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A glass-bonded ceramic material from chrysotile (white asbestos)

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A process has been developed for bonding chrysotile asbestos into a robust, dimensionally-stable lightweight ceramic material by fusing it with sodium silicate and/or ground waste glass. The chrysotile can retain its desirable properties of fibrous morphology and porosity, but the fibre bundles are stabilized by fusion into a glassy matrix, reducing the respirable fibre concentration. The glass-bonded materials have good resistance to mechanical abrasion, and any resulting dust is found by SEM to be particularly free of fibres. The thermal treatment also converts the chrysotile into crystalline forsterite, which should destroy its cell toxicity. Other methods of glass-bonding chrysotile compacts (hot pressing and impregnating with glaze) were also investigated, and the properties of the resulting materials are reported.

1. Introduction

Asbestos in both its white and blue forms (the minerals chrysotile, $Mg_3Si_2O_5(OH)_4$ and crocidolite, $Na_2(Fe^{2+},Mg)Fe_2^{3+}Si_8O_{22}(OH)_2$, respectively) has many useful properties for insulation and fireproofing, for friction surfaces, and, in cement-bonded sheets, for cladding buildings. However, increasing recognition of the health hazard caused by respiration of asbestos dusts has now led to its virtual abandonment in many of these applications. Current understanding of the physiological effects of inhaling fibrous materials is still incomplete, but suggests that the three factors which determine the hazard of fibres are their dimensions, their durability and their dose [1]. The fibre dimension is important in determining whether it will become airborne and therefore respirable; fibres greater than 3 μm diameter and 50–100 μm long are thought unlikely to enter the lungs [2]. Of the fibres which do enter the lungs, those shorter than about 3 μm can be removed by the bodily defence mechanisms, provided the concentrations do not become too high or the dose too prolonged; the most dangerous fibres in even small doses are therefore those which are chemically durable, 5–10 μm long and about 0–1 μm diameter [2]. Fibre bundles which are capable of splitting down to 0–1 μm without shortening are particularly dangerous. Chrysotile, which occurs in bundles of fibrils, each with an average diameter of 0.25 μm, falls into the highly dangerous category [1]. The primary importance of the fibre dimensions is also apparent from the fact that long, thin fibres of a range of other materials of different chemical composition, crystal structure and surface characteristics have all been shown to have biological activity [1].

Another hazard of asbestos minerals is their toxicity to living cells, which can be measured in terms of the effect on the macrophages, destruction of the red blood cells (haemolysis) and neurotoxicity. On the basis of all three criteria, chrysotile shows high toxicity.

Thermal treatment of chrysotile at about 750 °C converts it into the magnesium silicate forsterite, Mg_2SiO_4 [3], which retains the morphology of its precursor, but progressively loses mechanical strength with increasing temperature [4]. Thermal degradation followed by mechanical crushing to destroy the fibre structure has been proposed as a method for eliminating the biological hazards of asbestos [5, 6]. However, studies of heated chrysotile indicate that its neurotoxicity [7], macrophage destruction and haemolytic activity [8] are all increased by heating at 600–800 °C, but the toxicity disappears in samples heated to above 1000 °C [8]. These effects are suggested to be due to the disordered nature of the crystal surfaces during thermal transformation to forsterite, which is non-toxic when well crystallized [8].

Several chemical methods have been proposed for detoxifying chrysotile fibres, including coating the fibres with water-insoluble metal orthophosphates [9] which can be formed *in situ* by treatment with gaseous $POCl_3$ followed by heating to about 400 °C [10], treatment with organosilane to form organosiloxane polymers [11] and destruction of the fibres by treatment with a fluorine-containing weak organic acid [12].

Another possibility for removing the health hazards associated with the use of chrysotile is to convert it into forsterite, simultaneously bonding the fibres into a glassy matrix, thereby immobilizing them and reducing their tendency to split into individual fibrils. This should also compensate for their decrease in strength without adversely affecting their most valuable insulating and heat-resistant properties. Silicate bonding

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should also increase the fibre diameters by fusing them into sheaths or bundles, thereby reducing the physiological damage of any dust which might result from mechanical abrasion of the material. Silicate bonding could be achieved by the use of a process previously developed for granular materials [13], in which sodium silicate provides unfired (green) strength, and ground waste glass provides the fired strength.

The aim of this work was to develop a safe asbestos-based ceramic material, with particular reference to:

(i) the effect of sodium silicate impregnation on the size and morphology of the heated chrysotile fibres;

(ii) the bulk properties of silicate-bonded fibrous compacts;

(iii) the applicability of other silicate-bonding methods such as hot pressing of laminated compacts and glaze impregnation.

2. Experimental procedure

Two Canadian chrysotiles were used in this work – fibre bundles pulled from a massive sample from Quebec, and a processed material (AK 262 C91) from the Cassiar Mine, British Columbia. Both samples were found by X-ray diffraction (XRD) to be crystalline monophase chrysotile, containing about 3% Fe (determined by EDAX). The sodium silicate had an $SiO_2:Na_2O$ ratio of 2.32 and a pH of 12.2

TABLE I Composition of glazes used to impregnate chrysotile compacts

Component	glaze 1(%)	glaze 2(%)	glaze 3(%)
SiO_2	71.10	54.93	55.87
Al_2O_3	1.63	13.24	11.69
CaO	16.07	10.87	13.93
MgO	2.55	–	–
Na_2O	8.21	–	–
K_2O	0.44	1.44	2.20
BaO	–	13.47	2.83
ZnO	–	6.05	13.47

Two sets of fibre impregnation experiments were carried out, one using a saturated solution of this sodium silicate, and the other using the same solution diluted to 3 wt %. The uptake by the unheated chrysotile from these solutions on a dried weight basis was about 25% and 1%, respectively. The impregnated samples were heated at 900 °C for 80 min, then examined in a Hitachi S570 scanning electron microscope.

