

MORTAR COMPOSITION BASED ON A SLAG ACTIVATED BY A BY-PRODUCT

The present invention relates to a dry mortar composition comprising, as hydraulic binder, a calcium aluminosilicate derivative activated by an industrial
5 byproduct. The present invention also relates to a process for preparing an adhesive mortar by mixing said dry mortar composition.

There are currently on the market mortar formulations, in particular for tile adhesive, that comprise hydraulic binders based on calcium aluminosilicate derivatives such as activated blast-furnace slags. These binders make it possible
10 in particular to limit the amount of Portland cement in the adhesive mortar formulations and consequently to also reduce the carbon footprint of these products. Specifically, the processes for manufacturing clinker require operations of decarbonation, of calcining, of clinkering and of heating, in particular at very high temperatures of the order of 1450°C. Portland cements
15 and high-alumina cements are for example the cause of emissions of around 800 kg of CO₂ per tonne of cement produced. They also consume energy resources and natural resources. Formulations that are poor in Portland cement, for example comprising less than 1% by weight of cement relative to the total composition, make it possible to greatly reduce the CO₂ footprint and
20 to do away with the “corrosive product” safety marking. On the other hand, certain formulations based on blast-furnace slag activated by Portland cements and/or high-alumina cements may have limited performance at low temperatures, due to a low reactivity, in particular at cold temperatures, below 10°C. It is consequently sought to further improve this low-temperature
25 reactivity.

The present invention sits within this context, which invention provides a dry mortar composition based on calcium aluminosilicate derivatives, which comprises, as activator, a slag rich in the element aluminum, referred to hereinbelow as high-alumina slag, which is an industrial byproduct.

30 The present invention relates to a dry mortar composition comprising:

- a hydraulic binder comprising at least one calcium aluminosilicate derivative, at least one ground granulated high-alumina slag comprising less than 30% by weight of silica, and at least one source of calcium sulfate,
- 5 - aggregates and/or fillers, and
- at least one base in an amount of less than or equal to 0.5% of the total weight of the dry mortar composition.

Within the meaning of the present invention, a “high-alumina slag” is understood to mean a slag wherein alumina is the most abundant constituent.

10 In this document, the elementary chemical compositions are given as equivalent weight % of oxide. For example, saying that a substance contains X% of alumina means that this substance contains the element aluminum in an amount equivalent to that provided by X% of alumina; this does not necessarily mean that the substance contains alumina as a chemical compound or a
15 mineralogical constituent.

A slag is a byproduct from an industrial process involving the melting of a starting product, which melting is intended to separate metals from an oxide phase, the latter being referred to as “slag”.

Within the meaning of the present invention, the term “granulated”
20 means that the molten high-alumina slag has undergone thermal water quenching which results in grains being obtained, which grains are in general predominantly amorphous. The granulated slag is then ground in order to activate it, as explained in greater detail in the remainder of the text.

The ground granulated high-alumina slag preferably comprises between
25 30% by weight and 60% by weight, in particular from 30% to 50% by weight, preferably between 32% and 45% by weight, or even between 35% and 43% by weight of alumina.

Advantageously, the silica content of the ground granulated high-alumina slag is between 5% and 25% by weight, or even between 10% and 20% by weight
30 relative to all of the components of the granulated high-alumina slag.

Preferably, the ground granulated high-alumina slag comprises between 12% and 18% by weight of silica.

Preferably, the granulated high-alumina slag also comprises lime (CaO). The content of lime is less than the content of alumina - as indicated above; it is preferably between 20% and 40% by weight, in particular between 25% and 35% by weight.

In order not to negatively impact the activation properties of the high-alumina slag, the content of iron oxide in the high-alumina slag is preferably less than 5% by weight, in particular less than 3% by weight, and even less than 2% by weight.

The ground granulated high-alumina slag is advantageously predominantly, or even completely, amorphous. The content of amorphous material, as determined by x-ray diffraction according to the Rietveld method, is preferably at least 66%, in particular 90%, and even 95% or 98% by weight.

