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(54) **MATERIAUX FIBREUX LIES**
(54) **BONDED FIBROUS MATERIALS**

(57) Cette invention concerne un matériau composite qui comprend des fibres de silicates de terres alcalines liées de manière inorganique, et dans lequel tous les agents de liaisons ou matières de charge comprennent de faibles quantités d'aluminium de sorte que ledit matériau composite comprenne moins de 1 % en poids d'aluminium exprimé sous forme d' Al_2O_3 .

(57) A composite material comprises inorganic-bonded alkaline earth silicate fibres in which any bonding agents or fillers comprise low amounts of aluminium so that the composite material comprises less than 1 % by weight aluminium expressed as Al_2O_3 .

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<p>(54) Title: BONDED FIBROUS MATERIALS</p>		
<p>(57) Abstract</p> <p>A composite material comprises inorganic-bonded alkaline earth silicate fibres in which any bonding agents or fillers comprise low amounts of aluminium so that the composite material comprises less than 1 % by weight aluminium expressed as Al₂O₃.</p>		

BONDED FIBROUS MATERIALS

This invention relates to bonded fibrous materials and is particularly applicable to materials comprising saline soluble fibres bonded with a binder.

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Refractory ceramic fibres (RCF) are well known materials and typically comprise an aluminosilicate inorganic fibre formed from an oxide melt which is spun, blown, drawn, or otherwise formed into fibres. Such RCF fibres are used in the manufacture of various industrial and domestic articles. Typical uses of RCF are for applications in which resistance to temperatures
10 in excess of 800°C is required.

Much RCF fibre is used in the form of needled blankets of fibre in which structural integrity is provided by the fibres that are tangled together in the needling process. (Such products are known as "blanket"). Sometimes a binder is used to lock the fibres together subsequent to
15 exposure to high temperature. Blanket can be processed further to form cut shapes or folded to form insulating modules.

RCF fibre is also used in the production of so-called "Converted Products". Converted products comprise materials in which the RCF is processed further to provide materials in which the
20 RCF is present as either a minor or major constituent. Typical converted products include the following:-

- "Board" – substantially rigid flat sheets containing inorganic and/or organic binders produced by a wet process (for example made by dehydrating a suspension of RCF and binders);
- 25 "Paper" – a flexible fibrous insulating material with a thickness of less than or equal to 6mm, formed on paper making machinery (for example RCF in sheet form with a binder);
- "Shapes" – substantially rigid shapes made of ceramic fibre with the addition of inorganic and/or organic binder, fired or unfired (for example, RCF formed by vacuum
30 forming into a variety of shapes);
- "Fire shapes" – RCF formed by a vacuum forming route and used for domestic and industrial fires either as radiant bodies or for decorative appearance;

- “Castables” – ceramic fibre with inorganic and/or organic binder which may be cast (for example, RCF in the form of cements, concretes and mortars);
- 5 “Mastics” – A mouldable material containing RCF with binders and which may be trowelled, hand moulded, or dispensed from a pressure gun and which sets upon drying/heating;
- “Extrusion” - A mastic-like material that may be used in the manufacture of extruded sections and tubes;
- 10 “Textiles” – ceramic fibre which has been woven with or without the addition of other filaments, wires, or yarns (for example, RCF formed into rope, yarn, mats and the like by textile technology).

In many of the above mentioned applications binders are used. There are two broad classes of binders:-

- 15 “Organic binders” – which serve to improve the handling characteristics of the product concerned at low temperatures but which burn off at higher temperatures. Organic binders include, for example, such materials as starch.
- 20 “Inorganic binders” – which may be effective to improve the handling characteristics of the product concerned at low temperatures, but which also give integrity to the product after exposure to high temperatures. Inorganic binders include, for example, such materials as colloidal silicas, aluminas, and clays.

All of the above materials and concepts are well known in the refractory industry.

- 25 Although extremely useful, RCF is an inorganic fibrous material. Inorganic fibrous materials can be either glassy or crystalline. Asbestos is an inorganic fibrous material one form of which has been strongly implicated in respiratory disease.

It is still not clear what the causative mechanism is that relates some asbestos with disease but some researchers believe that the mechanism is mechanical and size related. Asbestos of a critical size can pierce cells in the body and so, through long and repeated cell injury, have a bad effect on health. Whether this mechanism is true or not regulatory agencies have indicated a desire to categorise any inorganic fibre product that has a respiratory fraction as hazardous, regardless of whether there is any evidence to support such categorisation. Unfortunately, for many of the applications for which inorganic fibres are used, there are no realistic substitutes.

