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Solvent effect of water on S-glass

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The dissolution of magnesium, aluminium, and silicon from S-glass rovings in water at 30, 40 and 50° C and from S-glass powders in water at 40° C has been studied. The concentrations of magnesium and silicon reached 2 mg l^{-1} or more depending upon the temperature and length of contact time, while the aluminium concentration reached no more than 0.2 mg l^{-1}. The preferential leaching out of Mg (or MgO) by water from S-glass could be the initial step which causes and aggravates the degradation of S-glass filament reinforced composites. Weak ammonia solutions ranging from 0.04 to 0.000 08 M enhanced the dissolution of aluminium and magnesium, especially that of the former. In the experiments with S-glass rovings in boiling water in Pyrex glass flasks, complications arose as a result of the interactions between the alkaline ingredients of the Pyrex wares and the ingredients of S-glass. Rate relations are proposed and discussed for the dissolution process.

List of symbols

C_g	concentration of Mg in bulk glass (g cm^{-3})
C_{gs}	concentration of Mg at the glass surface (g cm^{-3})
C_l	concentration of Mg in liquid film immediate to glass surface (g cm^{-3})
C_b	concentration of Mg in bulk liquid (g cm^{-3})
D_g	diffusivity of Mg in solid phase ($\text{cm}^2 \text{ sec}^{-1}$)
D_l	diffusivity of Mg in liquid phase ($\text{cm}^2 \text{ sec}^{-1}$)
E_a	dissolution activation energy of Mg for S-glass-water system (cal g.mol^{-1})
k_d	detachment rate coefficient of Mg from S-glass to water (cm sec^{-1})
m	reaction order for surface area
n	reaction order for concentration driving force
R	universal constant ($\text{cal g.mol}^{-1} \text{ K}^{-1}$)
S	surface area (cm^2)
T	temperature (° K)
V	liquid volume (cm^3)
W	mass of Mg in S-glass rovings used (g)
α	overall mass transfer coefficient, g Mg transferred per (sec) (cm^2) (g Mg cm^{-3}), or cm sec^{-1}
α'	proportionality coefficient in Equation 1
β	dimension correction factor between k_d and k_l, dimensionless
δ	solid phase diffusion path length (cm)
ϵ	equilibirum coefficient between Mg in the liquid phase and in the solid phase, dimensionless. $\epsilon = C_l/C_{gs}$
θ	time (sec)

1. Introduction

Fibre glass composites have been used to an increasing extent as structural components because of their high strength at relatively low densities. They are, in general, more resistant to moisture and weathering than most other structural materials. But under environments of high humidity and temperature, glass fibre composites have been found to be susceptible to degradation [1–4]. To meet rigid requirements of certain highly demanding applications it is necessary to improve our understanding of the degradation process, which

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lags far behind the glass fibre technology.

The extensive studies [4–9] made on the degradation of glass fibre composites cover a wide variety of areas. They include the properties of individual ingredients of the composites, interaction between the ingredients, and the influence of environmental conditions on the bonding and strength of the composites. As many ingredients and their interplays are involved, there have been various theories pertaining to the degradation mechanism.

Most experimental results and microscopic and submicroscopic observations reported in the literature [2–4, 10, 11] agree that the water molecule is the major transgressor in causing debonding between the fibres and the resin matrix. The mutual strengthening effect of the major components in the composite is thus adversely affected. It is likely also that the glass fibres themselves are weakened by the action of moisture on their surface composition and structure.

For high-strength reinforced composites, the preferred fibres are made from S-glass, the composition of which is given in wt% as Al_2O_3 25%, MgO 10%, and SiO_2 65% [8]. Converted to a molar basis, S-glass has an overall composition of $MgO \cdot Al_2O_3 \cdot 4.4SiO_2$ in comparison with cordierite which is represented as $MgO \cdot Al_2O_3 \cdot 5SiO_2$ [12].

This paper presents the dissolution rates and amounts of the ingredients of S-glass dissolved by water at several temperature and solution conditions. Rate relations for the dissolution process and possible degradation mechanisms are discussed in the light of the results.

2. Experimental

In the degradation studies, Type S-1014 S-glass rovings of Ferro Corporation were used, which came in spools. Each strand forming the rovings contains 204 filaments and the filaments have an average diameter of approximately 10 μm. The strands were made into coils about $1\frac{1}{2}$ in. diameter and tied together into knots so that there were no loose filaments to handicap weighing and transferring.

