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The kinetics of corrosion of E-glass fibres in hydrochloric acid

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The corrosion of glass fibres in acid solution is well known and is thought to be responsible for many instances of failure in glass reinforced plastic materials. Although it is generally accepted that cations are leached from the glass matrix into the acid solution, the precise chemical mechanism and rates of corrosion are still not fully understood. For example, it is not simply the hydrogen ion concentration of the corroding medium that affects the rate of corrosion, but in many cases the anion associated with the acid plays a major role. Anions that can form insoluble salts or complexes with cations in the glass matrix can increase the rate of leaching and hence accelerate the corrosion process. In the case of hydrochloric acid, it has been suggested that chloride anions form complexes with iron(III) ions leached from the glass and this in part increases the rate of corrosion. This paper investigates the corrosion rate of glass fibres exposed to hydrochloric acid at different concentrations and temperatures by measuring the residual strength of the fibres before and after exposure. The leaching rate of cations into solution is also measured using atomic absorption spectroscopy. As expected, increase in temperature increases the rate of corrosion and this can be modelled using a simple Arrhenius plot to determine the activation energy of the process. Strength retention and rates of leaching of individual cations are compared in an attempt to explain the mechanism of corrosion.

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1. Introduction

The chemical corrosion of E-glass fibres, particularly in acidic environments, is now well established [1–16]. E-glass fibre is still the major reinforcing material used in glass reinforced plastic (GRP) composites in Australia, although several reports of GRP failure have been attributed to chemical corrosion [1–4, 12, 13, 16]. Generally such failures occur when the composite material is exposed to strongly acidic environments and are particularly aggravated when the material is under mechanical stress [1–7]. Good design and fabrication procedures are able to reduce failure rates to acceptable levels, although this is not always the case. The constituent responsible for stress corrosion failures in GRP materials appears to be the glass fibre rather than the resin, as the latter appears to play a protective role by shielding the fibres from the corrosive environment [1–4]. However, if this is damaged in any way and the fibres are exposed to acidic media, corrosion becomes rapid and may often be catastrophic. The failure of a sulphuric acid elution column in a South African gold mine is believed to be an example of this [13].

The accepted mechanism of the corrosion process is an ion exchange reaction in which metal ions associated with the glass surface such as Ca^{2+} and Al^{3+} are replaced by H^+ from the acid medium [8–10]. The general reaction may be written as:

$$\overline{M^{n+}} + nH^+ \leftrightarrows \overline{nH^+} + M^{n+} \qquad (1)$$

where the bar denotes association of the species with the glass phase. Because 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]. Corrosion can be slowed considerably by addition of the appropriate metal ions to the acid solution, thus supporting the leaching mechanism [11]. Originally it was presumed that the corrosive effect was related to the acidic strength of the medium expressed as the hydrogen ion concentration, but later work has shown that the associated anion can also play a significant role if the anion can form complex ions or insoluble species with the cations found in the glass [11, 13–16]. Such complex formation will effectively remove the leached cations M^{n+} from the right hand side of the above equation, thus driving the reaction to the right. This complex ion formation has been invoked to explain the severe corrosive effects of relatively weak organic acids such as oxalic acid in which the strength retention versus concentration curves show a well-defined minima [15].

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TABLE I Percentage composition of E-glass fibres

SiO_2	CaO	Al_2O_3	B_2O_3	MgO	K_2O	Na_2O	Fe_2O_3
52.1	23.90	14.86	4.29	1.78	1.06	1.02	0.39

Such minima are observed because at low acid concentration the ion exchange reaction is not favoured on account of the low hydrogen ion concentration, and at high acid concentration the anions present bind to certain metal cations on the glass surface and prevent their dissolution. This passivating mechanism has been observed with hydrochloric acid solutions, the chloride ion complexing with iron(III) ions in this case [11, 14], and this paper describes a more detailed investigation of corrosion by hydrochloric acid, in particular the effect of temperature.

2. Experimental

All chemicals used were analytical reagent grade where available or the purest grade supplied commercially. The material used was an E-glass fibre roving kindly supplied by ACI Fibreglass, Belmont, WA, of chemical composition shown in Table I.

Specimens 200 mm long were cut and immersed in 25 mL acid solution for various times up to 7 days, after which the specimens were washed in deionised water, air dried and subjected to tensile testing. Control specimens were cut at intervals along the roving and immersed in deionised water to eliminate any handling damage defects. Sample containers were immersed in thermostatted baths to maintain constant temperature over the period of investigation.

