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Preliminary investigations of the dimensional stability of super-critically carbonated glass fibre reinforced cement

A.M.G. Seneviratne[a], N.R. Short[a,*], P. Purnell[b], C.L. Page[c]

[a]*School of Engineering and Applied Science, Aston University, Birmingham B4 7ET, UK*
[b]*School of Engineering, University of Warwick, Coventry CV4 7AL, UK*
[c]*School of Civil Engineering, University of Leeds, Leeds LS2 9JT, UK*

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Abstract

The dimensional changes occurring during the super-critical carbonation of glass fibre reinforced cement (GRC) and its subsequent environmental exposure have been investigated. Sheet samples, with embedded stainless steel pins 200 mm apart, were fabricated and then subjected to super-critical carbonation. Test coupons were subsequently exposed to a range of environments including continuous immersion in water, cyclic wetting/drying and outdoor exposure. The super-critical carbonation process resulted in a slight expansion of GRC. This is contrary to the behaviour observed during natural carbonation where irreversible shrinkage normally occurs. Exposure to the various environments mentioned above showed that super-critically carbonated samples had much greater resistance to swelling and shrinkage than uncarbonated specimens. These observations are particularly significant in relation to the practical application of GRC in environments of fluctuating moisture content.

Keywords: Carbonation; Stability; Shrinkage; Fibre reinforcement

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1. Introduction

Extensive use of glass fibre reinforced cement (GRC) products has not been achieved primarily because of concern about their long-term age-embrittlement in wet environments [1,2]. In addition, concerns have been raised about dimensional changes that may occur as a result of moisture or temperature fluctuations. Excessive dimensional changes can reduce the bond between GRC and, e.g., decorative tiles, or may result in cracking which is aesthetically unpleasant and can lead to structural unsoundness or other durability problems [3–5].

All cement-bonded materials, when exposed to wetting and drying, undergo dimensional changes which are caused by the stresses induced as water movement occurs within the microporous structure of the hydrated cement matrix [6–8]. The problem is aggravated in the case of GRC, however, since the mixtures used tend to be cement rich. While over time the aggregate–cement ratio of GRC has gradually been increased from 0.3 to about 1.0, these values are still much lower than those typical of concrete or mortar and dimensional changes can therefore still be problematic [3]. New cements that have low alkalinity and/or produce little calcium hydroxide on hydration have been developed to combat long-term age-embrittlement and these cements are also claimed to have greater dimensional stability when hydrated than Portland cement [4]. Results are based on rather limited studies however, and bearing in mind that these new cements are complex in composition and microstructure, it has been suggested that their actual behaviour is not well established and requires further investigation [5].

Recent work concerned with reducing the susceptibility of GRC to age-embrittlement has demonstrated the advantages of treating the hardened material with super-critical carbon dioxide ($scCO_2$), to produce a fully carbonated cement matrix [9,10]. The aim of the investigations reported in this paper was to study the dimensional changes occur-

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* Corresponding author. Tel.: +44-121-359-3611; fax: +44-121-333-3389.

E-mail address: n.r.short@aston.ac.uk (N.R. Short).

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Table 1
Oxide composition of Portland cement

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Alkalis	MgO	Free lime	Cl	LOI[a]
%w/w	62.8	19.1	4.91	2.87	3.19	0.85	1.50	1.19	0.014	2.34

[a] Loss on ignition.

ring during the super-critical carbonation treatment itself and on subsequent exposure of the samples to different environmental regimes.

2. Experimental

There are no standard methods for measuring the dimensional stability of GRC. While such methods are available for normal mortars and concretes, these involve casting large, square section, prisms. These are unrealistic for a material whose primary applications are for thin section cladding panels, formwork, etc., and it is generally accepted that measurements should be made on sheets. Stability is considered to be dependent on the sheet forming process used, the thickness of the specimen and the curing conditions but independent of the specimen size and Demec gauge used [11]. However, since different investigators have used different materials and exposure regimes, it can be difficult to compare results. In the present work, the specimen geometry was restricted by the size of sample that could be super-critically carbonated with the equipment available, as described elsewhere [9,10]. The procedures used were as outlined below.

