

CONCRETE WITH A LOW CONTENT OF CEMENT

FIELD OF THE INVENTION

The invention provides a concrete with a low content of Portland cement, as well as preparation processes of such a concrete and compositions useful for the implementation of these processes.

TECHNICAL BACKGROUND

Technological developments in the field of concretes in the last few years have led to the development of innovative cement formulations making it possible to obtain ultra-high-performance concretes notably in terms of compressive strength. These formulations generally involve the use of extra materials in addition to cement and aggregates and/or sand, which are for example fibers, organic additives or so-called ultrafine particles, generally smaller than cement grains.

For example the document EP 0518777 describes a mortar composition comprising, besides Portland cement: sand with a diameter from 80 μm to 1 mm (in particular from 125 to 500 μm), vitreous microsilica with a diameter from 0.1 to 0.5 μm and a water-reducing agent or plasticizer. The microsilica represents only 10 to 30% by weight relative to the cement.

The document WO 95/01316 describes a concrete composition comprising, besides Portland cement: sand with a diameter of 150 to 400 μm , fine elements with pozzolanic reaction (notably amorphous silica but also fly ash or blast furnace slags) with a diameter less than 0.5 μm , a small quantity of metal fibers and optionally ground quartz powder (average size 10 μm) and small quantities of other additives. The amorphous silica may be present at a rate of 10 to 40% by weight relative to the cement, and the ground quartz powder, when it is used, is typically present at a rate of 40% by weight relative to the cement. The concrete composition in this document therefore requires approximately 900 kg of cement per m^3 of concrete.

In the document WO 95/01317, a concrete composition very similar to the preceding one is disclosed, with exclusively steel wool as metal fibers and amorphous silica as elements with a pozzolanic reaction.

The cement compositions described in the document WO 99/23046 are more specifically devoted to cementing wells and comprise, besides a hydraulic binder: 20 to 35% by weight relative to the microsilica binder with a particle size distribution

from 0.1 to 50 μm , and from 20 to 35% by weight relative to the mineral or organic particle binder with a diameter from 0.5 to 200 μm , as well as a superplasticizer or plasticizer.

5 The document WO 99/28267 relates to a concrete composition comprising cement and metal fibers as well as: from 20 to 60% by weight relative to the cement matrix of granular elements of a type of sieved or ground sand smaller in size than 6 mm; elements with a pozzolanic reaction smaller in size than 1 μm ; acicular or flaky elements smaller in size than 1 mm; and a dispersing agent. In the examples, the elements with a pozzolanic reaction are constituted by vitreous silica at a rate of
10 approximately 30% by weight relative to the Portland cement.

In a relatively similar manner, the document WO 99/58468 describes a concrete composition in which are included at least: a small quantity of organic fibers, granular elements smaller in size than 2 mm, fine elements with a pozzolanic reaction smaller in size than 20 μm and at least one dispersing agent. In the different
15 mentioned examples, the composition comprises approximately 30% of quartz flour and approximately 30% by weight of silica fume relative to the cement.

These proportions between the different particle size ranges are not fundamentally modified in a later document (WO 01/58826) also disclosing other concrete compositions.

20 The document EP 0934 915 describes a concrete prepared from cement in which the grains have an average diameter from 3 to 7 μm , to which are added: sand, silica fume with a characteristic diameter less than 1 μm , an antifoaming agent and a superplasticizer, such that at least three particle size ranges are represented. In light of the different examples, it is noted that the silica fume is in a minority compared to the
25 cement, the latter being typically present in a proportion of approximately 900 kg per m^3 of concrete.

Analysis of the prior art shows:

1) that the optimization of the formulations is specifically directed towards the high or ultra-high-performance concretes and does not generally apply
30 to ordinary concretes; and

2) that all the currently known concretes have a relatively high cement content.

Thus, even if standard concretes, which provide less good performances in terms of compressive strength than the abovementioned concretes, for example the B25-type of concretes (i.e. the compressive strength 28 days after mixing is at least 25

MPa) are examined, it is noted that the quantity of cement is typically 260 to 360 kg per m³ of concrete. Moreover, current European standards do not provide cement levels below 260 kg/m³ for ordinary concretes.

Now, the processes for cement production, and more particularly its prime constituent, clinker, are responsible for high carbon dioxide emissions. The production of clinker grains in fact requires:

- a) preheating and decarbonation of the raw meal that is obtained by grinding the raw materials, which are notably limestone and clay; and
- b) firing or clinkering the meal at a 1500°C temperature, followed by rapid cooling.

