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- (71) **Applicant:** SAINT-GOBAIN PLACO [FR/FR]; 34 Avenue Franklin Roosevelt, Suresnes, F-92282 Paris (FR).
- (72) **Inventors:** BROOKS, Laura; BPB United Kingdom Limited, Technical Centre, East Leake, Loughborough Leicestershire LE12 6JT (GB). SPARKES, Joanna; BPB United Kingdom Limited, Technical Centre, East Leake, Loughborough Leicestershire LE12 6JT (GB). RIDEOUT, Jan; BPB United Kingdom Limited, Technical Centre, East Leake, Loughborough Leicestershire LE12 6JT (GB).
- (74) **Agents:** OXLEY, Rachel et al.; Mewburn Ellis LLP, 33 Gutter Lane, London Greater London EC2V 8AS (GB).
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(54) **Title:** FIRE-RESISTANT CALCIUM SULPHATE-BASED PRODUCTS

(57) **Abstract:** The present invention relates to a calcium sulphate-based product comprising gypsum and a clay additive. The clay additive, which may be a kaolinitic clay, is provided in an amount greater than 22 wt%. The product is formed by drying an aqueous slurry containing calcined gypsum and greater than 25wt% clay additive. The product (e.g. a gypsum wallboard) exhibits improved resistance to shrinkage and increased strength after heat exposure.



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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 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 2-5wt%) 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 unexpended 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.

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 wallboard may
15 have particular use for encasing ventilation/smoke extraction ducting.

SUMMARY OF THE INVENTION

Accordingly, in a first aspect, the present invention provides a calcium sulphate-based product comprising gypsum and a clay additive, wherein the clay additive is provided in an amount greater than 22 wt% (based on the amount of gypsum and clay additive).

20 In a second aspect, the present invention provides a calcium sulphate-based product comprising gypsum and a clay additive, wherein the product is formed from drying an aqueous slurry containing calcined gypsum and > 25wt% (relative to the total amount of calcined gypsum and clay additive) of said clay additive.

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 and >25wt% (based on the total weight of the calcined gypsum and the clay additive) of a clay additive.

In a fourth aspect, the present invention provides the use of a clay additive in an aqueous slurry of calcined gypsum in an amount greater than 25wt% (based on the total weight of the calcined gypsum and the clay additive) for reducing shrinkage and improving strength during heat exposure of a calcium sulphate-based product formed by drying said slurry.

In a fifth aspect, the present invention provides the use of a clay additive in an amount greater than 22 wt% (based on the weight of clay additive and gypsum) for reducing shrinkage and improving strength during heat exposure of a calcium sulphate-based product comprising gypsum.

The present inventors have found that adding a clay additive in an amount greater than 25wt% (based on the total weight of the calcined gypsum and the clay additive in the slurry) results in a calcium sulphate-based product (containing greater than 22wt% clay additive) which maintains its structural integrity, 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 and reduces shrinkage. Analysis of the clay structure after heating (and after the gypsum has been removed using EDTA) shows that the clay forms an interlinking network structure which helps to bind the gypsum and thus increase hardness and strength. The clay network helps delay sintering of the gypsum and thus helps reduce shrinkage.

Preferably, the clay additive is a kaolinitic clay material. 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. The clay is preferably un-calcined.

In the slurry used to form the calcium sulphate based product, the clay additive may be provided in an amount equal to or greater than 30wt%. The amount of clay additive in the
5 slurry may be equal to or greater than 35wt%. These wt% values are based on the total weight of the calcined gypsum and the clay additive in the slurry.

In the slurry used to form the calcium sulphate based product, the maximum amount of clay additive may be 70wt%, or, preferably, 60wt% and most preferably 50wt%. These wt% values are based on the total weight of the calcined gypsum and the clay additive in the
10 slurry.

In the calcium sulphate-based product, the clay additive may be provided in an amount equal to or greater than 26 wt%. The amount of clay additive in the product may be equal to or greater than 31 wt%. These wt% values are based on the total weight of the gypsum and the clay additive in the product.

15 In the calcium sulphate-based product, the maximum amount of clay additive may be 62 wt% or, preferably, 53 wt% and, most preferably, 44 wt%. These wt% values are based on the total weight of the gypsum and the clay additive in the product.

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

20 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).

In the slurry used to form the calcium sulphate based product, the calcined gypsum is provided in an amount of 75wt% or less. The calcined gypsum may be provided in an amount equal to or less than 70wt%. The amount of calcined gypsum in the slurry may be equal to or less than 65wt%. These wt% values are based on the total weight of the calcined gypsum and the clay additive in the slurry.

In the slurry used to form the calcium sulphate based product, the minimum amount of calcined gypsum may be 30wt%, or, preferably, 40wt% and most preferably 50wt%. These wt% values are based on the total weight of the calcined gypsum and the clay additive in the slurry.

In the calcium sulphate-based product, the gypsum is provided in an amount of 78 wt% or less. The gypsum may be provided in an amount equal to or less than 74 wt%. The amount of gypsum in the product may be equal to or less than 69 wt%. These wt% values are based on the total weight of the gypsum and the clay additive in the product.

