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Chemical durability studies on basalt fibres

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Chemical durability studies carried out on basalt fibres indicated that this fibre has excellent resistance to alkaline attack, but it has poor resistance to acids. Basalt compares very well with Cem-Fil† with respect to alkaline durability. Surface study by scanning electron microscopy and strength properties were used to ascertain the durability of basalt and Cem-Fil.

1. Introduction

Glass fibres which are used as a reinforcement in different matrices should have good chemical resistance as well as compatibility with the matrix. This property determines its application in different environments. Most of the fibres are affected by acid or alkali and this interaction with chemicals deteriorates its properties. Various reviews are available on the chemical durability of glasses [1–3]. Fibres which are used for cement reinforcement should have good resistance toward alkaline attack. Fibres like basalt [4] and Cem-Fil [5] have been developed and are found to have good resistance to alkaline attack. Both the strength measurements and surface morphology studies by scanning electron microscopy (SEM) have proved their resistance to alkaline attack [6, 7].

The present paper reports the results of a study on the effect of boiling NaOH solution on basalt and Cem-Fil fibres, and the effect of mineral acid (HCl) on basalt fibre. Tensile strength measurements and surface morphology studies by SEM were used to assess the suitability of these fibres in different environments. The results are compared with E-glass fibre results.

2. Experimental procedure

To study the effect of alkali, fibres of Cem-Fil, basalt and E-glass were refluxed in a solution of NaOH having a pH of 13 for 2 h. The compositions of these fibres are given in Table I. After refluxing the fibres were washed with water to remove all the reaction products. These fibres were dried at 100° C and then observed under SEM for surface defects. The same fibres were also tested in an Instron testing machine for their mechanical properties. In each batch, 15 to 20 fibres were tested and the average strength and modulus were computed. The gauge length was 10 mm.

Basalt fibre was also tested for its acid durability. Here fibres were treated with 4N HCl solution both at room temperature and 100° C (refluxing). The fibres were soaked for various periods of time (4, 8, 16 and 24 h) in 4N HCl at room temperature. The refluxing treatment with 4N HCl was carried out of 0.5 h. After washing, the treated fibres were used for SEM studies and mechanical property measurements.

3. Results and discussion

3.1. Alkaline durability

The alkaline durability of basalt and Cem-Fil with cement extract solution at room temperature has already been established [6, 7]. Basalt and Cem-Fil have very good resistance to alkali even at higher temperatures (100° C). Figs 1 and 2 show the excellent resistance of basalt and Cem-Fil fibre to alkali attack even after 2 h refluxing. The absence of surface damage indicates the excellent resistance of these fibres to alkali. The corrosion resistance of Cem-Fil is mainly due to the presence of ZrO_2. The hydrated ZrO_2 surface formed on the fibre is mainly responsible for the alkaline resistance [8, 9]. The excellent corrosion resistance of basalt is due to the presence of various oxides (TiO_2, MnO_2, Fe_2O_3 and Al_2O_3). Alumina reacts

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TABLE I Typical composition of fibres (wt %)

Fibres	SiO_2	Al_2O_3	B_2O_3	MnO	MgO	CaO	$Na_2O + K_2O$	ZrO_2	Li_2O	TiO_2	Fe_2O_3	Si/O	Na_2O/Al_2O_3
A-glass*	72.2	1.8	–	–	3.5	9.5	13	–	–	–	–	0.41	6
E-glass*	52.4	14.4	10.4	–	5.2	16.6	0.8	–	–	–	–	0.31	0.02
C-glass	65.0	4.0	5.0	–	3.0	14	8.5	–	–	–	–	0.36	2
Basalt†	49.1	13.8	–	0.21	5.25	9.43	4	–	–	3.16	13.98	0.297	0.289
Cem-Fil*	71.0	1.0	–	–	–	–	11	16	1	–	–	0.429	11.0

* From Majumdar *et al.* [5].
† From Subramanian *et al.* [4].

with silica to form a film over the surface which slows down the corrosion [10]. From consideration of thermodynamic activity Mn, Ti and Fe oxides always improve the alkaline durability.