Specimens were manufactured by a premix process to incorporate chopped strand Cem-FIL II (250/5B) AR glass fibres, length 15–20 mm, at a volume fraction of 3.0%. The matrix used was a 50:50 Portland cement: Chelford 50 sand with a 0.5 w/c. The composition of the cement is given in Table 1. The premix GRC was cast around stainless steel pins, which were kept in correct position and alignment by supporting in uPVC prism moulds. Dimensions of the test specimen, the pins and their relative positions are shown in Fig. 1. The longitudinal separation distance between pairs of pins was measured with a Demec gauge of length 200 mm. This arrangement of pins was chosen so that measurements could be made from casting through the super-critical carbonation treatment and then on subsequent environmental exposure. Simple glued Demec spots were not used since they may susceptible to debonding from the specimen during super-critical carbonation treatment.

Immediately after trowel finishing the specimens were contact covered with ‘cling film’ and cured at 20 °C, 95% RH for 24 h. After demoulding, the specimens were conditioned in a sealed box at 20 °C, 35% RH for 7 days, a regime which was found to promote effective super-critical carbonation within 24 h [10]. Half the samples were measured and then placed directly in the relevant exposure environment (uncarbonated control). The remaining samples were measured and then statically exposed to water-saturated $scCO_2$ at 60 °C and 100 bar for 48 h. Triplicate control and super-critically carbonated specimens were then

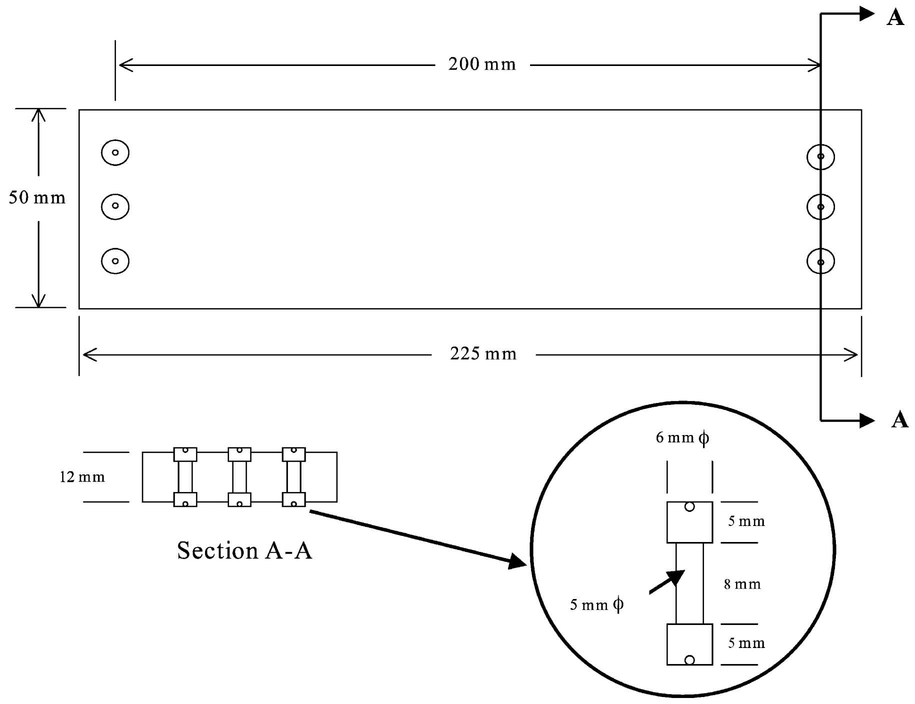

Fig. 1. Specimen configuration.

measured and placed in the relevant exposure environment as follows:

(a) Continuous exposure
A: Immersed in water for ~250 days
B: Immersed in water for 14 days
then 60% RH for ~250 days
C: Stored at 100% RH for ~250 days
D: Stored at 100% RH for 14 days
then 60% RH for ~250 days

(b) Cyclic wetting and drying
E: Immersed in water for 14 days
then 60% RH for 50 days; 4 cycles
F: Stored at 100% RH for 14 days
then 60% RH for 50 days; 4 cycles

(c) Outdoor exposure
G: Immersed in water for 14 days then outside for ~250 days
H: Stored at 100% RH for 14 days then outside for ~250 days

Apart from during outdoor exposure all temperatures were 20 ± 1 °C.

