

Strength loss in "E" glass fibres treated in strong solutions of mineral acids

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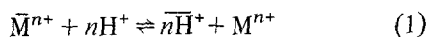
The strength loss of "E" glass fibres following treatment with solutions of nitric, sulphuric and hydrochloric acids have been studied as a function of hydrogen ion activities. The anion present in the corroding medium has at least as much influence on behaviour as does the hydrogen ion activity. Corrosion can be slowed considerably by the addition of metal ions to the acid solutions.

1. Introduction

Glass fibre reinforced composite materials are used in many applications involving strongly acidic environments. It is, however, becoming increasingly apparent that such materials are not immune from corrosive attack by such media, although good design and fabrication procedures are able, for the most part, to reduce failure rates to acceptable levels. Nevertheless a number of different types of corrosion related failure are observed [1]. Because of its sudden, potentially catastrophic nature, a particular type of failure that has recently been receiving considerable attention is one resembling stress corrosion cracking in metals. In this type of failure a stressed composite component exposed to an aggressive environment suffers rapid failure after a certain time interval [1-6] and, typically, the failure surfaces are relatively clean cut with very little fibre pull-out occurring.

The constituent responsible for stress corrosion failures in glass fibre composite materials appears to be the glass rather than the resin [1-3] and the resin appears to play a protective role in shielding the fibres from the environment. Indeed, it is well known that glass fibres suffer attack in acid solutions and may crack spontaneously after a period of immersion even when not subjected to an externally applied stress [7-9]. This is due to the occurrence of ion exchange reactions involving the replacement of cations such as sodium, calcium and aluminium near the surface of the glass by

protons. The general reaction may be written as:



where the bar denotes association of the species with the glass phase. Because the protons are smaller in size than the replaced cations, it is believed that tensile stresses are induced in the surface of the glass and that such stresses can become large enough to promote cracking [7]. For "E" glass fibres which form the bulk of material used for reinforcement, the major constituents leached from the surface appear to be calcium and aluminium. Recently it has been shown that glass fibres free from these elements appear to suffer no corrosion in sulphuric acid solutions [3].

Generally, degradation of "E" glass fibres is regarded simply as a function of hydrogen ion activity, i.e. pH, and little work seems to have been reported on the effect of the anions in the corroding medium. The aim of the present work is to investigate the mechanical performance of "E" glass fibres after immersion in solutions of sulphuric, hydrochloric and nitric acids and, for a given hydrogen ion activity, compare the effects of the different acids. Most previous investigations have expressed acid strengths in terms of the concentration of acid in the solution, i.e. in terms of either the normality or molarity of the solution. However, for solution strengths greater than 0.1 M, these quantities are not a true reflection of hydrogen ion activity and thus cannot be used for

TABLE I Composition of "E" glass fibres (wt %)

SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	B ₂ O ₃
52.10	14.86	23.90	1.78	0.39	1.02	1.06	4.29

comparing the effects of different acids in strong solutions. H⁺ activities are usually measured on the pH scale which assumes complete dissociation of acids into H⁺ and anions. On this scale H⁺ activity is equal to concentration in solution. In strong solutions, acids are not completely dissociated so that a true measure of H⁺ activity must use an alternative scale which takes into account the degree of association. Such an H⁺ activity scale is the H₀ acidity function scale [10] which, like the pH scale, is logarithmic and is identical to the pH scale at infinite dilutions. In the present investigation, H⁺ activities are expressed on the H₀ scale, values of H₀ having been determined from the solution strengths using tables from [10].

2. Experimental details

The material used was an "E" glass fibre roving, 2275 TEX of chemical composition shown in Table I. Specimens 200 mm long were cut and immersed in acid solutions for various times. After treatment the glass specimens were washed in distilled water and dried in air. Control specimens were cut at intervals along the roving and, although stored in air prior to testing, were subjected to the same handling and washing procedures as the corroded specimens to try and eliminate any handling damage effects.

Tensile tests were carried out on the specimens using an Instron testing machine of 50 kN capacity. The test length was 100 mm and a crosshead displacement rate of 2 mm min⁻¹ was used throughout. Flat rubber-faced grips were used to try and minimize specimen damage due to clamping. The failure load recorded was the maximum load that the roving could withstand in the tensile test.

