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ENVIRONMENTAL SCANNING ELECTRON AND FOCUSED ION BEAM MICROSCOPY OF NOVEL FILLERS AND BINDERS IN CEMENT-BASED COMPOSITES

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Abstract

Environmental scanning electron microscopy and focussed ion beam imaging have been used to characterise the morphology of some composite materials consisting of organic plant fibres in calcium aluminate cements and a lime based mortar. Energy dispersive X-ray maps show the locations of calcium, carbon and aluminium atoms in specially prepared cross sections in which fibrous material was exposed.

Focussed ion beam milling, ion induced electron images and environmental scanning electron microscopy show the microstructure of the additives in the mortars. Internal surfaces of the prepared materials were exposed by impact fracture. Subsequently the focussed ion beam (FIB) technique was found to be the most useful method for sectioning the exposed hemp fibres encapsulated in the cement matrix. Sectioning revealed relatively little ingress of the alkaline solution from the cement paste within the internal cells of the hemp fibres although there was some ingress into those at the periphery.

Keywords: calcium aluminate cement, hemp, Raman, ESEM, EDX, FIB

Introduction

Cements may be regarded as adhesive compounds with the ability to embed and hold together fragments of rocks, reinforcement and other solid materials in any required morphology and dimension. The constructional properties of such materials depend on loads being shared between two or more separate constituents or 'phases' and where paths for the propagation of cracks will be affected by the different mechanical properties of the components. The manner in which these adhere to each other becomes an important consideration. Hence the interfacial bond between constituents and the matrix is of fundamental importance.

The scanning electron microscope with its superior depth of focus compared to the optical instrument has played a prominent role in studies of the hydration reactions involved in cement chemistry (Taylor 1997, Steward and Bailey 1983, Bergstrom, T.G., and Jennings, H.M., 1992),

Though many studies have focused on the 'bulk' properties of the cements it is recognised that the early stages of hydration may well occur on the surface of the cement particles and in the near-surface liquid (Meredith et al 1995). Clearly the incorporation of additives would be expected to influence these processes.

This paper describes results obtained from the analysis of a novel composite which is compared with a fibre-containing 60 year old sample from the Channel Islands as part of a larger study concerned with developing new low embodied energy products for the building industry.

Experimental

Sample Preparation

The new composite matrix was prepared using calcium aluminate cement (Secar 71, Lafarge Aluminates), Fontainebleau sand and hemp. The weight percentage of sand with respect to the total weight of mineral solid (cement and sand) was 29% and the volume percentage of hemp was 10 %. The water over cement weight ratio was equal to 0.3. The composite matrix was left to cure at 20°C and 50% of relative humidity for 24h.

An external and internal cross-section of the hemp: sand: cement composite was analysed using Environmental Scanning Electron Microscopy (ESEM) and Focused Ion Beam (FIB) imaging. The location of calcium, carbon and aluminium was determined using Energy Dispersive X-ray Analysis (EDX) on the environmental scanning electron microscope (ESEM). The experimental methods used with each of these techniques is given below.

Environmental Scanning Electron Microscopy (ESEM) with Energy Dispersive X-ray Analysis (EDX)

Sample surfaces were examined using a Philips Electroscan 2020 ESEM, fitted with a Princeton Gamma-Tech Energy Dispersive X-ray (EDX) analysis system. The chamber was evacuated in "wet" mode (vacuum pressure 5 Torr) and "flooded" 3 times to introduce water vapour. Images were acquired using an accelerating voltage of 20keV and a working distance of 19mm. A long working distance secondary electron detector was used. Samples were prepared by mounting on 12mm diameter pin stubs with carbon sticky pads.

