

FIRE RESISTANT CALCIUM SULPHATE-BASED PRODUCTS

This invention relates to improved fire resistant calcium sulphate-based products and, in particular, to calcium sulphate-based building/construction products having improved strength after exposure to high temperatures.

5 BACKGROUND

Calcium sulphate-based products are widely used in the construction of buildings, for example, to form internal partitions (using wallboard, also known as dry wall, gypsum board or plaster board) and ceilings or to encase ducts (e.g. ventilation ducts) within buildings.

Calcium sulphate-based products such as wallboard are typically formed by drying an
10 aqueous slurry of the hemihydrate of calcium sulphate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), also known as calcined gypsum or stucco, between two sheets of lining paper or fibreglass matting. As the slurry dries and the calcined gypsum is hydrated, a hard, rigid core of gypsum (calcium sulphate dihydrate - ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)) sandwiched between the lining sheets/mats is formed.

When wallboard is exposed to high temperatures such as those experienced in a building
15 fire, or those experienced by wallboards used for encasing ducts carrying high temperature fluids, the water of crystallization contained within the gypsum is driven off to yield the anhydrite of calcium sulphate. Initially, this has the advantage that heat transfer across the wallboard is reduced thus helping to contain the heat emanating from a duct or generated during a building fire. However, at temperatures around 400-450°C, the initially formed All
20 phase anhydrite (also known as $\gamma\text{-CaSO}_4$ or "soluble" anhydrite) converts to the All phase (or "insoluble" anhydrite) and this phase change results in shrinkage of the wallboard i.e. a loss of dimensional stability. This shrinkage (which may be around 2% of the wallboard's length or width or around 6vol%) often causes the wallboards to pull away from their supporting structures. This is obviously undesirable. In situations where wallboard is used for internal
25 partitions and a fire breaks out, shrinkage can leaves gaps exposing rooms adjacent to the

fire source to the effects of the heat/fire. Gaps also allow ingress of oxygen into the fire source thus fuelling the fire and negating the effects of any fire doors.

At higher temperatures (in excess of 600°C), the insoluble anhydrite goes on to sinter resulting in large reductions in wallboard volume. This results in extreme shrinkage which eventually causes collapse of the internal walls/ceilings/duct casings as they are no longer held by their supporting structures.

Furthermore, once the chemical composition of the gypsum has been altered by the heat, the wallboard loses strength and, ultimately, structural integrity. Typically, the gypsum core of wallboard that has been exposed to high temperatures such as those generated during building fires crumbles to a fine dust and thus the wallboard effectively disintegrates.

Efforts have been made to improve the fire resistance of calcium sulphate-based products in an attempt to reduce shrinkage and/or maintain strength/structural integrity.

It is known e.g. from US2526066 and US2744022, to add a combination of unexpanded vermiculite and non-combustible fibres to the aqueous calcined gypsum slurry during the manufacture of wallboard.

During heat exposure the vermiculite contained within the wallboard core expands by an amount comparable to the amount of gypsum shrinkage thus resisting the shrinkage of the wallboard. The fibres, which are known to be asbestos and/or glass, form a network which mechanically bind the gypsum core together and reduces the likelihood of mechanical failure.

Wallboard containing unexpanded vermiculite and/or glass fibres has found extensive commercial excess.

US3616173 proposed adding small amounts (preferably about 2-5 wt%) of clay, colloidal silica or colloidal alumina to the gypsum core in addition to the glass fibres and vermiculite.

The intention was to reduce the density of the fire resistant wallboard. Amounts greater than 20wt% were found to result in a weak core that did not bind satisfactorily with the paper lining sheets.

5 US2003/0138614 discloses a fire resistant gypsum wallboard containing, in addition to unexpanded vermiculite and glass fibres, 3-25wt% of a mineral additive which may be a clay and 3-15wt% hydrated alumina. Best results are achieved using 10-15wt% of a clay which comprises 25% kaolinite.

US4664707 discloses a gypsum wall board made from a slurry containing glass fibres, calcium sulphate crystal fibres and 0.5-5wt% clay. The clay is preferably a kaolinitic clay.