To produce compact, silicate-bonded fibre mats, the chrysotile was blended with varying amounts of waste glass which had been crushed and graded to pass a 44

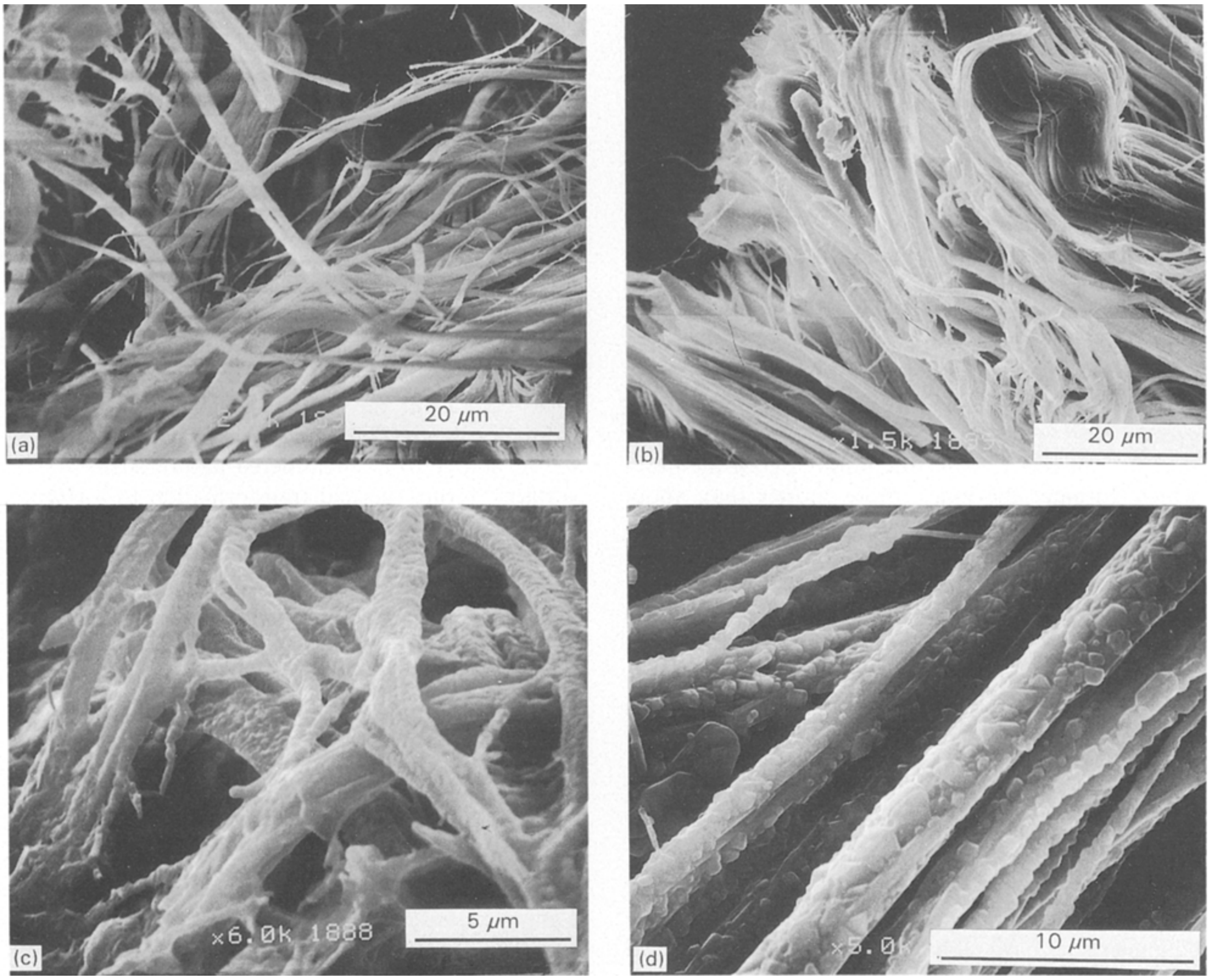


Figure 1 Scanning electron micrographs of chrysotile impregnated with sodium silicate and/or heated at 900 °C. (a) Unimpregnated, heated. (b) Impregnated with diluted sodium silicate, heated. (c and d) Impregnated with undiluted sodium silicate, heated.

mesh sieve. After the addition of 5 wt % saturated sodium silicate solution and sufficient water to permit mixing, the samples were pressed in a 25 mm diameter steel die at 1050 kPa then hardened by exposure to CO_2 gas as previously described [12] before removing from the mould. A parallel set of samples was also prepared without gassing. The pellets were heated at $6\,^{\circ}C\,min^{-1}$ to 1000 °C, held for 90 min then cooled at $8\,^{\circ}C\,min^{-1}$. The tensile strengths were measured by crushing the pellets across their diameter using an Instron Universal Tester at a crosshead speed of $3\,mm\,min^{-1}$. The tensile strength, T, is then given [14] by

$$T = 2P/\pi dt \qquad (1)$$

where P is the breaking load and d and t are, respectively, the diameter and thickness of the pellet, measured by vernier callipers.

The radial firing shrinkage and apparent density was calculated by measurements of pellet dimensions made by vernier callipers, the "true" density and porosity being determined by water absorption in a vacuum desiccator. To determine the resistance of these compacts to mechanical abrasion, attrition tests were carried out by dry ball milling in a 60 mm diameter plastic vessel with 138 g 12 mm enstatite balls. The resulting dust (> 100 mesh) was weighed and its morphology examined by SEM (Cambridge Stereoscan 250 Mk2). The bulk pellet material was also examined by SEM, X-ray diffraction (XRD, Philips PW 1700 automatic diffractometer with Co K_α radiation and graphite monochromator) and ^{29}Si high-resolution MAS MNR (Varian XL-200, 4.7T field strength, 4 kHz spinning speed). The delay between the 90° pulses was 0.5 s (longer delays did not affect the peak ratios).