A number of individual fibres had broken before this peak and a number were intact after the peak. A problem that clearly arises is to try and ensure that each fibre in the roving is subjected to the same load. While this was not possible, extreme examples of non-uniform loading gave rise to flat or extended peaks on the force-displacement diagram due to progressive failure of highly stressed fibres and the transfer of the load to others. These could be readily detected and only results showing sharp peaks in the load-deflection

curves were accepted. At least six specimens were tested for each acid-time condition and the mean and standard deviations of the peak loads calculated. Tests were repeated if the standard deviation was greater than 10% of the mean load. For less corroded (i.e. stronger) specimens, standard deviations were generally within 5% of the mean but, for more corroded specimens, standard deviations tended to increase, presumably because damage was not necessarily the same for each fibre nor uniform along the fibre length. The mechanical test results are presented in terms of percentage strength retention of corroded samples compared to control specimens.

3. Results

3.1. Strength after acid treatment

Figs. 1 to 3 show strength retention against immersion time curves for glass treated with acids of hydrogen ion activities H₀ of -0.3, -1.0 and -1.75 respectively (i.e. in order of increasing H⁺ activity). An activity value of -1.0 corresponds roughly to 3 molar solutions of nitric and hydrochloric acids and 1.5 molar sulphuric acid. The curve shapes for the three acids at a given H⁺ activity are similar but the behaviour with respect to time markedly different. Each curve shows that the strength falls sharply during the initial period of immersion which is followed by a region of slower attack rate. The second region indicates a continuing slowing of the attack rate but samples tested for longer times than those shown in Figs. 1 to 3 show that more or less complete mechanical strength loss eventually occurs in all three acids over the concentration ranges investigated. During the initial stage of attack, HCl and HNO₃ behave fairly similarly whereas the effect of H₂SO₄ is much more severe. In the second stage, the corrosion rate in HNO₃ and H₂SO₄ falls quite sharply yet continues at a relatively high rate in HCl.

Figs. 4 to 6 show curves of strength retention plotted against H⁺ activity for different immersion times in HNO₃, H₂SO₄ and HCl respectively. In Fig. 4 for HNO₃, the strength falls with increasing H⁺ activity, the effect being more pronounced for the longer immersion time. In H₂SO₄ the short time behaviour shows a similar trend to HNO₃ but

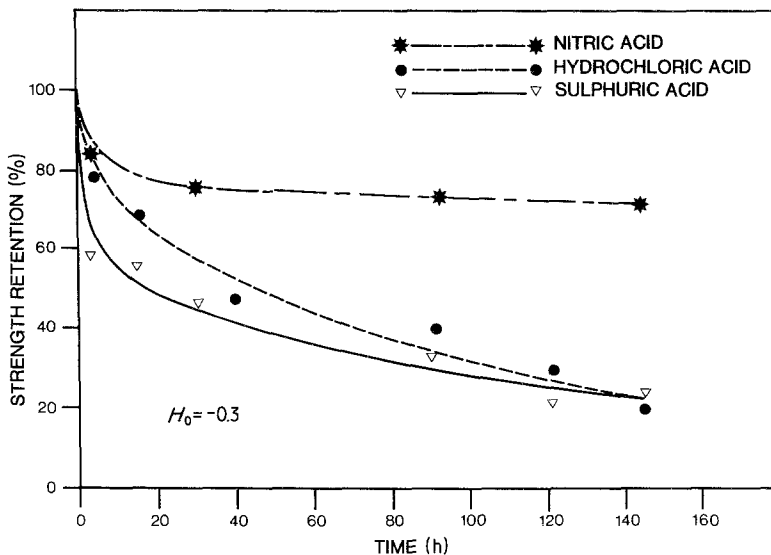


Figure 1 Strength retention plotted against immersion time for fibres treated in acid solutions of hydrogen ion activity -0.3 .

at longer times, the strength retention becomes more or less independent of H^+ for the range of acid concentrations used. Initial behaviour in HCl is similar to the other two but at longer times a dip appears in the curve indicating that attack is most severe in the region of $H_0 = -1$. Additionally it was observed that a pale yellow colour formed in the HCl solutions after the fibres had been immersed for some time, the colour being deepest when $H_0 = -1$.

