

BINDER BASED ON CALCIUM ALUMINOSILICATE DERIVATIVES FOR CONSTRUCTION MATERIALS

5 The present invention relates to a hydraulic binder based on calcium aluminosilicate derivatives, in particular based on blast-furnace slags, used for construction materials, to the mortar or concrete compositions comprising said binder, and also to the construction materials obtained from these compositions.

10 Most of the environmental problems linked to the production of cement relate to the manufacture of clinker which requires calcining and heating operations, in particular at very high temperatures, of the order of 1450°C. The production of one tonne of Portland cement generates between 0.7 and 1 tonne of carbon dioxide. Many efforts are therefore directed toward reducing
15 the carbon footprint of cement and one of the solutions envisaged consists in using alternative raw materials or binders based on industrial waste. It is also possible to reduce the clinker content of the cement, by incorporating supplementary cementing materials such as fly ash, optionally pozzolanic fly ash, ground granulated blast-furnace slag, silica fumes or metakaolin for
20 manufacturing compound cements, often referred to as blended cements. Such cements are in particular described in the standard EN197-1 which defines the specifications of 27 common cements and the constituents thereof.

 Due to a high reactivity and the reduction of carbon dioxide emissions,
25 cements comprising slags and/or fly ash are particularly advantageous. Blast-furnace slag is a coproduct resulting from the manufacture of cast iron from iron ore; it corresponds to the barren gangue of the iron ore, isolated from the liquid cast iron by the difference in density. The molten slag is lighter and floats on the bath of liquid steel. A blast furnace slag essentially comprises
30 calcium silicates or silicoaluminates. The vitrified slag obtained by sudden cooling of the molten slag using high-pressure water jets has a vitreous structure. This allows it to develop hydraulic properties: reference is made to granulated slag, the diameter of the particles of which is less than 5 mm. Granulated slags can be finely ground after drying and used in the cement

industry. Most ground granulated blast-furnace slags have a fineness of between 3800 and 4500 cm²/g (also expressed in Blaine units).

CEMII/A-S cements, also referred to as Portland slag cements, contain from 65% to 94% of clinker and from 6% to 35% of ground granulated blast-furnace slag. CEMIII/A-B-C cements or blast-furnace cements comprise from 36% to 95% of slag and from 5% to 64% of clinker. Studies carried out recently showed that it was possible to replace more than 95% of Portland cement with ground granulated blast-furnace slag, or even to use this slag as binder for construction materials. Mention will be made, for example, of patent FR-B-2 952 050 which describes high-performance binders based on ground granulated blast-furnace slag, that can be used under "mild" conditions, i.e. without requiring the use of an activator system which is highly basic and consequently dangerous to handle. The proposed solution consists in using, as activator, slag microparticles having a fineness of greater than 6000 Blaine, in the presence of a very small amount of base. However, with this type of system, in particular under conditions of low temperatures combined with a relatively high humidity, the setting time and hardening time of the binder remain too poor due to too slow a hydration rate.

Patent US-B1-6,451,105 describes a cementitious composition comprising Portland cement optionally substituted with blast-furnace slags and/or fly ash, to which a setting accelerator based on limestone ground to 150 µm is added. The type of activation proposed in that document is not sufficient, when the essential constituent of the binder is a calcium aluminosilicate derivative of slag and/or fly ash type. Specifically, the systems described in that patent all contain at least 40% Portland cement, which therefore significantly participates in the hydraulic setting mechanism of the blended cements described.

It has therefore been sought to develop an activation system which makes it possible to effectively activate the slags, known for being relatively unreactive compared to other hydraulic binders.

The present invention relates to a hydraulic binder predominantly comprising a calcium aluminosilicate derivative and at least one accelerator of the hardening reaction of the binder which is not classified under the group of irritant or corrosive products according to Directive 91/155/EEC and which

retains its accelerator properties, even under low-temperature conditions. Another subject of the invention relates to a mortar or concrete composition comprising such a binder. The binder according to present invention advantageously makes it possible to obtain good mechanical performances in the short term (start of setting).

The present invention also relates to construction materials such as tiling adhesives, pointing mortars, masonry mortars, screeds, wall coverings or renderings obtained from the above mortar or concrete compositions.

The hydraulic binder according to present invention comprises at least 80% by weight of a ground granulated blast-furnace slag and at least one accelerator of the hardening reaction comprising at least one source of calcium sulfate and at least one nucleating agent in the form of particles, the BET specific surface area of which is greater than $1\text{m}^2/\text{g}$ and the size of which is such that 50% of the particles have a mean diameter of less than $5\text{ }\mu\text{m}$, said particles being chosen from calcium carbonates, magnesium carbonates, calcium magnesium carbonates, calcium silicate hydrates, aluminum silicate hydrates, alone or as a mixture.