The high alumina Channel Island mortar was mounted in epoxy resin and polished down to ¼? m using a combination of alumina papers and diamond pastes. The sample was coated to minimise charging prior to introduction into the analysis chamber of a Hitachi S2300 scanning electron microscope. A four-quadrant solid-state backscattered electron detector (KE Developments Ltd) was used to image the sample. 200?m x 200?m energy dispersive X-ray element maps were acquired using a combination of an Oxford Instruments detector and electronics with Thomson Scientific WinEDX software. Figure 4 shows a scanning electron cross section of the sample obtained from an artillery post on the Channel Islands. The sample dates from 1942.

Focused Ion Beam Microscopy

An FEI FIB201 ion beam instrument was used for sectioning and high-resolution imaging of the sample. The instrument was capable of producing a gallium ion beam of 30eV and 7 nm diameter which was focused onto the sample using beam currents in the range 5-75pA. A platinum organometallic gas injector was used for ion-assisted deposition of platinum over selected regions of the sample to avoid electrical charging effects produced under ion bombardment. The principal of operation was similar to a scanning electron microscope, but in this instrument a gallium ion beam was scanned over the surface of the sample while secondary electrons were captured to produce an image. If the ion beam was allowed to dwell on a given part of the sample, sputtering occured, removing sample material, to reveal underlying structures (Gamo and Namba 1990).

X-ray Diffraction Measurements

For the Channel Island mortar, samples were carefully taken from regions between the bulk aggregates, to examine the cement paste regions. Methanol was used to disperse the powder sample evenly over the holder and evaporated to leave a dry sample for analysis. A Siemens D500 X-ray diffractometer was used to record diffraction data. Diffractograms with 2? values ranging from 10? to 80? were acquired, in steps of 0.05? and dwell times of 2s per step. Unfiltered CuK? radiation was used, generated at 40kV and 30mA. The sample was rotated during analysis and Siemens DIFFRACT-AT software used to process the results and compare them with the JCPDS database. After performing the initial analysis, it was found necessary to acquire data over a narrower range of 2? values, from 5? to 35? using a dwell time of 10s per step. This was done to improve the quality of the diffractogram over the range of angles required to investigate the presence of clay minerals.

Results and discussion

Figure 1a shows an ESEM image obtained from the free surface of the hemp-reinforced cement composite. The image shows that the hemp fibres were completely surrounded by the cement matrix. EDX analysis from this area indicated the presence of Ca, C and Al, shown in Figures 1b, 1c and 1d respectively. This confirmed that the cement in the composite matrix contained anhydrous calcium aluminate phases as well