In the calcium sulphate-based product, the minimum amount of gypsum may be 38 wt% or, preferably, 47 wt% and, most preferably, 56 wt%. These wt% values are based on the total weight of the gypsum and the clay additive in the product.

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 wallboards/tiles/panels etc.).

The calcium sulphate-based product may be a composite product e.g. it may be a wallboard having a gypsum matrix core (containing the shrinkage resistance additive) sandwiched between two liners (e.g. paper liners or fibreglass matting).

Preferably, the calcium-sulphate-based product contains substantially no vermiculite. The present inventors have found that the addition of increased amounts (>25wt% in the slurry)

of a clay additive can help minimise shrinkage of a calcium-sulphate-based product e.g. gypsum wallboard even in the absence of vermiculite.

Preferably, 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
5 increased amounts (>25wt% in the slurry) of a clay additive can help maintain strength and structural integrity after heating even in the absence of a fibrous network.

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.

10 In preferred embodiments of the present invention, the calcium sulphate-based product further comprises silicone oil. Silicone oil is known to help minimise water absorption in calcium sulphate-based products. However, it appears that there is an interaction between the silicone oil and the clay additive which provides a surprising enhancement of this effect. Silicone oil is preferably included in the slurry an amount of between 0.6 - 2wt% (and most
15 preferably around 2wt%) (based on the weight of the calcined gypsum and clay additive). This equates to an amount of 0.5 – 1.8wt% in the calcium sulphate-based product.

The calcium sulphate-based product may contain additives such as accelerators. The accelerators may be, for example, freshly ground gypsum having an additive of sugar or surfactant. Such accelerators may include Ground Mineral NANSO (GMN), heat resistant
20 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, ultrasound may be used to accelerate the setting rate of the slurry, e.g. as described in US2010/0136259.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows the linear shrinkage during heating;

Figure 2 shows the development of flexural strength during heating;

Figure 3 shows the development of Brinell hardness during heating; and

5 Figure 4 shows a TGA trace for kaolin obtained from Sigma Aldrich.

EXPERIMENTAL

The following examples are given by way of illustration only.

Control sample 1 – 25wt% kaolin plus 2wt% silicone oil, glass fibres and glass matting

585g of water at 40°C was mixed with 6.75g of John Mansville glass fibres and 15g of
10 silicone oil. 187.5g of kaolin and 562.5g 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 slurry was poured into the
mould and further layer of glass tissue was laid onto the top of the slurry. The sample was
15 dried at 40°C overnight (minimum 12 hours).

Control Sample 2 – 10wt% kaolin plus silicone oil, glass fibres and glass matting

585g of water at 40°C was mixed with 6.75g of John Mansville glass fibres and 15g of
silicone oil. 75g 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
20 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 3 – 5wt% kaolin plus silicone oil, glass fibres and glass matting

585g of water at 40°C was mixed with 6.75g of John Mansville glass fibres and 15g of silicone oil. 37.5g of kaolin and 712.5g 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 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 – 2wt% kaolin plus silicone oil, glass fibres and glass matting

585g of water at 40°C was mixed with 6.75g of John Mansville glass fibres and 15g of silicone oil. 15g of kaolin and 735g 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).

Control Sample 5 - no kaolin plus 2wt% silicone oil, glass fibres and glass matting

585g of water at 40°C was mixed with 6.75g of John Mansville glass fibres and 15g of silicone oil. 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 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 – no kaolin plus 2wt% silicone oil

140g of water at 40°C was mixed with 4g of silicone oil. 200g of calcined gypsum was added to the water and the mixture was blended by hand for 30 seconds to form a slurry. The slurry was poured into a cylindrical silicone mould (height 25mm, diameter 12mm) and the sample was dried at 40°C overnight (minimum 12 hours).

Control Sample 7 – no kaolin – no silicone oil

200g of calcined gypsum was added to 140g of water at 40°C and the mixture was blended by hand for 30 seconds to form a slurry. The slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and the sample was dried at 40°C overnight (minimum 12 hours).

Kaolin Sample 1 – 36wt% kaolin plus 2wt% silicone oil, glass fibres and glass matting

585g of water at 40°C was mixed with 6.75g of John Mansville glass fibres and 15g of silicone oil. 270g of kaolin and 480g 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).

Kaolin Sample 2 – 36wt% kaolin plus glass fibres and glass matting

600g of water at 40°C was mixed with 6.75g of John Mansville glass fibres. 270g of kaolin and 480g 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).

Kaolin Sample 3 – 36wt% kaolin plus glass fibres

600g of water at 40°C was mixed with 6.75g of John Mansville glass fibres. 270g of kaolin and 480g of calcined gypsum was added to the water and the mixture was mechanically blended for 10 seconds to form a slurry. The slurry was poured into a 320mm x 120mm x 12.5mm silicone mould and the sample was dried at 40°C overnight (minimum 12 hours).

Kaolin Sample 4 – 36wt% kaolin

270g of kaolin and 480g of calcined gypsum was added to 600g of water at 40°C and the mixture was mechanically blended for 10 seconds to form a slurry. The slurry was poured

into a 320mm x 120mm x 12.5mm silicone mould and the sample was dried at 40°C overnight (minimum 12 hours).