These two stages produce CO₂, on the one hand as a direct product of the decarbonation and on the other hand as a by-product of the combustion that is implemented in the firing stage in order to raise the temperature.

The emission level therefore reaches a minimum of approximately 560 kg of CO₂ per tonne of binder for a standard B25 concrete (based on an average 850 kg of CO₂ emitted per tonne of cement), and this is even greater for an ultra-high performance concrete.

Now, the high carbon dioxide emissions in standard production processes of cement and concrete compositions constitute a major environmental problem, and, in the current context, are subject to high economic penalties.

A strong need therefore exists for a process making it possible to produce concrete with reduced associated carbon dioxide emissions, the said concrete providing satisfactory mechanical properties, and in particular equivalent to those of existing ordinary concretes, in view of its use in the construction industry.

SUMMARY OF THE INVENTION

The invention therefore provides a mixture comprising in mass proportions:

- from 0.4 to 4%, preferably from 0.8 to 1.7%, of materials in the ultrafine particle size range, comprising particles with a D₉₀ less than 1 µm and/or a specific BET surface area greater than 6 m²/g;
- from 1 to 6%, preferably from 2 to 5%, of Portland cement;
- from 8 to 25%, preferably from 12 to 21%, of materials in the fine particle size range, comprising particles wherein the D₁₀ and the D₉₀ are from 1 µm to 100 µm and with a specific BET surface area less than 5 m²/g,

different from the cement;

- from 25 to 50%, preferably from 30 to 42%, of materials in the medium particle size range, comprising particles wherein the D10 and the D90 are from 100 μm to 5 mm; and
- 5 - from 25 to 55%, preferably from 35 to 47%, of materials in the larger particle size range, comprising particles wherein the D10 is greater than 5 mm.

The invention also provides a binder premix comprising:

- Portland cement;
- 10 - a fine particle size range as defined above; and
- an ultrafine particle size range as defined above;

in which the mass proportion of Portland cement in the premix is less than 50% and preferably from 5 to 35%, more preferably from 10 to 25%.

Advantageously, the mass proportion of the ultrafine particle size range in the
15 said binder premix is from 2 to 20%, preferably from 5 to 10%.

Advantageously, the binder premix according to the invention comprises in mass proportions:

- from 5 to 35% preferably from 10 to 25%, of Portland cement;
- from 60 to 90%, preferably from 65 to 85%, of materials in the fine
20 particle size range, and
- from 2 to 20%, preferably from 5 to 10%, of materials in the ultrafine particle size range.

According to one advantageous embodiment of the mixture or binder premix according to the invention, the ultrafine particle size range comprises materials chosen
25 from the group composed of silica fumes, limestone powders, precipitated silicas, precipitated carbonates, pyrogenated silicas, natural pozzolans, pumice stones, ground fly ash, ground hydrated or carbonated silicic hydraulic binder, and mixtures or co-grinds thereof, in dry form or aqueous suspension.

According to a particular embodiment of the mixture or binder premix
30 according to the invention, the mixture (Portland cement and fine particle size range) comprises:

- a first particle size sub-range, comprising particles wherein the D10 and the D90 are from 1 to 10 μm ; and
- a second particle size sub-range, comprising particles wherein the D10

and the D90 are from 10 to 100 μm ;

and in which the first particle size sub-range comprises Portland cement.

According to one alternative embodiment of the mixture or binder premix according to the invention, the mixture (Portland cement and fine particle size range)

5 comprises particles wherein the D10 and the D90 are from 1 to 20 μm .

According to one advantageous embodiment of the mixture or binder premix as defined above, the fine particle size range comprises one or several materials chosen from fly ash, pozzolans, limestone powders, siliceous powders, lime, calcium sulfate, slags.

10 Advantageously, the mixture or premix as defined above comprises:

- Portland cement and fly ash; or
- Portland cement and limestone powder; or
- Portland cement and slag; or
- Portland cement, fly ash and limestone powder; or
- 15 - Portland cement, fly ash and slag; or
- Portland cement, limestone powder and slag; or
- Portland cement, fly ash, limestone powder and slag.

According to one embodiment, the mixture or binder premix comprises Portland cement and fly ash and does not comprise slag.

20 According to one embodiment, the mixture or binder premix comprises Portland cement and slag and does not comprise fly ash.

Advantageously, the mixture or binder premix as defined above also comprises:

- a plasticizer
- 25 - optionally an accelerator and/or an air-entraining agent and/or a thickening agent and/or a retarder.

