A static fatigue model for the durability of glass fibre reinforced cement

P. PURNELL*
*School of Engineering (Civil & Mechanical Division), University of Warwick,
Coventry, CV4 7AL, UK*
E-mail: pp@eng.warwick.ac.uk

N. R. SHORT
School of Engineering & Applied Science, Aston University, Birmingham, B4 7ET, UK

C. L. PAGE
School of Civil Engineering, University of Leeds, Leeds, LS2 9JT, UK

This paper presents a model for predicting service lives for glass-fibre reinforced cement (grc) components using hot-water accelerated ageing. It improves on previous models, being derived from consideration of a specific proposed micro-mechanical strength loss mechanism based on static fatigue principles and can be applied from time = 0. The model fitted well to all available strength vs. time data pertaining to various grc formulations. The activation energies thus derived for the strength loss process (80–90 kJ mol^{-1}) were consistent with those derived previously and those proposed for general glass dissolution mechanisms. Updated acceleration factors for predicting service lives for grc are advanced. The model was also applied to grc made with modified cement matrices. For metakaolin modified matrices, the activation energy appeared similar to that for OPC-grc, thus the use of similar acceleration factors appears justified. There is some evidence that calcium sulphoaluminate modified grc degrades according to a different activation energy. More data are required for modified matrix grcs if the model is to be applied thereto with confidence. © *2001 Kluwer Academic Publishers*

1. Introduction

Glass-fibre reinforced cement (grc) made with Portland cement (OPC) and alkali-resistant (AR) glass fibre is known to suffer a marked loss in strength and ductility with time in wet environments [1, 2]. This has hampered expansion in the use of grc and has limited its specification to non-structural applications.

The loss of strength in grc is caused by the fibre reinforcement becoming weaker with time. The exact mechanisms underlying this weakening are still subject to debate [1, 3] but it is generally accepted that the alkalinity of the cement matrix is an important factor. The unit reinforcing element in grc is not a single filament but a 'strand' of about 200, into which the matrix does not initially penetrate. The propensity of a matrix to precipitate CH within or at the fibre/matrix interface of these strands, purportedly reduces their flexibility and is also considered to adversely affect durability. An understanding of these factors has led to enhanced durability through developments in fibre coating, incorporation of pozzolans and the development of new cement matrices (see eg. Ref. 1).

Whilst these strength loss mechanisms are known to influence ageing characteristics they are not linked to the model [4, 5] that is generally used for quantitative lifetime prediction by specifiers. The model is essentially empirical and suffers from other drawbacks as discussed in the next section.

This paper proposes a new model for strength degradation vs. time based on consideration of a proposed mechanism of strength loss in grc. The model is fitted to data extant in the literature (including that used to formulate the empirical model) both for first and second-generation fibre composites with OPC matrices and more recent data obtained for composites made with new matrix formulations.

1.1. Empirical model [4, 5]

In order that estimates of the durability characteristics of grc can be made, accelerated ageing tests are employed. The most common of these involves the immersion of coupons of grc in water, at temperatures elevated with respect to the in-service ambient condition, for varying lengths of time. Relatively short ageing regimes are then correlated with in-service weathering lifetimes via a model first advanced in the early 1980's [4]. This was based on studies of composites made with OPC and first-generation AR-glass fibres (O-I grc). Later studies by the same authors [5] implied that this original model could also be applied to OPC

*Author to whom all correspondence should be addressed.

containing second-generation fibres (O-II grc), which have been shown to impart a significant enhancement of durability.

Using the accelerated tests, plots of strength vs. log {time} for samples aged at different temperatures were made which can be approximated to a family of parallel lines. From these, and using a normalisation procedure, it was possible to plot a rate parameter versus $1/T$ giving an Arrhenius type of relationship. The rate parameter was defined as: the time taken for a given degree of absolute strength loss to be observed at a given ageing temperature divided by the time taken for a similar strength loss to be observed at a reference temperature of 50°C. This procedure allowed an activation energy for the strength loss process to be deduced (89–93 kJ mol^{-1}) and 'acceleration factors' to be advanced, e.g. that 1 day in water at 50°C is equivalent to $\approx$100 days weathering in UK climatic conditions.