Laminated samples were prepared by pre-forming 25 mm diameter mats, each containing 1 g chrysotile. The mats were assembled into triple sandwiches, interspersed with varying amounts of > 44 mesh glass powder. The laminates were then heated in a hot press at $20\,^{\circ}C\,min^{-1}$ to temperatures between 720 and 820 °C, held at temperature for 20 min at 10 MPa, then cooled at $10\,^{\circ}C\,min^{-1}$. A parallel series of experiments was carried out with mats which had previously been converted to crystalline forsterite at 1000 °C. The strength of these samples was measured by the biaxial ball-on-ring method, in which the specimen was supported by a circular ball-bearing race and loaded centrally with a ball [15]. The equibiaxial stress, S, at the centre is given by

$$S = [3P(1 + \nu)/4\pi t^2]\{1 + 2[\ln(a/b)] + [(1 - \nu)a^2/(1 + \nu)R^2][1 - (b^2/2a^2)]\} \qquad (2)$$

where P is the breaking load, t the disc thickness, a the radius of the support ring, b the radius of the central loading region (taken as $t/3$), R the radius of the sample disc and ν is Poisson's ratio (taken as 0.25). In other ceramic systems, this test method has been found to give tensile strengths about 8% lower than the more common four-point loading test of a bar-shaped specimen [16].

Other disc-shaped samples were prepared by outgassing pre-formed chrysotile mats in a vacuum desiccator, then exposing them to a slurry of finely ball-milled glass (> 75 μm), drying and firing at 1000 °C as above. In other experiments, commercial pottery glazes were substituted for the ball-milled glass. The compositions of these glazes and the ground glass are shown in Table I. These samples were subjected to the ball-on-ring test, and examined by SEM and XRD as above.

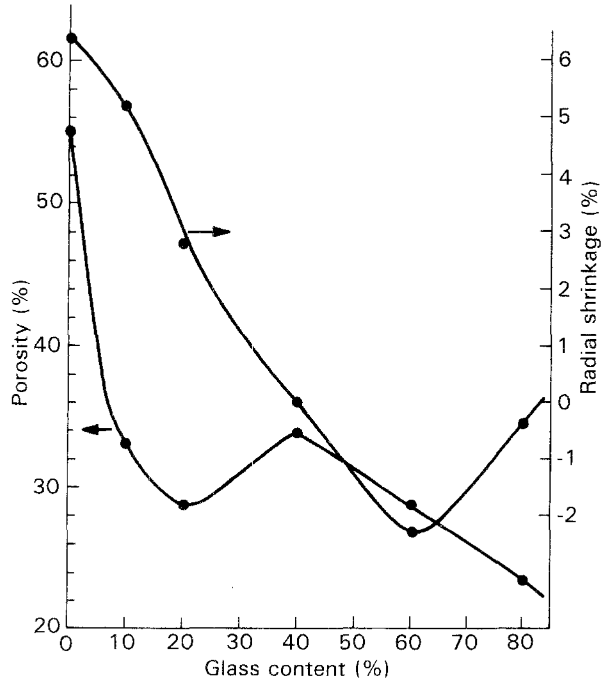


Figure 2 Porosity and radial shrinkage of chrysotile–glass powder–sodium silicate pellets fired at 1000 °C, as a function of their glass content.

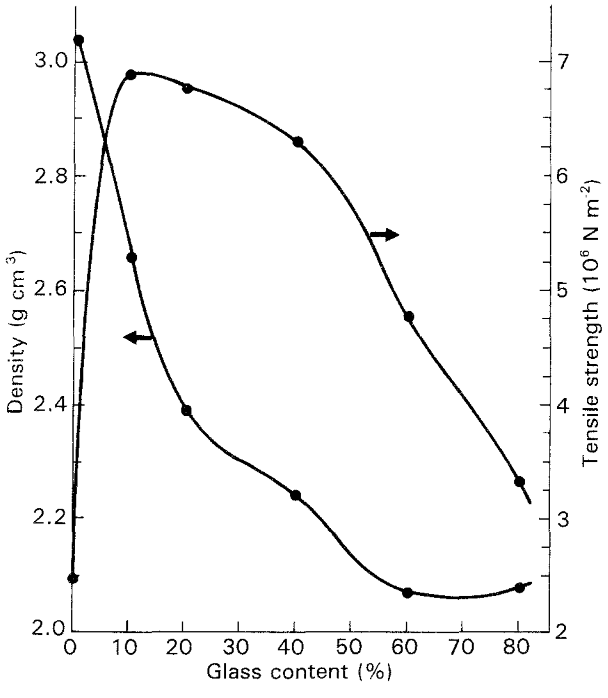


Figure 3 Bulk density and tensile strength of chrysotile–glass powder–sodium silicate pellets fired at 1000 °C, as a function of their glass content.

3. Results and discussion

3.1. Sodium silicate impregnation of chrysotile fibres

The scanning electron micrographs of Fig. 1 show that heating unimpregnated fibres at 900 °C produces a spaghetti-like morphology (Fig. 1a) of average diameter 1 μm, but exhibiting a few of the finer 0.1 μm diameter fibrils which compose the bundles in the unheated material.