Three samples containing no fibres were also made and carbonated. These were made to check the dimensional stability of the cement matrix during carbonation without the influence of the fibres. Measurements were made before and after treatment but these specimens were not subsequently exposed to the various environments. Values of the effective thermal expansion coefficient were determined by measuring lengths of specimens after allowing them to equilibrate at 37, 24 and 5 °C.

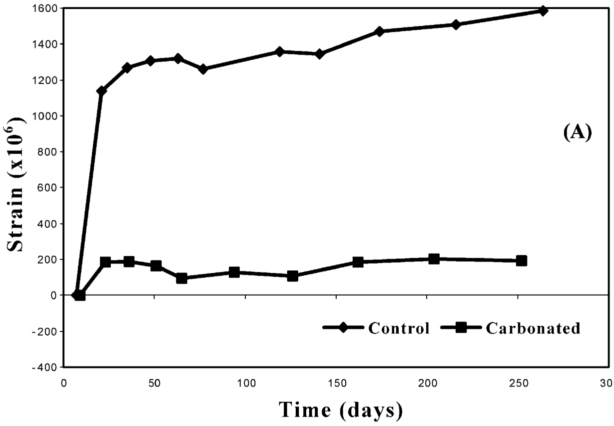

Fig. 2. Exposure A: Immersed in water for ~250 days.

3. Results and discussion

3.1. Dimensional changes due to the carbonation treatment

In the case of mortar samples without fibres, it was found that the carbonation process resulted in a small permanent expansion of about 50 microstrain (με). This result is contrary to the dimensional changes found during natural carbonation where a significant contribution to irreversible shrinkage is normally found [12]. The normal mechanism of carbonation shrinkage is still a subject of some debate [13]. Presumably, however, it has its roots in the changes in pore structure which, for Portland cements, involve a slight reduction in total porosity but an increase in the proportion of pores > 30 nm [14]. With super-critical carbonation, it was found [9] that the calcium hydroxide was virtually all converted to calcium carbonate probably through a dissolution and precipitation mechanism. In addition, most of the unhydrated material (C_3S/C_2S) was converted, via accelerated hydration, to calcium carbonate and silica gel. This resulted in considerable reduction in total porosity and a substantial decrease in the proportion of fine pores [9]. Values of the effective thermal expansion coefficient (Table 2) for carbonated samples, 11.9×10^{-6}/°C, were lower than those for uncarbonated samples, 13.4×10^{-6}/°C. The difference is such that on cooling from the treatment temperature of 60 °C to room temperature ~20 °C, a permanent expansion of 60 με may be calculated which is close to the value of 50 με measured after treatment. Thus, it would appear that shrinkage, as commonly observed in natural carbonation, does not occur during super-critical carbonation.

Table 2
Values of effective thermal expansion coefficient

Sample type	Thermal expansion coefficient (× 10^6/°C)
No fibres—uncarbonated	13.4
No fibres—carbonated	11.9
With fibres—uncarbonated	10.0
With fibres—carbonated	10.9