2.1. Degradation of S-glass in water at ambient temperatures

Degradation of S-glass in water was determined in terms of the amounts of magnesium, aluminium, and silicon dissolved. Approximately 10 g S-glass rovings were weighed into 250 ml wide-mouth polypropylene bottles. To each bottle 150 ml distilled water were added and the bottle was tightly capped. The bottles were placed in a constant-temperature water bath maintained at 40° C. After different time periods (up to 2000 h), the bottles were separately removed from the bath and the water in the bottles decanted into 150 ml polypropylene sample bottles. The concentrations of Mg, Al, and Si in the water were, respectively, determined by the following methods:

Mg – Perkin-Elmer (Model 305) atomic absorption spectroscope.

Al – Perkin-Elmer atomic absorption spectroscope with Al concentration above 1 ppm. The Aluminon colorimetric method [13] was used for Al concentrations below 1 ppm.

Si – Heteropoly Blue colorimetric method [14].

The runs were also made with the constant-temperature bath maintained at 30 and 50° C.

2.2. Effect of amounts of rovings

Different amounts (between 0.6 and 12.3 g) of S-glass rovings were placed in 100 ml distilled water contained in 250 ml polypropylene bottles. The bottles were maintained at 40° C in a water bath. After 9 days, the solutions decanted from the bottles were analysed for their Mg contents.

2.3. Degradation of S-glass powders in water

S-glass powders were obtained by crushing S-glass marbles supplied by Ferro Corporation. The powders were screened and the portions retained on 48-, 65- and 100-mesh screens were mixed and used in this series of runs. 2 g glass powder and 50 ml distilled water were placed in each of the five 2 oz polypropylene bottles maintained at 40° C. The bottles were shaken gently a few times a day, although it was learned later that the number of shakings had little effect on the rate of dissolution of the glass ingredients. The bottles were removed from the water bath after different time periods, and the water in each bottle was filtered and analysed for its magnesium, aluminium, and silicon contents.

2.4. Degradation of S-glass rovings in weak ammonia solutions

Into 100 ml ammonia solutions of different concentrations (from 0.000 081 to 0.0404 M) in

250 ml, polypropylene bottles were each placed 5.5 g S-glass rovings. The bottles were maintained at 40° C for 13 days and at 24° C for 14 days. The ammonia solutions were then separated from the glass rovings and analysed for their pH value and contents of Mg and Al.

2.5. Degradation of S-glass rovings in boiling water

A series of runs was made using four sets of 500 ml round-bottom Pyrex flasks, each being heated by an electric heating mantle and fitted with a reflux condenser. The amounts of S-glass rovings and water in each flask were, respectively, 9.5 g and 100 ml. After different time periods, boiling was stopped and the water from each flask was cooled and analysed for its pH value and contents of Mg and Al.

3. Results and discussion

The concentrations in milligrams of Mg and Si per litre of water (or parts per million by weight) after different time periods of contact between S-glass rovings and water at 30, 40 and 50° C are plotted, respectively, in Figs. 1 and 2. The figures show that the dissolution of both Mg and Si were relatively rapid in the early stage of contact, but the rate tapered off with time. The concentrations of Mg and Si reached up to several parts per million by weight, depending on the temperature. However, the concentrations of Al in the solutions obtained in the three series of runs were all below 0.2 $\mathrm{mg\,l^{-1}}$, barely analysable by the atomic absorption spectroscope and by the Aluminon colorimetric method. The concentration of Al could reach a few milligrams per litre under other temperature and solution conditions as will be discussed shortly.

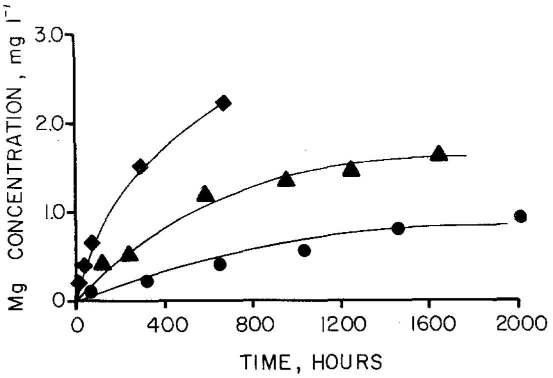

Figure 1 Variation of Mg dissolution with time. 10 g S-glass rovings in 150 ml water. ● 30° C, ▲ 40° C, ◆ 50° C.

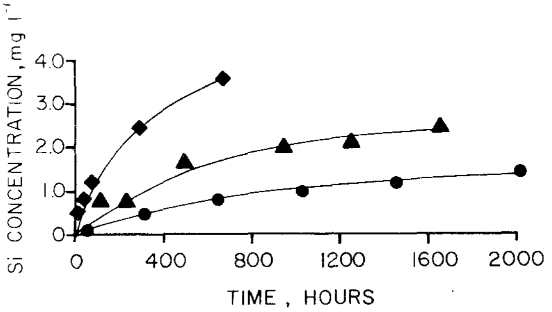

Figure 2 Variation of Si dissolution with time. 10 g S-glass rovings in 150 ml water. ● 30° C, ▲ 40° C, ◆ 50° C.