10 US6569541 discloses a water-resistant gypsum wallboard containing 5-15wt% of a mineral additive which may be a clay such as kaolinite.

US5985013 discloses an ablative type heat protecting material containing calcium sulphate hemihydrate and a hydrated salt. A number of hydrated salts are used including magnesium nitrate hexahydrate (used in an amount of 40wt% based on the weight of dry ingredients).

15 The time taken for heat transfer across the heat ablative material was recorded. No mention is made of any effect on the shrinkage of the material after heating.

Calcium sulphate-based products are also used to cast metal or glass objects. Calcium sulphate moulds are heated to 700-900°C prior to being filled with molten metal/glass. It is important to control high temperature shrinkage of such calcium sulphate-based moulds to ensure that the moulds do not leak and to ensure that the cast metal/glass products are not warped.

A preferred aim of the present invention is to provide an improved fire/heat resistant calcium-sulphate-based product having improved strength, hardness and structural integrity after heat exposure e.g. during a building fire. Such an improved fire resistant product may have particular use as a building product e.g. wallboard or panels for forming internal partitions in

buildings, ceiling tiles, wallboard or panels for encasing ventilation/smoke extraction ducting, joint filler materials for joining wallboard/panels/tiles or for moulds for use in metal/glass product casting.

SUMMARY OF THE INVENTION

5 Accordingly, in a first aspect, the present invention provides a calcium sulphate-based product comprising gypsum, a pozzolan source and a metal salt additive.

In a second aspect, the present invention provides a calcium sulphate-based product wherein the product is formed from drying an aqueous slurry containing calcined gypsum, a pozzolan source and a metal salt additive.

10 In a third aspect, the present invention provides a method of forming a calcium sulphate-based product by drying an aqueous slurry comprising calcined gypsum, a pozzolan source and a metal salt.

In a fourth aspect, the present invention provides the use of a combination of a pozzolan source and a metal salt additive for improving strength during heat exposure of a calcium
15 sulphate-based product.

In a fifth aspect, the present invention provides a calcium sulphate-based composition for use in forming a calcium sulphate-based product by drying an aqueous slurry of the calcium sulphate-based composition, the calcium sulphate-based composition comprising calcined gypsum, a pozzolan source and a metal salt.

20 The present inventors have found that adding a combination of a pozzolan source and a metal salt results in a calcium sulphate-based product which maintains its structural integrity and strength and dimensional stability even after heating up to 1000°C. It is thought that a sintering process occurs which binds the gypsum together and helps improve the structural integrity and hardness. Analysis of the product after heating (and after the gypsum has been

removed using EDTA) shows that the pozzolan source forms an interlinking network structure which helps to bind the gypsum and thus increase hardness and strength. The presence of the metal salt reduces the temperature at which the pozzolan source transforms to the interlinking network structure and allows a reduction in the amount of pozzolan source
5 needed. This may be as a result of the inclusion of the metal salt in the network structure.

The term “pozzolan source” is intended to refer to materials that are themselves pozzolanic (e.g. rice husk ash, fly ash, volcanic ashes and pumices or diatomaceous earth) or that yield pozzolanic material upon heating (e.g. a clay additive such as kaolinitic clay material which yields metakaolin upon heating).

10 The term “kaolinitic clay material” encompasses kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), polymorphs of kaolinite such as dickite, halloysite and nacrite, ball clay (which comprises 20-80% kaolinite, 10-25% mica, 6-65% quartz), fire clay and flint clay. An example of a suitable clay additive is Puroflo 31™ manufactured by Sibelco and which comprises 66% kaolinite, 23% mica, 6 % feldspar and 1% quartz.

15 The clay additive is preferably un-calcined clay.

In the slurry used to form the calcium sulphate-based product and in the calcium sulphate-based composition, the clay additive may be provided in an amount between 5 wt% and 30 wt%, preferably between 5 and 25 wt% and most preferably between 10 and 25 wt% (where wt% is based on the weight of the calcined gypsum, clay additive and metal salt).

20 In the slurry used to form the calcium sulphate-based product and in the calcium sulphate-based composition, the rice husk ash, fly ash, volcanic ashes or pumices or diatomaceous earth may be provided in an amount greater than 10wt%, preferably greater than 20wt% and most preferably equal to or greater than 25wt% (where wt% is based on the weight of the calcined gypsum, pozzolan source and metal salt).