The observations made under the SEM of these fibres are further substantiated by the change in mechanical properties. Table II compares the strength and modulus values before and after refluxing in alkali. The loss in strength and modulus is very marginal. Basalt [7] and Cem-Fil [12] retain their flexibility even after the refluxing.

Compared to basalt and Cem-Fil, E-glass has a very poor resistance to alkali. Alkali attacks the silica network itself. Fig. 3 shows the surface damages observed in E-glass. Strength measurements were not possible for E-glass.

3.2. Acid durability

Basalt fibres have poor resistance to acids on soaking with 4N HCl solution at room temperature. The fibre slowly corrodes. The calcium, iron and aluminium present in the basalt leaches out. Fig. 4 shows SEM pictures of basalt fibres which were soaked in 4N HCl solution. Some of the pictures show surface damage. The leachability of basalt can be explained using the Huggin's formula [13]. A smaller Si/O ratio means more non-bridging oxygens, resulting in the decreased stability of the silica lattice. The Si/O ratio was calculated for A-, C- and E-glass fibres, and also for basalt fibres. The values are given in Table I. A- and C-glass have a higher value (> 0.36) and they are found to have a higher resistance to acids [14]. Basalt and E-glass have a lower value (0.29 and 0.31, respectively). E-glass has a poor resistance to acid attack [14]. The presence of aluminium ions in four-fold co-ordination improves acid resistance and aluminium can enter four-fold co-ordination if enough sodium ions are present in the glass, i.e. if $Na_2O/Al_2O_3 > 1$. Basalt has a value of 0.2898

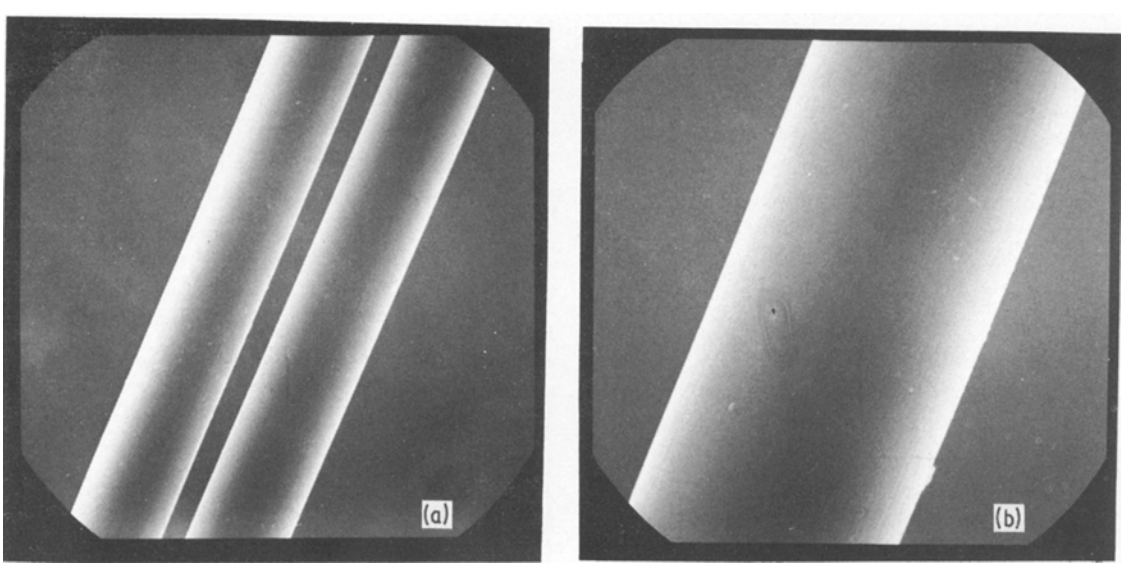

Figure 1 (a) and (b) SEM micrographs of basalt fibres refluxed in NaOH solution for 2 h. (a) 1 cm = 5 μm and (b) 1 cm = 2.5 μm.