The model, an apparently reasonable representation of the data, has been useful in comparing and contrasting varying matrix formulations over the years. However, it suffers from two intrinsic limitations: (a) it is not linked to any hypothesis concerning the strength loss mechanism in glass fibre composites but is simply an empirical representation of the data and (b) the relationship "strength $\propto$ log[time]" is fundamentally flawed in that strength is undefined at $t = 0$ and thus cannot provide a continuous representation of strength vs. time. Additionally, in modern grc second-generation fibres are incorporated into matrices modified with cement replacement materials, polymers or even non-OPC matrices, which have also been shown to increase durability [e.g. 6–8]. It is not clear whether the acceleration factors originally suggested for older grc formulations are valid for these newer materials. Hence there is a need for a new approach.

2. Static fatigue model

Many investigators [6, 9–13] have shown that fibre strength loss is not a result of gross fibre corrosion (i.e. loss of section). The surfaces of fibres extracted from degraded grc and examined using SEM rarely exhibit any significant visible corrosion. In fact it is known [e.g. 14] that the size and population density of surface flaws, which are very difficult to resolve in the SEM, chiefly governs the strength of glass fibres. It is inevitable that flaws will be introduced into the fibre surface during fibre handling, packaging and grc manufacture. This is borne out by comparing the relative, respectively decreasing strengths of virgin filaments, industrial strands [1, 15] and filaments removed from unaged grc [1, 16]. The tensile strength of grc reinforced with continuous, uniaxially aligned fibres is also only half that expected from theory [6]. Since fibre strength is closely related to the maximum flaw size, it would be reasonable to assume, given the lack of gross corrosion, that enlargement of these flaws is the cause of the weakening.

A possible mechanism for the enlargement of flaws is static fatigue or delayed failure, which is a well documented phenomenon in the glass technology literature [17, 18]. If a glass component is in an aqueous environ-ment under a constant stress (less than its bulk failure stress), then stress concentrations will be present at the tips of pre-existing flaws. At these stress concentrations, the glass network bonds at the tip of the flaws are preferentially attacked and broken, causing the flaws to grow. The process may *in extremis* cause spontaneous failure of glass components. Time to failure is thus a thermally activated process and found to be dependent on such factors as glass composition, pH, stress level, temperature and polymer coating, if applied [19].

In the case of grc such a process, rather than causing spontaneous failure, will reduce the strength of the fibres and hence the composite, since strength is related to critical flaw size. In alkaline environments (i.e. cement pastes, generally of pH $\sim$13.0 to 13.5 [6]) there is no stress level or 'static fatigue limit' below which sub-critical crack growth will not occur [20]. Hence even very small stresses may provide a sufficient driving force for the process.

AR glass fibres are generally resistant to alkali attack but are not completely inert [1, 21, 22]. It is thought that reaction in aqueous and cement extract media commences with immediate dissolution of sodium ions followed by hydroxyl ion attack of the Si—O—Si glass network and dissolution of silicate ions:

$$Si—O—Si—O^-Na^+ + H_2O \rightarrow Si—O—Si—OH + NaOH \tag{1}$$

$$Si—O—Si—OH + OH^- \rightarrow Si—OH + {}^-O—Si—OH \tag{2}$$
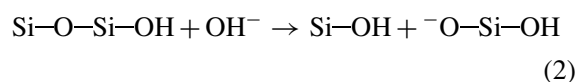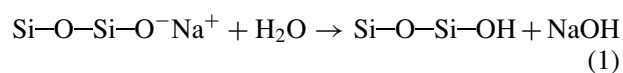
Evidence suggests that Na$^+$ removal (Equation 1) is diffusion controlled with an activation energy of 78 kJ mol^{-1} which is consistent with that found for a H$^+$ for Na$^+$ ion exchange mechanism, 73–85 kJ mol^{-1}. The Zr—O bonds are only slightly attacked by hydroxyl ions compared to the Si—O bonds (Equation 2), so that there is a marked increase in Zr content at the surface of the fibres. Whilst these reactions are not fully understood and do not appear to lead to extensive general surface corrosion, they may well provide a mechanism for dissolution of the glass network at the tips of flaws under stress.