Kaolin Sample 5 – 30wt% kaolin plus 2wt% silicone oil, glass fibres and glass matting

585g of water at 40°C was mixed with 6.75g of John Mansville glass fibres and 15g of silicone oil. 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).

Kaolin Sample 6 – 36% kaolin plus 2wt% silicone oil

140g of water at 40°C was mixed with 4g of silicone oil. 128g of calcined gypsum and 72g of kaolin was added to the water and the mixture was blended by hand for 30 seconds to form a slurry. The slurry was poured into a cylindrical silicone mould (height 25mm, diameter 12mm) and the sample was dried at 40°C overnight (minimum 12 hours).

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

	Kaolin/wt% in slurry (in product)	Silicone oil/g	Glass fibres/g	Glass matting/g
Control sample 1	25 (22.2)	√	√	√
Control sample 2	10 (8.8)	√	√	√
Control sample 3	5 (4.4)	√	√	√

Control sample 4	2 (1.8)	√	√	√
Control sample 5	0	√	√	√
Control sample 6	0	√	x	x
Control sample 7	0	x	x	x
Kaolin sample 1	36 (32)	√	√	√
Kaolin sample 2	36 (32)	x	√	√
Kaolin sample 3	36 (32)	x	√	x
Kaolin sample 4	36 (32)	x	x	x
Kaolin sample 5	30 (26.7)	√	√	√
Kaolin sample 6	36 (32)	√	x	x

Table 1 – Summary of sample formulations

Collapse test – horizontal fire test

Samples were placed in a furnace at room temperature with their ends supported such that the samples rested horizontally. 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. Results are shown in Table 2.

Sample	Observations
Kaolin sample 1 (36wt% kaolin)	Minor sagging – no visible cracks
Kaolin sample 2 (36wt% kaolin)	Minor sagging – no visible cracks
Kaolin sample 3 (36wt% kaolin)	Minor sagging – no visible cracks
Kaolin sample 4 (36wt% kaolin)	Minor sagging – no visible cracks
Kaolin sample 5 (30wt% kaolin)	Minor sagging – no visible cracks
Control sample 1 (25wt% kaolin)	Some sagging – cracks appearing
Control sample 2 (10wt% kaolin)	Collapse – major cracks
Control sample 5 (no kaolin)	Collapse – major cracks

Table 2 – Results of collapse test (wt% shown for slurry)

It can be seen that the addition of kaolin in the slurry an amount equal to or greater than 30% significantly improves the structural integrity of the sample (which will contain kaolin in an amount equal to or greater than 26.7 wt%). A comparison of kaolin samples 1-4 shows that the effect can be attributed exclusively to the kaolin in the sample and the inclusion of additional ingredients (silicone oil, glass fibres, glass matting) does not result in any further improvement.

Area shrinkage test

- 10 Dimensions of the samples were measured. Samples were placed in a furnace room at room temperature and heated to 1000°C over 1.5 hours. The samples were allowed to cool

to room temperature and then the dimensions were re-measured. Results are shown in Table 3.

Sample	Area Shrinkage
Kaolin sample 1 (36wt% kaolin)	18%
Kaolin sample 5 (30wt% kaolin)	18%
Control sample 1 (25wt% kaolin)	18%
Control sample 2 (10wt% kaolin)	22%
Control sample 5 (no kaolin)	26%

Table 3 – Results of area shrinkage test (wt% shown for slurry)

It can be seen that the inclusion of kaolin reduces the area shrinkage.

5 Linear shrinkage

Linear shrinkage was measured using a Netzsch dilatometer. The samples (kaolin sample 6 and control samples 6 and 7) were heated to 1000°C at a rate of 5°C/min. The shrinkage was measured in-situ using a transducer having a resolution of 8nm.

The dilatometer results are shown in Figure 1. It can be seen that kaolin sample 6 showed a linear shrinkage of 2.76% at 950°C whilst control sample 6 showed a linear shrinkage of 4.54% and control sample 7 (labelled DSG) showed a linear shrinkage of 18.64%. The effect of kaolin addition on reducing shrinkage was even more apparent at 995°C where kaolin sample 6 showed a linear shrinkage of 5.79% whereas control samples 6 and 7 showed a linear shrinkage of 18.91% and 18.64% respectively.

Flexural strength

Samples measuring 50 x 300mm x 14mm were supported on two supports separated by a span of 200mm. Force was applied to the centre of the board using a Zwick™ universal testing machine and the peak load to break the board (i.e. the flexural strength) was measured.

The measurement was repeated for samples heated to and subsequently cooled from 1000°C. Results are shown in Table 4.

Sample	Average Flexural strength small scale (N)	Standard deviation
Control sample 5 (before heating)	175.4	18.8
Kaolin sample 1 (before heating)	88.1	15.1
Control sample 5 (after heating)	1.9	1.9
Kaolin sample 1 (after heating)	49.9	4.8

Table 4 – Results of flexural strength test

It can be seen that the addition of the clay additive significantly (x25) improves flexural strength after heating to 1000°C.

The flexural strength development of control sample 5 and kaolin sample 1 during heating was also tested and the results are shown in Figure 2.