3.2. Strength in acid plus cation solutions

Table II shows strength retention results for glass fibre samples which were immersed in acid solutions of $H_0 = -1$ and similar solutions contain-

ing 1 molar calcium and/or aluminium ions for 72 h (saturated Ca^{2+} in the case of solutions containing H_2SO_4). For equilibrium of the ion exchange reaction, which is reversible, it might be expected that addition of Al^{3+} and Ca^{2+} to the corroding solution would inhibit the leaching of Al^{3+} and Ca^{2+} respectively from the glass surface. In many instances such reduction of corrosion is observed with the effects being different for each of the three acids. In HNO_3 solutions, additions of both Al^{3+} and Ca^{2+} suppress attack to some extent with Al^{3+} being slightly more effective. Addition of Al^{3+} suppresses attack in H_2SO_4 solutions whereas saturating the solution with Ca^{2+} has little effect. In HCl solutions, additions

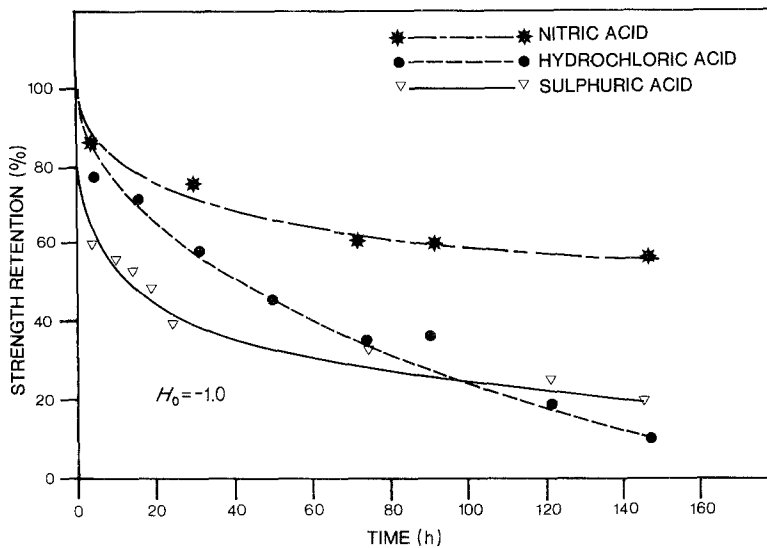


Figure 2 Strength retention plotted against immersion time for fibres treated in acid solutions of hydrogen ion activity -1.0 .

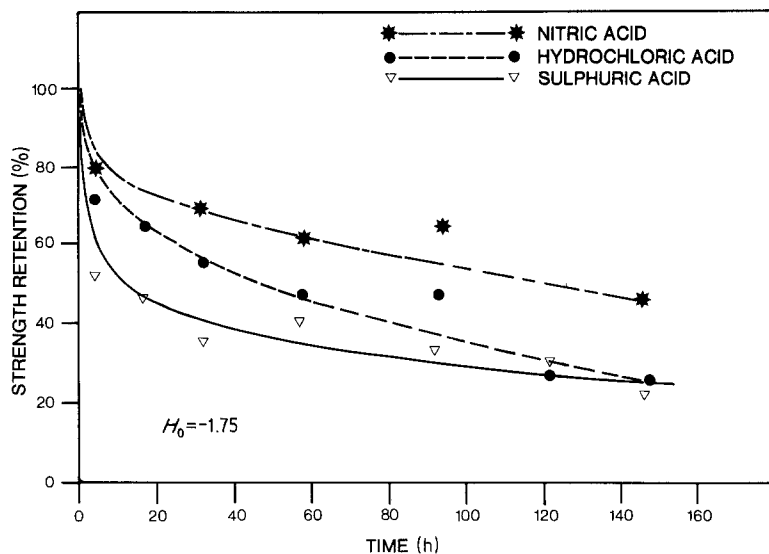


Figure 3 Strength retention plotted against immersion time for fibres treated in acid solutions of hydrogen ion activity -1.75 .

of AlCl_3 and $\text{Al}(\text{NO}_3)_3$ have the greatest effect, addition of $\text{Al}_2(\text{SO}_4)_3$ has some effect and Ca^{2+} additions appear to have little effect on corrosion.

4. Discussion

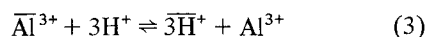
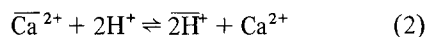
In the glass-acid system, the major factors expected to influence equilibrium of the ion exchange reaction are [11]:

- Activity of H^+ and M^{n+} in the solution.
- Preference of the glass for higher valence ions.
- Preference of glass for ions with a smaller hydrated volume.

(d) Preference of glass for more strongly bound ions.

(e) Metal ions which become involved in anionic complex formation are more likely to be removed from the glass.