The ground granulated high-alumina slag is preferably derived from the recycling, by complete melting, of catalysts used for the desulfurization of petroleum products, in particular of catalysts based on molybdenum and/or cobalt. These catalysts are recycled and a certain number of waste products or byproducts are obtained during the recycling cycles. One of the byproducts obtained is a high-alumina slag, the silica content of which is less than 30% by weight. The high-alumina slag preferably comprises molybdenum or cobalt, in a weight content of at most 0.5% expressed by weight of oxide.

This byproduct is, at the end of the recycling of the catalyst, in the form of aggregates having a mean size generally of between 2 and 5 mm. At this diameter, the aggregates of high-alumina slags are generally inert. In order to render them reactive, it is preferable to grind them in order to obtain fine particles. This grinding operation must be taken into consideration for calculating the carbon footprint during the manufacture of the binder. However, if it is compared to the carbon footprint of a process for manufacturing a high-alumina or sulfoaluminate cement, the grinding operation makes it possible to reduce the CO₂ emissions by more than 90%.

The ground granulated high-alumina slag is preferably in the form of ground granules having a D50 particle diameter of less than 20 μm , preferably of less than 15 μm . The D50 diameter is the diameter such that 50% by weight of the particles have a diameter smaller than this D50 value. This fineness of the particles makes it possible in particular to give the granulated high-alumina slag a good reactivity enabling it to be used in a mortar composition and to obtain the expected properties in terms of setting time and mechanical strength.

The high-alumina slag, by its activator action, makes it possible in particular to improve the reactivity of the binder at relatively low temperatures, such as for example at 5°C.

The base also participates in the activation of the hydraulic binder. However, the amounts of base needed are very low which makes it possible to consider the activation system to be a mild activation system compared to systems where it is necessary to add an alkaline activator in a significantly larger amount, giving rise to a high pH capable of causing severe skin irritation during the handling of the products. Its content is preferably less than 0.3% by weight relative to the weight of the dry mortar composition.

The base is preferably chosen from alkali or alkaline-earth metal hydroxides, alkali or alkaline-earth metal carbonates or alkali or alkaline-earth metal silicate derivatives. Mention may in particular be made of KOH, $\text{Ca}(\text{OH})_2$, Na_2CO_3 , K_2CO_3 , Li_2CO_3 , Na_2SiO_3 . It may be a mixture of bases, so that the total amount of the mixture of bases is less than 0.5%, in particular 0.3%, of the total weight of the mortar composition.

The calcium aluminosilicate derivative is preferably an industrial byproduct. Advantageously, alumina is not the most abundant constituent of the calcium aluminosilicate derivative.

The calcium aluminosilicate derivative is preferably chosen from ground granulated blast-furnace slags, fly ash such as aluminosilicate fly ash, calcined clay and/or expanded clay dust, or calcium aluminosilicate fly ash, in particular of coal, in particular of lignite, of sub-bituminous coal, of bituminous coal, etc.

Preferably, at least one calcium aluminosilicate derivative has a fineness of less than 6000 Blaine. The term “Blaine” is a unit for measuring the fineness of grinding of a solid ingredient, expressed in cm^2 per gram of solid. This unit is used to measure the working surface area of the grains of solid.

- 5 The hydraulic binder may also comprise microparticles of ground granulated blast-furnace slag, the fineness of which is between 6000 and 15000 Blaine.

The source of calcium sulfate is advantageously chosen from plaster, hemihydrate, gypsum and/or anhydrite, alone or as a mixture.

- 10 The hydraulic binder may also comprise sulfates of an alkali metal such as lithium, sodium and/or potassium, preferentially in an amount of less than or equal to 0.5% of the total weight of the dry mortar composition.

- 15 The hydraulic binder may also comprise Portland cement, a high-alumina cement and/or a sulfoaluminate cement, preferably in an amount of less than or equal to 1% of the total weight of the dry mortar composition.

- 20 The hydraulic binder preferably represents from 5% to 70%, in particular from 10% to 60% of the total weight of the dry mortar composition. The total amount of calcium aluminosilicate derivative (other than the high-alumina slag) is preferably between 5% and 60%, in particular between 20% and 50% by weight relative to the dry mortar composition. The total amount of ground granulated high-alumina slag is preferably between 0.1% and 5%, in particular between 0.5% and 3% of the total weight of the dry mortar composition. The total amount of the source of calcium sulfate is preferably between 0.5% and 4%, in particular between 1% and 3% of the total weight of the dry mortar composition.