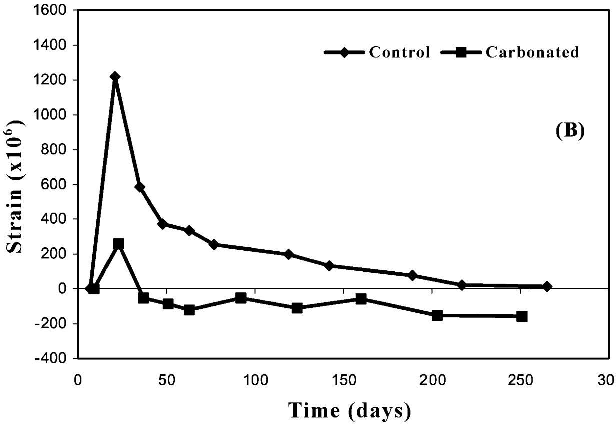

Fig. 3. Exposure B: Immersed in water for 14 days then 60% RH for ~250 days.

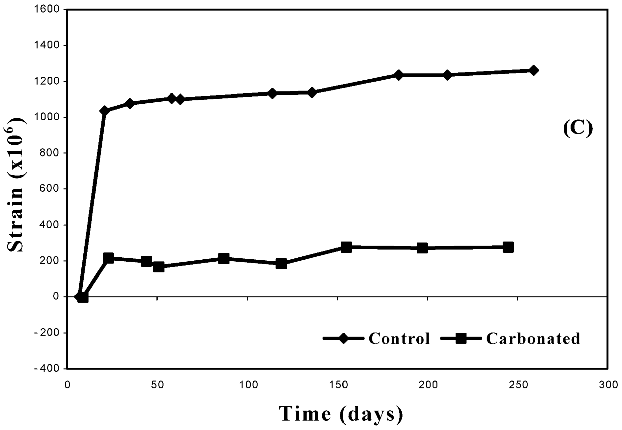

Fig. 4. Exposure C: Stored at 100% RH for ~250 days.

When samples containing fibres were treated, these showed a residual permanent expansion of about 350 ± 50 με after the carbonation treatment. Values of the effective thermal expansion coefficient (Table 2) were lower than those for samples without fibre while similar to those quoted for commercial GRC, 7.0–12.0 [15] and 12.5 × 10^{-6}/°C [16]. In this case, the residual expansion cannot be accounted for in terms of changes in thermal expansion coefficient. However, densification of the matrix results in an increased fibre matrix bond [10] that may inhibit contraction of the composite on cooling. Thus, while the samples with no fibres recover to leave an overall expansion of only 50 με on cooling to room temperature, the samples with fibres do not. In any event, it should not be a problem to take this residual expansion into account when designing with GRC.

3.2. Dimensional changes due to environmental changes

During exposure to the various conditions A–H, it was noted that the mean values of dimensional change as measured on the top face (rough trowelled surface) of the specimens were slightly different from those measured on the bottom face (smooth cast surface), i.e., a slight warping had occurred. The difference was greater for the uncarbonated samples as compared with the carbonated samples but values were within ± 100 με at maximum and often less. Since these differences do not affect the conclusions drawn, the results are presented as an average of the measurements taken on the top and bottom faces. To determine the stability of this type of measurement, an uncarbonated sample was held at 35% RH for a period of 90 days. This sample achieved equilibrium within about 15 days, and thereafter, dimensional stability did not vary by more than ± 3 με.

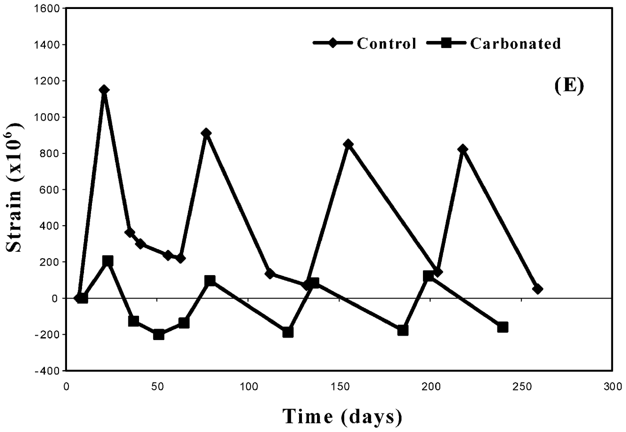

Fig. 6. Exposure E: Immersed in water then 60% RH.