Tensile tests were carried out on the specimens using a LLOYD L6000R tensiometer, fitted with a 1 kN load cell, at a crosshead displacement rate of 2 mm/min. The failure load recorded was the maximum load that the roving could withstand in the test. At least six specimens were tested for each data point and only results showing sharp peaks in the load-deflection curves were recorded. This was necessary to eliminate non-uniform loading that sometimes occurred in the individual rovings. The mean and standard deviations of the peak loads were calculated, and 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 the 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. All elemental analyses were performed using flame atomic absorption spectroscopy, with the exception of boron, which was analysed by inductively coupled plasma mass spectrometry (ICP-MS).

3. Results

3.1. Temperature effects

As anticipated, increasing the temperature led to an increase in the rate of corrosion, and at 50°C the corrosion is particularly severe, as illustrated in Fig. 1. The rate of corrosion is particularly rapid in the initial stages of the process and slows gradually as time of exposure increases, although at 50°C complete strength loss occurs after only a few hours. Even so the rate of strength loss depicted in Fig. 1 can be modelled using a first order kinetic decay of the type:

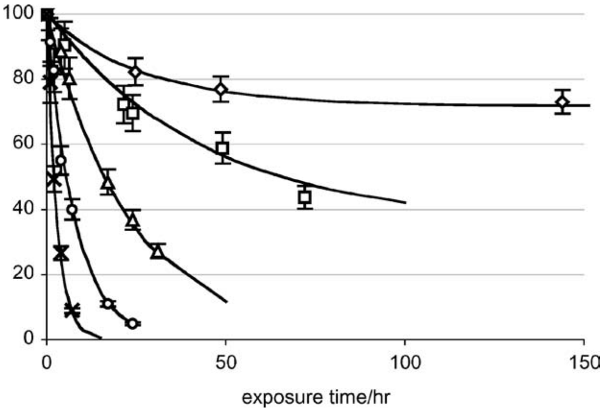

Figure 1 Corrosion of E-glass fibres in 3 M HCl at varying temperatures.

$$\text{Strength retention} = Ae^{-\mathrm{kt}}$$

where A is the overall strength loss, k is a rate constant for the decay, and t is the time of exposure in hours. The lines in Fig. 1 represent this model where the symbols are the actual data points. For corrosion at 10°C, strength loss is comparatively slow and appears to reach some limiting value rather than decay to zero as is the case at higher temperatures. Consequently this was modelled using a modified equation:

$$\text{Strength retention} = B + Ae^{-\mathrm{kt}}$$

where B is the limiting strength retention at that temperature.

The curves for the higher temperatures show an Arrhenius type of dependence where the first order rate constant k varies with temperature according to:

$$k = Ae^{-\mathrm{E_a/RT}}$$

where A is a pre-exponential factor related to the frequency of collisions of the reacting species, R is the universal gas constant, T is the absolute temperature, and E_a is the activation energy of the reaction. The result for 10°C is not included as the strength retention does not decay to zero. This behaviour is illustrated in Fig. 2. The slope of this curve yields an activation energy of 90.8 ± 0.9 kJ mol^{-1}, which represents the energy of activation required to replace a cation in the glass phase with a hydrogen ion.

3.2. Concentration effects

Fig. 3 shows the effect of concentration and temperature on strength retention and is in accordance with earlier data [11, 14]. It is clear that a corrosion maximum occurs at a concentration of 3 molar, but the definition of this maximum reduces with decreasing temperature

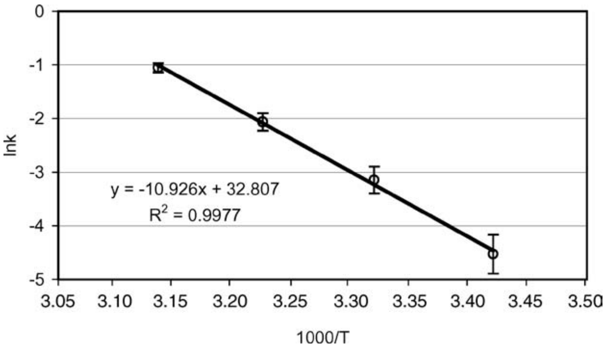

Figure 2 Arrhenius plot for the temperature dependence of strength loss of E-glass fibres in 3 M HCl.