According to one advantageous embodiment of the binder premix as defined above, the proportion of plasticizer is from 0.05 to 3%, preferably from 0.1 to 0.5% expressed as a mass ratio of dry extract of plasticizer to the mass of binder premix.

30 The invention also provides a mixture comprising:

- a binder premix as defined above;
- a medium particle size range as defined above; and
- a larger particle size range as defined above.

Advantageously, the said mixture comprises, in mass proportions:

- from 10 to 35%, preferably from 15 to 25%, of binder premix;
- from 25 to 50%, preferably from 30 to 42%, of materials in the medium particle size range; and from 25 to 55%, preferably from 35 to 47%, of materials in the larger particle size range.

5 According to one advantageous embodiment of the abovementioned mixture:

- the medium particle size range comprises sand and/or fine sand; and
- the larger particle size range comprises aggregates and/or gravel and/or pebbles and/or fine gravel.

10 According to one advantageous embodiment of the abovementioned mixture, the spacing coefficient of the skeleton to the binder is from 0.5 to 1.3, preferably from 0.7 to 1.0.

The invention also provides a composition of wet concrete, comprising:

- a mixture according to the invention, mixed with
- water,

15 Advantageously, the said composition of wet concrete comprises:

- from 10 to 100 kg/m³, preferably from 20 to 40 kg/m³ of materials in the ultrafine particle size range as defined above;
- from 25 to 150 kg/m³, preferably from 50 to 120 kg/m³, more preferably, from 60 to 105 kg/m³, of Portland cement;
- 20 - from 200 to 600 kg/m³, preferably from 300 to 500 kg/m³ of materials in the fine particle size range as defined above;
- from 600 to 1200 kg/m³, preferably from 700 to 1000 kg/m³ of materials in the medium particle size range as defined above;
- from 600 to 1300 kg/m³, preferably from 800 to 1100 kg/m³ of materials in the larger particle size range as defined above; and
- 25 - optionally, a plasticizer.

Advantageously, the said composition of wet concrete also comprises:

- an accelerator and/or an air-entraining agent and/or a thickening agent and/or a retarder.

30 According to one advantageous embodiment of the composition of wet concrete according to the invention, the W/C ratio, where W designates the quantity of water and C the quantity of Portland cement, is from 1 to 2.5, preferably from 1.3 to 1.5. Other possible ranges for the W/C ratio are for example: from 1 to 1.3; from 1 to 1.5; from 1.3 to 2.5; and from 1.5 to 2.5.

According to one advantageous embodiment of the composition of wet concrete according to the invention, the W/B ratio, where W designates the quantity of water and B the quantity of materials in the mixture (Portland cement and fine particle size range), is from 0.1 to 0.45, preferably from 0.18 to 0.32. Other possible
 5 ranges for the W/B ratio are for example: from 0.1 to 0.18; from 0.1 to 0.32; from 0.18 to 0.45; and from 0.32 to 0.45.

The W/C and W/B ratios are notably adjusted according to the desired amount of cement and final mechanical properties. With a lower amount of cement, the ratio will also be relatively lower. Routine testing by a person skilled in the art will
 10 determine the amount of water as related to the amount of cement, fine and ultrafine particles of the composition, according to the compressive strength measurements of the samples.

Advantageously the composition of wet concrete according to the invention comprises from 60 to 180 l/m³, preferably from 80 to 150 l/m³, more preferably from
 15 95 to 135 l/m³ of water.

According to one advantageous embodiment, the composition of wet concrete according to the invention is a self-placing concrete.

The invention further provides a concrete composition comprising less than 150 kg/m³, preferably less than 120 kg/m³, more preferably, from 60 to 105 kg/m³, of
 20 Portland cement and having a compressive strength greater than or equal to 4 MPa 16 hours after mixing, and greater than or equal to 25 MPa, preferably greater than or equal to 30 MPa, 28 days after mixing.

The invention also provides an object of hardened concrete of the composition defined above.

25 The invention further provides an object of hardened concrete, comprising:

- from 10 to 100 kg/m³, preferably from 20 to 40 kg/m³ of materials in the ultrafine particle size range as defined above;
- Portland cement hydrates in a quantity corresponding to a quantity of Portland cement of 25 to 150 kg/m³, preferably from 50 to 120 kg/m³,
 30 more preferably, from 60 to 105 kg/m³;
- from 200 to 600 kg/m³, preferably from 300 to 500 kg/m³ of materials in the fine particle size range as defined above;
- from 600 to 1200 kg/m³, preferably from 700 to 1000 kg/m³ of materials in the medium particle size range as defined above;

- from 600 to 1300 kg/m³, preferably from 800 to 1100 kg/m³ of materials in the larger particle size range as defined above.