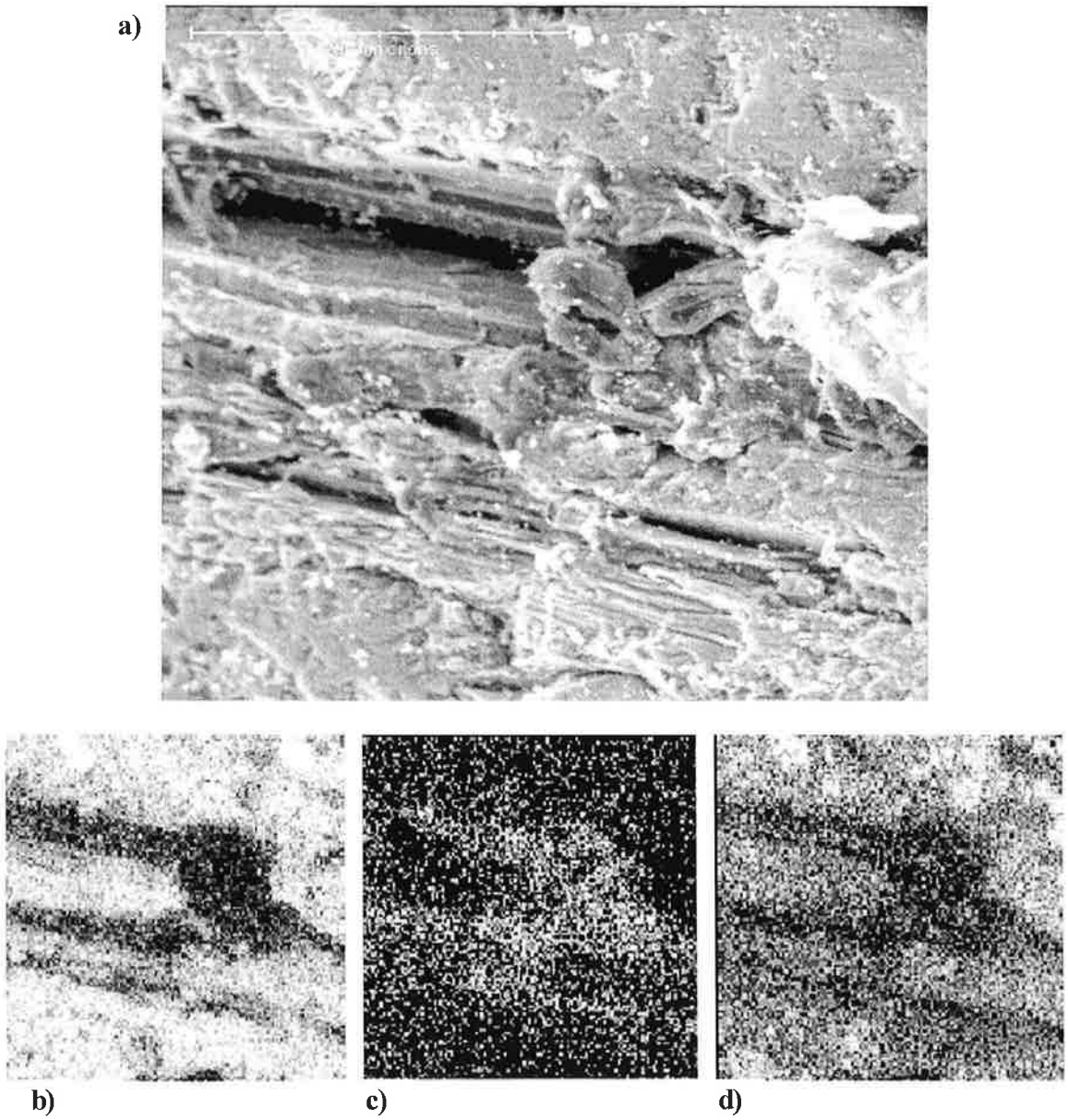

Figure 1: a) ESEM image of as-cast external surface of the hemp - cement composite. EDX maps of b) calcium c) carbon and d) aluminium.

as calcium aluminate hydrates. An ESEM image obtained from a fracture surface of from a fracture surface of the same sample is shown in Figure 2. Hemp fibres are clearly visible protruding from the cement matrix.

The Focused Ion Beam was used to section the hemp fibres. Sample sectioning was achieved using a 12nA ion current to produce a trench in the material. A finer beam of lower current (1nA) was then used to 'polish' the larger vertical face of the trench by scanning the beam in a line and moving it progressively upwards to remove further material. The sample was then tilted to an angle of 45 degrees and the