Treatment with diluted sodium silicate solution makes no great difference to the morphology of the unheated material, which appears as a mesh of interwoven, predominantly fine fibrils. When heated at 900 °C, this morphology is largely maintained, al-

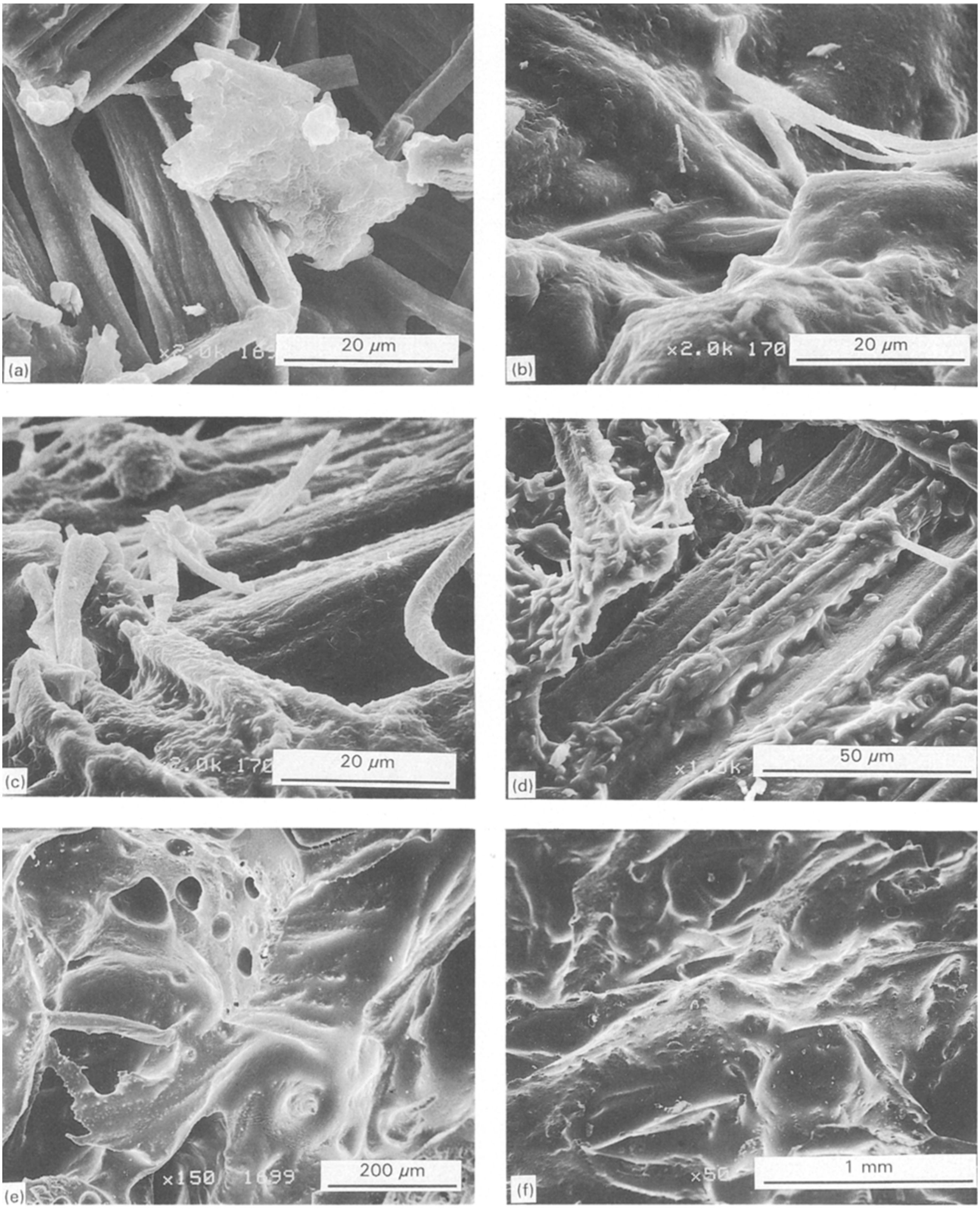


Figure 4 Scanning electron micrographs of fracture surfaces of chrysotile–glass powder–sodium silicate pellets fired at 1000 °C. (a, b) Bonded with sodium silicate only. (c) Containing 20% glass. (d) Containing 40% glass. (e) Containing 60% glass. (f) Containing 80% glass.

though fibre strands of 2–3 μm are not uncommon, and appear to be stabilized by the sodium silicate treatment (Fig. 1b).

Undiluted sodium silicate solution produces an even more pronounced effect; although the unheated samples still show cobwebs of unstranded fibrils hanging from thicker bundles, heating at 900 °C fuses these into glassy-looking structures (Fig. 1c) in which the 1–2 μm diameter fibres are covered with fine crystals (Fig. 1d). These results suggest that the forsterite fibres can be stabilized and bonded together by glass-forming reactions with sodium silicate alone, especially at higher silicate concentrations.

3.2. The properties of silicate-bonded chrysotile compacts

All the fired glass-asbestos compacts, including the control pellet bonded with sodium silicate but containing no ground glass, were durable and quite hard, with colours ranging from pale fawn through greyish-white with increasing glass content. At lower glass contents, the pellets had the appearance of a solidified mat of fibres, but with increasing glass content, the pellet surfaces became rougher and pitted with pinholes.

The fired shrinkage of all these pellets is very low, and decreases with increasing glass content (Fig. 2), as the densification is increasingly offset by bloating at high glass concentrations. The porosity of the pellets remains high over the entire range of glass content (Fig. 2); the porosity at lower glass contents arises from the residual fibrous structure, which is progressively replaced at higher glass contents by a more closed porosity due to bloating of the glass by the water released in the thermal decomposition of the chrysotile. This progressive increase in closed porosity is also reflected in the decrease in bulk density with increasing glass content (Fig. 3), and in a corresponding decrease in tensile strength, which has its maximum values at the lowest glass contents (Fig. 3). The tensile strength results indicate, however, that compacts bonded with sodium silicate alone have very low strength, which develops only in the presence of glass.

Because no significant differences were detected between the mechanical properties of the CO_2-gassed and ungassed pellets, the results were combined in Figs 2 and 3, giving quadruplicate samples for each composition.