From Figs. 1 and 2, the atomic ratio Mg/Si based on the amounts of Mg and Si dissolved in water for the same temperature and after the same time period may be calculated. At the temperatures and time covered in these two figures, the atomic ratio Mg/Si in water is in the neighbourhood of 0.7 as compared with 0.199 based on the composition in wt% given for S-glass. The atomic ratio Mg/Si obtained for S-glass powders in water at 40° C was found to be approximately 0.45 as will be discussed later. The higher Mg/Si ratio in water than in S-glass indicates that Mg is leached out of solid phase more readily than the other two major ingredients, Al and Si. This may be attributed to the higher solubility of MgO in water than those of Al_2O_3 and SiO_2 [15]. The Mg removed could be from the silicate network in the glass through hydrolysis or from those not incorporated in the network.

In any case, the excessive proportion of Mg removed from S-glass indicates a change in the surface composition of the filaments. The preferential removal of one of the ingredients tends to produce voids on the surface which, in turn, would aggravate further deterioration of the glass filaments [5, 10] and weaken the reinforcing effect between the filaments and the resin matrix in a glass fibre-reinforced composite.

The nearly linear relation in Fig. 3 between the amount of Mg in the water and the amount of S-glass rovings used suggests that compared at the same contact time of nine days the amount of dissolved Mg is directly related to the total surface area of the glass filaments.

The activation energy for the dissolution of Mg from S-glass was calculated based on Equation 1 and the Mg dissolution curves in Fig. 1.

$$\frac{\mathrm{d}\ln(1/\theta)}{\mathrm{d}(1/T)} = \frac{-E_\mathrm{a}}{R}. \qquad (1)$$

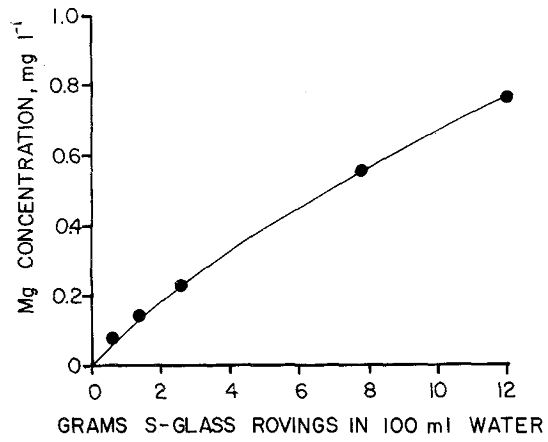

Figure 3 Variation of Mg dissolution with amount of S-glass rovings. 40° C, 9 days, 100 ml water.

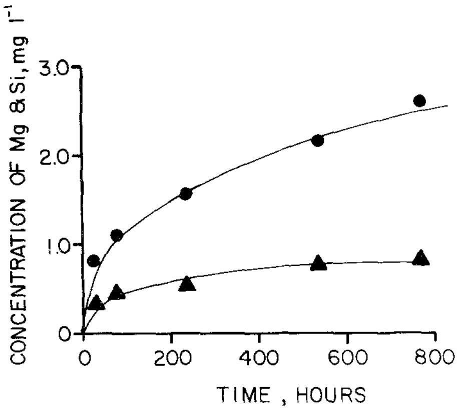

Figure 4 Variation of Mg and Si dissolution with time from S-glass powders. 2 g S-glass powders in 50 ml water. 40° C; ▲ Mg, ● Si.

For the calculation, two horizontal lines were drawn (at Mg concentrations of 0.5 and 0.7 mg^{-1}) to obtain the respective time (θ) required for each of the three temperatures. The average activation energy, E_a calculated for the temperature range is equal to 2.4×10^4 cal g.mol^{-1}.

Fig. 4 shows the dissolution of Mg and Si from S-glass powders made by crushing finish-free S-glass marbles. The dissolution curves for Mg and Si in water display the same general trend for both the powders and the rovings (Figs. 1 and 2). Although a quantitative comparison between the powders and the rovings is not possible because of the difference in their specific surface areas, the results seem to indicate that the thin film of finish (about 0.1 μm thick) on the S-glass filaments has no significant effect on the rate and amount of dissolution.

