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Chemical corrosion of E-glass fibres in neutral phosphate solutions

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Following local reports of failure of glass reinforced plastic (GRP) tanks used for the storage of ammonium orthophosphate fertilizer, the effect of phosphate solutions on the strength retention of E-glass fibre was investigated. Although solutions (1 to 5 mol dm^{-3}) of mineral acids are known to corrode E-glass fibre, phosphoric acid solution (3 mol dm^{-3}; pH 1.55) is essentially inert and strength retention of the glass fibre after 15 days exposure is the same as the water control. However, as the pH is raised strength retention is diminished and a minimum is observed around pH 7 to 8. A chemical explanation of this behaviour is put forward in terms of leaching and complex formation with calcium and magnesium ions. Although not nearly as corrosive as other agents, evidence suggests that phosphate solutions do corrode E-glass fibre and this should be borne in mind when GRP materials are used in such chemical environments.

1. Introduction

The chemical corrosion of E-glass fibres, particularly in acidic environments, has been the subject of several recent investigations [1–5]. E-glass fibre is the major reinforcing material used in glass reinforced plastic (GRP) composites and several reports of GRP failure have been attributed to chemical corrosion [6–9]. Normally such failures occur when the GRP material is exposed to strongly acidic environments and is particularly aggravated when the material is also under mechanical stress. 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 [10–12]. The general reaction may be written as:

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

where the bar denotes association of the species with the glass phase. Originally it was presumed that the corrosive effect was related to the acidic strength of the medium, expressed as the hydrogen ion concentration. However, recent work [3–5] has shown that the anion too plays a significant role, particularly when the anion can form complex ions or insoluble species with the cations found in the glass. Such complex ion formation will effectively remove the leached cations M^{n+} from the right hand side of Equation 1, thus driving the reaction to the right. This complex formation has been put forward to explain the severe corrosive effects of relatively weak organic acids such as oxalic and mesoxalic acids, in which the strength retention versus concentration curves show well defined minima [5]. 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 also been observed with hydrochloric acid solutions, the chloride ion complexing with ferric ions in this case [4].

Recently, cases of failure have been observed locally in GRP tanks used for the storage of ammonium orthophosphate fertilizer (50% aqueous solution) under conditions of approximately neutral pH. Examination of these tanks, which have been used successfully to store water, suggests that corrosion of the glass fibres was a contributing factor in the failure, the ammonium phosphate solution in this case corroding the E-glass fibre of the tank material. This paper investigates the strength retention behaviour of E-glass fibres on exposure to phosphate solutions of varying pH, and attempts to explain the fertilizer tank failure in terms of corrosion. To our knowledge this is the first case of GRP failure in neutral environments which has been attributed to corrosion.

2. Experimental procedure

All chemicals used were analytical grade reagents. Glass specimens 200 mm long were cut from an E-glass fibre roving, 2275 TEX, of chemical composition shown in Table I. Exposure of the glass fibres to aqueous phosphate solutions of varying concentration and pH was allowed to proceed for 360 h after which the specimens were washed, air dried and subjected to tensile testing. Ammonium, sodium and potassium salts of phosphoric acid (3 mol dm^{-3}) were used to cover the pH range from 2 to 10 as well as phosphoric acid solution (3 mol dm^{-3}; pH 1.55). Different cations were necessary to achieve the required concentrations over the pH range; overlaps were arranged in order to correlate any specific cationic effects. A time curve

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TABLE I Composition of E-glass fibres

SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O	B_2O_3
52.10	14.86	23.90	1.78	0.39	1.02	1.06	4.29