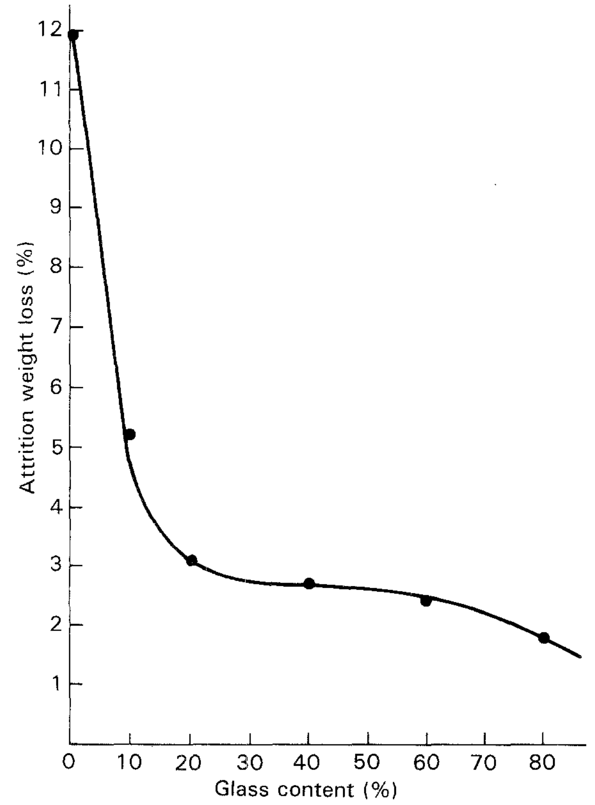


Figure 5 Attrition behaviour of chrysotile–glass powder–sodium silicate pellets fired at 1000 °C (in terms of their weight loss after dry ball-milling for 30 min) as a function of their glass content.

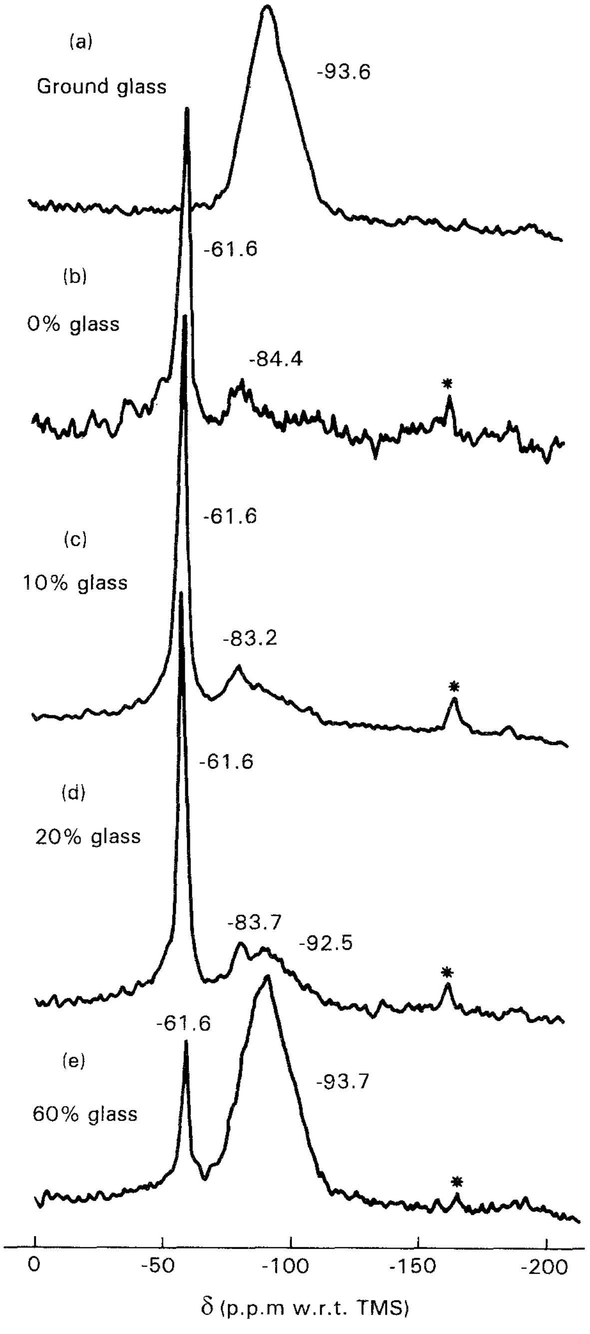


Figure 6 ^{29}Si MAS NMR spectra of chrysotile–glass powder–sodium silicate pellets fired at 1000 °C, with various glass contents. *Spinning side bands.

Examination of the pellet fracture surfaces by SEM and EDAX shows that in the sample bonded with sodium silicate but not containing glass, the forsterite fibres have thickened into bundles which appear to be fused together in some areas (Fig. 4a). The sodium silicate is reasonably uniformly spread throughout the fibres, the excess appearing in some places as whitish unreacted crystals, but in other areas as a glassy melt in which the chrysotile fibres can also be seen (Fig. 4b). The crystalline phases in this material were found by XRD to be forsterite and a little enstatite ($MgSiO_3$), a product which normally occurs later in the thermal decomposition sequence of chrysotile [3], but whose appearance here is probably due to the fluxing action of the sodium silicate.

With the addition of increasing amounts of ground glass, the microstructure of the pellets becomes increasingly glassy in appearance (Fig. 4c–f), but even in the sample containing 80% glass, relicts of the original fibres are still visible (Fig. 4f). XRD indicates the presence of crystalline phases in even the most glassy samples; in addition to forsterite, aluminium diopside, $Ca(Mg,Fe,Al)(Si,Al)_2O_6$ (JCPDS file number 38-0466) appears in increasing amount with increasing glass content, suggesting that reaction has occurred between the added glass and the other components of the pellet. The sodium apparently remains in the glassy phase.

The results of ball-milling tests on these pellets are shown in Fig. 5, which indicates very low rates of attrition in all the pellets containing glass. Moreover, SEM examination of the powder resulting from the ball-milling shows its morphology to be almost exclusively granular, with little evidence of fibrous structures, even in the sample bonded only with sodium silicate. The absence of fibres in this and the other low-glass samples reflects the fragility of fibrous forsterite, which has been broken down by the ball milling. The lack of fibres in the other samples is as expected from their higher glass content. These results suggest that the silicate bonding technique has considerable potential for converting asbestos into non-hazardous materials with useful physical properties.