In weak ammoniacal solutions ranging from 0.0404 to 0.000 080 8 M, it was found that dissolution of Al became measurable. The dissolution of Mg and Al in the ammonia solutions of different pH values is shown in Fig. 5.

The rapid increase of Al concentration with increasing pH appears to be parallel to the results reported for borosilicate glasses [16]. The rate of attack on Corning Code 7740 borosilicate glass by aqueous alkaline solutions increases very rapidly with pH. The effect of pH on the Mg dissolution is, however, not as drastic. Ammonia and amines are possible products when amino silanes and curing agents used in glass-reinforced composite formulations undergo decomposition in the presence of moisture, micro-organisms, and other agents. Deterioration of glass reinforced composites by this sequence of processes is conceivable. Further work is required to establish the effect of decomposition products of amino finishing materials on the stability of S-glass-reinforced composites. Unavailability of proprietary information on the finish composition for the glass fibre rovings from the manufacturers has been a handicap.

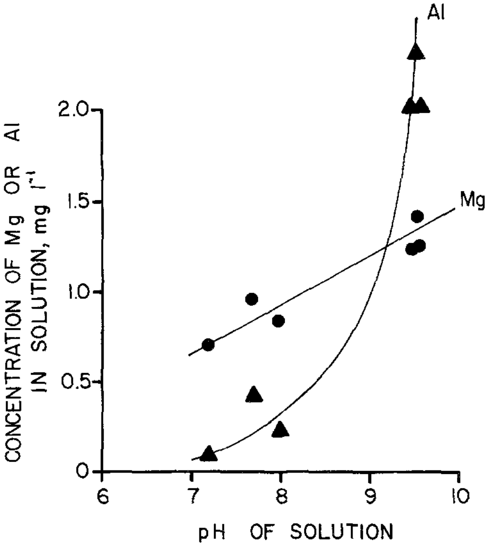

Figure 5 Dissolution of Mg and Al from S-glass rovings – variation with pH of solution. 5.5 g rovings in 100 ml ammonia solutions of 0.0404 to 0.000 080 8 M. Contact time: 27 days at room temperature.

The action of boiling water on S-glass rovings was complicated by the presence of the Pyrex glass flask and reflux condensers. The alkaline ingredients of the Pyrex wares apparently interacted with those of S-glass at the elevated temperature, affecting considerably the dissolution process. Fig. 6

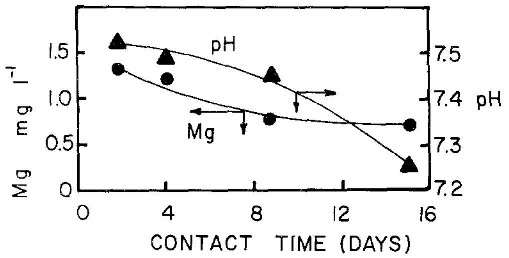

Figure 6 Effect of boiling water on S-glass rovings in Pyrex flasks. Variation of Mg dissolution and pH with contact time. 9.6 g S-glass rovings in 100 ml of water.

shows the changes, with time, of the pH value and Mg concentration of the resulting water. The water was found to contain approximately 3 mg l^{-1} of Al, which could come from both the S-glass rovings and the Pyrex glass wares. Attempts were made to identify the translucent solid deposits which formed along the air–water interface on the inside surface of the Pyrex flasks. The particles collected failed to show any significant crystallinity by powder X-ray diffraction.

The rate of dissolution of Mg from the filament is expected to be affected by the surface area and concentration difference and may be represented by the following relation.

$$\frac{-\mathrm{d}W}{\mathrm{d}\theta} = \alpha' S^m (C_g\epsilon - C_b)^n \qquad (2)$$

where W is mass of Mg in the glass; θ, time; S, total surface area of glass filaments used, $(C_g\epsilon - C_b)$ concentration difference between those in the glass, C_g, and in the bulk water, C_b; ϵ, coefficient of equilibrium between Mg in the liquid phase and in the solid phase; m and n, exponents signifying, respectively, the orders of effect of S and concentration driving force on the rate process; and α', a proportionality constant. Fig. 3 verifies that m is essentially equal to 1.0. For mass transfer, the rate is in general related to the first power of concentration difference, i.e. $n = 1.0$. Rewriting Equation 1, including replacement of α', we have

$$\frac{-\mathrm{d}W}{\mathrm{d}\theta} = V\left(\frac{\mathrm{d}C_b}{\mathrm{d}\theta}\right) = \alpha S(C_g\epsilon - C_b). \qquad (3)$$