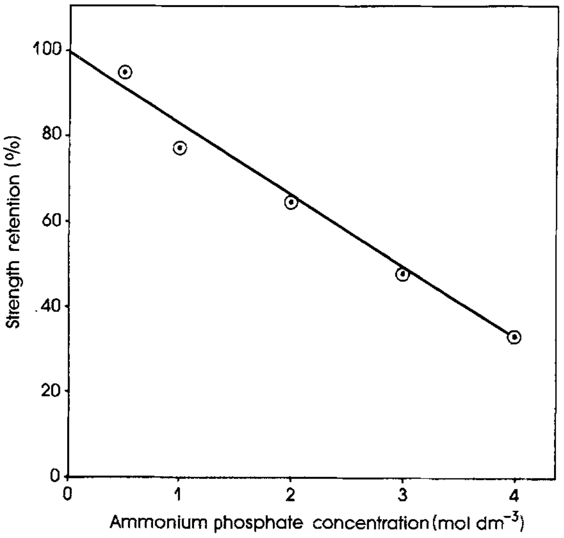

Figure 2 Strength retention against concentration for fibres exposed to ammonium phosphate solutions for 360 h; pH 7.

(0 to 360 h; 3 mol dm^{-3}) and a concentration curve (0 to 4 mol dm^{-3}; 360 h), were also done for ammonium phosphate at pH 7. The tensile testing procedure followed was identical to that described previously [3].

At least six specimens were tested for each data point 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, which had been kept in distilled water and subjected to the same handling procedures as the experimental samples.

3. Results

Strength retention against time and strength retention against concentration graphs for ammonium phosphate solutions are shown in Figs 1 and 2, respectively. Both curves show a steady decline in strength retention as time or concentration increases. The strength retention against pH curve is shown in Fig. 3 and shows a well defined minimum at around pH 8. No strength loss was observed in samples exposed to solutions of pH 4 and below. Strength loss depends only on the concentration of hydrogen and phosphate ion and is independent of associated cations such as Na^+, K^+ and NH_4^+. Weight losses in the samples after exposure to the phosphate solutions were in all cases insignificant.

4. Discussion

Corrosion of E-glass fibres is known to occur in solutions of high hydrogen ion concentration but corrosion in neutral solutions has not been reported. The corrosion mechanism even in acids is thought to involve factors besides that of high acidic strength, as severe corrosion of E-glass has been observed in organic acid solutions of relatively low acidic strength [5]. It is interesting to note from the present results that no corrosion is observed following treatment with 3 mol dm^{-3} phosphoric acid, but corrosion is observed as the acid is neutralized, and reaches peak severity around pH 8. Obviously factors other than hydrogen ion concentration are involved here.

Recent reports [3–5] have indicated that the formation of complex ions, from anions in the corroding medium and cations leached from the glass, plays a role in the corrosion process by effectively driving the ion exchange reaction (Equation 1) over to the right. Phosphates are known to form particularly stable complex ions with many metals [13, 14] including aluminium, calcium, magnesium and iron, all of which are present in E-glass fibres. However, there must still be an appreciable hydrogen ion concentration to

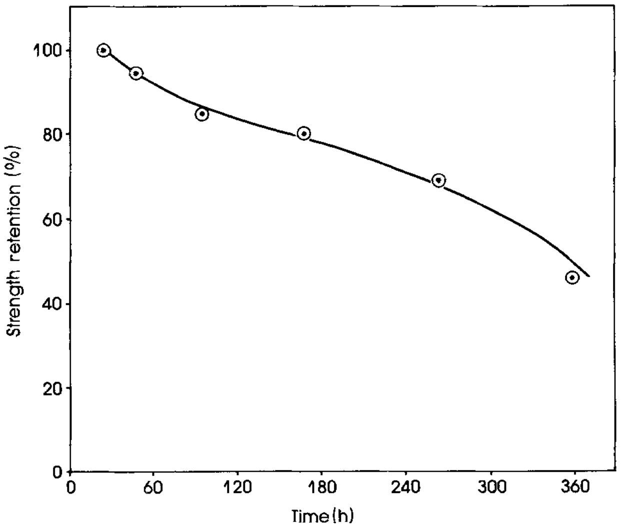

Figure 1 Strength retention against time for fibres exposed to 3 mol dm^{-3}; pH 7 ammonium phosphate.