3.2.1. Continuous exposure

Uncarbonated samples immersed in water (Fig. 2) swelled rapidly to give expansions of about 1200 με within 10 days. The rate of expansion then slowed down considerably reaching a value of 1600 με after 250 days. If samples were removed from the water after 14 days and then held at 60% RH (Fig. 3), the expansion was reversed, quickly at first, then more slowly so that they regained their original dimensions after just over 200 days. In contrast, super-critically carbonated samples immersed in

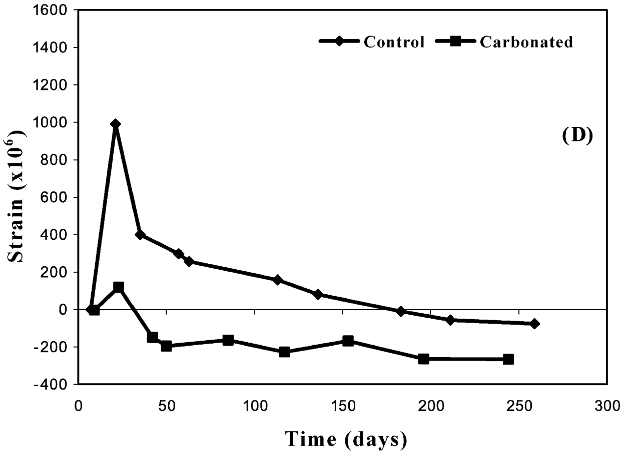

Fig. 5. Exposure D: Stored at 100% RH for 14 days then 60% RH for ~250 days.

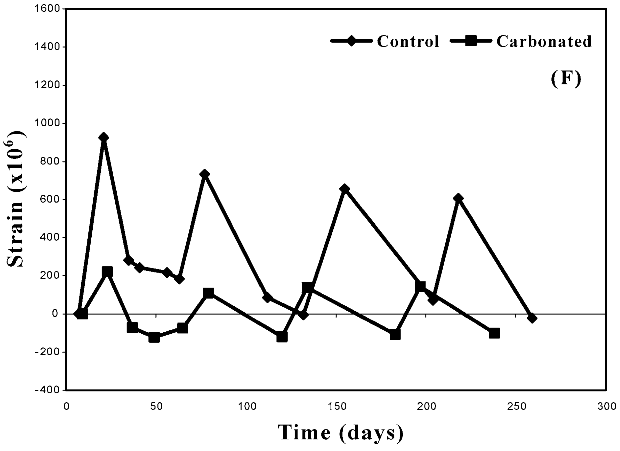

Fig. 7. Exposure F: Stored at 100% RH then 60% RH.

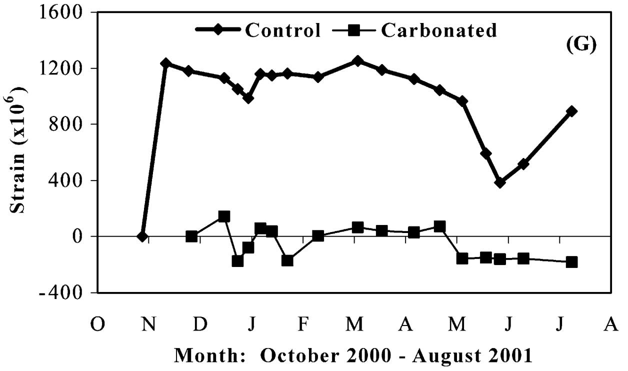

Fig. 8. Exposure G: Immersed in water for 14 days then outside for ~250 days.