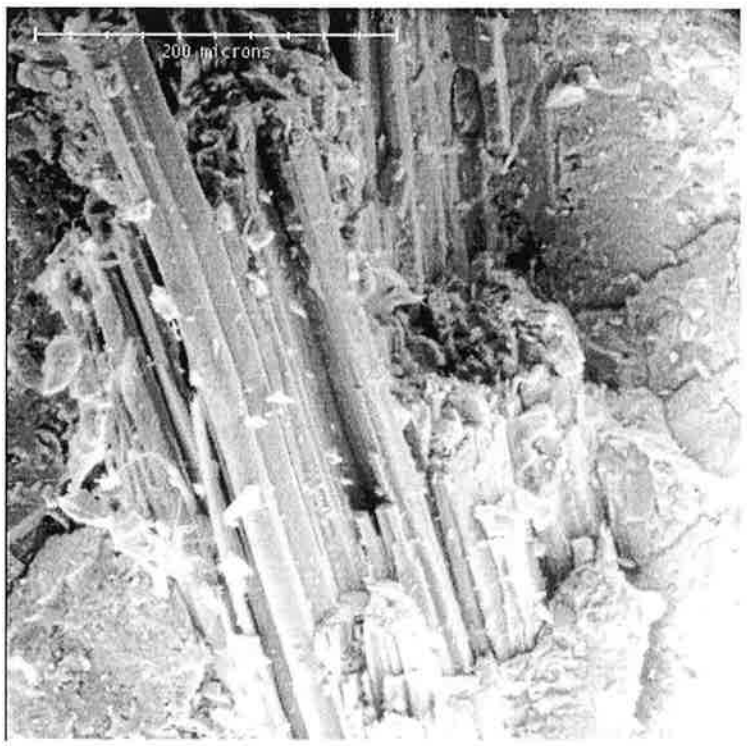

Figure 2: ESEM image of fracture cross-section surface of sample showing hemp fibre.

polished face imaged using the same ion beam, at a few picoamperes current to obtain high-resolution images.

Figure 3a shows a section produced at the interface between a hemp fibre and the cement matrix. Pores in the fibre are visible and the lower ones in the image appear to be hollow. The upper pores and those bordering the cementitious phase appear dark in colour. This is consistent with a small degree of cement ingress within some pores at the periphery and their consequential charging under the ion beam.

Images at higher magnification (Figures 3b and 3c) revealed structure in the hemp fibres themselves.

X-ray diffraction studies of a high alumina cement mortar from the Channel Islands artillery post indicated the presence of the hydration products $CaO.Al_2O_3.6H_2O$ and $Al_2O_3.H_2O$. This sample was imaged and mapped in a scanning electron microscope revealing the presence of fibrous material, most probably wood or

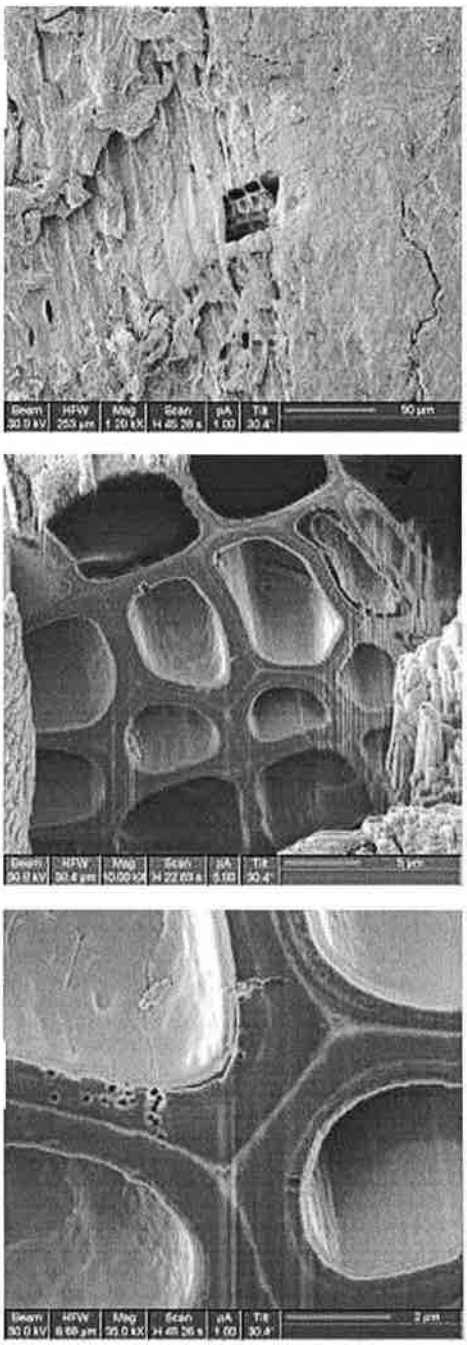

Figure 3: FIB images showing a section produced at the interface between a hemp fibre and the cement matrix.