In the calcium sulphate-based product, the clay additive may be provided in an amount between 5 wt% and 30 wt%, preferably between 5 and 25 wt% and most preferably between 10 and 25 wt% (where wt% is based on the weight of the gypsum, clay additive and metal salt).

- 5 In preferred embodiments, the amount of clay additive (e.g. kaolin) in the slurry/calcium sulphate-based composition and in the finished product is less than 25 wt%.

In the calcium sulphate-based product, the rice husk ash, diatomaceous earth, fly ash, volcanic ashes or pumices may be provided in an amount greater than 10wt%, preferably greater than 15wt% and most preferably equal to or greater than 20wt% (where wt% is based on the weight of the gypsum, pozzolan source and metal salt).

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The metal salt is preferably a metal salt which decomposes between a temperature of 300-500°C to yield a metal oxide.

The metal in the metal salt may be an alkaline earth metal e.g. calcium or magnesium. The metal may be a transition metal e.g. copper or zinc. The metal may be aluminium.

- 15 Preferably the metal is magnesium.

The salt may be a nitrate, a carbonate, a hydrogen carbonate, a sulphate, a hydroxide or chloride. The salt may be hydrated.

Preferred metal salts are the nitrates of magnesium, copper, aluminium, calcium and zinc, magnesium chloride and magnesium hydroxide.

- 20 Magnesium nitrate (e.g. the hexahydrate) and magnesium chloride (e.g. the hexahydrate) are preferred metal salts.

In the slurry used to form the calcium sulphate-based product and in the calcium sulphate-based composition, the metal salt may be provided in an amount between 5 and 25 wt%,

preferably between 10 and 25 wt% e.g. between 10 and 20 wt% (where wt% is based on the weight of the calcined gypsum, pozzolan source and metal salt).

In the calcium sulphate-based product, the metal salt may be provided in an amount between 5 and 25 wt%, preferably between 10 and 25 wt% e.g. between 10 and 20 wt%
5 (where wt% is based on the weight of the gypsum, pozzolan source and metal salt).

In preferred embodiments, the wt% of clay additive and metal salt in the slurry/calcium sulphate-based composition and in the product are equal and, preferably, between 10 and 25 wt%.

The term "gypsum" is intended to refer predominantly to calcium sulphate dihydrate
10 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

The term "calcined gypsum" is intended to refer predominantly to calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) but may also encompass any other calcium sulphate compound having a lower bound water content than calcium sulphate dihydrate (e.g. calcium sulphate anhydrite).

15 In the slurry used to form the calcium sulphate-based product and in the calcium sulphate-based composition, the calcined gypsum is preferably provided in an amount between 50 wt% and 85 wt%, more preferably between 50 and 80 wt% e.g. between 60 and 80 wt% (where wt% is based on the weight of the calcined gypsum, pozzolan source and metal salt).

In the calcium sulphate-based product, the gypsum is preferably provided in an amount
20 between 50 wt% and 85 wt%, more preferably between 55 and 80 wt% e.g. between 60 and 80 wt% (where wt% is based on the weight of the gypsum, pozzolan source and metal salt).

In a particularly preferred embodiment, the calcium-sulphate based product comprises 50 wt% - 85 wt% gypsum, a pozzolan source and 10 wt% - 25 wt% metal salt and may be

formed from drying an aqueous slurry containing 50-85 wt% calcined gypsum, a pozzolan source and 10 wt% to 25 wt% metal salt (where wt% is based on the weight of the gypsum, pozzolan source and metal salt).

For this embodiment, the amounts and nature of the pozzolan source, the preferred amounts
5 of gypsum/calcined gypsum and the preferred amounts/nature of the metal salt may be as described above.

In another particularly preferred embodiment, the calcium-sulphate based product comprises 50 wt% - 85 wt% gypsum, 20 wt% or more of a pozzolan source and metal salt, wherein the pozzolan source is rice husk ash or diatomaceous earth and may be formed from drying an
10 aqueous slurry containing 50-85 wt% calcined gypsum, 25 wt% or more of the pozzolan source and a metal salt (where wt% is based on the weight of the (calcined) gypsum, pozzolan source and magnesium nitrate).