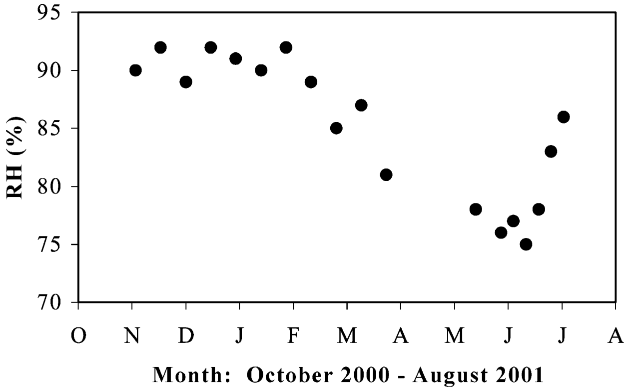

Fig. 10. Average values of RH over the outdoor exposure period.

water (Fig. 2) swelled to give expansions of only 200 με within 10 days and the lengths effectively remain constant thereafter. Similarly, if carbonated samples were removed after 14 days and stored at 60% RH they quickly regained their original dimensions and then underwent a slight shrinkage (Fig. 3).

Similar observations were made with samples exposed to 100% RH rather than being immersed in water (Figs. 4 and 5), although the maximum swelling achieved was slightly less. This confirmed changes found for uncarbonated GRC during other investigations [11] where the influence of immersion was compared with that of exposure at a high RH.

3.2.2. Cyclic wetting and drying

Uncarbonated samples subjected to a cyclic regime of immersion in water (Fig. 6) or 100% RH (Fig. 7), and then stored at 60% RH, showed expansions of up to 1200 με and then underwent shrinkage, during each cycle. The behaviour appeared to be almost completely reversible. In contrast, the carbonated samples exhibited a much greater dimensional stability with a reversible, maximum expansion and contraction of about ±200 με.

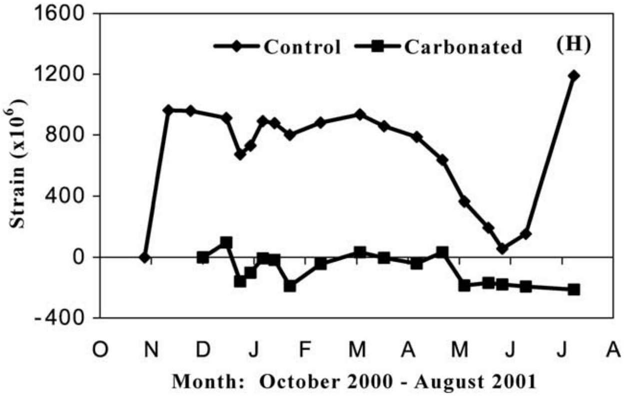

Fig. 9. Exposure H: Stored at 100% RH for 14 days then outside for ~250 days.

3.2.3. Outdoor exposure

Samples were either immersed in water (Fig. 8) or held at 100% RH (Fig. 9) for 14 days and then exposed, unsheltered from rain outside the NE facade of a laboratory in Birmingham, UK, in the late autumn 2000. The initial large and small swellings of uncarbonated and carbonated samples, respectively, were confirmed. Thereafter, the dimension changes followed the prevailing weather conditions and it is quite evident from these figures that fluctuations of the carbonated specimens were much smaller than those of the uncarbonated samples. Comparing the changes with local meteorological data [17], it was observed that average relative humidity (Fig. 10) was the most important factor influencing the dimensional changes.

3.3. General comments

It is evident from the data shown in Figs. 2–9 that the super-critically carbonated samples showed a much greater resistance to swelling and shrinkage than the uncarbonated specimens. The reasons for this are not, at the moment, fully understood. Several mechanisms have been proposed to explain the swelling and shrinkage behaviour of cement pastes, although none has been universally accepted [7]. Of particular importance is the influence of microporosity which is known to be significantly changed by the super-critical carbonation reactions [9]. However, to explain the observations, a much better understanding of the modifications in pore structure and CSH/silica gel composition, taking place during super-critical carbonation, is required. This is being studied using a range of techniques, including NMR, and will be reported elsewhere [18].