TABLE II Fibre properties before and after treatment

Treatment	Basalt		Cem-Fil	
	Tensile strength ($\times 10^3$ psi)	Modulus ($\times 10^6$ psi)	Tensile strength ($\times 10^3$ psi)	Modulus ($\times 10^6$ psi)
(Untreated)*	190 (183–196)	7–8	280 (262–297)	8–9
Alkali				
30 days in cement*	170 (162–188)	7–8	260 (251–268)	8–9
Extract (room temperature 25° C)				
NaOH refluxing (100° C)	159 (150–170)	5–6	219 (170–250)	6–7
4N HCl				
Room temperature:				
4 h	162 (140–170)	7–8	–	–
8 h	120 (117–130)	6–7	–	–
16 h	120 (115–125)	6–7	–	–
24 h	103 (90–116)	5–6	–	–
Refluxing (100° C)	Measurement was not possible			

The figures in the brackets indicate the minimum and maximum of the test results.
10^3 psi = 6.89 N mm^{-2} = 6.89 Pa.
Diameter: Basalt untreated 10–13 μm, treated 10–12 μm. Cem-Fil untreated 12–14 μm, treated 12–14 μm.
Virgin strengths: Basalt 390 $\times 10^3$ psi [4]. Cem-Fil 370 $\times 10^3$ psi [5].
* Velpari *et al.* [7].

and hence the aluminium ion should be in six-fold co-ordination which also accounts for its poor resistance to acid attack.

Boiling HCl solution has a very severe effect on basalt fibres. It leaches out most of the ions. The fibre becomes brittle and loses its brown colour due to the removal of Fe^{3+} ions. It was not possible to conduct mechanical property measurements as the treated fibres were very brittle. Fig. 5 shows the brittleness of treated basalt fibres under SEM.

Room-temperature leached fibres had a reasonable amount of flexibility. The strength and modulus values are given in Table II. With the increase in time of soaking the strength reduces drastically. Modulus values also decrease with time of soaking.

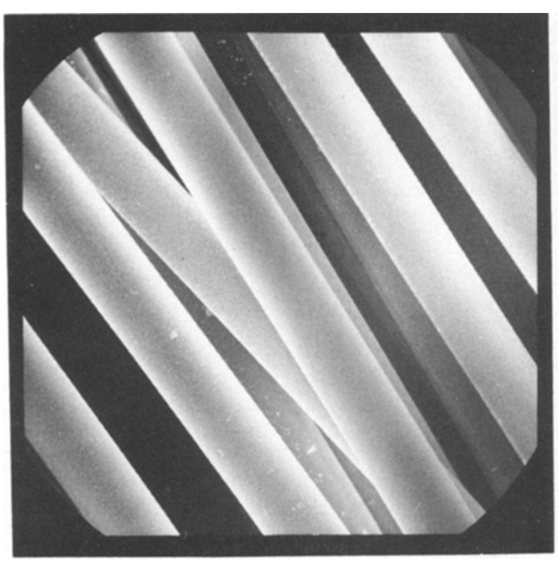

Figure 2 SEM of Cem-Fil fibre refluxed in NaOH solution for 2 h. 1 cm = 10 μm.

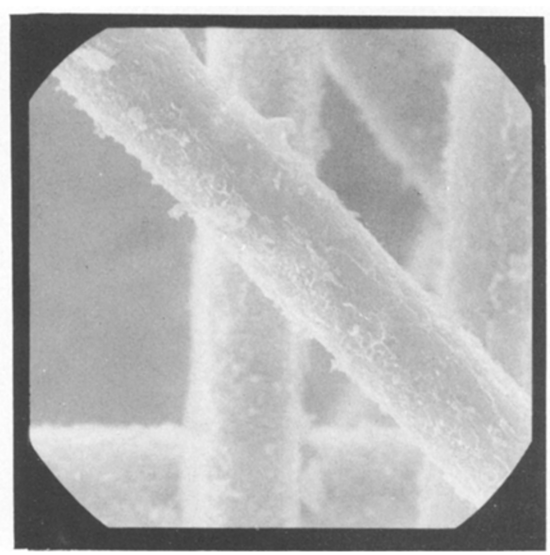

Figure 3 SEM of E-glass fibre refluxed in NaOH solution for 2 h. 1 cm = 5 μm.