- 25 The fillers are finely ground inert mineral materials, of calcareous or siliceous type. Their content is generally between 0 and 30% by weight relative to the dry mortar composition. The aggregates used generally in the mortar compositions have a diameter of less than 8 mm. The aggregates are mineral grains, in particular grains of stone, gravel, grit, pebbles and/or sands. The content of aggregates preferably varies between 20% and 95% by weight relative to the dry mortar composition.
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The composition is a dry composition since the majority of its constituents are in pulverulent form. The percentages of each of the constituents are given as weight percentages relative to all of the components of said composition.

5 The composition may also comprise one or more additives, chosen from rheological agents, water-retaining agents, air-entraining agents, thickeners, biocidal protecting agents, dispersants, pigments, accelerators and/or retarders, or polymeric resins. The total content of additives and admixtures conventionally varies between 0.001% and 10% by weight relative to the total weight of the dry mortar composition.

10 The presence of these various additives makes it possible in particular to adapt the setting time or the rheology of the wet mortar composition, i.e. after mixing with water, so as to meet the expectations as a function of the desired product.

15 The present invention also relates to a process for preparing a wet mortar composition, in particular an adhesive mortar composition, by mixing the dry mortar composition according to the invention with water. The presence of high-alumina slag as activator advantageously makes it possible to accelerate the hardening kinetics of the mortar composition, both at 20°C and at lower temperature, for example at 5°C.

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

A ground granulated high-alumina slag, derived from the recycling, by complete melting, of catalysts for desulfurization of petroleum products that are based on cobalt and molybdenum, is used in the following examples. The
25 main constituents of this slag are alumina (41%), lime (32.6%), silica (12.6%), magnesium oxide (8.9%), iron oxide (1.6%) and sulfur (1.6%). Other oxides in particular of molybdenum, nickel, cobalt, chromium, vanadium, zinc, manganese, phosphorus, potassium, titanium, as well as chlorine are also present in the slag, but at minimal contents, of less than 0.5%.

30 The granules of this high-alumina slag which have a maximum diameter of 5 mm were ground, in order to obtain a fineness equivalent to that of a cement.

The particle size distribution of the ground granulated high-alumina slag is the following: D_{10} of 0.7 μm , D_{50} of 10 μm and D_{90} of 34 μm .

This ground granulated high-alumina slag was used in the following examples, as activator of the hydraulic binder.

- 5 Various formulations of mortar compositions were prepared by mixing the constituents in the proportions indicated below in table 1. Composition 1 is given by way of comparison and does not contain the ground granulated high-alumina slag acting as activator. Compositions 2 and 3 are mortar compositions according to the present invention.

Components in %	Composition 1	Composition 2	Composition 3
Slag (4500 Blaine)	35	35	35
Slag (>6500 Blaine)	4.5	4.5	0.0
Fine calcareous filler	5	5	9.5
Cellulose ether	0.40	0.40	0.40
Polymer powder (ethylene-vinyl acetate copolymer)	3.50	3.50	3.50
Siliceous sand	48.9	47.4	47.4
Calcium sulfate	1.5	1.5	1.5
Alkali metal sulfate	0.1	0.1	0.1
Alkali metal carbonate	0.1	0.1	0.1
Portland cement	0.9	0.9	0.9
Ground granulated high-alumina slag	0	1.5	1.5
Lime	0.1	0.1	0.1

Table 1

10

These pulverulent mixtures were mixed with water with a mixing ratio of 26%, at a temperature of 20°C.

Tests were carried out on the mortars having the dry compositions given in table 1; they are summarized in table 2 below.

The consistency of the adhesive mortar is evaluated by measuring the Brookfield viscosity.

The initial adhesion corresponds to a tensile strength test carried out according to the method described in the standard EN 12004. The pull-off
 5 strength expressed in MPa is measured by pulling off after 24 h, according to the method described in the standard EN 1348 § 8.2.

The setting times are given by measuring the Vicat start of setting and the Vicat end of setting.

The jointing time is the time after which the tiles are held sufficiently to
 10 enable the premises to be reopened to traffic and the joints to be created. In order to estimate it under the most unfavorable conditions, it is carried out at 5°C and by simulating a renovation test on nonporous old tiling. Tiles are bonded using a 9x9x9 mm³ comb on an enameled earthenware mockup. The jointing time is defined by qualitatively determining the moment when it
 15 becomes impossible to move the tiles by applying a shearing force.