Accordingly there is an industry and regulatory demand for inorganic fibres that will pose as little risk as possible (if any) and for which there are objective grounds to believe them safe.

A line of study has proposed that if inorganic fibres were made that were sufficiently soluble in physiological fluids that their residence time in the human body was short; then damage would not occur or at least be minimised. As the risk of asbestos linked disease appears to depend very much on the length of exposure this idea appears reasonable. Asbestos is extremely insoluble.

As intercellular fluid is saline in nature the importance of fibre solubility in saline solution has long been recognised. If fibres are soluble in physiological saline solution then, provided the dissolved components are not toxic, these fibres should be safer than fibres that are not so soluble. Accordingly, in recent years, a number of different types of fibre have been proposed which are refractory and yet soluble in body fluids. Such fibres comprise alkaline earth silicates (e.g. WO87/05007, WO89/12032, WO93/15028, WO94/15883, WO96/02478, and WO97/49643) which are soluble to varying extent in body fluids.

A problem with saline soluble fibres is that by their nature they are more reactive than RCF and therefore cannot always be used as a direct replacement for RCF. The applicants have found that one aspect of this reactivity is that the performance of materials at temperatures in excess of 1100°C is extremely adversely affected by the presence of aluminium in the binders and fillers conventionally used with RCF. The applicants speculate that this adverse effect is due to a eutectic composition that has been reported to lie at about 1238°C in the CaO-Al₂O₃-MgO-SiO₂ phase field.

The applicants have further found that sodium and boron badly affect performance of fibres above 1200°C.

Accordingly the present invention provides a composite material comprising bonded alkaline earth silicate fibres in which any bonding agents or fillers comprise low amounts of aluminium so that the composite material comprises less than 1% aluminium expressed as Al_2O_3 . Preferably the composite material comprises less than 0.5% by weight of aluminium expressed as Al_2O_3 . More preferably the composite material comprises less than 0.1% by weight of aluminium expressed as Al_2O_3 . Yet more preferably the composite material is essentially free of aluminium.

In a further feature the composite material comprises less than 1%, preferably less than 0.5%, more preferably less than 0.1% by weight of sodium expressed as Na_2O and is still more preferably essentially free of sodium.

In a still further feature the composite material comprises less than 0.5% by weight of boron, preferably less than 0.1% of boron expressed as B_2O_3 .

Further features of the invention are apparent from the claims and the following description, which refers to various applications in which the invention is applicable.

Insulation board and shapes.

The invention can be illustrated in its broadest concept by reference to Table 1 which indicate the results of making board using alkaline earth silicate fibres of the SUPERWOOL™ 612™ composition (available from Thermal Ceramics de France SA or Thermal Ceramics Limited). Such fibres have a nominal composition (by weight) of SiO_2 64%, CaO 17%, MgO 13.5%, ZrO_2 5%, and impurities < 0.5%, and are usable at temperatures in excess of 1200°C and up to 1250°C.

Boards and some shapes are conventionally made by first formulating a suspension of fibre with a cationic organic binder such as a starch and an anionic inorganic binder such as colloidal silica. The cationic organic binder and anionic inorganic binder flocculate, drawing the fibre into a flocculated suspension.

The suspension is placed in contact with mesh moulds and vacuum is applied to the moulds to vacuum form articles either on the outside of the mesh (male mould) or on the inside of the mesh (female mould). Vacuum is applied to the mould until a sufficient thickness of fibre has built up and the mould is then removed from the suspension, the vacuum remaining on for a little while to promote dewatering. This process produces a wet green article containing about 50%-70% water.

At this stage the product is extremely fragile having the consistency of wet cardboard. The wet green article is dried, for example at a temperature of about 150°C and the organic binder then gives some handling strength. Relatively low amounts of inorganic binder are used in the formation of such materials. A typical recipe for use in vacuum forming would comprise 100kg of fibre, 25kg of colloidal silica (a 30% solution i.e. 7.5 kg dry weight), 6.5kg starch and 1000 gallons (approximately 4500 litres) water. The silica in this formulation amounts to about 0.16% of the suspension formulation and about 7% of the dry materials.

When first fired by the end user of the shape or board the organic binder burns off and the inorganic binder binds the fibres.