Typical ^{29}Si MAS NMR spectra of ground samples of these pellets are shown in Fig. 6. The spectrum of the ground glass used in these experiments is very broad (Fig. 6a), and thus at the highest glass concentrations, some of the interesting minor phases are obscured. All the spectra show a sharp peak at -61.6 p.p.m. which agrees well with the reported chemical shift for forsterite (-61.6 to -61.9 p.p.m. [17, 18]). The sample containing only sodium silicate (Fig. 6b) contains a minor peak at -84.4 p.p.m., approximately in the position expected for enstatite [18], in agreement with the XRD pattern for this sample. The samples with low glass contents also show a small peak in this region, in addition to the broader glass resonance (Fig. 6c and d). The XRD patterns of these samples indicate the presence of aluminium diopside rather than enstatite; the structures of both these pyroxenes are closely related, as reflected by the similar ^{29}Si chemical shift in diopside (-84.7 to -85 p.p.m. [19, 20]). The MAS NMR spectra of these pellets are therefore consistent with the X-ray results.

For the glass-containing samples, the chemical compositions of the corresponding fully-reacted glass/chrysotile systems were calculated from the known compositions of the glass and chrysotile, and compared with spot analyses by EDAX of selected areas of the microstructure. All the glass-containing samples contained regions corresponding to the ideal homogeneous composition, but the compositions of other regions suggested more chrysotile and less glass, and vice versa. Evidence was also found in some regions for preferential reaction between the sodium silicate and chrysotile, but this may have been the result of inhomogeneities arising from difficulty experienced in blending together the fibrous and granular components of the original mix. For this reason, two alternative fabrication methods were investigated.

3.3. Hot pressing of chrysotile/glass laminates

The temperature range of these experiments (720–820 °C) was much lower than in the previous experiments, and was chosen to span the dehydroxylation temperature of chrysotile (730 °C) which is fortuitously similar to the lower working temperature of the glass (720 °C). The specimens were pre-pressed chrysotile mats interspersed with ground glass; sodium silicate was not used in these experiments. Parallel experiments made using mats which had been converted to crystalline forsterite by pre-firing to 1000 °C produced consistently poorer, more friable

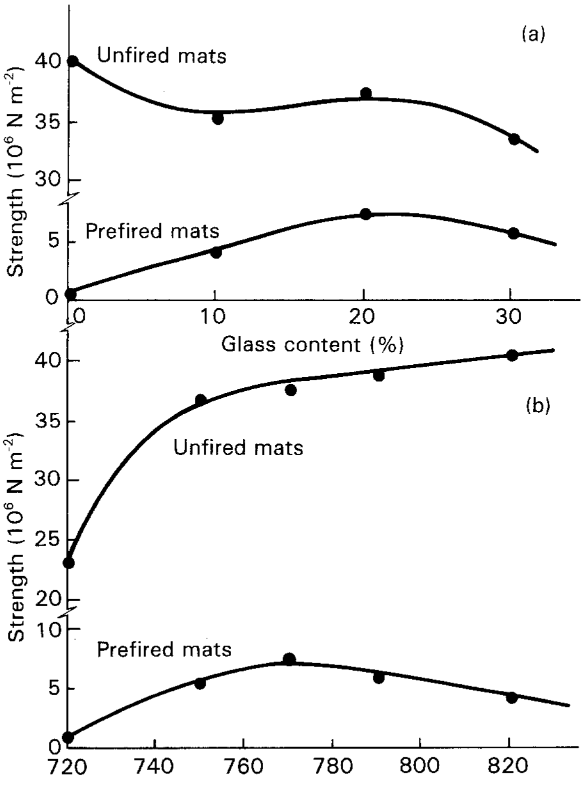
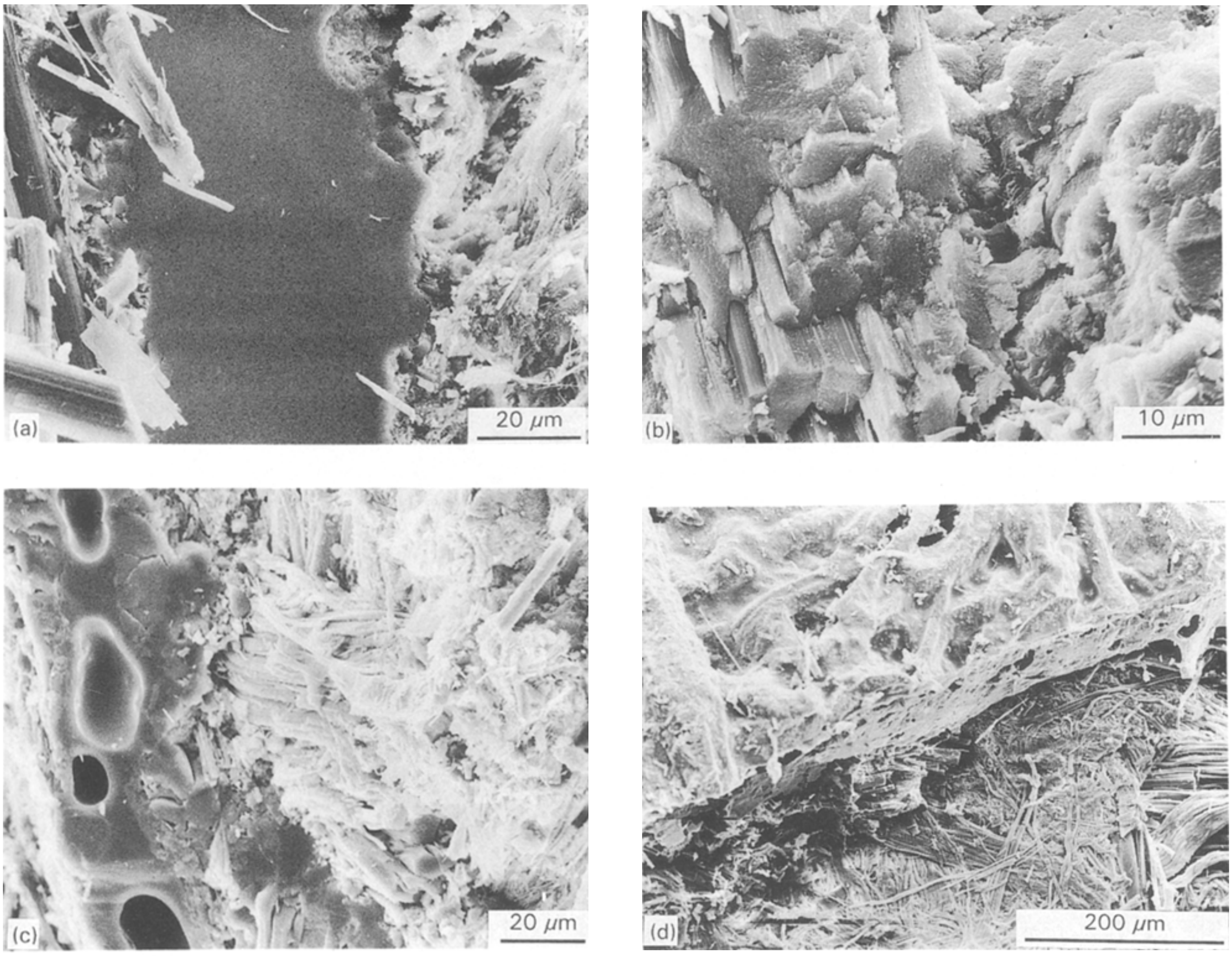