Particular reactions likely to govern corrosion of "E" glass fibres are:



For corrosion to occur, these reactions obviously proceed from left to right and would be favoured

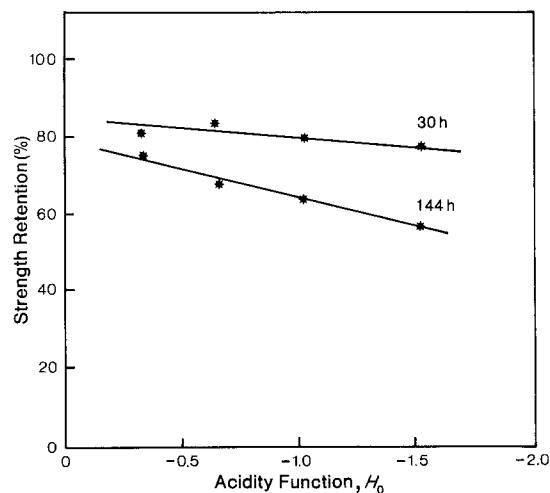


Figure 4 Strength retention plotted against hydrogen ion activity for fibres treated in nitric acid solutions.

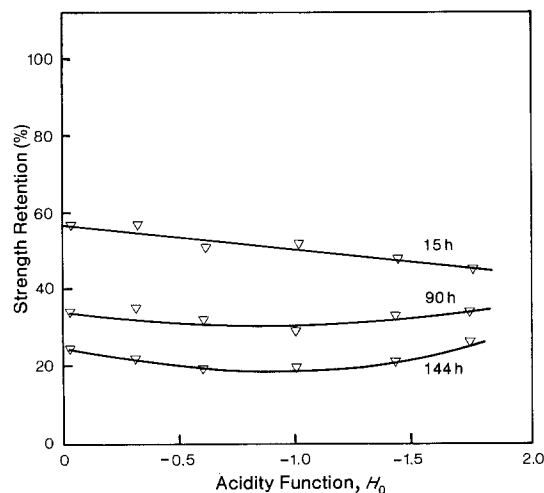


Figure 5 Strength retention plotted against hydrogen ion activity for fibres treated in sulphuric acid solutions.

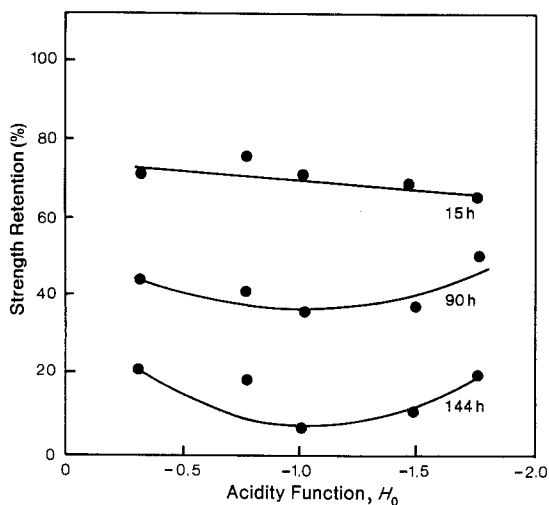


Figure 6 Strength retention plotted against hydrogen ion activity for fibres treated in hydrochloric acid solutions.

by an increase in H^+ activity and depressed by high concentrations of Ca^{2+} and Al^{3+} respectively. Factors (b), (c) and (d) suggest that Reaction 2 would be more favourable than Reaction 3 since Al^{3+} has a higher valence, a smaller hydrated volume and tends to be covalently bound in the lattice rather than occurring as an interstitial.

Kinetically, the rates of ion exchange reactions are governed by diffusion processes. The rate limiting step may be either diffusion of ions through the liquid phase (film diffusion controlled), or through the solid phase (particle diffusion controlled). As glass has a relatively compact structure, it is likely that corrosion is a particle diffusion controlled process and this is indicated from Figs. 1 and 2 as an initially high reaction rate followed by a sharp falling off which is a characteristic of this type of reaction.

Corrosion by HNO_3 is less severe than by the other two acids but is, however, extremely detrimental to the mechanical properties. The behaviour is very much as expected from consideration of

Reactions 2 and 3 in that increasing the H^+ activity increases the rate of corrosion and addition of Ca^{2+} and Al^{3+} reduces attack. Adding Al^{3+} and Ca^{2+} separately shows that the former has a greater inhibiting effect which may indicate slight favouring of Reaction 3. However, it is clear that as far as corrosion in HNO_3 is concerned, leaching of both Ca^{2+} and Al^{3+} plays a significant role.