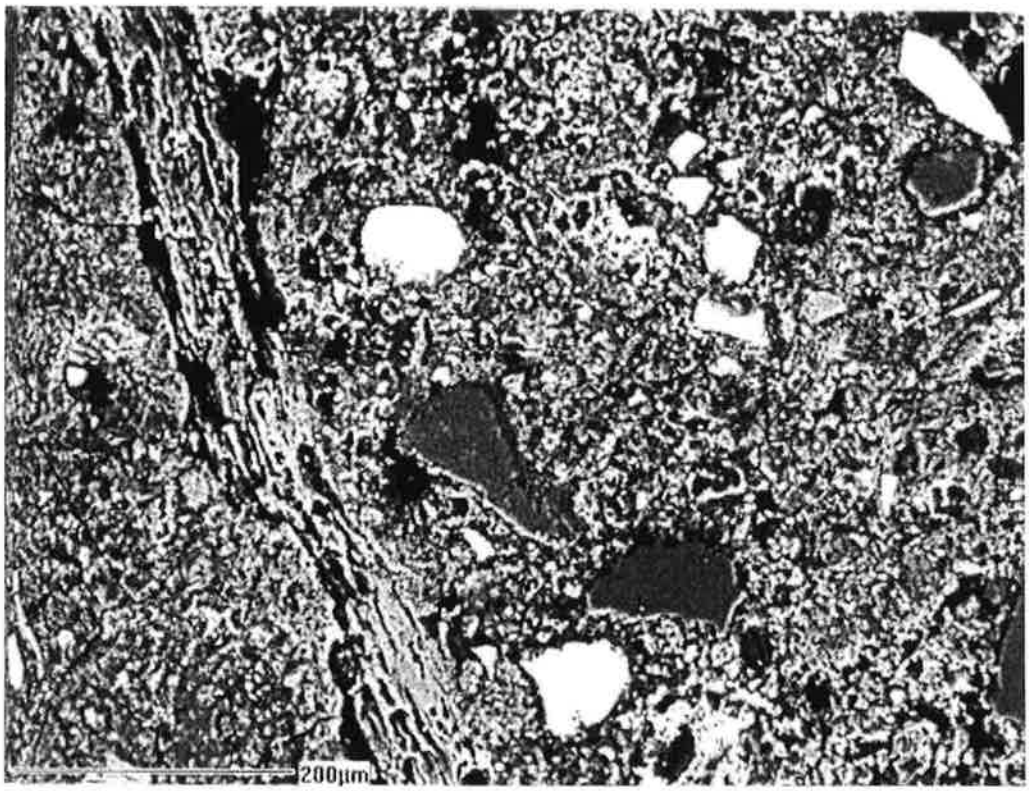

Figure 4: Backscattered electron image and element maps from a high alumina cement

straw in the matrix. In contrast to the hemp fibres in the cementitious phase described above, the elemental maps from this mortar sample shown in Figure 4 indicated extensive calcification of the organic material. The EDX maps shown in Figure 5 confirmed that migration of calcium from the cement pore solution in the fibrous material had occurred while aluminum and silicon remained in the paste. This is not unlike the situation noted for the behaviour witnessed in cement-bonded particle-board (CBPB) (Fan et al 1999). Here the deformation of the cellular structure of wood fragments adjacent to the cement paste and full or partial blocking of the space between the cell walls is known to occur.

Whether this difference in behaviour is one produced by diffusion of calcareous material as a process of ageing or is a consequence of the matrix of the fibrous material itself is uncertain. However a 2000 year old sample of a mortar from King Herod's palace in Masada containing reed-like material indicated that delignification may have occurred but there was no evidence of ingress from the lime matrix (Radonjic et al 2001). Moreover the cellulose structure of the outer walls of the fibrous material was virtually intact favouring the view that the nature of the fibrous material is the controlling factor in these fibre matrix composites.