Figure 7 Unibiaxial strength of hot-pressed chrysotile–glass laminates, (a) as a function of glass content at 770 °C, (b) as a function of pressing pressure at 20% glass content.



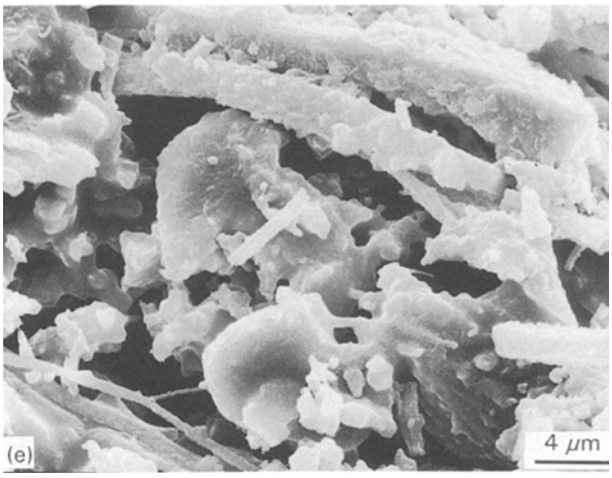


Figure 8 Scanning electron micrographs of fracture surfaces of hot-pressed and glaze-impregnated chrysotile pellets. (a) Hot-pressed at 770 °C, prefired (forsterite) mats; (b) hot-pressed at 770 °C, unprefired (chrysotile) mats; (c) as (b), showing bubbles in residual glass layer; (d) vacuum-impregnated with ball-milled glass before firing at 1000 °C, showing glassy surface crust and fibrous pellet interior; (e) stirred with glaze 3 slurry, pressed and fired at 1000 °C.

compacts over the complete range of temperatures and glass contents used. Specimens prepared from unreacted chrysotile mats were also found to be an order of magnitude stronger (Fig. 7). The strength increased with increasing pressing temperature, especially with the unfired mats (Fig. 7b), but was essentially independent of glass content (Fig. 7a). The relatively high strength of samples hot pressed without glass is noteworthy, and may reflect an effect similar to that reported in kaolinite pressed at its decomposition temperature [21]. The lack of an analogous enhancement of strength in the pre-fired asbestos samples is also consistent with results reported for pre-reacted kaolinite subjected to "reactive hot pressing" [21].

Meaningful direct comparison of the absolute strengths of the hot-pressed laminates with the strengths of the silicate-bonded pellets is not possible because of the different measuring techniques, and the fact that the silicate-bonded compacts exhibit reasonably brittle fracture, whereas the laminates fail in a more complex manner. Although the difference between the biaxial and uniaxial strength measurements is known to be about 8% for conventional brittle ceramics [16], this difference has not been established for other types of failure.

SEM examination of the hot-pressed specimens fractured across the laminated plane (Fig. 8) shows marked lack of wetting and penetration of the glass into the fibre mat of pre-fired samples (Fig. 8a), whereas the unfired mats have generally taken up the glass throughout their volume (Fig. 8b); in areas where residual glass is still visible, its porous nature is due to the elimination of hydroxyl water above the glass softening temperature (Fig. 8c).

X-ray diffraction shows no unexpected phases in the hot-pressed samples; all the pre-fired specimens contain crystalline forsterite and a small amount of enstatite which is formed at about 1000 °C, whereas the unprefired samples contain only forsterite, with the exception of the samples pressed at 720 °C, which contain only unreacted chrysotile.

These results suggest that the strength of the hot-pressed samples results from a combination of the strength of the glass layer, together with strength resulting from the reactive hot-pressing of the chrysotile (the latter is only significant in the unprefired samples which have been hot-pressed above the dehydroxylation temperature). Fig. 7 suggests that the most significant strength component arises from the reactive hot pressing.