Recipes 1, 2 and 3 of Table 1 were tested in the discontinuous manufacture of special shapes. As can be seen Recipe 1 of Table 1 melts at 1250°C due to the presence of aluminium in the clay. The aluminium reacts with the CaO, MgO, and SiO₂ of the fibre to form a eutectic mixture. Although Recipe 1 failed at temperature Recipes 2 and 3 appear to give similar results. Recipes 4 to 10 were tested in the continuous manufacture of board.

Recipe 4 refers to Table 2 to show the effect of aluminium compounds (as aluminium sulphate present in re-cycled wastewater) on high temperature behaviour. This appears to be extremely detrimental.

Recipes 5 and 6 show the effect of adding talc as filler. This appears to improve modulus of rupture and compressive strength. Recipes 5, 7 and 8 allow comparison with other fillers, talc giving the best result.

Recipes 5, 9 and 10 allow comparison of the variation of the amount of colloidal silica. Recipe 9 appears the best.

TABLE 1

Recipe	1	2	3	4	5	6	7	8	9	10
Fibre	64.0%	73.3%	76.1%	80.3%	78.1%	75.2%	78.1%	78.1%	76.0%	74.1%
Clay	24%									
Talc			14.2%	15.0%	14.6%	17.5%			13.2%	11.8%
Wollastonite								14.6%		
Fumed Silica							14.6%			
Colloidal silica (30%)	7.0%	22.8%	6.3%		3.9%	3.9%	3.9%	3.9%	7.6%	11.1%
Cationic Starch	5.0%	3.9%	2.8%							
Starch				4.1%	2.9%	2.9%	2.9%	2.9%	2.8%	2.7%
Xanthan gum			0.6%	0.6%	0.5%	0.5%	0.5%	0.5%	0.4%	0.3%
Density	313	320	277	305	316	320	304	313	307	296
Modulus of rupture by bending (MPa)	1.4	0.69	1.2	0.9	0.75	0.87	0.78	0.73	1.26	1.22
M.O.R. at 1150°C				0.04						
M.O.R. at 1200°C				N.A.	0.2	0.24	0.16	0.11	0.77	0.68
M.O.R. at 1250°C					0.3	0.39	0.15	N.A.	N.A.	N.A.
Loss on ignition at 800°C	5.2	4.5	4.2	3.6	3.6	3.6	3.4	3.4	3.4	3.6
Linear shrinkage 24h -1200°C (%)				see Table 2	2.1	2	2.3	1.9	2.6	2.6
Linear shrinkage 24h -1250°C (%)	melted	2.1	1.2	2	2.3	2.2	2.5	N.A.	N.A.	N.A.
Compressive strength @ 10% (MPa)				0.22	0.13	0.15	0.13	0.12	0.22	0.24
Compressive Strength at 1150°C for 10% (MPa)				0.1						
Compressive Strength at 1200°C for 10% (MPa)				N.A.	0.07	0.09	0.05	0.03	0.20	0.19

Al ₂ O ₃ content (wt%)	10.2	6.7	6.3	5.1	0.4
Shrinkage at 1150°C - 24 hours	melted	1.8	1.7	1.6	
Shrinkage at 1200°C - 24 hours	melted	glazed	glazed	glazed	2.3

The recipes of Table 1 resulted in boards having the composition set out in Table 3.

Recipe	1	2	3	4	5	6	7	8	9	10
Fibre	67.3%	87.2%	79.7%	80.3%	80.3%	77.3%	80.3%	80.3%	80.3%	80.3%
Clay	25.2%									
Talc			14.8%	15.0%	15.0%	18.0%			13.9%	12.8%
Wollastonite								15.0%		
Fumed Silica							15.0%			
Colloidal silica (30%)	2.2%	8.2%	2.0%		1.2%	1.2%	1.2%	1.2%	2.4%	3.6%
Cationic Starch	5.3%	4.6%	2.9%							
Starch				4.1%	3.0%	3.0%	3.0%	3.0%	3.0%	3.0%
Xanthan gum			0.6%	0.6%	0.5%	0.5%	0.5%	0.5%	0.4%	0.3%

- 5 A typical and useful range of ingredients for making insulating board and shapes by vacuum forming is (in weight percent):-

Alkaline earth metal silicate fibre	70-85%
Colloidal silica (30% SiO ₂ by weight)	3-25%
10 Organic binder	1-6%
Filler	11-20%

and from such ingredients typical and useful compositions in the finished board are:-