According to one advantageous embodiment of the object of hardened concrete according to the invention, the spacing coefficient of the skeleton by the binder is from 0.5 to 1.3, preferably from 0.7 to 1.0.

Advantageously, the object of hardened concrete according to the invention shows shrinkage less than 400 µm/m, preferably less than 200 µm/m, after 80 days.

The invention further provides a method for the preparation of a composition of wet concrete comprising a step of:

- mixing a mixture according to the invention with water.

The invention moreover provides a process for preparation of a composition of wet concrete comprising a step of:

- mixing a binder premix according to the invention with materials in the medium particle size range as defined above, materials in the larger particle size range as defined above and water.

According to one embodiment of the process for preparation of a composition of wet concrete according to the invention, the amount of Portland cement used is less than 150 kg/m³, preferably less than 120 kg/m³, more preferably from 60 to 105 kg/m³.

The invention moreover provides a process for preparation of a composition of wet concrete comprising a step of mixing:

- from 10 to 100 kg/m³, preferably from 20 to 40 kg/m³, of materials in the ultrafine particle size range as defined above;
- from 25 to 150 kg/m³, preferably from 50 to 120 kg/m³, more preferably, from 60 to 105 kg/m³ of Portland cement;
- from 200 to 600 kg/m³, preferably from 300 to 500 kg/m³ of materials in the fine particle size range as defined above;
- from 600 to 1200 kg/m³, preferably from 700 to 1000 kg/m³ of materials in the medium particle size range as defined above;
- from 600 to 1300 kg/m³, preferably from 800 to 1100 kg/m³ of materials in the larger particle size range as defined above; and
- optionally, a plasticizer and/or an accelerator and/or an air-entraining agent and/or a thickening agent and/or a retarder; with
- water.

According to one advantageous embodiment of the process for preparation of a composition of wet concrete according to the invention, the mixing is carried out with a W/C ratio, where W designates the quantity of water and C the quantity of Portland cement, from 1 to 2.5, preferably from 1.3 to 1.5.

5 According to one advantageous embodiment of the process for preparation of a composition of wet concrete according to the invention, the mixing is carried out with a W/B ratio from 0.1 to 0.45, preferably from 0.18 to 0.32, where W designates the quantity of water and B the quantity of materials in the mixture (Portland cement and fine particle size range).

10 According to one advantageous embodiment of the process for preparation of a composition of wet concrete according to the invention, the quantity of water used is from 60 to 180 l/m³, preferably from 80 to 150 l/m³, more preferably from 95 to 135 l/m³.

15 According to one embodiment of the process for preparation of a composition of wet concrete according to the invention, the compressive strength is greater than or equal to 4 MPa 16 hours after mixing.

According to one embodiment of the process for preparation of a composition of wet concrete according to the invention, the compressive strength is greater than or equal to 25 MPa, preferably greater than 30 MPa 28 days after mixing.

20 The invention further provides a process for preparation of a cast wet concrete, comprising a step of:

- casting a composition of wet concrete according to the invention, or obtainable by the abovementioned process.

25 The invention also provides a process for the production of an object in concrete, comprising a step of:

- hardening a composition of wet concrete according to the invention or obtainable by the process for preparation of an abovementioned composition of wet concrete, or of a composition of cast wet concrete as described above.

30 The invention makes it possible to meet the need to reduce CO₂ emissions, hitherto unsatisfied, by known concretes. Indeed, the quantity of cement (and in particular of clinker) used within the scope of this invention is less than that which is conventionally necessary. For example, for a formula according to the invention with 70 kg of clinker per m³ of concrete, the CO₂ emission is of the order of 110 kg per

tonne of binder, which represents a reduction of almost 80% in the CO₂ emission compared to a standard B25 type of concrete, while not inducing any significant reduction of the mechanical performances of the concrete, since the invention provides a concrete with a mechanical compressive strength greater than or equal to
 5 25 MPa 28 days after mixing.

The concrete obtained according to the invention also has the following advantages:

- its behavior to corrosion of the reinforcements in reinforced concrete is at least as good or even better compared to a standard B25 type of concrete;
- 10 - its porosity and permeability are less than those of a standard B25-type concrete;
- its shrinkage is less than that of a standard B25-type concrete;
- its resistance to chloride diffusion is better compared to a standard B25 type of concrete.