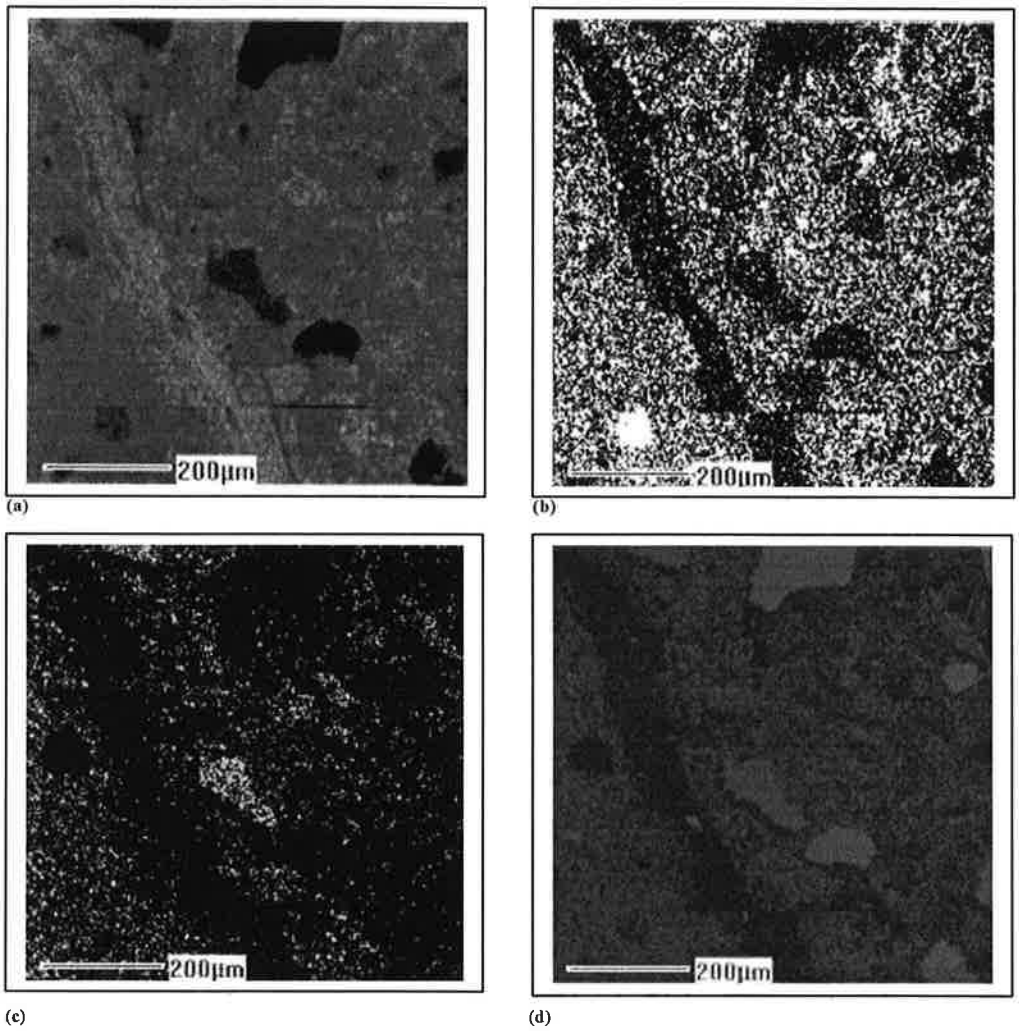

Figure 5: Element maps from a high alumina cement (a) calcium; (b) silicon; (c) iron; (d) aluminium.

Conclusion

Environmental scanning electron microscopy was used to determine the structure of a hemp reinforced cement composite. EDX elemental mapping successfully identified the presence of carbon, aluminium and calcium in a cement matrix. A focused ion beam (FIB) was found to be most useful in sectioning hemp fibres which were encapsulated in a cement matrix but exposed by a fracture surface. Sectioning revealed that no cement paste had entered the internal cells of the hemp fibres, although there was some ingress into those at the periphery.

Acknowledgements

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