3.4. Impregnation of chrysotile mats with finely-divided glass and glaze frits

Vacuum impregnation of pre-pressed chrysotile mats with an aqueous slurry of finely ball-milled glass or glaze was found to be very difficult to control; the amount of glass taken up was variable, and the mats tended to disintegrate when allowed to remain in contact with the slurry for more than a minute or so. Under vacuum conditions, glass uptake by prefired mats was in all cases less than with unfired mats, by an order of magnitude in some samples. Several samples were also prepared by stirring the unheated chrysotile fibres up in the slurry, removing them and drying at 100 °C, then pressing into mats and firing. This method gave the highest glass uptakes (35%–69%). All the vacuum-impregnated mats were seen by SEM to have a surface crust of glass-bonded material, but less glass had penetrated the inner spaces, which were more fibrous (Fig. 8d). By contrast, glass uptake by the samples exposed to the slurry before pressing was more homogeneous, and in the samples incorporating glazes maturing at lower tempertures (1 and 3), all the fibres were well coated with glass (Fig. 8e).

The apparent bulk densities of all these samples are low, indicative of high porosity, but increase progressively with glaze content, irrespective of the glaze composition (Fig. 9). This behaviour is different to that of the silicate-bonded pellets, in which the apparent bulk densities decrease with increasing glass content (Fig. 9), due to the bloating effect of water from the decomposition of chrysotile and sodium silicate. The more open porous structure of the impregnated samples allows the vapour to escape more readily and bloating does not occur.

The strengths of the glaze-impregnated pellets, measured by the ball-on-ring method, increase in a linear manner with glaze content, again irrespective of the glaze composition (Fig. 10). Irrespective of the glaze composition, the phases formed in these samples (by XRD) are similar to those in silicate-bonded pellets (primarily forsterite, with aluminium diopside becoming increasingly significant at higher glass contents). Thus, the properties of these compacts are controlled by the ability of the glaze to enter the pore structure of the fibrous mats (a function of the particle size) rather than by the chemistry of the glaze.

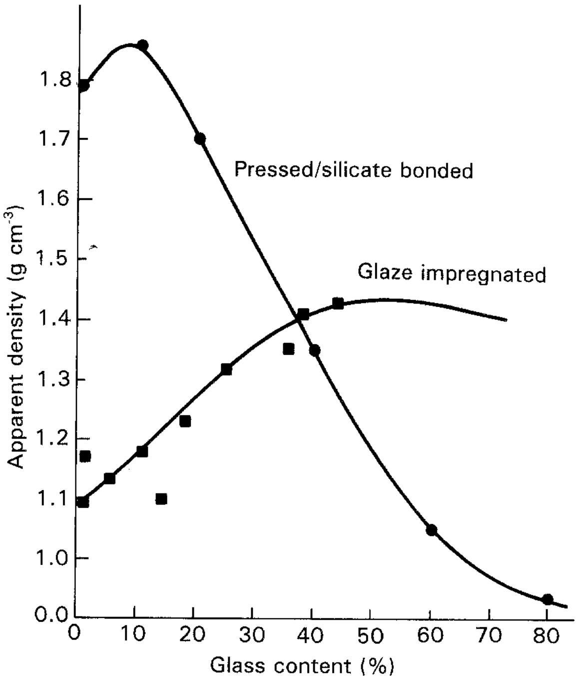


Figure 9 Apparent bulk density of glaze-impregnated chrysotile pellets fired at 1000 °C, as a function of glass content, compared with chrysotile–glass powder–sodium silicate compacts fired under the same conditions.

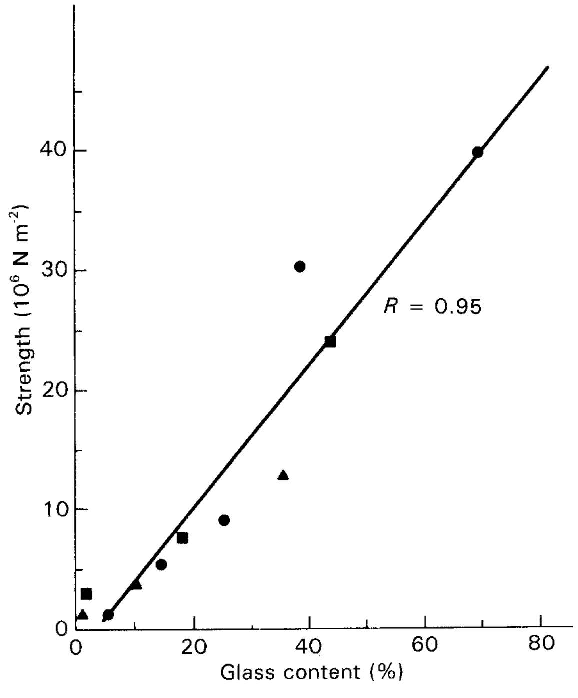


Figure 10 Unibiaxial strength of glaze-impregnated chrysotile pellets fired at 1000 °C, as a function of their glaze content. (●) Glaze 1, (▲) glaze 2, (■) glaze 3.

4. Conclusions

1. Silicate bonding of chrysotile asbestos by impregnation with sodium silicate followed by thermal decomposition to forsterite allows the sample to retain its fibrous morphology while fusing and stabilizing the fibre bundles in a glassy matrix. The process thus has the potential for reducing the respirable fibre concentration of the asbestos, simultaneously destroying the

cell toxicity of raw chrysotile by converting it to crystalline forsterite.

2. The addition of glass powder before firing produces strong, porous materials whose properties can be adjusted by varying the glass content. In the present samples, maximum strength is achieved with 10%–20% glass. These materials show good resistance to mechanical abrasion, and the abraded glass-impregnated forsterite dust is virtually free of fibres, suggesting that the health hazard from these materials should be low.

3. Other bonding methods (hot pressing chrysotile/glass laminates or impregnation by an aqueous slurry of finely divided glass or glaze) work well with raw chrysotile, but give much poorer results with chrysotile which has previously been thermally converted into fibrous forsterite. The strength of hot-pressed laminates is derived principally from reaction bonding of the chrysotile, and is probably weakened by the interpolation of glass layers. The glass does not penetrate or wet the fibre bundles of pre-reacted chrysotile, which has no strength or cohesiveness. Impregnation with a glass or glaze slurry gives dimensionally stable pellets with good strength and porosity at higher glass contents (30%–60%).

Acknowledgements

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