15 The different purposes and advantages of the invention are obtained by means of full optimization of all of the formulation parameters, and notably by means of:

- the development of binder compositions having a compartmentalization of the materials into separate particle size ranges, notably into a fine range, a medium range, a larger range, and an ultrafine range, which allows
 20 optimization of the packing of the different particles, and optimization of the spacing coefficient of the skeleton by the binder;
- the presence, in addition to the cement, of non-cement binder materials belonging to the fine particle size range, which are the majority as related to the cement the choice and proportions of which are optimized;
- 25 - the use of ultrafines, notably elements with a pozzolanic reaction, capable of participating in the hydraulic binding function;
- adjustment of the water demand;
- optimization of the different additives.

30 BRIEF DESCRIPTION OF THE FIGURES

Figures 1a to 1d represent the particle-size distribution profiles of various materials used to prepare dry compositions according to the invention as well as associated mixed concretes. The size in μm is shown on the x-axis and the percentage by volume on the y-axis. Reference may be made to the examples section for the

meaning of the names of the materials. **Figure 1a** thus provides the profile of the materials used for example in the formulae FA1, FA 2, FA 7 or FA 8 below; **Figure 1b** provides that of the materials used for example in the formula FA 3 below; **Figure 1c** provides that of the materials used for example in the formulae FA 4 or FA 5 below; **Figure 1d** provides that of the materials used for example in the formulae FC1, FC2 or FC3 below.

Figure 2 is a photograph that provides a diagrammatic representation of a typical composition of dry mortar according to the invention (on the left) compared with a standard B25 type of composition of dry mortar (on the right). The different constituents are the following: A, filler (limestone filler in the specimen on the right, fly ash in the specimen on the left); B, cement; C, sand; D, aggregates; E, water; F, silica fumes.

Figure 3 represents the shrinkage measured on a concrete according to the invention (x) compared with a control standard B25 concrete ($\square$). The time, in days, is shown on the x-axis and the dimensional variation of the concrete, as a %, on the y-axis.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

The invention will now be described in more detail and not limited to the following description.

Distribution of the particle size ranges

The invention provides dry mortar compositions in the form of mixtures of various constituents, in the following mass proportions:

- from 1 to 6%, preferably from 2 to 5% of Portland cement;
- from 0.4 to 4%, preferably from 0.8 to 1.7% of materials in the ultrafine particle size range;
- from 8 to 25%, preferably from 12 to 21%, of materials in the fine particle size range, different from the cement;
- from 25 to 50%, preferably from 30 to 42%, of materials in the medium particle size range;
- from 25 to 55%, preferably from 35 to 47%, of materials in the larger particle size range.

The materials that comprise the above mixture are present in the form of

particles, i.e. unitary elements of materials. The particle-size distribution makes it possible to establish a division of the constituents into several “particle size ranges”, i.e. into essentially separate compartments.

Thus, the ultrafine particle size range is constituted of:

- 5 (i) particles with a D90 less than 1 μm or
- (ii) particles with a specific BET surface area greater than 6 m^2/g or
- (iii) particles with a D90 less than 1 μm and with a specific BET surface area greater than 6 m^2/g .

10 The fine particle size range corresponds to a group of particles wherein the D10 and the D90 are from 1 μm to 100 μm and the specific BET surface area is less than 5 m^2/g . The medium particle size range corresponds to a group of particles wherein the D10 and the D90 are from 100 μm to 5 mm. And the larger particle size range corresponds to a group of particles wherein the D10 is greater than 5 mm.

15 The D90 corresponds to the 90th percentile of the particle-size distribution, i.e. 90% of the particles are smaller than the D90 and 10% are larger than the D90. Similarly the D10 corresponds to the 10th percentile of the particle-size distribution, i.e. 10% of the particles have a size smaller than the D10 and 90% have a size larger than the D10.

The D10 and the D90 are the D_{V10} and the D_{V90} as shown on the drawings.

20 In other words: at least 80% of the particles in the fine particle size range (preferably at least 90%, more preferably at least 95% or even at least 99%) have a size from 1 μm to 100 μm ; at least 80% of the particles in the medium particle size range (preferably at least 90%, more preferably at least 95% or even at least 99%) have a size from 100 μm to 5 mm; at least 90% of the particles in the larger particle size range (preferably at least 95% or even at least 99%) have a size larger than 5 mm; and, according to the embodiments corresponding to cases (i) and (iii) above, at least 90% of the particles in the ultrafine particle size range (preferably at least 95%, more preferably at least 99%) have a size smaller than 1 μm . The four particle size ranges (ultrafine, fine, medium and larger) then correspond to essentially separate size compartments.