4. Conclusions

(1) The super-critical carbonation process, undertaken at 60 °C and 100 bar in water-saturated CO_2, resulted in a small residual expansion of GRC, measured at 20 °C. This is contrary to the behaviour observed during natural carbo-

nation of cement-bound materials where irreversible shrinkage normally occurs.

(2) Exposure to a number of different environments showed that super-critically carbonated samples of GRC had a much greater resistance to swelling and shrinkage than uncarbonated specimens. This observation, which is particularly significant in relation to the practical applications of GRC, was thought to be associated with changes in the microporosity of the mortar matrix induced by the super-critical carbonation process.

Acknowledgments

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References

[1] A.J. Majumdar, V. Laws, Glass Fibre Reinforced Cement, BSP Professional Books, Oxford, 1991.

[2] P. Purnell, N.R. Short, C.L. Page, A.J. Majumdar, P.L. Walton, Accelerated ageing characteristics of glass-fibre reinforced cement made with new cementitious matrices, Composites, Part A 30 (1999) 1073–1080.

[3] T.G. Harmon, Effect of sand gradation on shrinkage of GRC, Proceedings of 8th Biennial Congress, GRC '91 Maastricht, GRCA, Glassfibre Reinforced Cement Association, Wigan, UK, 1991, pp. 61–69.

[4] M. Hayashi, T. Suenaga, Y. Izawa, A. Noguchi, Ten year natural weathering tests of GFRC-CGC, Proceedings of 11th Biennial Congress, GRC '98 Cambridge, Glassfibre Reinforced Cement Association, Wigan, UK, 1998, pp. 1–10 (Session 3, paper 3).

[5] T.G. Harmon, H.G. Molloy, Some issues of durability and shrinkage in GRC, Proceedings of 8th Biennial Congress, GRC '91 Maastricht, Glassfibre Reinforced Cement Association, Wigan, UK, 1991, pp. 23–35.

[6] A.M. Neville, Properties of Concrete, fourth ed., Longman, Harlow, UK, 1995, p. 425.

[7] Y. Xi, H.M. Jennings, Relationship between microstructure and creep and shrinkage of cement paste, in: J.P. Skalny (Ed.), Materials Science of Concrete, vol. 3, American Ceramic Society, Westerville, OH, 1992, pp. 37–69.

[8] P. Acker, F.J. Ulm, Creep and shrinkage of concrete: Physical origins and practical measurements, Nucl. Eng. Des. 203 (2001) 143–158.

[9] N.R. Short, P. Purnell, C.L. Page, Preliminary investigations into the super-critical carbonation of cement pastes, J. Mater. Sci. 36 (1) (2001) 35–41.

[10] P. Purnell, N.R. Short, C.L. Page, Super-critical carbonation of glass-fibre reinforced cement: Part 1. Mechanical testing and chemical analysis, Composites, Part A 32 (12) (2001) 1777–1787.

[11] D.D. Theodorakopoulos, Shrinkage behaviour of GRC thin sheets, Cem. Concr. Compos. 17 (1995) 229–238.

[12] A.M. Neville, Properties of Concrete, fourth ed., Longman, Harlow, 1995, p. 443.

[13] F.M. Lea, The Chemistry of Cement and Concrete, third ed., Edward Arnold, London, 1970, p. 546.

[14] V.T. Ngala, C.L. Page, Effects of carbonation on pore structure and diffusional properties of hydrated cement pastes, Cem. Concr. Res. 27 (7) (1997) 995–1007.

[15] NEG ARG Fibre Data Sheet, Nippon Electric Glass, June 1997.

[16] Technical Committee of fachvereinigung faserbeton e.v. Glassfibre Reinforced Concrete, Practical Design and Structural Analysis, Beton-Verlag, Dusseldorf, 1995, p. 20.

[17] www.bham.ac.uk/BrumMet/home.htm.

[18] A.R. Brough, N.R. Short, A.M.G. Seneviratne, P. Purnell, C.L. Page, Preliminary Investigations of the Fine Pore Structure of Super-Critically Carbonated Cement Pastes, in preparation.