It can be seen that before heating, flexural strength of control sample 5 was greater than that of kaolin sample 1. Up to 750°C, both samples lose roughly the same amount of strength.

At 920°C, both samples have no strength. At 975°C, kaolin sample 1 is beginning to gain

strength whilst control sample 5 still has no strength. At 1000°C, kaolin sample 1 has gained more strength whilst control sample 5 still has none.

This shows that the strength improvement arising from the addition of the clay additive does not occur until high temperatures (975°C).

5 Brinell hardness

A jig mounted with a 10mm diameter steel ball was lowered onto the samples and a 200N force applied for 15 seconds. The resulting indentation was measured using a Zwick universal tester machine and this was used to calculate the hardness using the Brinell indentation hardness principle.

- 10 The hardness development of control sample 5 and kaolin sample 1 during heating was tested and the results are shown in Figure 3.

It can be seen that before heating, Brinell hardness of control sample 5 was greater than that of kaolin sample 1. Up to 750°C, both samples lose roughly the same amount of hardness. At 920°C, both samples have no strength. Above 975°C, kaolin sample 1 has gained

- 15 considerable strength whilst control sample 5 still has none.

This shows that the hardness/strength improvement arising from the addition of the clay additive does not occur until high temperatures (975°C).

Thermal gravimetric analysis

- 20 Thermal Gravimetric Analysis (TGA) was carried out on samples of Kaolin from three different suppliers – Sigma Aldrich, Sibelco and Goonvean.

In all cases, a large endothermic peak was observed at around 540°C associated with a weight loss of around 11wt%. This can be attributed to dehydration of the clay. In all cases, a second, large exothermic peak was observed at around 993°C. This peak was not

associated with any weight change and this peak can be attributed to a structural change occurring in the clay. This structural change is occurs at around the same temperature region at which the strength and hardness develop. It therefore appears likely that that the improvement in strength and hardness are directly attributable to the structural change of the clay.

A TGA trace of the Sigma Aldrich kaolin is shown as Figure 4.

Core cohesion

Samples measuring 300mm x 45mm x 14mm were clamped at one end in a horizontal position with a 400g weight hooked onto the opposite end. Propane burners were either side of the sample, spaced from the sample by 25mm. The time taken for the weight to drop by 10mm was measured. Results are shown in Table 5.

Sample	Time to drop 10mm
Control sample 5	37 mins 52 secs
Kaolin sample 1	Burner turned off after 2 hours and sample had dropped 4mm

Table 5 – Results of core cohesion test

It can be seen that the addition of kaolin in amounts greater than 30wt% results in greater structural integrity and dimensional stability.

Water absorption

Samples were dried at 40°C overnight (at least 12 hours). The weight of the dried samples was measured. The samples were then immersed in water for 2 hours and the weight re-measured. The percentage increase in weight is shown below in Table 7.

Sample	Water absorption
Control sample 1	10%
Control sample 2	34%
Control sample 3	31%
Control sample 4	34%
Control sample 5	34%
Kaolin sample 1	1.5%
Kaolin sample 2 (no silicone oil)	45%
Kaolin sample 5	4%

5 Table 7 – Results of water absorption test

The results show that inclusion of silicone oil results in a kaolin/silicone oil interaction which surprisingly increases resistance to water absorption.

CLAIMS

1. A calcium sulphate-based product comprising gypsum and a clay additive, wherein the clay additive is provided in an amount greater than 22 wt%.
2. A calcium sulphate-based product according to claim 1 wherein the clay additive is provided in an amount equal to or greater than 26wt%.
3. A calcium sulphate-based product according to claim 2 wherein the clay additive is provided in an amount equal to or greater than 31wt%.
4. A calcium sulphate-based product according to any one of the preceding claims wherein the amount of gypsum is equal to or greater than 38 wt%.
5. A calcium sulphate-based product according to any one of the preceding claims wherein the amount of gypsum is equal to or greater than 47wt%.
6. A calcium sulphate-based product according to any one of the preceding claims wherein the amount of gypsum is equal to or greater than 56wt%.
7. A calcium sulphate-based product comprising gypsum and a clay additive, wherein the product is formed from drying an aqueous slurry containing calcined gypsum and greater than 25wt% of said clay additive
8. A calcium sulphate-based product according to claim 7 wherein the amount of clay additive in the slurry is equal to or greater than 30wt%.
9. A calcium sulphate-based product according to claim 8 wherein the amount of clay additive in the slurry is equal to or greater than 35wt%.
10. A calcium sulphate-based product according to any one of claims 7 to 9 wherein the amount of calcined gypsum in the slurry is equal to or greater than 30wt%.