A number of mechanisms can be postulated as providing sub-failure driving stresses for the stress corrosion process. In hot water aged coupons, stress can be generated via mismatch in the thermal coefficients of expansion (α) of the glass and the matrix; typical values of α for fibre and matrix respectively are 7.5×10^{-6} and 12–20×10^{-6} °C^{-1} [1, 23]. For in-service components, the thermally induced driving stress will fluctuate with the ambient temperature. Live and dead loads on the components will provide additional driving stresses. In matrices containing calcium hydroxide (CH), it is known that CH has a tendency to precipitate at the glass surface and within the strands [11, 24]. It would be reasonable to assume that CH thus precipitated would nucleate at pre-existing imperfections on the glass surface—i.e. flaws. As these crystals grow in the confined spaces in and around the fibre strands pressures will be exerted, further aggravating the stress corrosion process. Preferential leaching of components from the glass surface is also likely to induce stresses in the glass network [18].

The rate at which a surface flaw, of critical length a, will grow is therefore a function of the induced stress (σ_I), the OH$^-$ concentration of the pore solution (C) and the temperature, T:

$$\frac{\partial a}{\partial t} = f(\sigma_I, C, T) \qquad (3)$$

If we assume, for a first approximation;

- that σ_I is a (probably linear) function of temperature and will be accounted for in the term k_T (i.e. $k_T = f(T)$),
- that $\partial a / \partial t \propto C$,
- that $\partial a / \partial t \propto e^{-\Delta G^*/RT}$ where $-\Delta G^*$ is the activation energy of the corrosion process assuming a single temperature dependent rate determining step

and that all these quantities are constant with time t then we can write:

$$a = k_C k_T C e^{(-\Delta G^*/RT)} t + a_0 \qquad (4)$$

where a_0 is the initial flaw size (induced by manufacturing processes). The strength of a filament can be expressed as [25];

$$\sigma_f = \frac{K_{IC}}{1.12\sqrt{\pi a}} \qquad (5)$$

where K_{IC} is the critical stress intensity factor for the glass. The strength of the composite made thereof can be expressed as [eg. 1];

$$\sigma_c = \eta_o \eta_l V_f \sigma_f \qquad (6)$$

where η_o and η_l are efficiency factors for fibre orientation and length respectively and V_f is the fibre volume fraction. Substituting Equation 4 into Equation 5 then Equation 5 into Equation 6 we obtain a formula for composite strength vs. time;

$$\sigma_c = \frac{\eta_o \eta_l V_f K_{IC}}{1.12\sqrt{\pi \left(k_C k_T C e^{(-\Delta G^*/RT)} t + a_0 \right)}} \qquad (7)$$

To compare data sets from different composites and investigators, it is necessary to define a normalised strength S, defined as the current strength σ_c (at time $= t$) divided by the original, unaged strength. The advantages of this approach are that it accounts for the strength variations caused by differing fibre volume fractions, fibre orientations etc. and also those caused by different test methods i.e. flexural modulus of rupture (MOR) or tensile strength (TS). The strength of an unaged composite is given by setting $t = 0$ in Equation 7. It can then be shown that;

$$S = \frac{\sigma_c}{\sigma_{c,t=0}} = \frac{1}{\sqrt{1 + \frac{k_C k_T C e^{(-\Delta G^*/RT)} \cdot t}{a_0}}} \qquad (8)$$

For comparative purposes e.g. rank ordering of matrix suitabilities, formulation of accelerated ageing coefficients etc. this essentially simplifies to;

$$S = \frac{1}{\sqrt{1 + kt}} \qquad (9)$$

where $k = f(T, [CH], pH \dots)$.

