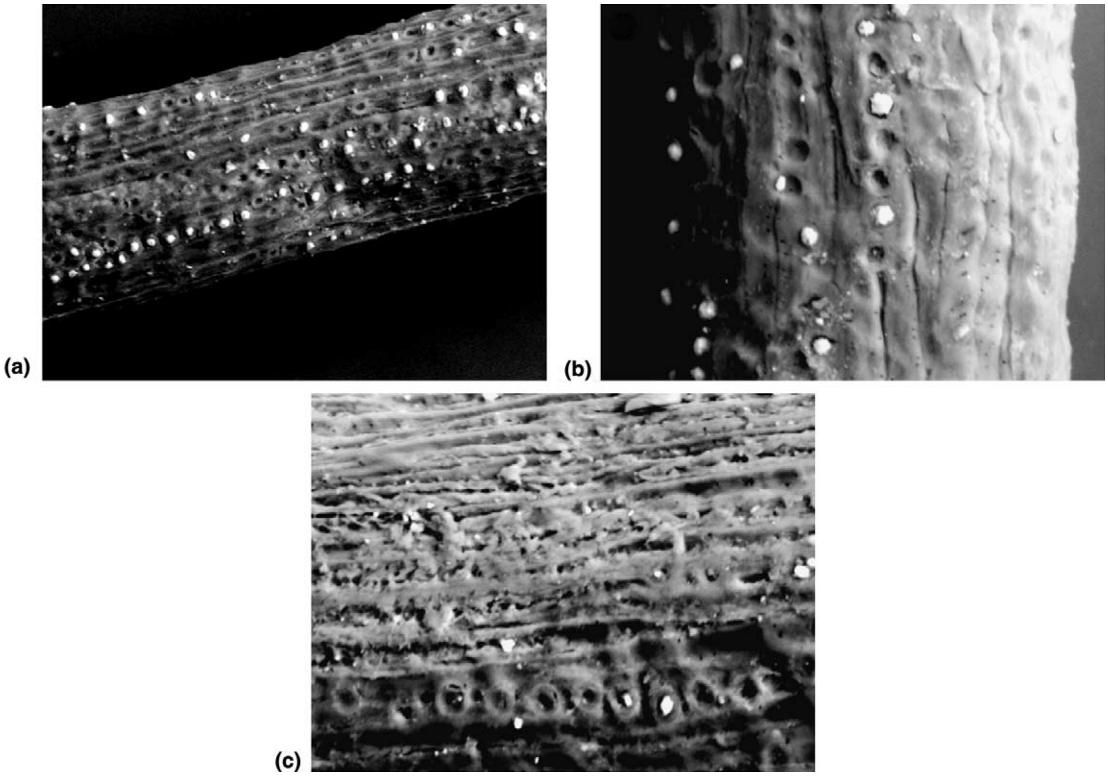

Fig. 7. Representative BSE (3D mode) micrograph from fibres removed from samples (a) external and (b) internal wall samples after acid cleaning and (c) new fibre sample. The bright dots are silicon occlusions over the surface pits.

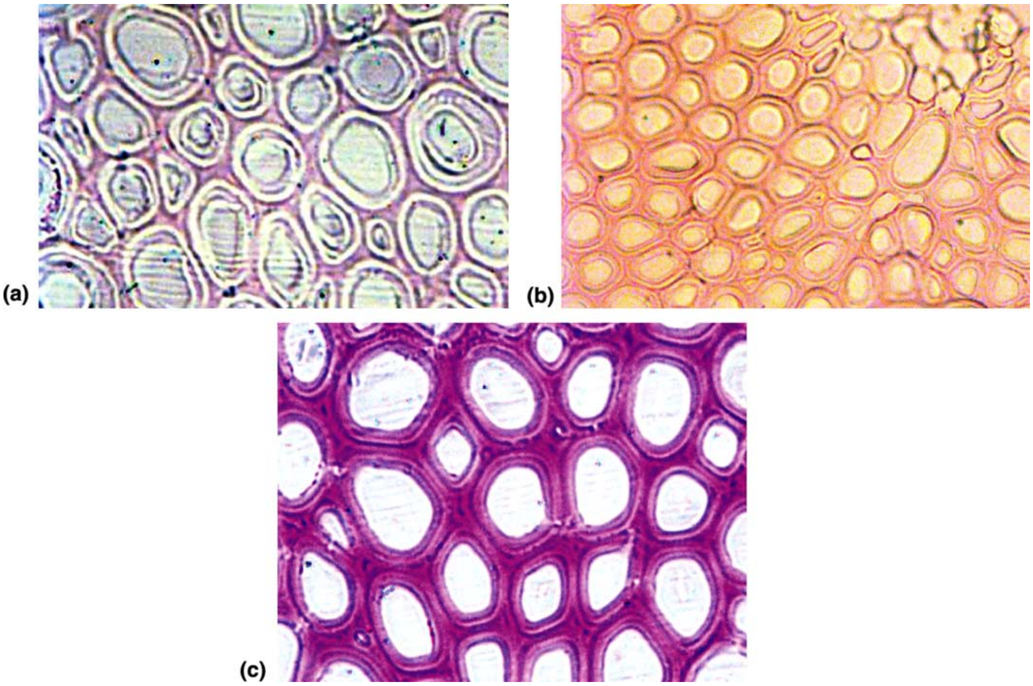

Fig. 8. Optical micrographs of Wiesner reaction samples from (a) external wall, (b) internal wall and (c) new fibres. The more intense the red/purple colour the higher is the content of guayacil lignin groups. (For interpretation of colour in this figure legend, the reader is referred to the web version of the article.)

gypsum and calcite were found between samples from external and internal walls. The DTG of the sample from the internal wall revealed an unexplained peak just above 100 °C. The same sample presented a slightly higher total volatile content than the one from the external wall. Differences in carbonation processes and leaching of soluble phases like gypsum can explain this difference. Further research is needed to clarify this point.

The pore water of carbonated cement with about the same chemical composition, presented mainly Ca^{2+} and possible SO_4^{2-} groups. The pH was as low as 10.3.

The average lignin content in coir fibre samples removed from both external and internal walls was around 35%, higher than the average content found in the references. However, the possibility of lignin decomposition can not be dismissed, because new fibres have been reported to have lignin contents as high as 48%. But, since no statistically significant difference in the lignin content was found between external and internal samples, this difference is probably smaller than the natural variability.

Weisner reaction revealed that samples from the wall contained a lower content of guaiacyl lignin units than the new fibres. External wall sample, exposed to wetting and drying cycles, had the lowest guaiacyl content, followed by the internal wall sample. This measurement reinforces the conclusion that some lignin had been leached from the fibre.

Fibres extracted from the samples appeared to be integer when examined under SEM. Analysis of polished samples of the composite confirmed the occurrence of a gap between the fibres and the matrix as well as the impregnation of the fibre walls by calcium and, a to a minor extent, by silicon. But total impregnation of fibre's lumen void space was rarely found.

The low alkaline cement was not able to prevent some lignin from being decomposed and leached from the fibres. Further experiments are being conducted to elucidate this point as well as the carbonation process of the cement.

Finally, it is necessary to point out that an eventual leaching of lignin has not proved to have had any effect on the walls in-use performance.

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