The distinguishing features of corrosion in H_2SO_4 as compared to the other two acids are the relatively high initial rate of attack and the apparent independence of attack from H^+ activity at longer immersion times. This may be explained in terms of the relative insolubility of $CaSO_4$ in aqueous solutions. Being relatively insoluble, $CaSO_4$ is effectively removed from the right-hand side of Reaction 2 encouraging the left to right reaction with a consequent rapid initial attack rate. Crystals which were formed in solutions of H_2SO_4 were identified as $CaSO_4$. As attack proceeds from the surface into the fibre it is likely that $CaSO_4$ is precipitated in interstitial spaces in the glass, thus providing a physical barrier to ionic diffusion and slowing the rate of attack. This effect is probably the reason for the independence of attack from H^+ activity for longer corrosion times. With reference to Table II, although saturating the solution with Ca^{2+} produces no effect as expected, addition of Al^{3+} partially inhibits attack thus indicating that, as is the case with HNO_3 , corrosion is affected by leaching of both Ca^{2+} and Al^{3+} with, again, leaching of Al^{3+} having possibly the greater influence.

A further potential problem regarding the presence of SO_4^{2-} (and probably other ions producing insoluble reaction products) is shown in Table II where the corrosion inhibiting effect of $Al_2(SO_4)_3$ additions to HCl solutions is less than additions of either $AlCl_3$ or $Al(NO_3)_3$. This is probably due to $CaSO_4$ formation.

Corrosion in HCl is characterized by a relatively high rate of second stage attack following an initial

TABLE II Strength retention and weight loss of fibres treated for 72 h in solutions containing acids of hydrogen ion activity = -1.0 and metal ions

Addition	Nitric acid		Sulphuric acid		Hydrochloric acid	
	Strength (%)	Wt. loss (%)	Strength (%)	Wt. loss (%)	Strength (%)	Wt. loss (%)
None	60	7	30	15	35	15
Al^{3+}	87	1	67	7	88	1
Ca^{2+}	80	3	33	15	39	10
$Ca^{2+} + Al^{3+}$	100	1	72	7	94	1
$Al(NO_3)_3$	—	—	—	—	90	2
$Al_2(SO_4)_3$	—	—	—	—	71	4

region which is fairly similar to HNO₃. In addition, Fig. 6 indicates that attack after longer times is most severe at a particular value of H⁺ activity. Table II indicates that, unlike the other two acids, corrosion in HCl is governed more by removal of Al³⁺ than Ca²⁺ since addition of AlCl₃ inhibits attack to a greater extent than does addition of CaCl₂. The results could be explained in terms of reactions which result in the formation of anionic complexes. However, the only component of "E" glass which would be involved in such a reaction would appear to be Fe³⁺ which, as the oxide, is present only to the extent of 0.39%. The reaction is:



The reaction would be expected to be favoured at a particular HCl concentration as, although increasing the HCl concentration favours the left to right reaction, an increase in H⁺ favours right to left. Removal of Fe³⁺ in HCl solutions gave rise to the yellow colour described above and its presence was confirmed by ultraviolet spectroscopy. Fe³⁺ together with Al³⁺ would be mostly associated with the covalent lattice and the results suggest that removal of Fe³⁺, although present in very small quantities, possibly has a destabilizing effect on the structure facilitating removal of Al³⁺. Since Al³⁺ does not form complexes in HCl solutions, its removal from the glass would not be expected to be a maximum for a particular acid strength unless influenced by a complexing agent.

5. Conclusions

Tests on "E" glass fibres following immersion in solutions of nitric, sulphuric and hydrochloric acids suggest that corrosion is as much a function of the anion present as it is of the hydrogen ion activity. Nitric acid is the least corrosive of the three. Sulphuric acid has a high initial rate of attack due to the insolubility of calcium sulphate formed during the reaction. Whereas leaching of

both calcium and aluminium ions contributes to the strength loss in nitric and sulphuric acids, the relatively high rate of attack in hydrochloric acid appears to be mainly due to leaching of aluminium.

The rate of attack can be slowed by adding metal ions to the corroding media. Addition of calcium and aluminium ions to nitric acid solutions retards corrosion, as does the addition of aluminium ions to sulphuric and hydrochloric acids.

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