11. A calcium sulphate-based product according to claim 10 wherein the amount of calcined gypsum in the slurry is equal to or greater than 40wt%.
12. A calcium sulphate-based product according to claim 11 wherein the amount of calcined gypsum in the slurry is equal to or greater than 50wt%.
- 5 13. A calcium sulphate-based product according to any one of the preceding claims wherein the clay additive is a kaolinitic clay material.
14. A calcium sulphate-based product according to any one of the preceding claims wherein the calcium sulphate-based product is a building material.
15. A calcium sulphate-based product according to claim 14 wherein the product is a wall
10 board, tile, panel or joint filler material.
16. A calcium sulphate-based product according to claim 15 wherein the calcium sulphate-based product is a composite product having a gypsum matrix core sandwiched between two liners.
17. A calcium sulphate-based product according to any one of the preceding claims
15 containing substantially no vermiculite.
18. A calcium sulphate-based product according to any one of the preceding claims containing substantially no inorganic fibres.
19. A calcium sulphate-based product according to any one of the preceding claims further comprising silicone oil.
- 20 20. A calcium sulphate-based product according to any one of the preceding claims further comprising an accelerator.
21. A method of forming a calcium sulphate-based product by drying an aqueous slurry comprising calcined gypsum and >25wt% of a clay additive.

22. A calcium sulphate-based product according to claim 21 wherein the amount of clay additive in the slurry is equal to or greater than 30wt%.
23. A method according to claim 22 wherein the amount of clay additive in the slurry is equal to or greater than 35wt%.
- 5 24. A method according to any one of claims 21 to 23 wherein the amount of calcined gypsum in the slurry is equal to or greater than 30wt%.
25. A method according to claim 24 wherein the amount of calcined gypsum in the slurry is equal to or greater than 40wt%.
- 10 26. A method according to claim 25 wherein the amount of calcined gypsum in the slurry is equal to or greater than 50wt%.
27. A method according to any one of claims 21 to 26 wherein the clay additive is a kaolinitic clay material.
28. A method according to any one of claims 21 to 27 wherein the calcium sulphate-based product is a building material.
- 15 29. A method according to claim 28 wherein the product is a wall board, tile, panel or joint filler material.
30. A method according to claim 29 wherein the method comprises sandwiching the product between two liners.
- 20 31. Use of a clay additive in an aqueous slurry of calcined gypsum in an amount greater than 25wt% for reducing shrinkage and improving strength during heat exposure of a calcium sulphate-based product formed by drying said slurry.
32. Use according to claim 31 wherein the amount of clay additive in the slurry is equal to or greater than 30wt%.

33. Use according to claim 32 wherein the amount of clay additive in the slurry is equal to or greater than 35wt%.
34. Use according to any one of claims 31 to 33 wherein the amount of calcined gypsum in the slurry is equal to or greater than 30wt%.
- 5 35. Use according to claim 34 wherein the amount of calcined gypsum in the slurry is equal to or greater than 40wt%.
36. Use according to claim 35 wherein the amount of calcined gypsum in the slurry is equal to or greater than 50wt%.
- 10 37. Use of a clay additive in an amount greater than 22 wt% for reducing shrinkage and improving strength during heat exposure of a calcium sulphate-based product comprising gypsum.
38. Use according to claim 37 wherein the clay additive is used in an amount equal to or greater than 26wt%.
- 15 39. Use according to claim 38 wherein the clay additive is used in an amount equal to or greater than 31wt%.
40. Use according to any one of claims 37 to 39 wherein the amount of gypsum is equal to or greater than 38 wt%.
41. Use according to claim 40 wherein the amount of gypsum is equal to or greater than 47wt%.
- 20 42. Use according to claim 41 wherein the amount of gypsum is equal to or greater than 56wt%.
43. Use according to any one of claims 31 to 42 wherein the clay additive is a kaolinitic clay material.

44. Use according to any one of claims 31 to 43 wherein the calcium sulphate-based product is a wallboard, tile, panel or joint filler material.

45. A calcium sulphate-based product substantially as any one embodiment herein described.

5 46. A method of forming a calcium sulphate-based product substantially as any one embodiment herein described.

