BINDER BASED ON ALUMINA-RICH SLAG

The present invention relates to a hydraulic binder for a mortar composition based on an industrial byproduct, to a mortar composition comprising said binder and also to floor products or technical mortars obtained from such a composition.

Many mortar compositions used in the construction field employ high-alumina cements (also known under the abbreviation CAC for “calcium aluminate cements”) or sulfoaluminate cements (also known under the abbreviation CSA for “calcium sulfoaluminate cements”). These types of CAC cements were developed many years ago and the use thereof is widespread today. Specifically, these cements make it possible in particular to shorten the setting time and therefore to accelerate the hardening of the composition but also to control the dimensional variations during the hardening or also to increase the mechanical strength. Thus, high-alumina or sulfoaluminate cements are used as a mixture with Portland cements in order to achieve rapid setting. The accelerator power of the binary system depends on the CAC/OPC ratio. It is also known that high-alumina or sulfoaluminate cements are used as a mixture with sources of calcium sulfate and optionally of Portland cement in order to control the dimensional variations or else in order to obtain rapid endogenous drying.

One of the current concerns remains to significantly reduce the carbon footprint of construction products. The processes for manufacturing clinker require operations of decarbonation, of calcining, of clinkering by heating, in particular at very high temperatures of the order of 1450°C. High-alumina and Portland cements are for example the cause of emissions of around 800 kg of CO_2 per tonne of cement produced. They also consume energy resources and natural resources.

An alternative solution to high-alumina or sulfoaluminate cements would therefore be of potential interest to manufacturers. The present invention sits within this context, which invention provides a hydraulic binder based on an

industrial byproduct, considered to be a byproduct and therefore recycled very little or not at all until now. The process for preparing the byproduct with a view to the use thereof in construction materials generates a lower amount of CO_2 emissions and therefore makes it possible to improve the carbon footprint.

The present invention relates to a hydraulic binder for a mortar composition, which comprises at least one ground granulated high-alumina slag comprising less than 30% by weight of silica. Within the meaning of the present invention, a “high-alumina slag” is understood to mean a slag wherein alumina is the most abundant constituent.

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 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” 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 inventors have been able to demonstrate that such a slag could replace high-alumina cements, by imparting the same properties of acceleration of the hardening of the composition, of control of the dimensional variations during hardening and of improving the mechanical strength. These properties make the addition of such a binder to mortar compositions for floor products, in particular screeds and coatings, particularly advantageous.

The ground granulated high-alumina slag preferably comprises between 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 relative to all of the components of the ground granulated high-alumina slag. Preferably, the ground granulated high-alumina slag comprises between 12% and 18% by weight of silica.

Preferably, the ground 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 setting time, 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 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 CO_2 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 binder preferably comprises the ground granulated high-alumina slag and at least one of the following constituents:

- one or more cements chosen from Portland cements, belite cements, high-alumina or sulfoaluminate cements, cements formed of pozzolanic mixtures optionally comprising fly ash, silica fumes, limestone, calcined schist and/or natural or calcined pozzolans, and/or
- a source of calcium sulfate chosen from plaster, hemihydrate, gypsum and/or anhydrite, alone or as a mixture.

The binder according to the present invention may be a binary binder, in the sense that it is the mixture of two constituents, or a ternary binder if it is a mixture of three constituents. The binder may also be more complex in its composition and comprise more than three different constituents.

In a binary system comprising the ground granulated high-alumina slag and a cement, advantageously, the binder is constituted of ground granulated high-alumina slag and of Portland cement. Preferentially in a binary system of

this type, the content of ground granulated high-alumina slag is less than 40% by weight, the remainder being the Portland cement. Even more preferentially, the content of ground granulated high-alumina slag is less than 20% by weight. This limited amount of high-alumina slag makes it possible to maintain mechanical strengths that are compatible with the desired applications.