8

Alkaline earth metal silicate fibre	70-90%
Colloidal silica (30% SiO ₂ by weight)	1-10%
Organic binder	1-6%
Filler	11-20%

5

The examples given above have compositions in the range:-

Alkaline earth metal silicate fibre	77.3-87.2%
Colloidal silica (30% SiO ₂ by weight)	1.2-8.2%
10 Organic binder	3.3-4.7%
Filler	12.8-18%

In all of the above tested compositions the colloidal silica used was Nyacol™ 1430 which has a sodium content of about 0.4% by weight. The amount of colloidal silica binder present was sufficiently low (3.9-22.8% by weight of the colloidal silica translating as approximately 1.2-7 wt% silica binder in the finished product) that the sodium in the binder did not have an appreciable deleterious effect on the properties of the material.

Papers

20

The same principles apply in the manufacture of papers. In the conventional manufacture of refractory paper slurry is made in like manner to vacuum forming and is cast upon a wire former as in paper making machinery.

25 The normal flocculant used is alum. The applicants have been able to make refractory fibre paper using acrylic latex binders and an organic flocculant. Such papers have been tested to 1250°C and while collapsing at 1200°C the fibres remain in place providing some insulating effect. In contrast, if alum is used as a flocculating agent the paper melts.

30 A typical recipe (by weight percent) for the paper is:-

SUPERWOOL™ 612™	90-95%
Acrylic latex (PRIMAL HA8™ from Rohm & Haas)	5-10%
Organic flocculants	<1%

Suitable organic flocculants comprise the PERCOL L Series™ from Allied Colloids. These are polyacrylamide based products. In particular PERCOL 230L works well.

Fire beds, artificial coals, and fire shapes.

5

Articles that are directly exposed to flames are in an aggressive environment with temperatures in excess of 1000°C and exposure to combustion products. Use of conventional binders with alkaline earth metal silicate fibres (SUPERWOOL™ 612™) led to cracking of shapes. The applicants tested a series of compositions by making pieces using different colloidal silica binders each present at the same amount (about 6% by weight). These pieces were heated to 1000°C for one hour and assessed for cracking, friability, and hardness (Shore 'o'). The results of these tests are given in Table 4 below:-

10

Colloid	pH	Na ₂ O (wt%)	Specific Surface Area (m ² /g)	Silica (wt%)	Cracking	Friability	Hardness
Nyacol™ 1430	10.2	0.4	230	30	Bad fracturing	Friable	10-17
Syton™ X30	9.9	0.3	250	30	Some fracture	Fibrous	57
Levasil™ 200-A-30	9.5	0.17	200	30	Minor fracture	Friable	40
Bindzil™ 40/220	9.7	0.42	220	40	Some fracture	Friable	40
Bindzil™ 30NH ₃ /220	9.5	<0.1	220	30	Some fracture	Fibrous	47

15 From this it was deduced that:-

- a) Alkaline pHs were associated with fractured pieces and could be indicative of poor thermal shock resistance; and
- b) A reduction in Na₂O content appears to correlate with friability of the product.

Accordingly, and in view of the growing perception that aluminium, sodium and boron are detrimental to the high temperature performances of alkaline earth metal silicate fibres, the applicants requested their suppliers of colloid (Univar of Croydon, England - distributors for Akzo Nobel) to supply colloidal silica meeting the following requirements not usually called for commercially:-

- a) The colloidal silica should have a slightly acid to roughly neutral pH, preferably in the range 6.5 to 7.5
- b) The soda content of the colloidal silica should be low, preferably below 0.1wt%
- c) The silica should not have appreciable amounts of aluminium present.

A preliminary experimental product supplied under the reference Bindzil 30/220LPN comprised 30wt% silica, had a pH of 7.0 and comprised 0.08wt% Na₂O. The same trial as above was repeated using this silica and a product was produced which did not crack and remained fibrous with a Shore 'o' hardness of 50. Further samples were made and subjected to a 250 hours cycling test (2 hours on and 2 hours off under gas flame) and passed this test.

Preliminary specifications for the typical colloidal silicas usable to achieve these results are:-

SiO ₂ content (by weight)	30	25
Viscosity	<10cP	<10cP
pH	6.5 - 8.0	6.5 - 8.0
Specific Surface Area (m ² /g)	220 - 240	220 - 240
Density (g/cm ³)	1.192-1.199	1.155-1.175
Na ₂ O content (by weight)	<0.1	<0.1

Such silicas are obtainable from Akzo Nobel under the reference Bindzil 30/220LPN or the mark THERMSOL™.