For this embodiment, the preferred amounts and nature of the pozzolan source, the preferred amounts of gypsum/calcined gypsum and the preferred amounts and nature of the
15 metal salt may be as described above.

In yet another particularly preferred embodiment, the calcium-sulphate based product comprises 50 wt% - 85 wt% gypsum, 5-30 wt% of a pozzolan source and metal salt, wherein the pozzolan source is a kaolinitic clay and may be formed from drying an aqueous slurry containing 50-85 wt% calcined gypsum, 5-30 wt% of the pozzolan source and a metal salt
20 (where wt% is based on the weight of the (calcined) gypsum, pozzolan source and magnesium nitrate).

For this embodiment, the preferred amounts and nature of the pozzolan source, the preferred amounts of gypsum/calcined gypsum and the preferred amounts and nature of the metal salt may be as described above.

In some embodiments, the calcium sulphate-based product contains substantially no inorganic fibres e.g. no glass or asbestos fibres. The present inventors have found that the addition of a combination of a pozzolan source and a metal salt can help maintain strength and structural integrity after heating even in the absence of a fibrous network.

- 5 However, in some embodiments, the calcium sulphate-based product may contain inorganic fibres (e.g. glass fibres) and/or matting (e.g. glass matting) as this may help improve strength of the product prior to heating.

The calcium sulphate-based product may contain additives such as accelerators, retarders, foaming/anti-foaming agents, fluidisers etc.. The accelerators may be, for example, freshly
10 ground gypsum having an additive of sugar or surfactant. Such accelerators may include Ground Mineral NANSO (GMN), heat resistant accelerator (HRA) and ball milled accelerator (BMA). Alternatively, the accelerator may be a chemical additive such as aluminium sulphate, zinc sulphate or potassium sulphate. In certain cases, a mixture of accelerators may be used, e.g. GMN in combination with a sulphate accelerator. As a further alternative,
15 ultrasound may be used to accelerate the setting rate of the slurry, e.g. as described in US2010/0136259.

The term "calcium sulphate-based product" may include building materials such as wallboards (with or without liners) (with or without fibrous reinforcement), tiles (e.g. ceiling tiles), duct encasement panels, joint filler materials (e.g. for joining adjacent
20 wallboards/tiles/panels etc.), plaster compositions or moulds for metal casting.

The term "calcium sulphate-based" will be readily understood as meaning that the product comprises gypsum as a major component i.e. that gypsum is the largest single component in terms of wt% of the product. The term may mean that the product comprises gypsum in 40
25 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt% or greater based on the total weight of the product.

The calcium sulphate-based product may be a composite product e.g. it may be a wallboard having a gypsum matrix core (containing the clay and metal salt additives) sandwiched between two liners (e.g. paper liners or fibreglass matting).

5 EXPERIMENTAL

The following examples show products having improved strength after exposure to high temperatures and are given by way of illustration only.

Control sample 1

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres. 750g of calcined
10 gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

15 Control Sample 2 – kaolin (30wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres. 225g of kaolin
and 525g of calcined gypsum was added to the water and the mixture was mechanically
blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a
320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to
20 the base of the mould. The remaining slurry was poured into the mould and further layer of
glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight
(minimum 12 hours).

Control Sample 3 – magnesium nitrate (10wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g of magnesium nitrate hexahydrate. 750g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the
5 slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Control Sample 4 – calcium nitrate (10wt%)

10 600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g of calcium nitrate tetrahydrate. 750g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the
15 mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Control Sample 5 – magnesium hydroxide (10wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g magnesium hydroxide. 750g of calcined gypsum was added to the water and the mixture
20 was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Control Sample 6 – aluminium nitrate (10wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g aluminium nitrate nonahydrate. 750g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the
5 slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 1 – Magnesium nitrate (9wt%)/Kaolin (27wt%)