30

The D10 or D90 of a group of particles may generally be determined by laser particle-size analysis for particles smaller than 200 μm , or by sieving for the particles larger than 200 μm .

Nevertheless, when the individual particles tend to aggregate, their size should

be determined by electron microscopy, given that the apparent size measured by laser diffraction particle-size analysis is then greater than the real particle size, which could falsify the interpretation.

The specific BET surface area is a measurement of the total real surface area of the particles that takes into account the presence of reliefs, irregularities, surface or internal cavities, and porosity.

According to one alternative embodiment, there may be an overlapping from the sizes of the particles in the fine and ultrafine ranges, i.e. more than 10% of the particles in the ultrafine and fine ranges respectively may be located in the same size range. In this case, the distinction of the fine and ultrafine range is ensured by the specific BET surface area, the ultrafine particles being those that have the largest specific surface area (and therefore high reactivity). In particular, in this case, the specific BET surface area of the materials in the ultrafine range is preferably greater than $10 \text{ m}^2/\text{g}$, advantageously greater than $30 \text{ m}^2/\text{g}$, and more preferably greater than $80 \text{ m}^2/\text{g}$. It should moreover be noted that the materials in the ultrafine range may also have these preferred specific BET surface area values even in the case where their D_{90} is less than $1 \text{ }\mu\text{m}$.

One example of a case where the ultrafine and fine ranges differ only by the specific BET surface area and not by the size of the particles may be that where the ultrafine particles comprise ground hydrated hydraulic binder. In this example, the ultrafine particles may have a size of the order of $10 \text{ }\mu\text{m}$, for a specific surface area that may be of the order of $100 \text{ m}^2/\text{g}$ (due to the porosity of this material).

Another particular embodiment of the present invention allows the subdivision of the mixture comprising the cement and the fine particle size range into two particle size sub-ranges:

- a first particle size sub-range, constituted of particles wherein the D_{10} and D_{90} are from 1 to $10 \text{ }\mu\text{m}$; and
- a second particle size sub-range, constituted of particles wherein the D_{10} and D_{90} are from 10 to $100 \text{ }\mu\text{m}$.

In this case, the cement belongs in particular to the first particle size sub-range.

In other words, according to this embodiment, at least 80% of the particles in the first particle size sub-range (preferably at least 90%, most preferably at least 95% or even at least 99%) have a size from 1 to $10 \text{ }\mu\text{m}$, and at least 80% of the particles in

the second particle size sub-range (preferably at least 90%, most preferably at least 95% even at least 99%) have a size from 10 to 100 μm . Still according to this embodiment, the mixture comprises 5 particle size ranges or 5 essentially separate compartments: the ultrafine range (less than 1 μm); the first sub-range of the cement + fine range mixture (1 μm - 10 μm); the second sub-range of the cement + fine range mixture (10 μm - 100 μm); the medium range (100 μm - 5 mm); and the larger range (greater than 5 mm).

According to one alternative embodiment, the mixture comprising the cement and the fine particle size range comprises particles wherein the D10 and D90 are from 1 to 20 μm . In other words, according to this embodiment, at least 80% of the particles of cement or of materials in the fine particle size range (preferably at least 90%, most preferably at least 95% even at least 99%) have a size from 1 to 20 μm . This embodiment corresponds to the case where the particle-size distribution profile comprises a discontinuity: the mixture comprises almost no particles with a diameter from 20 to 100 μm .

The different embodiments described above correspond to optimized packing modes of grains or particles. The invention also provides, as described above, the binder premixes that correspond to these mixtures for dry mortars, and which contain no materials in the medium particle size range, nor materials in the larger particle size range. The said binder premixes are intended to be mixed with materials in the medium and larger particle size range before or at the time of preparation of the concrete.

Preferably, the mixtures according to the invention are characterized by a spacing coefficient of the skeleton by the binder comprised from 0.5 to 1.3, preferably from 0.7 to 1.0. The “skeleton” designates the materials in the medium and larger particle size range, and the “binder” designates the cement as well as the materials in the fine and ultrafine particle size range. The “spacing coefficient” in question therefore designates the ratio between the volume of binder and the pore volume of the skeleton. This coefficient is calculated notably from the vibrated porosity of the skeleton.