	Composition 1	Composition 2	Composition 3
Viscosity (Pa.s)	400	470	380
Initial adhesion at 24 h (MPa)	0.3	0.5	0.4
Setting time (h): start of setting/end of setting at 20°C	13/14	7/8.5	7.5/9
Jointing time at 5°C on old tiling	72h	< 24h	< 24h

Table 2

The activation by the ground granulated high-alumina slag makes it possible to greatly accelerate the hardening kinetics at 20°C and also at 5°C.
 20 The jointing time, even under very unfavorable conditions (application at 5°C on old tiling), is bought from 72 h to less than 24 h, i.e. to a performance level

equivalent to that of a conventional adhesive mortar formulation based on Portland cement.

CLAIMS

1. A dry mortar composition comprising:
 - 5 - a hydraulic binder comprising at least one calcium aluminosilicate derivative, at least one ground granulated high-alumina slag comprising less than 30% by weight of silica, said high-alumina slag being a slag wherein alumina is the most abundant constituent, and at least one source of calcium sulfate,
 - aggregates and/or fillers, and
 - 10 - at least one base in an amount of less than or equal to 0.5% of the total weight of the dry mortar composition.
2. The mortar composition as claimed in the preceding claim, such that the
15 ground granulated high-alumina slag comprises between 30% by weight and 60% by weight of alumina, preferably between 32% and 45% by weight of alumina.
3. The mortar composition as claimed in either of the preceding claims, in
20 which the silica content of the ground granulated high-alumina slag is between 5% and 25% by weight, in particular between 10% and 20% by weight.
4. The mortar composition as claimed in one of the preceding claims, such
25 that the ground granulated high-alumina slag is predominantly amorphous.
5. The mortar composition as claimed in one of the preceding claims, such
30 that the ground granulated high-alumina slag is in the form of ground granules having a D50 particle diameter of less than 20 μm , preferably of less than 15 μm .
6. The mortar composition as claimed in one of the preceding claims, such
 that the ground granulated high-alumina slag is derived from the

recycling, by complete melting, of catalysts used for the desulfurization of petroleum products, in particular of catalysts based on molybdenum and/or cobalt.

- 5 7. The mortar composition as claimed in one of the preceding claims, such that the total amount of ground granulated high-alumina slag is between 0.1% and 5% of the total weight of the dry mortar composition.
- 10 8. The mortar composition as claimed in one of the preceding claims, such that the calcium aluminosilicate derivative is chosen from ground granulated blast-furnace slags, fly ash such as aluminosilicate fly ash, calcined clay and/or expanded clay dust, or calcium aluminosilicate fly ash, in particular of coal, in particular of lignite, of sub-bituminous coal or of bituminous coal.
- 15 9. The mortar composition as claimed in the preceding claim, such that at least one calcium aluminosilicate derivative has a fineness of less than 6000 Blaine.
- 20 10. The mortar composition as claimed in one of the preceding claims, such that the binder comprises microparticles of ground granulated blast-furnace slag, the fineness of which is between 6000 and 15000 Blaine.
- 25 11. The mortar composition as claimed in one of the preceding claims, such that the hydraulic binder comprises Portland cement, in an amount of less than 1% of the total weight of the dry mortar composition.
- 30 12. The mortar composition as claimed in one of the preceding claims, wherein the source of calcium sulfate is chosen from plaster, hemihydrate, gypsum and/or anhydrite, alone or as a mixture.
13. The mortar composition as claimed in one of the preceding claims, wherein the base is chosen from alkali or alkaline-earth metal

hydroxides, alkali or alkaline-earth metal carbonates or alkali or alkaline-earth metal silicate derivatives.

5 14. The mortar composition as claimed in one of the preceding claims, further comprising one or more additives, chosen from rheological agents, water-retaining agents, air-entraining agents, thickeners, biocidal protecting agents, dispersants, pigments, accelerators and/or retarders, or polymeric resins.

10 15. A process for preparing a wet mortar composition, in particular an adhesive mortar composition, by mixing the dry mortar composition as claimed in one of the preceding claims with water.