10 600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g of magnesium nitrate hexahydrate. 225g of kaolin and 525g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was
15 poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 2 – Magnesium nitrate (23wt%)/Kaolin (23wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 225g of magnesium nitrate hexahydrate. 225g of kaolin and 525g of calcined gypsum was added to
20 the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 3 – Magnesium nitrate (16.5wt%)/Kaolin (16.5wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 150g of magnesium nitrate hexahydrate. 150g of kaolin and 600g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A
5 small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 4 – Magnesium nitrate (13wt%)/Kaolin (13wt%)

10 600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 112.5g of magnesium nitrate hexahydrate. 112.5g of kaolin and 637.5g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining
15 slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 5 – Magnesium nitrate (11wt%)/Kaolin (11wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 93.75g of magnesium nitrate hexahydrate. 93.75g of kaolin and 565.25g of calcined gypsum was
20 added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 6 – Magnesium nitrate (9wt%)/Kaolin (9wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g of magnesium nitrate hexahydrate. 7g of kaolin and 675g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 7 – Magnesium hydroxide (9wt%)/Kaolin (27wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g of magnesium hydroxide. 225g of kaolin and 525g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 8 – Magnesium chloride (9wt%)/Kaolin (27wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g of magnesium chloride hexahydrate. 225g of kaolin and 525g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 9 – Magnesium chloride (11wt%)/Kaolin (11wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 93.75g of magnesium chloride hexahydrate. 93.75g of kaolin and 656.25g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a
5 slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 10 – Calcium nitrate (9wt%)/Kaolin (27wt%)

10 600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g of calcium nitrate tetrahydrate. 225g of kaolin and 525g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was
15 poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 11 – Zinc nitrate (9wt%)/Kaolin (27wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g of zinc nitrate hexahydrate. 225g of kaolin and 525g of calcined gypsum was added to the water
20 and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 12 – Copper nitrate (7wt%)/Kaolin (28wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 60g of copper nitrate tetrahydrate. 225g of kaolin and 525g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 13 – Aluminium nitrate (9wt%)/Kaolin (27wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 75g of aluminium nitrate nonahydrate. 225g of kaolin and 525g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 14 – Magnesium nitrate (13wt%)/rice husk ash (13wt%) 600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 93.75g of magnesium nitrate hexahydrate. 93.75g of diatomaceous earth and 525g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 15 – Magnesium nitrate (11wt%)/diatomaceous earth (27wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 93.75g of magnesium nitrate hexahydrate. 225g of diatomaceous earth and 525g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

Example 16 – Magnesium nitrate (11wt%)/rice husk ash (27wt%)

600g of water at 40°C was mixed with 3.75g of John Mansville glass fibres and 93.75g of magnesium nitrate hexahydrate. 225g of rice husk ash and 525g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. A small amount of the slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and glass tissue was pressed into the slurry to the base of the mould. The remaining slurry was poured into the mould and further layer of glass tissue was laid onto the top of the slurry. The sample was dried at 40°C overnight (minimum 12 hours).

A summary of the sample formulations is shown in Table 1.

Sample	Amount of stucco /g (wt%)	Amount of pozzolan source/g (wt%)	Amount of metal salt/g (wt%)
Control 1	750 (100)	0	0
Control 2	525 (70)	225 (30) kaolin	0
Control 3	750 (90)	0	75 (10)
Control 4	750 (90)	0	75 (10)
Control 5	750 (90)	0	75 (10)

Control 6	750 (90)	0	75 (10)
Example 1 Mg nitrate	525 (64)	225 (27) kaolin	75 (9)
Example 2 Mg nitrate	525 (54)	225 (23) kaolin	225 (23)
Example 3 Mg nitrate	600 (67)	150 (16.5) kaolin	150 (16.5)
Example 4 Mg nitrate	637.5 (74)	112.5 (13) kaolin	112.5 (13)
Example 5 Mg nitrate	656.25 (78)	93.75 (11) kaolin	93.75 (11)
Example 6 Mg nitrate	675 (82)	75 (9) kaolin	75 (9)
Example 7 Mg hydroxide	525 (64)	225 (27) kaolin	75 (9)
Example 8 Mg chloride	525 (64)	225 (27) kaolin	75 (9)
Example 9 Mg chloride	656.25 (78)	93.75 (11) kaolin	93.75 (11)
Example 10 Ca nitrate	525 (64)	225 (27) kaolin	75 (9)
Example 11 Zn nitrate	525 (64)	225 (27) kaolin	75 (9)
Example 12 Cu nitrate	525 (65)	225 (28) kaolin	60 (7)
Example 13 Al nitrate	525 (64)	225 (27) kaolin	75 (9)