In Equation 3, V is the volume of water holding the S-glass rovings and α is the overall dissolution rate coefficient, the reciprocal of which represents the total resistance. It is assumed here that the total resistance to the dissolution of Mg from S-glass consists of three resistances in series: diffusion of Mg from glass interior to glass surface, detachment of Mg from glass surface to become dissolved in the liquid film immediate to the glass surface, the diffusion of Mg across the interfacial film to the bulk liquid phase. Thus, we have

$$\frac{1}{\alpha} = \frac{\epsilon\delta}{D_g} + \frac{1}{k_d} + \frac{\beta}{k_l} \qquad (4)$$

Extraction of α from Equations 3 and 4 yields

$$\alpha = \frac{1}{\dfrac{\epsilon\delta}{D_g} + \dfrac{1}{k_d} + \dfrac{\beta}{k_l}} = \frac{V(\mathrm{d}C_b/\mathrm{d}\theta)}{S(C_g\epsilon - C_b)}. \qquad (5)$$

In the above equations, D_g and δ represent, respectively, the diffusivity and diffusion distance in the solid phase, k_d and k_l are, respectively, the rate coefficients for Mg to detach from the solid surface and for Mg to diffuse across the interfacial liquid film, and β is a dimension factor between the rate coefficients k_d and k_l and is probably nearly equal to 1.0. The driving forces corresponding to these three component resistances are: $(C_g\epsilon - C_{gs}\epsilon)$, $(C_{gs}\epsilon - C_l)$, and $(C_l - C_b)$, where C_{gs} is the Mg concentration at glass surface and C_l is the Mg concentration in the liquid film immediate to the glass surface.

Rate coefficient for mass transfer from an infinite cylinder of diameter D_c to the surrounding fluid has been given as $k_l = 2D_l/D_c$ [17, 18]. For a bundle of cylinders as in a strand of glass filaments, corrections for geometry and available surface area are needed. In the Mg dissolution from S-glass, the resistance β/k_l is probably relatively small in comparison with the other two resistances as discussed below.

In the dissolution of a solid in a slow moving or stagnant liquid medium, the rate has been reported to be controlled by the detachment of solute molecules from the solid surface [19]. That is, the detachment resistance $1/k_d$ is much larger than the liquid diffusion resistance $1/k_l$. In the early stage of dissolution, in which the Mg atoms on the surface are dissolved, the resistance δ/D_g is negligible. With the detachment resistance controlling, $(C_g\epsilon - C_{gs}\epsilon)$ and $(C_l - C_b)$ would be relatively small compared with $(C_{gs}\epsilon - C_l)$, or $C_g\epsilon \cong C_{gs}\epsilon$ and $C_l \cong C_b$. Keeping the dominant driving force and resistance, Equation 5 may be written as

$$\frac{\mathrm{d}C_b}{\mathrm{d}\theta} = \frac{k_d S}{V}(C_{gs}\epsilon - C_l) \cong \frac{k_d S}{V}(C_{gs}\epsilon - C_b). \qquad (6)$$

Equation 6 represents Mg dissolution in the early stage, which is shown by the left segments of the curves in Fig. 1. However, the concentration driving force $(C_{gs}\epsilon - C_b)$ decreases with time as C_{gs} decreases and C_b increases.

When Mg atoms on the glass surface are leached out, further supply of Mg must come by diffusion from within the solid phase. Here, surface detachment is replaced by the much slower solid-phase diffusion as the rate-controlling step. By retaining δ/D_g and omitting the relatively small $1/k_d$ and β/k_1, the rate equation may now be written as

$$\frac{dC_b}{d\theta} = \frac{D_g S}{V\delta}(C_g\epsilon - C_{gs}\epsilon); \qquad (7)$$

The levelling-off segments of the curves in Fig. 1 represent the extremely slow Mg dissolution in this stage.

The preliminary analysis proposed for Mg dissolution so far seems to be supported by the experimental results. Quantitative verification of the rate relations for the individual stages would shed more light in elucidating the complex S-glass degradation process.

4. Conclusions

The disproportionately excessive removal of magnesium from S-glass by water probably creates voids on the surface of S-glass filaments, which are expected to detrimentally affect the structure and strength of the filaments. The presence of these voids could be of particular significance, as the strength of glasses is known to be highly sensitive to surface cracks. Also, the voids would allow water to penetrate and spread into the interface between S-glass filaments and the resin matrix. The overall degradation process is probably accelerated when a composite is under stress. To stabilize S-glass fibre-reinforced composites, the glass filaments perhaps should undergo some passivation treatment, so that the dissolution of the more soluble MgO may be curtailed. The results on the increased dissolution of Al and Mg, especially of the former, in the presence of weak ammonia solutions call for investigation of the decomposition of amino curing agents used in glass fibre composite formulations.

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