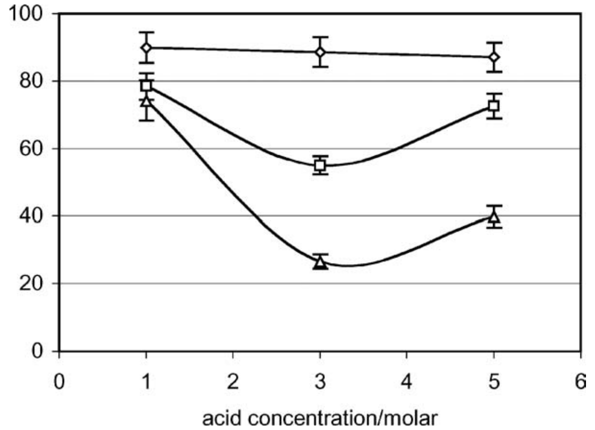

Figure 3 Effect of concentration and temperature on the strength retention of E-glass fibres after 4 h exposure.

after 4 h exposure. At longer exposure times (e.g., 24 h) the curve at 30°C has a similar form to that observed at 50°C. A yellow colour was observed in the more corroded specimens whose intensity increased as the corrosion became more severe. This corresponds to the dissolution of iron(III) as the chloride complex, verified by ultraviolet spectroscopy, and is again in accordance with earlier reports [11, 14].

3.3. Leaching of ions

The leaching patterns of all elements other than silicon were determined for all samples tested. Ions are leached into solution from the glass matrix by an ion exchange mechanism denoted by Equation 1, and all elements tested were found in varying quantities in the leached solution. A plot of dissolved ion concentration *versus* time for 3 M hydrochloric acid at 50°C is illustrated in Fig. 4. To represent all elements on the same graph, the concentrations of calcium and aluminium have been reduced by factors of 20 and 10 respectively.

Similar graphs were obtained for other concentrations and temperatures. It can be seen that the initial rate of dissolution of ions (denoted by the gradient) is quite large, and as the dissolution proceeds the rate decreases and eventually equilibrium is reached. This is consistent with the results obtained from strength loss data indicating a direct relationship between strength loss and cation dissolution from the glass matrix. The leaching rate can be described by a second order kinetic equation where the rate of leaching is proportional to the square of the leached ion concentration, rate $= k[x]^2$, and an integrated rate equation of the form:

$$x = \frac{at}{(1/ak) + t}$$

where a is the estimated equilibrium concentration of the leached ion, k is the rate constant, and t is time. The lines in Fig. 4 show this model and the points are the actual data points. This model is consistent with a mechanism involving initial equilibrium dissolution of the ions from the glass matrix, followed by complexing of the leached ion with the anion in solution, according to the following scheme:

$$\overline{\mathrm{M}^+} + \mathrm{H}^+ \leftrightarrows \overline{\mathrm{H}^+} + \mathrm{M}^+ \qquad (1)$$

$$\mathrm{M}^+ + \mathrm{A}^- \longrightarrow \mathrm{MA} \qquad (2)$$

where the bar denotes association with the glass matrix and A^- is the ion in solution associated with the original

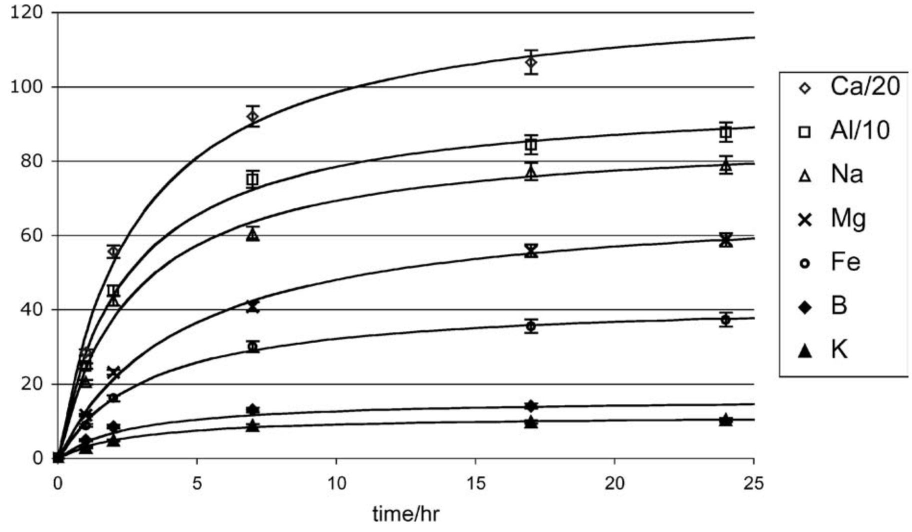

Figure 4 Leached ions from 3 M HCl at 50°C.

TABLE II Relative leaching of cation from 3 M HCl at 50°C and 50% strength retention

Cation	Ca	Al	B	Mg	K	Na	Fe
Relative wt% leached	39	34	4	14	4	28	35

acid which complexes the dissolved ion, in this case the chloride ion. A feature to note is that the iron(III) ion is leached to a much greater extent than would probably be expected, given the relatively low occurrence of this species in the glass matrix. This is shown in Table II for 3 M hydrochloric acid at 50°C, at a strength retention of 50%. This mechanism will be discussed later. The relative percentage weight was obtained by calculating the total weight of fibres in a typical sample and relating the amount of each cation leached to its total amount present in the original sample.