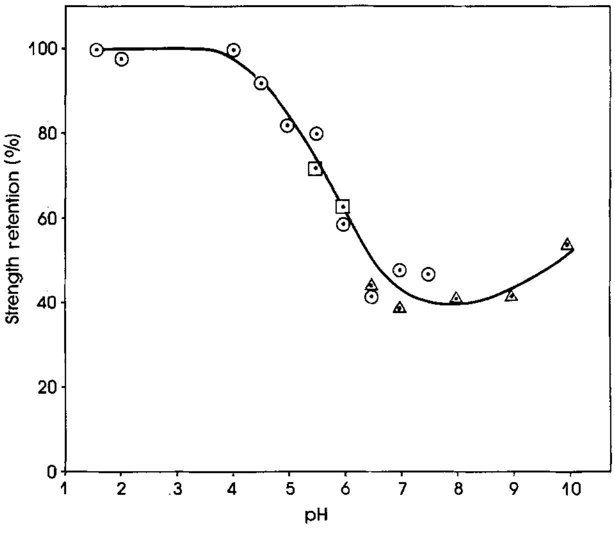

Figure 3 Strength retention against pH for fibres exposed to phosphate solutions (3 mol dm^{-3}) for 360 h. Associated cations: ○, NH_4^+; □, Na^+; △, K^+.

remove the metal cations from the glass surface in the first place.

In a solution containing hydrogen, calcium and phosphate ions there will be competition for the phosphate anions between the calcium and hydrogen ions, and reactions such as the following will take place:

$$Ca^{2+} + H_2PO_4^- \rightleftharpoons CaHPO_4 + H^+ \qquad (2)$$

$$Ca^{2+} + HPO_4^{2-} \rightleftharpoons CaPO_4^- + H^+ \qquad (3)$$

If these reactions lie predominantly to the right, calcium ions will be effectively removed from the solution and leaching of calcium ions from the glass fibre (Equation 1) will be promoted. If a right to left reaction in Equations 2 or 3 is favoured, leaching of calcium and hence corrosion will be suppressed. It would therefore appear that the corrosion process is critically dependent on the position of equilibrium of these reactions. The thermodynamic equilibrium constants, K, of the reactions can be deduced from the appropriate stability constants [13] of reactions involving calcium, hydrogen and phosphate ions. Thus:

$$H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^- \qquad \log K = 7.2 \quad (4)$$

$$Ca^{2+} + HPO_4^{2-} \rightleftharpoons CaHPO_4 \qquad \log K = 2.7 \quad (5)$$

Subtracting Equation 4 from Equation 5 gives Equation 2, and the equilibrium constant for Equation 2 is obtained from a similar combination of the stability constants. Thus for Equation 2, $\log K = -4.5$ or $K = 10^{-4.5}$. In the same way the equilibrium constant for Equation 3 can be deduced from:

$$H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-} \qquad \log K = 12.4 \quad (6)$$

$$Ca^{2+} + PO_4^{3-} \rightleftharpoons CaPO_4^- \qquad \log K = 6.5 \quad (7)$$

Thus for Equation 3, $\log K = -5.9$ or $K = 10^{-5.9}$.

It now becomes apparent why calcium ions are effectively leached in neutral phosphate solutions. At pH = 4.5 where the effective hydrogen ion concentration is $10^{-4.5}$ and the predominant phosphate species is $H_2PO_4^-$, neither side of Equation 2 will predominate, as at that pH

$$K = \frac{(CaHPO_4)(H^+)}{(Ca^{2+})(H_2PO_4^-)} = 10^{-4.5}$$

and

$$\frac{(CaHPO_4)}{(Ca^{2+})(H_2PO_4^-)} = 1$$

Using similar arguments for the divalent phosphate species (which will become the favoured one as the pH rises), Equation 3 will be evenly balanced at pH 5.9. Therefore as the pH rises above 4.5 complex formation between calcium and phosphate ions will become favourable, and this in turn will drive the initial leaching reaction (Equation 1) over to the right despite the low hydrogen ion concentration. As the pH decreases calcium ions are no longer bound by the phosphate ions and the leaching reaction is not assisted in any way. Phosphoric acid, even at $3\,\mathrm{mol\,dm^{-3}}$ concentration, does not generate a sufficiently large hydrogen ion concentration to remove enough calcium ions without the additional assistance of complexing anions. Conversely, at high pH, even though complex formation is highly favourable, there is insufficient hydrogen ion activity to leach any calcium ions from the glass surface. In addition the favourability of complex formation could lead to binding of phosphate anions on the glass surface, which at high pH would inhibit the leaching process by passivation. This is the observed behaviour as shown in Fig. 3.