3. Initial fit—shape of the curves
To test the suitability of the shape of the curves for representing strength vs. time data, Equation 9 was fitted using a least squares approach to the three most complete grc data sets available. These are those for natural weathering of O-I grc (nwUK-I) and those for O-I and O-II grc aged at 50°C (Fig. 1). The relevant values of k were found to be 9.22×10^{-4}, 6.71×10^{-2} and 9.34×10^{-3} (day)$^{-1}$ respectively. It can be seen that the curves adequately model the data and tend to 1 as time tends to zero. A complete reference summary of the data sets used is given in Table I.

4. Temperature dependence—OPC-grc
Curves were fitted to all available strength vs. time data (as detailed in Table I) and values of k obtained. By

TABLE I Data sets used in model formulation

Matrix	Fibre	Ageing temperature	Reference	No. of data sets
OPC	I	UK weathering[a]	1, p.71	1 (MOR & TS)
			1, p.80	3 (MOR & TS)
		20°C	1, p.71	1 (MOR & TS)
			1, p.80	3 (MOR & TS)
		35°C	4	1 (MOR)
		50°C	1, p.83	1 (MOR)
			4	1 (MOR)
			27	1 (MOR & TS)
		60°C	2	1 (MOR)
			4	1 (MOR)
		80°C	4	1 (MOR)
	II	UK weathering	1, p.83	1 (MOR & TS)
		50°C	1, p.83	1 (MOR & TS)
			5	1 (MOR)
		38°C	b	1 (TS)
		65°C	6[b]	1 (TS)
MK	II	38°C	6[b]	1 (TS)
		50°C	27	1 (MOR)
		65°C	6	1 (TS)
		83°C	b	1 (TS)
C	II	38°C	6[b]	1 (TS)
		65°C	6	1 (TS)

[a]Plotted at $T = 10.4$°C.
[b]Indicates data set consists of or is augmented by new data not previously published.
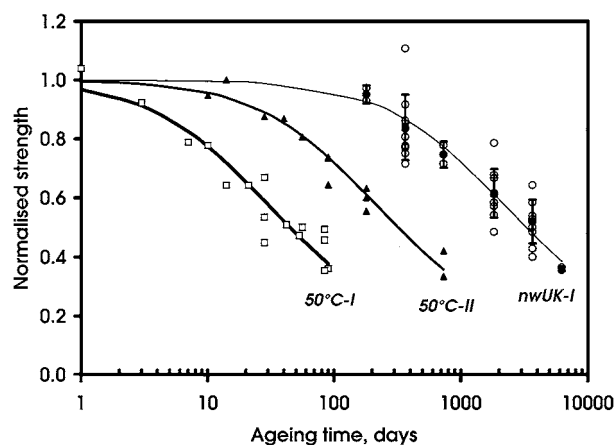

Figure 1 Fit of $S = (1 + kt)^{-1/2}$ curves to extant data sets for OPC-grc with 1st (I) and second (II) generation fibres. (nwUK = UK natural weathering environment: open circles-individual data sets; closed circles & bars—mean & standard deviation of all data sets [see Table I, OPC-I-UK weathering]).
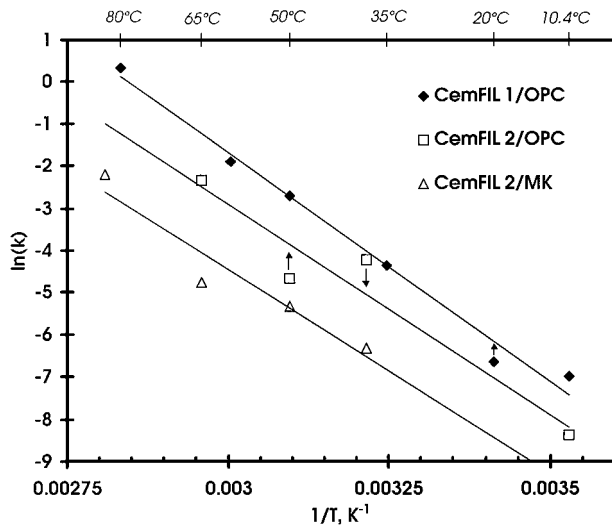
Figure 2 Arrhenius plots of ln k vs. $1/T$ for three grc formulations.