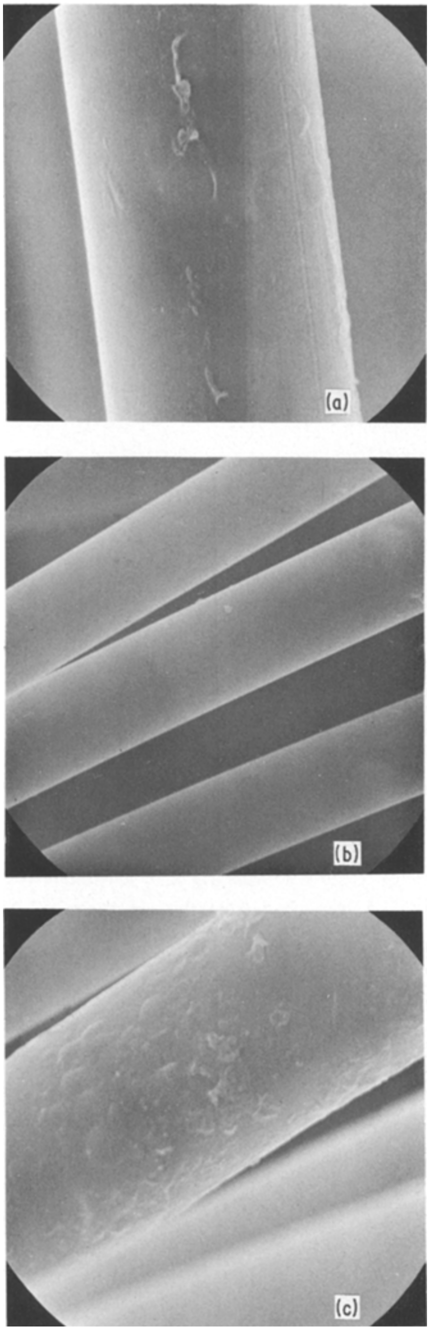

Figure 4 SEM micrographs of basalt fibres soaked in 4N HCl solution. (a) 4 h, 1 cm = 2.5 μm, (b) 8 h, 1 cm = 5 μm and (c) 16 h, 1 cm = 2.5 μm.

4. Conclusions

Basalt and Cem-Fil fibres have an excellent resistance to alkaline attack both at room temperature and at elevated temperatures. Basalt fibres do not have a good resistance to acids. The acid attack is marginal at room temperature and very severe at elevated temperatures.

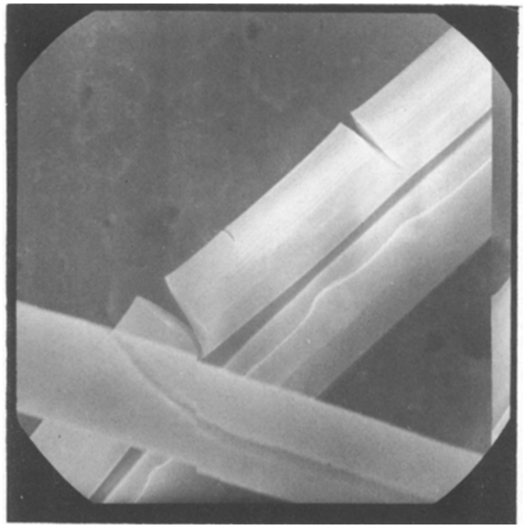

Figure 5 SEM of basalt fibre refluxed in 4N HCl solution for 0.5 h. 1 cm = 5 μm.

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