The nucleating agents advantageously make it possible to accelerate the hydration of the hydraulic binder, in particular at relatively low temperature, without requiring the addition of other, often toxic additives. It is necessary for at least 50% of the nucleating agent particles to have a mean diameter of less than $5\text{ }\mu\text{m}$. These nucleating agents play the part of seeds even better when they are as fine as possible and have a high specific surface area, of greater than $1\text{ m}^2/\text{g}$.

The binder according to the present invention may comprise fly ash, such as aluminosilicate fly ash and calcium aluminosilicate fly ash, or calcined or expanded clay dust. The difference between Class F and Class C fly ash lies in the respective calcium content thereof. Class F fly ash comprises less than 8% of calcium and is less reactive than Class C fly ash. The content of fly ash, or calcined or expanded clay dust in the binder according to the present invention is less than or equal to 15% by weight.

Preferentially, the binder according to the invention comprises between 85% and 98% by weight of ground granulated blast-furnace slag.

The binder according to the present may further comprise another hydraulic binder chosen from Portland cements, high-alumina cements, sulfoaluminate cements, belite cements or cements formed of pozzolanic mixtures, taken alone or as a mixture. Preferably, the amount of this type of hydraulic binder is less than or equal to 15% by weight, or less than or equal to 10% by weight, or even preferentially less than or equal to 5% by weight.

The binder according to present invention also comprises at least one accelerator of the hardening reaction. Specifically, it is necessary, given that binders based on calcium aluminosilicate derivatives are binders that are not considered to be very hydraulic, to add an accelerator which comprises at least one source of calcium sulfate and at least one nucleating agent that promotes the hydration of the binder due to the presence of seeds that act as activator.

The source of calcium sulfate is chosen from gypsum, calcium sulfate hemihydrate, anhydrite and phosphogypsum, alone or as a mixture, in an amount between 1% and 5% by weight relative to the total weight of binder. Preferentially, the amount of source of calcium sulfate is between 2% and 4% by weight of the total weight of binder. The source of calcium sulfate, in such an amount, makes it possible to control the activation at the start of the reaction and to guarantee sufficient trapping of water, while preventing too considerable a delayed ettringite formation which would result in a weakening of the material after the binder setting steps.

The amount of nucleating agent present in the hydraulic binder according to the present invention represents between 0.1% and 20% of the total weight of the binder. The nucleating agent is a pulverulent agent, the size of the particles of which is such that 50% of the particles have a mean diameter of less than 5 μm . The activation is particularly improved when the particles are of small size. Specifically, the finer the seeds, the more reactive they are. They are chosen from calcium carbonates, magnesium carbonates, calcium magnesium carbonates, calcium silicate hydrates, aluminum silicate hydrates, alone or as a mixture. These seeds may be obtained for example by precipitation and/or by grinding.

The nucleating agent particles are characterized by their specific surface area (BET surface area expressed in m^2/g) and by the median

diameter D_{50} which corresponds to the size for which 50% of the population of particles has a size of less than D_{50} .

Advantageously, the nucleating agent is chosen from ground or precipitated natural calcium and/or magnesium carbonates, the BET specific surface area of which is greater than $4 \text{ m}^2/\text{g}$. Precipitated calcium and/or magnesium carbonates are preferred.

It may also be a hydrated calcium silicate hydrate, the BET specific surface area of which is greater than $2.5 \text{ m}^2/\text{g}$. The nucleating agent may also be a finely ground zeolite. By choosing a nucleating agent as described above, it is possible to obtain an activation system that operates quite suitably for the binders considered to be not very hydraulic and therefore not very reactive.

When the nucleating agent is chosen from calcium silicate hydrates and aluminum silicate hydrates, the amount of nucleating agent is advantageously between 0.2% and 3% by weight relative to the total weight of the binder. This amount is relatively low with respect to the activation systems known from the prior art, in particular with respect to the solution proposed in patent application WO 2011/055063 which makes provision for adding up to 11% by weight, relative to the total weight of binder, of slag microparticles.

When the activation agent is of carbonate type, it may be necessary to add up to 20% of the total weight of the binder thereof in order to obtain a satisfactory activation. The amount of calcium and/or magnesium carbonates therefore varies between 0.2% and 20% by weight relative to the total binder weight.