Choice of materials

In the compositions as defined above, the cement is Portland cement chosen from among the standard CPA-type (Artificial Portland Cement) of Portland cements,

and notably from the cements described in the European Standard EN 197-1. It is possible to use for example a CEM1 or CEM2 52.5 N or R or PM (for marine construction) cement or PMES cement (for marine construction, sulfated water). The cement may be of the HRI type (High Initial Strength). In some instances, notably for

5 the CEM2 type, the Portland cement does not comprise pure clinker but is provided admixed with at least one additional material (slag, silica fume, pozzolan, fly ash, calcined schist, lime etc.) in an amount of up to 37%. In these cases, the abovementioned amounts of cement more particularly correspond to the amounts of clinker, whereas the additional materials are counted within the appropriate particle

10 size range (e.g. typically the fine particle size range for the slag component, the ultrafine particle size range for the silica fume component, etc.).

The larger particle size range may comprise aggregates and/or gravel and/or pebbles and/or fine gravel.

The medium particle size range may notably comprise sand or fine sand.

15 The fine particle size range may comprise one or more materials chosen from among fly ash, pozzolans, limestone powders, siliceous powders, lime, calcium sulfate (in particular gypsum in anhydrous or semi-hydrated form), slags.

The word “fillers” is sometimes used to designate most of the above materials.

It is particularly interesting to mix the cement with the following products: fly

20 ash alone; or limestone powder alone; or slag alone; or fly ash and limestone powder; or fly ash and slag; or limestone powder and slag; or fly ash, limestone powder and slag.

According to one variant, the fine particle size range comprises fly ash (optionally in association with yet other materials) but does not comprise slag.

25 According to one alternative variant, the fine particle size range comprises slag (optionally in association with yet other materials) but does not comprise fly ash. These two variants limit the total CO₂ cost of the premix and the mixture, since the production of slag and fly ash is associated with CO₂ emissions. This advantage in terms of limiting the CO₂ cost is particularly clear as far as the first variant is

30 concerned.

The ultrafine particle size range may comprise materials chosen from among the group comprising silica fumes, limestone powders, precipitated silicas, precipitated carbonates, pyrogenated silicas, natural pozzolans, pumice stones, ground fly ash, ground hydrated or carbonated siliceous hydraulic binder, and mixtures or co-

grinds thereof, in dry form or aqueous suspension.

The term “ground hydrated siliceous hydraulic binder” notably designates the products described in the document FR 2708592.

Any standard plasticizer (or superplasticizer) may advantageously be added to a mixture or binder premix according to the invention, preferably at a concentration of 0.05 to 3%, preferably from 0.2 to 0.5%, expressed as a mass ratio of dry extract of the plasticizer to the mass of binder premix. The plasticizer may be used at saturation or not. The amount of plasticizer is also determined as a function of the desired quality of the paste, notably depending on whether a self-placing concrete is desired or not. Slump measurements make it possible to determine the type and quantity of plasticizer that should be used in the formulation.

Other known additives or admixtures may also be used within the framework of the invention, for example superplasticizers, accelerators, air-entraining agents, thickening agents, retarders etc.

Concrete

The concrete according to the invention is prepared by mixing the above mixtures or the above binder premixes with water. In this case, the quantity of Portland cement that is used is advantageously less than 150 kg/m^3 , preferably less than 120 kg/m^3 , more preferably comprised from 60 to 105 kg/m^3 . It may also be prepared by directly mixing the different ingredients with each other and with the water, in the following proportions:

- from 10 to 100 kg/m^3 , preferably from 20 to 40 kg/m^3 of materials in the ultrafine particle size range;
- from 25 to 150 kg/m^3 , preferably from 50 to 120 kg/m^3 , more preferably from 60 to 105 kg/m^3 , of Portland cement;
- from 200 to 600 kg/m^3 , preferably from 300 to 500 kg/m^3 of materials in the fine particle size range;
- from 600 to 1200 kg/m^3 , preferably from 700 to 1000 kg/m^3 of materials in the medium particle size range;
- from 600 to 1300 kg/m^3 , preferably from 800 to 1100 kg/m^3 of materials in the larger particle size range; and
- optionally, a plasticizer.

“ kg/m^3 ” is understood as the mass of materials to be used per m^3 of produced

concrete.

The materials in question, depending on the particular embodiments, have the same characteristics as those that have been described above in relation to the mixtures and binder premixes according to the invention.