A typical mixture for use in the manufacture of fire shapes comprises:-

Fibre (e.g. SUPERWOOL 612™)	60 parts by weight
Colloidal silica (e.g. THERMSOL™ =Bindzil 30/220LPN [30%by weight SiO ₂])	12 - 14 parts by weight
Starch (e.g. PLV available from Avebe, Netherlands)	2.5 parts by weight

The amount of water used in forming the slurry varies according to application but may for example range from 2700-4500 litres (600-1000 gallons). The fibre typically represents about 0.5-4% by weight of fibre in water. Not all of the ingredients will be incorporated into a vacuum formed product formed from this mixture but typically such a mixture leads to a product comprising approximately 6% by weight colloidal silica, 3.5-5% starch with the balance fibre. The tolerable range for colloidal silica is usually from about 4% to about 9% by weight in the finished product.

Alternative compositions excluding organic binders (useful for such high temperature applications as cooker rings) may be made for example from slurry compositions 1 and 2 below:-

Component	COMPCSION 1	COMPOSITION 2
"White water" component	50-80% by volume of 30% solids THERMSOL™ =Bindzil 30/220LPN with 20-50% by volume mains water	90-100% by volume of 30% solids THERMSOL™ =Bindzil 30/220LPN with 10-0% by volume mains water
Fibre (SUPERWOOL™ 612)	0.5-4% by weight of solids to white water component	2-3% by weight of solids to white water component

"White water" is the industry term for a mixture of water and colloidal silica. Such slurry compositions lead to products comprising 15-30% by weight silica with the balance fibre.

Typical ring slurry compositions are, in parts by weight:-

Ring slurry composition 1

THERMSOL colloidal silica 355

Fibre (SUPERWOOL™ 612) 3 - 5

Fresh water 95

5 Ring slurry composition 2

LEVASIL 200-A-40 colloidal silica 750

Fibre (spun and chopped SUPERWOOL™ 612) 30

Fresh water 250

10 LEVASIL 200-A-40 differs from LEVASIL 200-A-30, mentioned in Table 4 above, in that in proportion to the amount of silica present LEVASIL 200-A-40 has a lower amount of sodium. Additionally, and very importantly, LEVASIL 200-A-30 is aluminate modified whereas LEVASIL 200-A-40 avoids alumina. LEVASIL 200-A-40 has the characteristics:-

Silica content (wt%) 40-41.5

15 Na₂O content (wt%) 0.16-0.24

Specific Surface Area (m²/g) 180-220

pH 8.5-9.5.

The applicants find no deleterious effects in cooker ring production or performance in using
20 LEVASIL 200-A-40. Suitable slurry compositions for rings using a 40% colloidal silica are:-

Component	
"White water" component	65-100% by volume of 40% solids low sodium content colloidal silica having a pH of less than 10 with 35%-0% by volume mains water
Alkaline earth metal silicate fibres, for example chopped spun fibre	2-3wt% by weight of solids to white water component

The materials described above under the heading "fire beds, artificial coals, and fire shapes"
25 (see Table 6) can also be used in wider applications such as boards and shapes.

A typical composition for forming boards and shapes is, in parts by weight:-

	Starch (Solvitose PLV)	4.8
	THERMSOL colloidal silica	32
5	Fibre (SUPERWOOL™ 612)	80

Generally, the fibre content should preferably be between 0.5 and 5% of the weight of the water. Selection of particular compositions for the wide variety of applications that such bonded fibrous materials are used in is a matter of experiment.

10

From the above results it can be seen that where the amount of binder used is high the amount of sodium in the binder is best kept low. Similar considerations apply for boron. It should be noted that some colloidal silicas contain aluminium as a counter-ion and such colloidal silicas should be avoided.

15

CLAIMS

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1. A composite material comprising colloidal silica-bonded alkaline earth silicate fibres in which any bonding agents or fillers comprise low amounts of aluminium so that the composite material comprises less than 1% by weight aluminium expressed as Al_2O_3 .

10

2. A composite material as claimed in claim 1 in which composite material comprises less than 0.5% by weight by weight of aluminium expressed as Al_2O_3 .