The accelerator may also comprise one or more sulfates of an alkali metal, chosen from lithium, sodium and/or potassium, preferably in an amount of less than or equal to 0.5% by weight relative to the total weight of the binder. More preferentially still, the accelerator comprises between 0.2% and 0.4% by weight, relative to the total weight of the binder, of alkali metal sulfates. The sulfates advantageously make it possible to promote the setting of the binder and are in particular favorable when they are combined with a source of calcium sulfate.

The activator may optionally comprise a small amount of a pH regulator chosen from alkali metal silicates or carbonates, in an amount of less than or equal to 0.5% by weight relative to the total weight of the binder, and preferably in an amount of between 0.2 and 0.4% of the total weight of the binder.

The activator may comprise an additive that acts as chemical activator, in particular chosen from calcium nitrate, calcium formate or hydraulic binders such as Portland cement or high-alumina and/or sulfoaluminate cements as mentioned above. The amount of chemical activator is less than or equal to 5% of the total weight of the binder, preferably less than or equal to 4% of the total weight of the binder. If the chemical activator is a hydraulic binder, it may be added in addition to the amount that may be introduced as hydraulic binder mentioned above.

The activation system according to the present is a mild activation system, based on products that are in pulverulent form and that easily make it possible to produce ready-to-use premixes and that do not contain irritant and corrosive substances.

The hydraulic binder according to the present invention may be hydrated at low temperatures (winter conditions) or at high temperatures, depending on the desired applications.

The present invention also relates to a mortar or concrete composition comprising the binder described above in combination with extenders, fillers, sand and/or aggregates. The extenders may be mineral or organic, low-density lightening extenders such as expanded perlite, expanded vermiculite, expanded glass beads, hollow glass microspheres, cenospheres, expanded clays, expanded shales, pumice stones, expanded polystyrene. The fillers are conventionally of siliceous, calcareous and/or siliceous/calcareous type and have a particle size ranging up to 150 μm . The aggregates or sands, the particle size of which varies between 100 μm and 5 mm make it possible to act on the thickness, the hardness, the final appearance and the permeability of the mortar.

The mortar or concrete composition according to the present invention may also comprise, in addition, one or more additives, chosen from rheological agents, water-retaining agents, air-entraining agents, thickeners,

biocidal protecting agents, dispersants, pigments, accelerators and/or retarders. The rheological agents may in particular be plasticizers, for example products based on polycarboxylic acids such as polycarboxylic ethers, lignosulfonates, polynaphthalenesulfonates, melamine-based
5 superplasticizers, polyacrylates and/or vinyl copolymers, and optionally modified cellulose ethers. These additives, when they are present, each represent less than 1% of the total weight of the mortar composition.

The present invention also relates to construction materials, in particular adhesive mortars or adhesives for tiling, obtained by mixing the
10 mortar composition described above with water. The adhesives obtained very advantageously have a very satisfactory short-term hardening (i.e. after 24 hours). The performance in terms of adhesion strength of the adhesives according to the present invention meet the specifications that make it possible to be classed as C2TE-S1 according to the standard EN 12004: 2007.

15 The construction materials may also be pointing mortars that make it possible to fill the existing voids between various masonry elements. They may also be screeds, facade mortars such as resurfacing mortars, undercoats, monocouche renders, organic facing mortars and waterproofing mortars.

20 The examples below illustrate the invention without limiting the scope thereof.

Example 1

A tiling adhesive formulation comprising a binder, the main constituent
25 of which is a ground granulated blast-furnace slag, with an accelerator system comprising calcium silicate hydrate seeds according to the present invention was prepared by mixing the various constituents given in table 1 below.

Component	Percentage by weight
Silica sand	52.5
Slag (4000 Blaine)	40.0
Polymer (ethylene-vinyl acetate copolymer) powder	3.4

CaSO ₄	1.5
CSH seeds (BET surface area 2.5 m ² /g) D ₅₀ 2.5 µm	1.0
Portland cement 52.5	1.0
Cellulose ether	0.4
Alkali metal sulfate	0.1
Alkali metal carbonate	0.1

Table 1

A pasty preparation of creamy consistency is obtained by adding 25% of water to this pulverulent composition, at a temperature of around 22.1°C.