In a binary system constituted of ground granulated high-alumina slag and of a source of calcium sulfate, the content of ground granulated high-alumina slag may be higher. Such a system may comprise up to 90% by weight of ground granulated high-alumina slag.

The binder may also advantageously be a ternary binder and be constituted of ground granulated high-alumina slag, Portland cement and calcium sulfate in one of its various mineralogical forms such as for example plaster. The relative proportions of each of the constituents may vary as a function of the application desired for the mortar. For example, the binder may comprise between 10% and 50% by weight of Portland cement, between 30% and 70% by weight of ground granulated high-alumina slag, and between 10% and 50% by weight of calcium sulfate.

The binder according to the present invention may optionally comprise high-alumina or sulfoaluminate cement. Preferably, said binder is however free of high-alumina or sulfoaluminate cement.

The present invention also relates to a dry mortar composition comprising at least one hydraulic binder according to the invention and aggregates and/or fillers.

The composition is referred to as dry since the majority of these 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.

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 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 which varies generally between 30% and 95 % by weight relative to the dry mortar composition.

Advantageously, the mortar composition according to the present invention comprises a binary hydraulic binder which is a mixture of the ground granulated high-alumina slag comprising less than 30% by weight of silica and Portland cement.

It may also comprise a ternary hydraulic binder which is the mixture of the ground granulated high-alumina slag and of two other binders chosen from:

- a cement chosen from Portland cements, belite cements, high-alumina or sulfoaluminate cements, cements formed of pozzolanic mixtures optionally comprising fly ash, silica fumes, limestone, calcined schist and/or natural or calcined pozzolans, and/or
- a source of calcium sulfate chosen from plaster, hemihydrate, gypsum and/or anhydrite, alone or as a mixture.

Preferably, the mortar composition according to the present invention comprises a ternary hydraulic binder which is the mixture of the ground granulated high-alumina slag comprising less than 30% by weight of silica, Portland cement and a source of calcium sulfate chosen from plaster, hemihydrate, gypsum and/or anhydrite, alone or as a mixture.

Very preferentially, the mortar composition is free of high-alumina or sulfoaluminate cement.

The hydraulic binder preferably represents between 5% and 50% by weight of the total dry mixture of the various pulverulent compositions, as a function of the use selected for the composition.

The mortar composition according to the present invention may comprise an activator chosen from the activators known for their use in compositions for mortars based on ternary binders or on cements.

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 5% by weight relative to the total weight of the dry composition.

The presence of these various additives makes it possible, in particular but not solely, 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.

The present invention also relates to floor products such as coatings or screeds and also to technical mortars capable of being obtained by mixing the dry mortar composition with water.

By way of example, for a self-levelling floor coating, the start of setting is generally less than 2 hours. The spreading values of the wet composition must be generally greater than 150 mm when they are measured at 2 minutes and greater than 135 mm when they are measured at 20 min.

The product obtained after drying and hardening of the wet mortar composition which may be a floor coating or a screed must satisfy certain mechanical characteristics. For example, the flexural strength of these products must in particular be greater than 4 MPa after 28 days, and the compressive strength must be greater than 18 MPa after 28 days for a P3 class.

For floor applications, it is also important that the shrinkage during the drying of the wet composition is controlled. This shrinkage is generally less than 1 mm/m.

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 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%.

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 floor formulations comprising a ternary binder of Portland cement/high-alumina cement/calcium sulfate type. The high-alumina cement is replaced by the byproduct based on ground granulated high-alumina slag.