47. Use of a clay additive substantially as any one embodiment herein described.

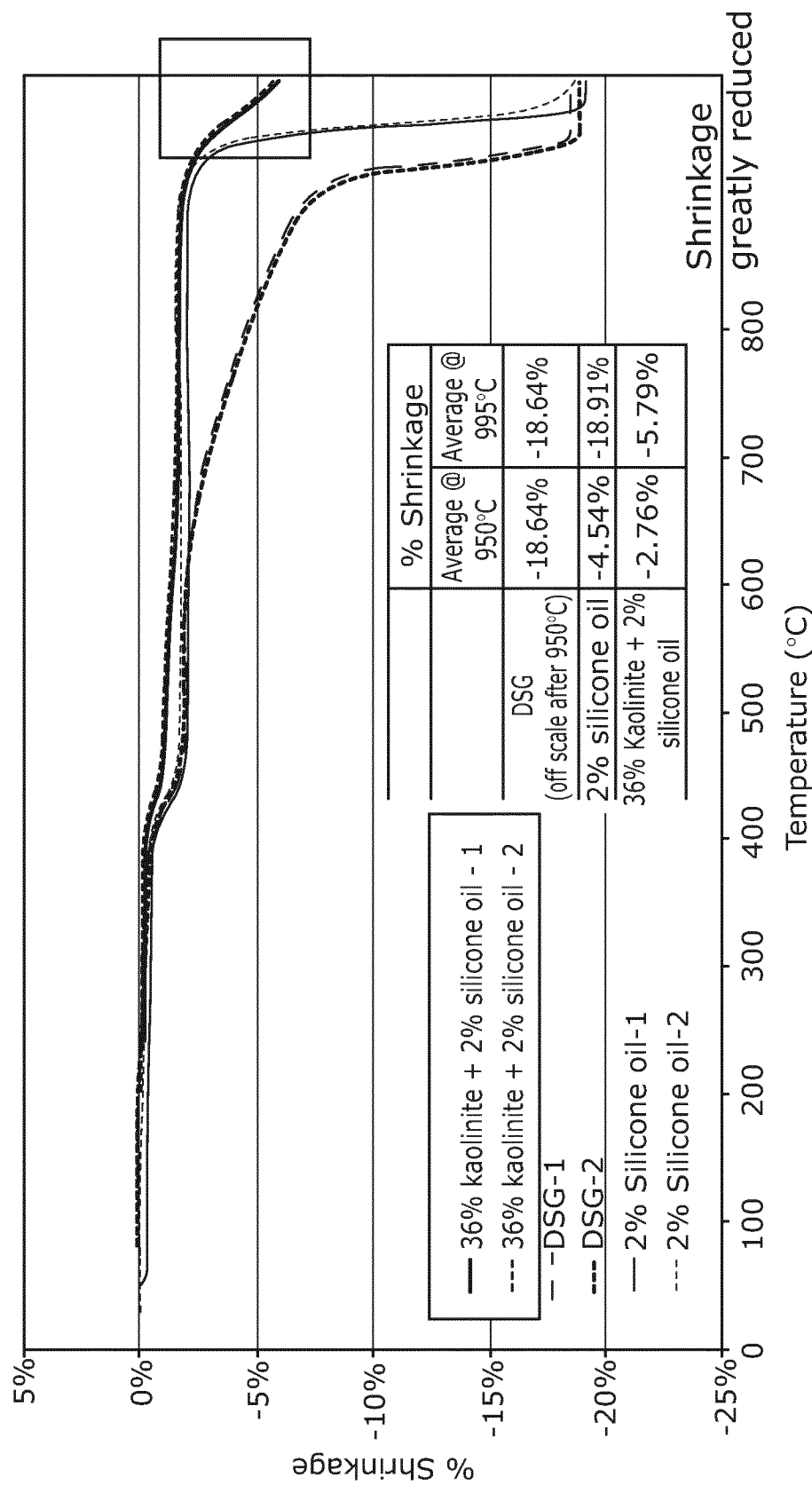


Figure 1

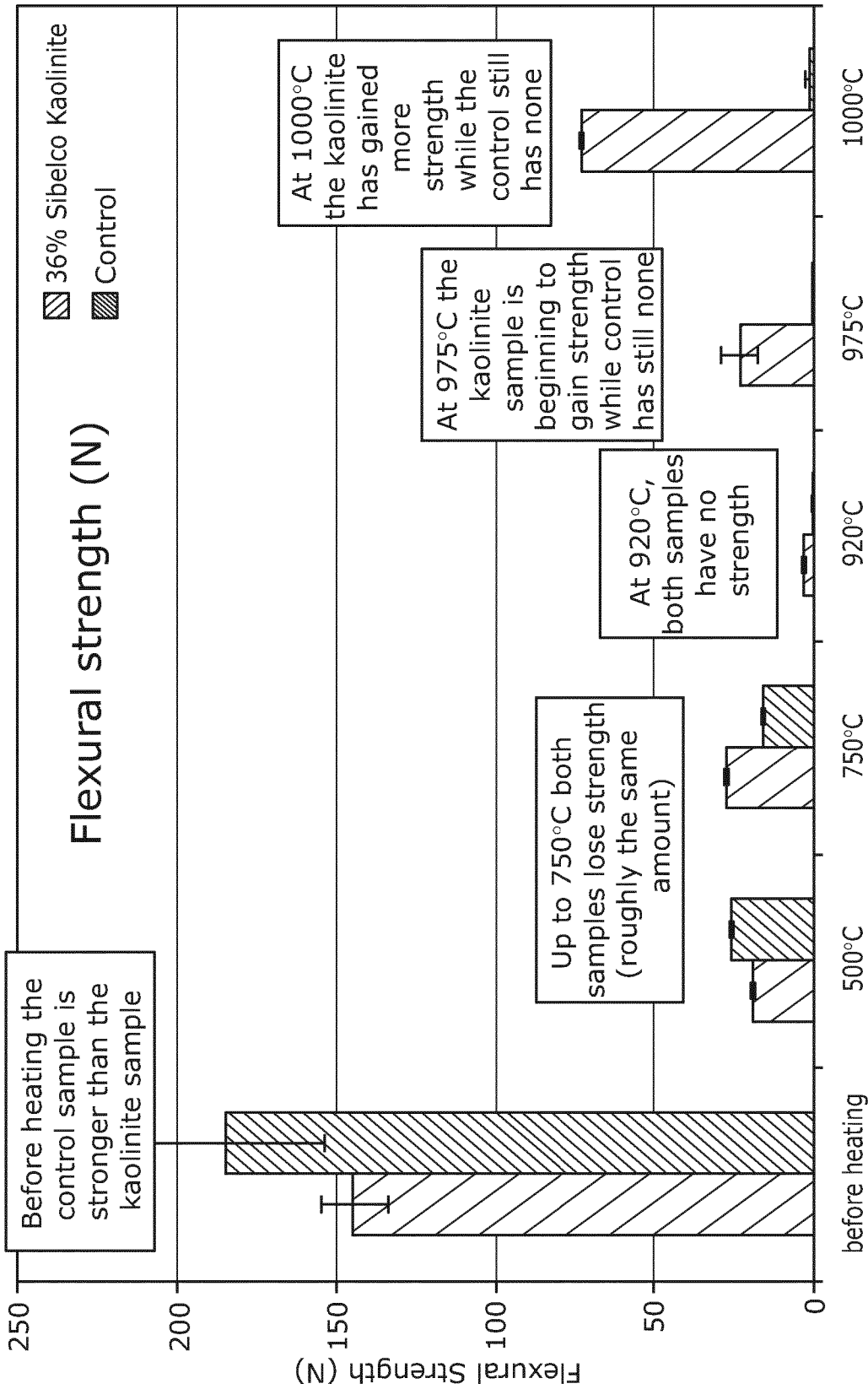


Figure 2

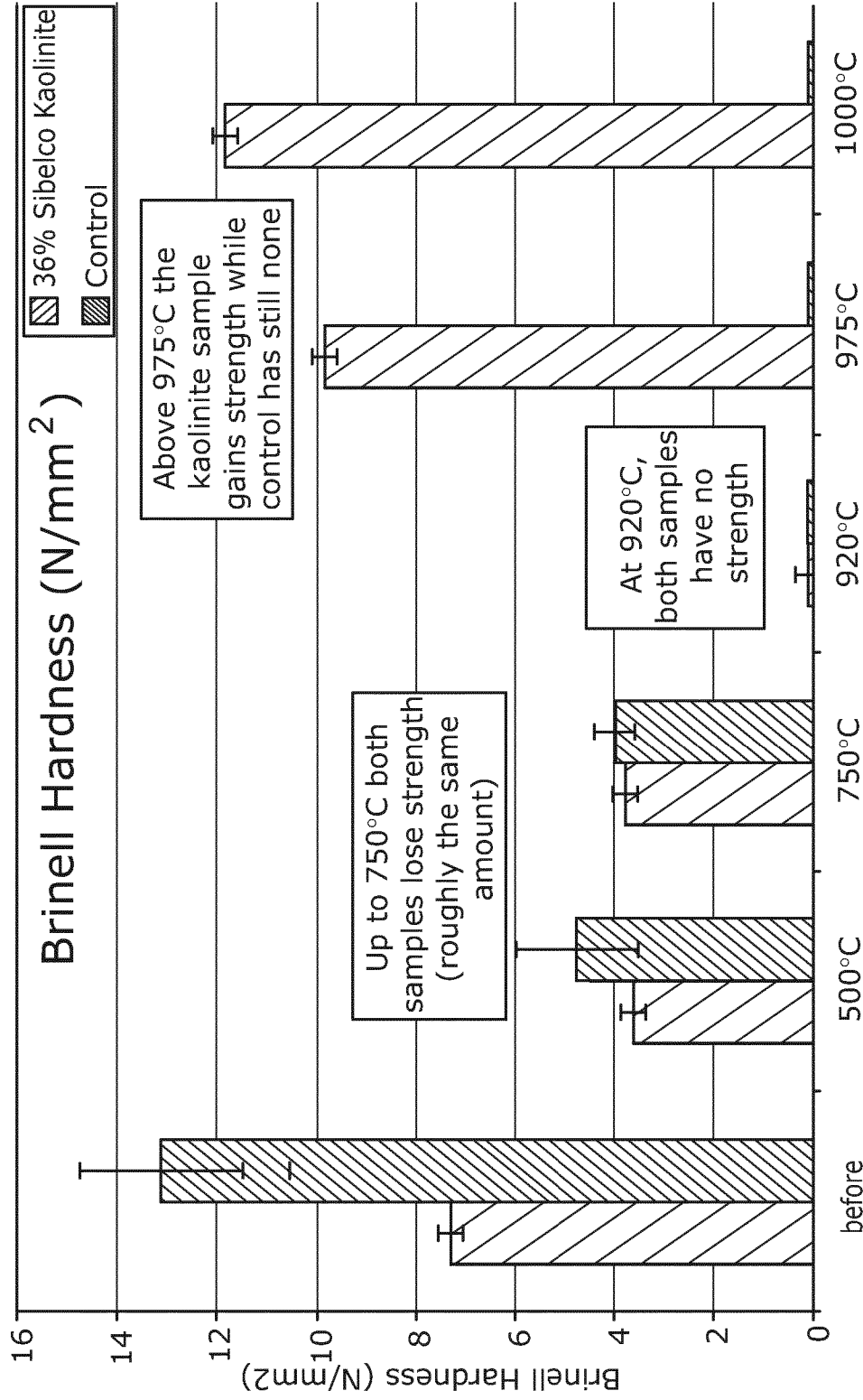


Figure 3

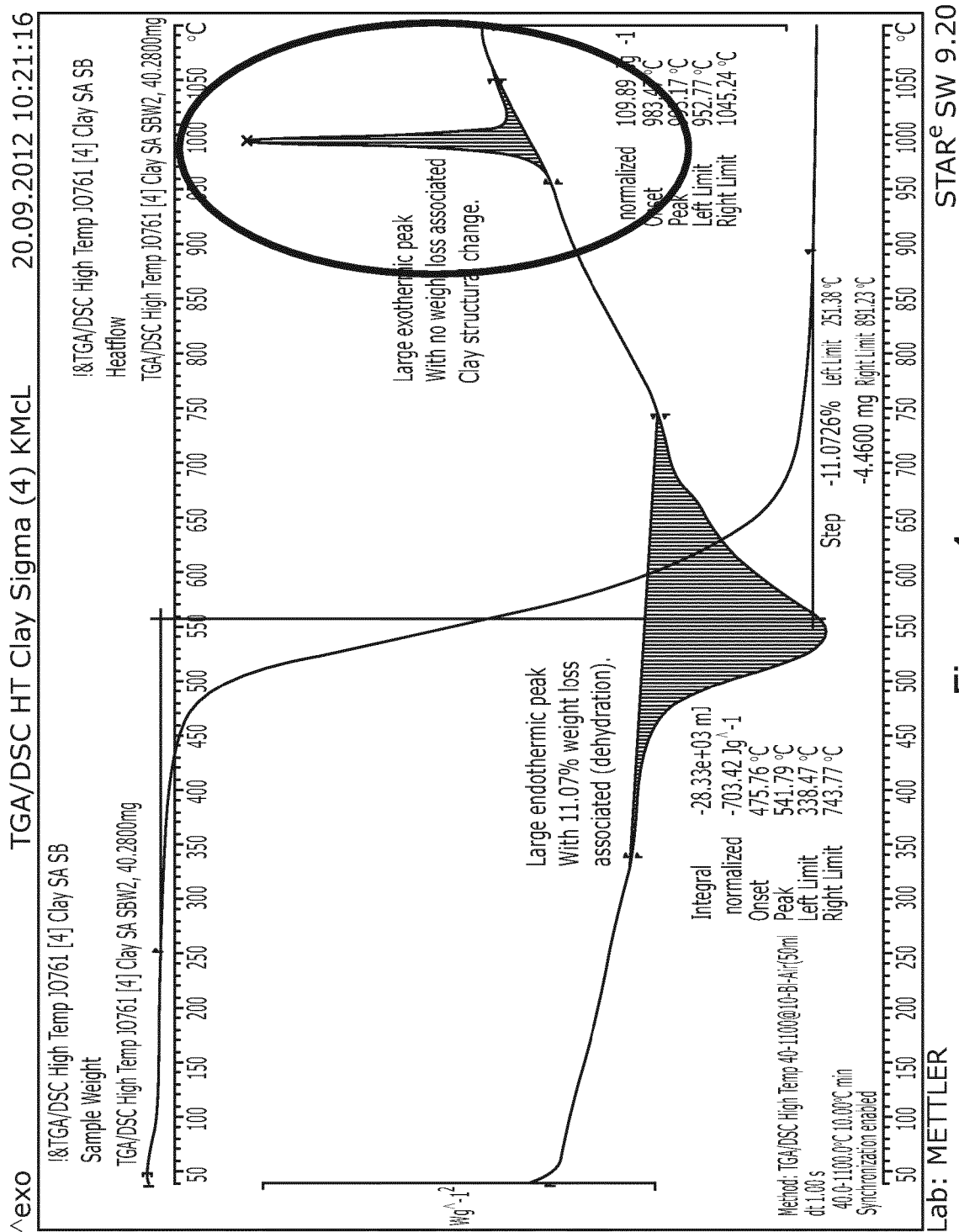


Figure 4

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/059783

A. CLASSIFICATION OF SUBJECT MATTER

INV. C04B28/14

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

17 October 2014

Date of mailing of the international search report

31/10/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Büscher, Olaf

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/059783

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	WO 03/004432 A1 (G P GYPSUM CORP [US]) 16 January 2003 (2003-01-16) paragraphs [0009], [0010], [0016] - [0030], [0035] - [0038], [0040] - [0105]; claims 1-20; table 1 -----	1,7,21, 31,37, 45-47
A	US 5 723 226 A (FRANCIS HUBERT C [US] ET AL) 3 March 1998 (1998-03-03) espec. col. 9, line 20-29; column 2, line 30 - column 12, line 62; claims 1-21; examples 1,2 -----	1-47
A	FARID ALFAWAKHIRI ET AL: "Fire Resistance of Loadbearing Steel-Stud Wall Protected with Gypsum Board: A Review", FIRE TECHNOLOGY, KLUWER ACADEMIC PUBLISHERS, BO, vol. 35, no. 4, 1 November 1999 (1999-11-01), pages 308-335, XP019241421, ISSN: 1572-8099, DOI: 10.1023/A:1015401029995 chapter: "Gypsum Board"; page 330 - page 331 -----	1-47

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International application No

PCT/EP2014/059783

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