- 5 Various tensile strength tests to determine the adhesion of the adhesive mortar thus obtained were carried out according to the standard EN 1348. Pieces of tiles are fixed to a flat support by applying a layer of the adhesive mortar obtained. The pull-off strength, expressed in N/mm², is measured by pulling off after 1 day, 7 days and 28 days of storage under standard conditions, i.e. at a temperature of 23°C with a relative humidity of 50%. A measurement "after wet immersion" is also carried out by measuring the pull-off strength after 7 days of storage under standard conditions, followed by 21 days of storage immersed in water at 23°C. An adhesion measurement "after freeze/thaw cycle" is carried out, in accordance with the standard EN 12004: 10 2007 which itself makes reference to the standard EN 1348: 2007. The samples are subjected to successive freeze-thaw cycles. A measurement "after exposure to heat" is carried out after 14 days of storage under standard conditions, followed by 14 days of storage at 70°C, then again 1 day under standard conditions.
- 15 2007 which itself makes reference to the standard EN 1348: 2007. The samples are subjected to successive freeze-thaw cycles. A measurement "after exposure to heat" is carried out after 14 days of storage under standard conditions, followed by 14 days of storage at 70°C, then again 1 day under standard conditions.
- 20 An adhesive strength test was also carried out on a piece of earthenware tile which is laid on a flat support, 20 minutes after the application of an adhesive mortar layer to the piece of tile and/or to the flat support; the pull-off strength is measured by pulling off the sample after 28 days of storage under standard conditions. This measurement is entitled "after 20 min open time".
- 25 The values obtained for these various measurements are compared to the minimum values required in order to obtain the desired certification (standard EN 12004).

Measurements were also carried out to measure the resistance to deformation of the adhesive mortar used and were compared to the expected values according to the standard EN 12002. All of the results obtained are given in table 2 below.

5

Adhesion strength (EN 1348)	measured	Expected (EN 12004)
1 day (N/mm ²)	0.72	
7 days (N/mm ²)	1.92	
28 days (N/mm ²)	2.35	1
After wet immersion (N/mm ²)	1.98	1
After freeze-thaw cycle	1.60	1
After exposure to heat (N/mm ²)	1.90	1
After 20 min open time (N/mm ²)	1.2	0.5
Deformation		
Force (N)	6.52	
Deformation (mm)	2.98	2.5

Table 2

The values obtained show that the tests satisfy the criteria required by the standard.

10

Example 2

A tiling adhesive formulation was prepared in the same way as in example 1, by replacing 5% of the slag with Class C fly ash. The composition is given in table 3 below:

15

Component	Percentage by weight
Silica sand	52.5
Slag (4000 Blaine)	35.0
Fly ash	5.0
Polymer (ethylene-vinyl acetate copolymer) powder	3.4
CaSO ₄	1.5
CSH seeds (BET surface area 2.5 m ² /g) D ₅₀ 2.5 μm	1.0
Portland cement 52.5	1.0
Cellulose ether	0.4
Alkali metal sulfate	0.1
Alkali metal carbonate	0.1

Table 3

Table 4 above gives the mechanical performances obtained for this tiling adhesive.

Adhesion strength (EN 1348)	measured	Expected (EN 12004)
1 day (N/mm ²)	0.68	
7 days (N/mm ²)	1.82	
28 days (N/mm ²)	2.21	1
After wet immersion (N/mm ²)	1.85	1
After freeze-thaw cycle	1.52	1
After exposure to heat (N/mm ²)	1.79	1
After 20 min open time (N/mm ²)	0.9	0.5
Deformation		
Force (N)	6.12	
Deformation (mm)	2.84	2.5

Table 4

Example 3

A tiling adhesive formulation comprising a binder, the main constituent of which is a ground granulated blast-furnace slag, with an accelerator system comprising ultrafine particles of magnesium and calcium carbonates according to the present invention was prepared by mixing the various constituents given in table 5 below.

Component	Percentage by weight
Silica sand	53.5
Slag (4000 Blaine)	35.0
Particles of calcium and magnesium carbonates (BET surface area of 4 m ² /g and D ₅₀ of 2.5 µm)	5.0
Polymer (ethylene-vinyl acetate copolymer) powder	3.4
CaSO ₄	1.5
Portland cement 52.5	1.0
Cellulose ether	0.4
Alkali metal sulfate	0.1
Alkali metal carbonate	0.1

Table 5

Adhesion tests are carried out as in example 1. The results obtained are presented in table 6 below:

Adhesion strength (EN 1348)	measured	Expected (EN 12004)
1 day (N/mm ²)	0.55	
7 days (N/mm ²)	1.33	
28 days (N/mm ²)	1.76	1
After wet immersion (N/mm ²)	1.24	1
After freeze-thaw cycle	1.18	1
After exposure to heat (N/mm ²)	1.59	1
After 20 min open time (N/mm ²)	0.7	0.5
Deformation		
Force (N)	5.8	
Deformation (mm)	2.62	2.5

5

Table 6

The values obtained show that the tests satisfy the criteria required by the standard.