performing an Arrhenius plot of the natural logarithm of k against the reciprocal of the ageing temperature (Fig. 2), values for the activation energy ΔG^* and the pre-exponential term k_0 for strength loss (expressed as in Equation 10) were obtained.

$$S = \frac{1}{\sqrt{1 + k_0 e^{(-\Delta G^*/RT)} \cdot t}} \qquad (10)$$

The activation energies for both O-I and O-II grc were found to be broadly similar (90.3, 83.3 kJ mol^{-1} respectively) although the difference between the two was somewhat greater that implied by Litherland *et al.* [4, 5] who quoted 89–93 kJ mol^{-1} for both fibres. It is interesting to note that these activation energies are similar to those for the glass dissolution mechanisms discussed in Section 2. The difference in durability between O-I and O-II grc can be attributed to factors affecting the pre-exponential term k_0 in Equation 10 (derived as 26×10^{12} and 0.61×10^{12} [day]$^{-1}$ respectively). Fibres I and II differ only in that the latter have an improved coating (size) which was applied during the fibre drawing process. That the activation energies are similar for the two fibres suggests that the coating does not alter the degradation mechanism. However, since the values of k_0 are reduced, it must influence the reaction kinetics by e.g. restricting inter-diffusion at the interface.

The similarity between the activation energies confirms the postulate of Litherland *et al.* that, broadly speaking, similar acceleration factors can be applied to both materials. A comparison of those authors' acceleration factors with those derived here (cf. UK weathering, assumed to be an annual mean temperature of 10.4°C) is given as Table II. The application of the acceleration factors is that e.g. for O-II grc, 1 day of accelerated ageing at 70°C causes the same degradation as 460 days of natural weathering. It will be noticed that the difference in activation energy derived for the two fibre types results in ~30–40% differences in acceleration factors, the effect being more pronounced at higher temperatures. Insufficient data exist concerning the strength vs. time/temperature behaviour of O-II grc at this juncture to confirm or refute the significance

TABLE II Comparison of acceleration factors (cf. 10.4°C i.e. natural UK weathering) advanced by Litherland *et al.* with those derived in this study

Ageing temperature	Ref. [4, 5]	O-I grc	O-II grc	MK-II grc
80	1672	1900	1100	800
70	693	780	460	400
60	272	300	190	200
50	101	110	76	70

of this effect. However, since the acceleration factors for O-II grc are lower, these should be used in preference to those previously advanced to provide a factor of safety against over-optimistic prediction of service life. Acceleration factors with respect to other temperatures can be expressed simply as the ratio of the experimental values of k (Equation 7) at the temperatures of interest, or derived from Equation 11;

$$A_{(a,b)} = e^{\frac{\Delta G^*}{R} \cdot \left(\frac{1}{T_a} - \frac{1}{T_b}\right)} \qquad (11)$$

where $A_{(a,b)}$ is the acceleration factor of (high) ageing temperature T_b with respect to (lower) weathering temperature T_a. The acceleration factors thus derived should be regarded as an improvement on those previously advanced.

5. Temperature dependence—new matrix grc
Rather fewer data are available concerning the variation of strength with time/temperature in grc made with the modified or non-OPC matrices currently in use in the grc industry. The model has thus been applied to only two such matrices: metakaolin modified matrices (matrix MK) and calcium-sulphoaluminate modified matrices (matrix C). Fig. 2 includes the Arrhenius plot of grc made with the MK matrix and second-generation fibre. The activation energy was ~80 kJ mol^{-1}, not significantly different from that for OPC-matrix composites made with the same fibre; the relevant acceleration factors are given in Table II. The enhanced durability can thus again be attributed to the lower pre-exponential term, $k_0 = 0.04 \times 10^{12}$.