Example 14 Mg nitrate	525 (74)	93.75 (13) rice husk ash	93.75 (13)
Example 15 Mg nitrate	525 (62)	225 (27) diatomaceous earth	93.75 (11)
Example 16 Mg nitrate	525 (62)	225 (27) rice husk ash	93.75 (11)

Table 1 – Summary of sample formulations

Collapse test – horizontal fire test

Samples (250mm x 50mm) were placed in a furnace at room temperature with their ends supported such that the samples rested horizontally (span between support 210mm). The samples were heated to 1000°C over 1.5 hours and then allowed to cool to room temperature. The samples were assessed for collapse after cooling. The distance from the bottom of the sample to the base support was measured in mm. This value was subtracted from 50mm to give a collapse measurement. The maximum possible collapse measurement (i.e. total collapse) is 50mm and the minimum possible collapse measurement (i.e. no collapse) is 0mm. The collapse measurements are shown in Table 2.

Sample	Amount of pozzolan source in slurry (in dried sample) /wt%	Amount of metal salt in slurry (in dried sample) /wt%	Collapse/mm
Control 1	0	0	50
Control 2	30 (26.5)	0	22
Control 3	0	10 (8.5)	50
Control 4	0	10 (8.5)	50
Control 5	0	10 (8.5)	50
Control 6	0	10 (8.5)	40
Example 1 - Mg nitrate	27 (24)	9 (8)	9
Example 2 - Mg nitrate	23 (21)	23 (21)	4.2
Example 3 - Mg nitrate	16.5 (15)	16.5 (15)	4.5

Example 4 - Mg nitrate	13 (11)	13 (11)	3.5
Example 5 - Mg nitrate	11 (10)	11 (10)	5.5
Example 6 - Mg nitrate	9 (8)	9 (8)	8
Example 7 - Mg hydroxide	27 (24)	9 (8)	14
Example 8 - Mg chloride	27 (24)	9 (8)	7
Example 9 - Mg chloride	11 (10)	11 (10)	5
Example 10 - Ca nitrate	27 (24)	9 (8)	12
Example 11 - Zn nitrate	27 (24)	9 (8)	12.5
Example 12 - Cu nitrate	28 (25)	7 (6)	14
Example 13 - Al nitrate	27 (24)	9 (8)	15
Example 14 – Mg nitrate/ rice husk ash	13 (11.5)	13 (11.5)	28
Example 15 – Mg nitrate/ diatomaceous earth	27 (24)	11 (10)	15
Example 16 – Mg nitrate/ rice husk ash	27 (24)	11 (10)	19

Table 2 – Results of collapse test

It can be seen that the addition of a combination of pozzolan source and a metal salt significantly improves the structural integrity of the sample. Control Example 2 shows that whilst kaolin alone provides some effect, the combination of kaolin with a metal salt provides a much greater effect.

The effect is greatest if:

- the wt% amounts of kaolin and metal salt in the slurry and in the product are equal and between 10 and 25 wt%;
- the amount of kaolin in the slurry and in the product is less than 25 wt%;
- the amount of rice husk ash or diatomaceous earth in the slurry is equal to or greater than 25w%;
- the metal salt is magnesium nitrate or magnesium chloride.