3. A composite material as claimed in claim 2 in which the composite material comprises less than 0.1% by weight by weight of aluminium expressed as Al_2O_3 .

15

4. A composite material as claimed in claim 1 in which the composite material is essentially free of aluminium.

20

5. A composite material as claimed in any preceding claim and comprising less than 1% by weight sodium expressed as Na_2O .

6. A composite material as claimed in claim 5 and comprising less than 0.5% by weight sodium expressed as Na_2O .

25

7. A composite material as claimed in claim 6 and comprising less than 0.1% by weight sodium expressed as Na_2O .

8. A composite material as claimed in any preceding claim and in which the composite material is essentially free of sodium.

30

9. A composite material as claimed in any preceding claim and comprising less than 0.5% by weight boron expressed as B_2O_3 .

10. A composite material as claimed in claim 9 and comprising less than 0.1% by weight boron expressed as B_2O_3 .
11. A composite material as claimed in any preceding claim in which the alkaline earth silicate fibre is itself capable of use without excessive shrinkage at temperatures in excess of $1200^\circ C$.
12. A composite material as claimed in any preceding claim in which the material is obtainable by vacuum forming from a slurry containing the following ingredients (in weight %):-
- | | |
|--|--------|
| Alkaline earth metal silicate fibre | 70-85% |
| Colloidal silica (30% SiO_2 by weight) | 3-25% |
| Organic binder | 1-6% |
| Filler | 11-20% |
13. A composite material as claimed in claim 12 comprising:-
- | | |
|--|--------|
| Alkaline earth metal silicate fibre | 70-90% |
| Colloidal silica (30% SiO_2 by weight) | 1-10% |
| Organic binder | 1-6% |
| Filler | 11-20% |
14. A composite material as claimed in claim 13 comprising:-
- | | |
|--|------------|
| Alkaline earth metal silicate fibre | 77.3-87.2% |
| Colloidal silica (30% SiO_2 by weight) | 1.2-8.2% |
| Organic binder | 3.3-4.7% |
| Filler | 12.8-18% |
15. A composite material as claimed in any of claims 1 to 11 in which the material is a paper comprising:-
- | | |
|-------------------------------------|--------|
| Alkaline earth metal silicate fibre | 90-95% |
| Organic binder | 5-10% |
| Organic flocculants | <1% |

16. A composite material as claimed in claim 15 in which the organic binder is an acrylic latex.

5 17. A composite material as claimed in any of claims 1 to 11 in which the material is a material obtainable by vacuum forming from a slurry comprising the ingredients:

- Alkaline earth silicate fibre 60 parts by weight
- Colloidal silica (30%by weight SiO₂) 12 - 14 parts by weight
- Starch 2.5 parts by weight

and in which the colloidal silica has a pH of less than 8.

10 18. A composite material comprising 4-12% by weight colloidal silica, 3-6.5% starch, balance to 100% alkaline earth silicate fibre.

19. A composite material as claimed in claim 18 and comprising 4-9% by weight colloidal silica, 3.5-5% starch, balance to 100% alkaline earth silicate fibre.

15 20. A composite material as claimed in claim 18 comprising about 6% colloidal silica.

21. A composite material as claimed in any of claims 1 to 11 in which the material is a material obtainable by vacuum forming from the ingredients:-

- "White water" 50-80% by volume of 30% solids colloidal silica component with 20-50% by volume mains water
- Alkaline earth metal silicate fibre 0.5-4% by weight of solids to white water component

20 and in which the colloidal silica has a pH of less than 8.

22. A composite material as claimed in any of claims 1 to 11 in which the material is a material obtainable by vacuum forming from the ingredients:-

"White water" component	90-100% by volume of 30% solids colloidal silica with 10-0% by volume mains water
Alkaline earth metal silicate fibre	2-3% by weight of solids to white water component

and in which the colloidal silica has a pH of less than 8.

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23. A composite material as claimed in claim 21 or claim 22 and which comprises 15-30% by weight colloidal silica, balance fibre.

24. A composite material as claimed in claim 17 in which the fibre is present in amounts comprising 0.5-5% by weight of the water in the slurry.

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25. A composite material as claimed in any of claims 1 to 11 in which the material is a material obtainable by vacuum forming from the ingredients

"White water" component	65-100% by volume of 40% solids low sodium content colloidal silica having a pH of less than 10 with 35%-0% by volume mains water
Alkaline earth metal silicate fibres	2-3wt% by weight of solids to white water component