Using similar arguments the corresponding reactions for the leaching of magnesium ions (Equations 2 and 3 where Mg^{2+} replaces Ca^{2+}) are found to have equilibrium constants corresponding to $\log K = -5.9$ and $\log K = -7.4$ which again suggests leaching will only become effective in neutral solutions. This also would be a contributing factor to corrosion in neutral solution even though the magnesium content of the E-glass sample is low (1.78%).

The binding of ferric ions with phosphate is extremely strong over the whole pH range and it is more than likely that phosphate ions would bind to ferric ions on the glass surface thus preventing any further leaching.

Aluminium ions form relatively weak complexes at low pH and stronger ones as the pH rises [14], but these tend to have low solubilities and would precipitate from the solution. This of course would also contribute to the corrosion process by disturbing the ion exchange equilibrium (Equation 1). However the effectiveness of this mechanism, which would increase with increasing pH, is offset by the decrease of hydrogen ion concentration which would become too inefficient to leach aluminium ions to any great extent, as the forward ion exchange reaction is much less favourable for small trivalent cations. Solubility considerations also apply to calcium and magnesium ions which form relatively insoluble phosphates at high pH.

The effect of strongly acidic phosphate solutions on glass fracture has been examined using soda-lime glass rods [15] or plates [16]. Ray [15] shows that attack by orthophosphoric acid is inappreciable at temperatures below 200° C and is mainly concerned with attack by polymerized phosphoric acids above that temperature, where an insoluble solid identified as silicon phosphate, $SiO_2P_2O_5$, was formed on the glass surface. This solid passivates the glass and renders it resistant to hydrofluoric acid. This however does not seem likely to happen in the neutral solutions used in this current investigation. Fox [16] investigates the effects of strong solutions of phosphoric and lactic acids on the fracture behaviour of a glass under point loading and shows that the acidic environment has a marked effect on the dynamic hardness. In both acids, hardness minima are observed at particular pH values. These results are explained in terms of binding to the silica lattice of protons or anions depending on the pH of the environment and the point of zero charge of the glass surface. It is concluded that the effect is due only to the hydrogen ion concentration and not the associated anion. However these ideas would not explain leaching in neutral solutions observed here.

An alternative explanation for the behaviour in phosphoric and lactic acid solutions would be based on the thermodynamic ideas put forward in this paper. The minima observed in the case of phosphoric acid [16] corresponds to the leaching and complexing of calcium ions by phosphoric acid according to the equation:

$$\mathrm{Ca^{2+} + H_3PO_4 \rightleftharpoons CaH_2PO_4^+ + H^+} \qquad (8)$$

Using stability constants [14] for the appropriate complexes, calculation of the equilibrium constant for this equation gives a value of $K = 10^{-0.75}$ from which one would predict optimum leaching and hence minimum strength or hardness at $\mathrm{pH} = 0.75$ which agrees well with the value obtained of 0.8. Similar calculations for the complexing of calcium by lactic acid predict an effective leaching pH of 2.2, reasonably close to the observed value of 1.5. Stability constant data for magnesium ions give similar results; data for aluminium are not available.

5. Conclusion

Corrosion of E-glass fibres has been observed in phosphate solutions at neutral pH. Corrosion is pH dependent, being more effective at pH 8, and virtually non-existent in $3\,\mathrm{mol\,dm^{-3}}$ phosphoric acid. It is dependent only on the phosphate ions in solution and not the associated cation ($\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{NH_4^+}$). The mechanism involves leaching of cations from the glass (e.g. $\mathrm{Ca^{2+}}$, $\mathrm{Mg^{2+}}$, $\mathrm{Al^{3+}}$) which can form complex species with phosphate ions. Corrosion does not occur in acidic solutions where the formation of such complex species is unfavourable. The possibility of corrosion should therefore be considered where GRP vessels are designed for use in such environments, for example the storage of phosphate fertilizers.

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