CLAIMS

1. A calcium sulphate-based product comprising gypsum, a pozzolan source and a metal salt additive.
2. A calcium sulphate-based product according to claim 1 wherein the pozzolan source
5 is a kaolinitic clay additive and is included in an amount between 5 and 30wt% (based on the weight of the gypsum, clay additive and metal salt additive).
3. A calcium sulphate-based product according to claim 2 wherein the clay additive is included in an amount between 10 and 25 wt%.
4. A calcium sulphate-based product according to claim 1 wherein the pozzolan source
10 is rice husk ash or diatomaceous earth and is included in an amount equal to or greater than 20 wt%.
5. A calcium sulphate-based product according to any one of claims 1 to 4 wherein the metal salt additive is included in an amount between 5 and 25 wt% (based on the weight of the calcined gypsum, pozzolan source and metal salt additive).
- 15 6. A calcium sulphate-based product according to claim 5 wherein the metal salt additive is included in an amount between 10 and 25 wt%.
7. A calcium sulphate-based product according any one of the preceding claims wherein the wt% amount of metal salt and the wt% amount of pozzolan source is equal.
- 20 8. A calcium sulphate-based product according to any one of the preceding claims comprising 50-85 wt% gypsum.
9. A calcium sulphate based product according to any one of the preceding claims comprising 50-85 wt% gypsum and 10-25 wt% metal salt.
10. A calcium sulphate-based product according to any one of the preceding claims
25 comprising 50-85 wt% gypsum and 20 % or more pozzolan source, wherein the pozzolan source is rice husk ash or diatomaceous earth.

11. A calcium sulphate-based product according to any one of the preceding claims comprising 50-85 wt% gypsum and 5-30 wt% or more pozzolan source, wherein the pozzolan source is a kaolinitic clay additive.
12. A calcium sulphate-based product formed from drying an aqueous slurry containing
5 calcined gypsum, a pozzolan source and a metal salt additive.
13. A calcium sulphate-based product according to claim 12 wherein the pozzolan source is a kaolinitic clay additive and is included in the slurry in an amount between 5 and 30 wt% (based on the weight of the calcined gypsum, clay additive and metal salt additive).
- 10 14. A calcium sulphate-based product according to claim 13 wherein the clay additive is included in an amount between 10 and 25 wt%.
15. A calcium sulphate-based product according to claim 12 wherein the pozzolan source is rice husk ash or diatomaceous earth and is included in the slurry in an amount equal to or greater than 25 wt%.
- 15 16. A calcium sulphate-based product according to any one of claims 12 to 15 wherein the metal salt additive is included in an amount between 5 and 25 wt% (based on the weight of the calcined gypsum, pozzolan source and metal salt additive).
17. A calcium sulphate-based product according to claim 16 wherein the metal salt additive is included in an amount between 10 and 25 wt%.
- 20 18. A calcium sulphate-based product according to any one of claims 12 to 17 wherein the wt% amount of metal salt and the wt% amount of clay additive is equal.
19. A calcium sulphate-based product according to any one of claims 12 to 18 wherein the calcined gypsum is included in the slurry in an amount of 50-85 wt%.
20. A calcium sulphate based product according to any one of claims 12 to 19 wherein
25 the slurry comprises 50-85 wt% calcined gypsum and 10-25 wt% metal salt.
21. A calcium sulphate-based product according to any one of claims 12 to 20 wherein the slurry comprises 50-85 wt% gypsum and 20 % or more pozzolan source, wherein the pozzolan source is rice husk ash or diatomaceous earth.

22. A calcium sulphate-based product according to any one of claims 12 to 20 wherein the slurry comprises 50-85 wt% gypsum and 5-30 wt% or more pozzolan source, wherein the pozzolan source is a kaolinitic clay additive.
23. A calcium sulphate-based composition for forming a calcium sulphate-based product
5 by drying an aqueous slurry of the composition, wherein the composition contains calcined gypsum, a pozzolan source and a metal salt additive.
24. A calcium sulphate-based composition according to claim 23 wherein the pozzolan source is a kaolinitic clay additive and is included in the composition in an amount between 5 and 30 wt% (based on the weight of the calcined gypsum, clay additive
10 and metal salt additive).
25. A calcium sulphate-based composition according to claim 24 wherein the clay additive is included in an amount between 10 and 25 wt%.
26. A calcium sulphate-based composition according to claim 24 wherein the pozzolan source is rice husk ash or diatomaceous earth and is included in an amount equal to
15 or greater than 25 wt%.
27. A calcium sulphate-based composition according to any one of claims 23 to 26 wherein the metal salt additive is included in an amount between 5 and 25 wt% (based on the weight of the calcined gypsum, pozzolan source and metal salt additive).
- 20 28. A calcium sulphate-based composition according to claim 27 wherein the metal salt additive is included in an amount between 10 and 25 wt%.
29. A calcium sulphate-based composition according to any one of claims 23 to 28 wherein the wt% amount of metal salt and the wt% amount of clay additive is equal.
30. A calcium sulphate-based composition according to any one of claims 23 to 29
25 wherein the calcined gypsum is included in an amount of 50-85 wt%.
31. A calcium sulphate based composition according to any one of claims 23 to 30 wherein the composition comprises 50-85 wt% calcined gypsum and 10-25 wt% metal salt.