4. Discussion

4.1. Temperature effects

The rate of corrosion shows a dramatic increase as the temperature is increased and can be modelled according to a first order or exponential decrease in strength retention. Using the model previously described, first order rate constants can be evaluated for each temperature run and these are found to fit an Arrhenius type model where $k = Ae^{-\mathrm{E/RT}}$. From this an activation energy can be found for the strength loss of the glass, which is related to the removal of an ion from the glass surface. Although this may not be a precise description of the molecular process, it does serve as a predictive model to relate the severity of strength loss to the prevailing temperature.

4.2. Concentration effects

The fact that there is an optimum concentration at which corrosion occurs is indicative of something other than hydrogen ion concentration that is causing it. This has been observed before in the case of hydrochloric acid [11, 14], hydrobromic acid [14], organic acids [15], and more recently in the case of perchloric acid [17]. The explanation offered is related to the complexing nature of the anion associated with the acid. At low acid concentration, the hydrogen ion concentration is too low for effective leaching of the cation from the glass surface, whereas at higher acid concentrations the anion binds to the ion on the glass surface and prevents the dissolution of cations from the glass. Evidence for the dissolution of iron(III) ions was the intensity of the yellow colour observed at 3 M concentration as opposed to higher or lower concentrations. This optimum was observed to become more pronounced as the temperature increased, as would be expected from an increased reaction rate.

4.3. Leaching of ions

All ions are leached into solution to varying extents, and in general the more abundant ions are leached to a greater extent than the less abundant. The notable exception here is the iron(III) ion which is leached to the same extent as the much more abundant aluminium and calcium ions. A possible reason for this is the fact that chloride ions complex iron(III) and this drives the leaching reaction to the right as depicted by Equations 1 and 2. The observed yellow colour, identified as the $FeCl_3$ complex by uv spectroscopy, is evidence of the complex formation. The kinetics of ion leaching for all ions follows a second order model consistent with the scheme denoted by Equations 1 and 2, even though no other ions form stable complexes with chloride ion. It is possible that the leaching of iron(III) opens a pathway for other ions to be leached and that the kinetics of iron(III) leaching determines the overall rate of leaching of all other ions. This would explain the decreased leaching rate at higher and lower acid concentrations, and the concentration dependence of the corrosion process, even though the iron is only a minor component of the glass. This is in contrast to a report by Qui and Kumosa [18] which states that the leaching of iron is of little influence because of the low amount of iron in the glass composition, although these authors did not study concentrations above 0.1 M, and were consequently far away from the optimum concentration which causes maximum corrosion, nor did they perform a detailed analysis of all the ions leached from the glass. The fact that the corrosion process may be suppressed by incorporation of iron(III) in the acid solution [14] further supports the importance of iron leaching in the corrosion by hydrochloric acid. Data from perchloric acid corrosion [17] also show a dependence on concentration and in this particular case the binding of perchlorate and potassium is thought to determine the overall leaching rate. Again, the influence of a minor component of the glass has a major influence on the corrosion process.

5. Conclusions

The corrosion of E-glass fibres in hydrochloric acid has been studied at different temperatures and concentrations in an attempt to elucidate the mechanism of the corrosion process. Increasing the temperature causes a dramatic increase in the corrosion rate, which can be described by an Arrhenius activation energy, and thus the corrosion rate at varying temperatures can be confidently predicted. The corrosion of E-glass in hydrochloric acid is concentration dependent with a maximum corrosion rate at 3 M concentration. It is thought that this is indicative of complex formation where leaching is influenced by the anion associated with acid rather than hydrogen ion concentration. At low acid concentrations there are insufficient hydrogen ions for effective leaching of the ions in the glass and at higher acid concentrations the complexing anion binds to the particular ion in the glass surface and prevents the leaching of other ions. The corrosion and hence strength loss of the glass is caused by an ion exchange reaction which leaches ions from the glass surface and replaces them with hydrogen ions. This causes surface tensile stresses, which eventually lead to cracking and consequent weakening of the individual fibres. All non-silicaceous ions are leached from the surface with the more abundant ions being leached to a greater extent. However in the case of hydrochloric acid there is an unusually high concentration of iron(III) leached into solution and it is thought that this arises from complex formation of iron(III) chloride, and that this has an overall influence on the leaching of other ions. A kinetic analysis of the corrosion and leaching process is consistent with this type of behaviour.

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