A mortar formulation for a floor coating is given in table 1 below:

Constituent	Content %
Portland cement	9.4
Ground granulated high-alumina slag	9.4
Calcium sulfate	6.3
Sand	45
Limestone filler	28
Set retarder	0.05
Redispersable polymer powder	1.3
Accelerators from the family of lithium salts, sodium carbonate	0.35
Rheological agents of cellulose ether type	0.08
Superplasticizer	0.12

Table 1

This pulverulent mixture is mixed with water with a mixing ratio of 24%, at a temperature of 23°C. Measurements for characterizing the flexural and

compressive strength according to EN 13892-2, and also the shrinkage and the spreading according to TECHNICAL DOCUMENT of the certification standard of the CERTIFIE CSTB CERTIFIED brand relating to FLOOR COATINGS are carried out in order to evaluate the performance of the hardened product. The mechanical strengths and dimensional variations are measured on 4x4x16 cm test specimens, stored at 23°C, at 50% relative humidity, after 28 days. The results obtained are collated in table 2 below:

	Requirements	Deadlines	Values
Compressive strength (MPa)	>16 (EN 13813)	28 days	22
Flexural strength (MPa)	>4 (EN 13813)	28 days	7.4
Shrinkage 23°C, 50% RH (mm/m)	< 1	28 days	-0.8
Spreading (mm)	>150 (self-levelling)	2 min	150
	>135	20 min	140

Table 2

The performances obtained are in accordance with the specifications required for a self-levelling P3 class floor coating. The compressive strengths are greater than 18 MPa at 28 days, the flexural strengths are greater than 4 MPa. The shrinkage is also less than 1 mm/m at 28 days. The application properties of the coating (in particular the setting time) and also its final mechanical properties are similar to those obtained by mortars based on a ternary binder comprising a high-alumina cement instead of the ground granulated high-alumina slag.

This mortar composition is classed as CT-C20-F7 according to the standard EN 13813.

CLAIMS

1. A hydraulic binder for a mortar composition comprising at least one ground granulated high-alumina slag comprising between 10% to 30% by weight of silica, said high-alumina slag being a slag wherein alumina is the most abundant constituent, said ground granulated high-alumina slag is predominantly amorphous.

2. The binder as claimed in claim 1, such that the 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 binder as claimed in either of the preceding claims, such that the silica content of the ground granulated high-alumina slag is between 10% and 25% by weight, in particular between 10% and 20% by weight.

4. The binder as claimed in the preceding claim, such 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.

5. The binder 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.

6. The binder as claimed in one of the preceding claims comprising said ground granulated high-alumina slag and at least one of the following constituents:

- one or more cements chosen from Portland cements, belite cements, high-alumina or sulfoaluminate cements, cements formed of pozzolanic mixtures optionally comprising fly ash, silica fumes, limestone, calcined schist and/or natural or calcined pozzolans, and/or
- a source of calcium sulfate chosen from plaster, hemihydrate, gypsum and/or anhydrite, alone or as a mixture.

7. The binder as claimed in one of the preceding claims, which is constituted of said ground granulated high-alumina slag and of Portland cement, the content of ground granulated high-alumina slag being less than 40% by weight, preferably less than 20% by weight.

8. The binder as claimed in one of claims 1 to 6, comprising between 10% and 50% by weight of Portland cement, between 30% and 70% by weight of said ground granulated high-alumina slag, and between 10% and 50% by weight of calcium sulfate.

9. A dry mortar composition comprising at least one binder as claimed in one of the preceding claims and aggregates and/or fillers.

10. The composition as claimed in claim 9, which is free of high-alumina or sulfoaluminate cement.

11. The composition as claimed in either of claims 9 and 10, 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.

12. Floor products such as coatings or screeds, or technical mortars, capable of being obtained by mixing the dry mortar composition as claimed in one of claims 9 to 11 with water.

PATENT

Applicant: **SAINT-GOBAIN WEBER**

ABSTRACT

One subject of the invention is a hydraulic binder for a mortar composition comprising at least one ground granulated high-alumina slag comprising less than 30% by weight of silica. Other subjects of the invention are:

- a dry mortar composition comprising at least one such binder and aggregates and/or fillers
- floor products such as coatings or screeds, or technical mortars, capable of being obtained by mixing such a dry mortar composition with water.