32. A calcium sulphate-based composition according to any one of claims 23 to 31 comprising 50-85 wt% gypsum and 20 wt% or more pozzolan source, wherein the pozzolan source is rice husk ash or diatomaceous earth.
33. A calcium sulphate-based composition according to any one of claims 23 to 31
5 comprising 50-85 wt% gypsum and 5-30 wt% or more pozzolan source, wherein the pozzolan source is a kaolinitic clay additive.
34. A calcium sulphate-based product/composition according to any one of the preceding claims where the metal salt additive is a metal salt which decomposes between a temperature of 300-500°C to yield a metal oxide.
- 10 35. A calcium sulphate-based product/composition according to any one of the preceding claims wherein the metal salt additive comprises calcium, magnesium, copper, zinc or aluminium.
36. A calcium sulphate-based product/composition according to any one of the preceding claims wherein the metal salt is a nitrate, carbonate, hydrogen carbonate, sulphate,
15 hydroxide or chloride.
37. A calcium sulphate-based product/composition according to any one of the preceding claims wherein the metal salt is magnesium nitrate or magnesium chloride.
38. A method of forming a calcium sulphate-based product by drying an aqueous slurry comprising a calcium sulphate-based composition according to any one of claims 23
20 to 37.
39. Use of a combination of a pozzolan source and a metal salt additive for improving strength during heat exposure of a calcium sulphate-based product comprising gypsum.
40. Use according to claim 39 wherein the pozzolan source is a kaolinitic clay additive
25 and is used in an amount between 5 and 30 wt% (based on the weight of the gypsum, clay additive and metal salt additive).
41. Use according to claim 40 wherein the clay additive is used in an amount between 10 and 25 wt%.

42. Use according to claim 39 wherein the pozzolan source is a rice husk ash or diatomaceous earth and is used in an amount equal to or greater than 20 wt%.
43. Use according to any one of claims 39 to 42 wherein the metal salt additive is used in an amount between 5 and 25 wt% (based on the weight of the gypsum, pozzolan source and metal salt additive).
44. Use according to claim 43 wherein the metal salt additive is included in an amount between 10 and 25 wt%.
45. Use according to any one of claims 39 to 44 wherein the product comprises 50-85 wt% gypsum.
46. Use according to any one of claims 39 to 45 wherein the product comprises 50-85 wt% gypsum and 10-25 wt% metal salt.
47. Use according to any one of claims 39 to 46 wherein the product comprises 50-85 wt% gypsum and 20 % or more pozzolan source, wherein the pozzolan source is rice husk ash or diatomaceous earth.
48. Use according to any one of claims 39 to 46 wherein the product comprises 50-85 wt% gypsum and 5-30 wt% or more pozzolan source, wherein the pozzolan source is a kaolinitic clay additive.
49. Use according to any one of claims 39 to 48 wherein the metal salt additive is a metal salt which decomposes between a temperature of 300-500°C to yield a metal oxide.
50. Use according to any one of claims 39 to 49 wherein the metal salt additive comprises calcium, magnesium, copper, zinc or aluminium.
51. Use according to any one of claims 39 to 50 wherein the metal salt is a nitrate, carbonate, hydrogen carbonate, sulphate, hydroxide or chloride.
52. Use according to any one of claims 39 to 51 wherein the metal salt is magnesium nitrate or magnesium chloride.
53. Product substantially as any one embodiment herein described.
54. Composition substantially as any one embodiment herein described.
55. Method substantially as any one embodiment herein described.

56. Use substantially as any one embodiment herein described.