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It is also noted for these three examples according to the invention that the short-term resistance measurements (i.e. at 1 day) are greater than 0.5 N/mm², which is particularly advantageous for the desired applications.

CLAIMS

- 5 1. A hydraulic binder comprising at least 80% by weight of a ground granulated blast-furnace slag and at least one accelerator of the hardening reaction, characterized in that said accelerator comprises at least one source of calcium sulfate and at least one nucleating agent in the form of particles, the BET specific surface area of which is greater than 1 m²/g and the size is such that 50% of the particles have a mean diameter of less than 5 μm, said particles being chosen from calcium carbonates, magnesium carbonates, calcium magnesium carbonates, calcium silicate hydrates, aluminum silicate hydrates, alone or as a mixture.
- 10 2. The binder as claimed in one of the preceding claims, characterized in that it comprises between 85% and 98% by weight of a ground granulated blast-furnace slag.
- 15 3. The binder as claimed in either of the preceding claims, characterized in that it further comprises fly ash, such as aluminosilicate fly ash and calcium aluminosilicate fly ash, or calcined or expanded clay dust.
- 20 4. The binder as claimed in one of the preceding claims, characterized in that it further comprises another hydraulic binder chosen from Portland cements, high-alumina cements, sulfoaluminate cements, belite cements or cements formed of pozzolanic mixtures, taken alone or as a mixture.
- 25 5. The binder as claimed in one of the preceding claims, characterized in that the amount of nucleating agent represents between 0.1% and 20% of the total weight of the binder.
- 30 6. The binder as claimed in one of the preceding claims, characterized in that the accelerator further comprises a pH regulator chosen from alkali metal silicates or carbonates, in an amount of less than or equal to 0.5% of the total weight of binder, preferably from 0.2% to 0.4% of the weight of the binder.
- 35 7. The hydraulic binder as claimed in one of the preceding claims, characterized in that the accelerator further comprises a sulfate of an

alkali metal chosen from lithium, sodium and/or potassium in an amount of less than or equal to 0.5% of the total weight, preferably between 0.2% and 0.4% of the total weight.

- 5 8. The binder as claimed in one of the preceding claims, characterized in that the accelerator further comprises a chemical activator chosen from calcium nitrate, calcium formate, Portland cement, calcium sulfoaluminate cement, calcium aluminate cement, alone or as a mixture, in an amount of less than or equal to 5% of the total weight.
- 10 9. The hydraulic binder as claimed in one of the preceding claims, characterized in that the source of calcium sulfate comprises one or more of the elements chosen from gypsum, calcium sulfate hemihydrate, anhydrite and phosphogypsum, in an amount between 1% and 5% of the total weight, preferably between 2% and 4% of the total weight.
- 15 10. The binder as claimed in one of the preceding claims, characterized in that the nucleating agent is chosen from ground or precipitated natural calcium and/or magnesium carbonates, the BET specific surface area of which is greater than or equal to 4 m²/g, preferably in an amount of between 0.2% and 20% by weight relative to the total binder weight.
- 20 11. The binder as claimed in the preceding claim, characterized in that the nucleating agent is a precipitated calcium and/or magnesium carbonate.
12. The binder as claimed in one of claims 1 to 9, characterized in that the nucleating agent is a zeolite.
- 25 13. The binder as claimed in one of claims 1 to 9, characterized in that the nucleating agent is a hydrated calcium silicate hydrate, the BET specific surface area of which is greater than or equal to 2.5 m²/g, preferably in an amount of between 0.2% and 3% by weight relative to the total binder weight.
- 30 14. A concrete or mortar composition, characterized in that it comprises at least one binder as claimed in one of the preceding claims, optionally lightening extenders, sand, aggregates, fillers.
15. The composition as claimed in claim 14, characterized in that it further comprises one or more additives, chosen from rheological agents,

water-retaining agents, air-entraining agents, thickeners, biocidal protecting agents, dispersants, pigments, accelerators and/or retarders.

16. Construction materials such as tiling adhesives, pointing mortars, masonry mortars, screeds, resurfacing mortars, undercoats, monocouche renders, organic facing mortars, waterproofing mortars, obtained by mixing the mortar or concrete composition as claimed in either of claims 14 and 15 with water.