With regard to C-II grc, even fewer data are available, primarily because of the extra-ordinary durability of this composite under accelerated ageing. However, the data that are available indicate strongly that the activation energy for ageing of C-II grc is likely to be significantly higher than that for other matrices. Under ageing at 65°C, both matrices C-II and MK-II grc exhibit very similar strength-time curves, becoming completely degraded between 6 months and 1 year of ageing [6, 26]. Under 38°C ageing, the curves were very different. After 3 years, MK-II grc was almost completely degraded while C-II grc suffered no significant loss in strength. Thus the Arrhenius plot for C-II grc will be much steeper and preliminary results indicate a lower bound for the activation energy significantly in excess of those given above.

6. Discussion
The continuous nature of the model advanced above has an added advantage over the previous model in that

it can be simply applied to predict service lives for grc components.

A grc component will not degrade indefinitely and can be considered completely degraded when the 'ultimate' strength has been reduced to a value comparable to the first-crack strength (which, for the relatively low fibre volume fractions used in grc products, is generally indistinguishable from the matrix strength). At this point, on first cracking (i.e. matrix failure, termed 'bend-over' point, BOP, in tensile tests and 'loss of proportionality', LOP, in flexural tests) the fibres will be insufficiently strong to carry the load thus thrown upon them and a brittle fracture will result. Hence the service life of a grc component can be determined from the intersection of the TS or MOR vs. time curve with the BOP or LOP vs. time curve.

Such predictions are slightly complicated by the fact that the 'normalised' first cracking strength (e.g. LOP ÷ MOR at $t = 0$) will not be independent of fibre parameters such as volume fraction or orientation. As volume fraction is increased, the first cracking strength represents a smaller fraction of the ultimate strength and vice versa, hence a general rule similar to Equations 8, 9 or 10 cannot be formulated. The normalised first cracking strength (i.e. proportion of the MOR or TS represented by the LOP or BOP) will be unique to each grc formulation. Also, the first cracking strength, dependent primarily on the matrix strength, will increase with ageing time as the cement matrix hydrates, although the magnitude of the increase is relatively small; for well-cured grc it should generally be less than 20%.

As an example, a typical sprayed commercial grc made with an OPC/sand matrix and 5% volume fraction of second generation fibre has an MOR of about 30 MPa and an LOP of about 11 MPa after a 28 day cure [1]. If the LOP is assumed not to increase by more than 20% then the critical normalised strength, S_{crit}, will be $1.2 \times 11/30 = 0.44$. Setting $S = 0.44$ in Equation 10 and solving for t gives a service lifetime of 42 years in UK weathering conditions. (The corresponding figures for O-I and MK-II grc would be 19 and 160 years respectively.) Reducing the fibre content to 4% and hence the MOR to 24 MPa without significantly affecting the LOP would increase S_{crit} to 0.55, reducing the service life to 23 years i.e. a 1% reduction in fibre volume fraction would lead to a 44% reduction in service life.

7. Conclusions
An improved model of strength loss vs. time has been successfully applied to data sets for grc made with first and second-generation fibres. The values calculated from the new static fatigue model are in reasonable agreement with those derived from the previous empirical model and also those advanced for more general glass dissolution processes. Thus, for OPC matrix grc, slightly adjusted values of previously suggested acceleration factors for hot water ageing may be used with increased confidence. However, research focussing on many more points within the time-temperature envelope is required for a more accurate determination of the activation energy of the degradation process in composites reinforced with second-generation fibre.

For modified matrix grcs, it is possible that the activation energy of the strength loss process in hot water ageing will depend on the matrix formulation. According to the best data available, for metakaolin-modified matrices the activation energy and hence acceleration factors appear to be similar to those for second-generation OPC matrix grc. Preliminary data strongly suggest that this will not be the case for sulphoaluminate modified matrices. The data sets for new matrix grcs are insufficiently detailed to draw firmer conclusions at this stage and must be expanded to include a greater range of matrix formulations.

If the model is used for service life predictions, it is important to note that the value of k_0 to be used in Equation 10 is specific to a given matrix formulation at a given temperature. It is not simply a function of the activation energy but also the pre-exponential term. Current research is concentrating on determining the effect of matrix modification on these parameters.

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