5 The quantity of mixing water is reduced compared to a standard concrete, from 60 to 180 l/m³, preferably from 80 to 150 l/m³, more preferably from 95 to 135 l/m³ of water. The W/B ratio, where W designates the quantity of water and B the quantity of binder (materials of the mixture (Portland cement + fine particle size range)), is therefore reduced compared to a standard concrete, and is typically from
10 0.1 to 0.45, preferably from 0.18 to 0.32. On the other hand, the W/C ratio, where W designates the quantity of water and C the quantity of cement, is greater than in the case of standard concrete, due to the small quantity of cement that is present. The W/C ratio is preferably from 1 to 2.5, most preferably from 1.3 to 1.5.

15 The mixing is carried out using a conventional mixer, for the usual mixing period in the field.

20 According to one embodiment, the compositions of concrete formulated according to the invention are the result of a complex optimization of the different parameters involved (choice of materials and concentration thereof) in order to guarantee optimized packing (choice of particle size and choice of the admixturization), optimized hydration chemistry (numerous components indeed participate in the reaction: limestone powder, fly ash, silica fumes etc.) and an optimized water demand.

25 The constituents of the ultrafine range, notably the silica fumes, may have multiple functions, namely a filling role of free spaces between particles, a role providing heterogeneous hydrate nucleation sites, an adsorption role of the alkalis and the calcium that are attracted by the surface silanol groups and a pozzolanic role.

30 The concrete compositions obtained according to the invention have comparable mechanical properties, preferably at least as good even better compared to standard B25 types of concretes, notably in terms of 28-day compressive strength, setting, shrinkage, and durability kinetics.

In particular, according to one embodiment of the invention, the compressive strength is greater than or equal to 4 MPa 16 hours after mixing, and greater than or equal to 25 MPa, preferably greater than or equal to 30 MPa, 28 days after mixing. Moreover, shrinkage after 80 days is advantageously less than 400 µm/m, preferably

less than 200 $\mu\text{m}/\text{m}$.

Preferably, the concretes according to the invention are fluid or self-placing concretes.

A concrete is considered to be fluid when the slump value measured using the
 5 Abrams cone (according to the French standard NF P 18-451, of December 1981) is at least 150 mm, preferably at least 180 mm. A concrete is considered to be self-placing when the spread value is greater than 650 mm for the concretes (and in general less than 800 mm) according to the operating procedure described in *Specification and Guidelines for Self Compacting Concrete*, EFNARC, February 2002, p. 19-23.

10 The quantity of cement used to prepare the concrete according to the invention is much less than that which is necessary to prepare a standard B25 type of concrete, which makes it possible to make spectacular savings in terms of CO_2 emissions. Compared to a reference B25 formula that contains 95 kg/m^3 of limestone and 260 kg/m^3 of cement, a concrete according to the invention containing for example 70
 15 kg/m^3 of clinker makes it possible to make savings in CO_2 emissions of approximately 80%. These savings may reach more than 85% if only 50 kg/m^3 of clinker is used.

The concrete according to the invention may be cast according to the usual methods; after hydration/hardening, hardened concrete objects are obtained, such as
 20 construction elements, engineering structural elements or others.

EXAMPLES

The following examples illustrate the invention without limiting it.

Example 1: laser granulometry method

25 The particle size curves of the different powders are obtained using a Malvern MS2000 laser granulometer. The measurement is carried out by the wet method (aqueous medium); the particle size must be from 0.02 μm to 2 mm. The light source is provided by a red He-Ne laser (632 nm) and a blue diode (466 nm). The Fraunhofer
 30 optical model is used, the calculation matrix is of the polydisperse type.

A measurement of background noise is first carried out at a pump speed of 2000 rpm, a stirrer speed of 800 rpm and a noise measurement over 10 s, in the absence of ultrasounds. Then the light intensity of the laser is verified to be at least equal to 80%, and that a decreasing exponential curve for the background noise is

obtained. Otherwise, the cell lenses must be cleaned.

A first measurement is then carried out on the sample with the following parameters: pump speed 2000 rpm, stirrer speed 800 rpm, absence of ultrasounds, obscuration limit from 10 to 20 %. The sample is introduced so as to have an obscuration slightly greater than 10 %. After stabilization of the obscuration, the measurement is carried out for a duration between immersion and the measurement set at 10 s. The duration of the measurement is 30 s (30000 diffraction images analyzed). In the obtained particle size diagram, the fact that part of the population of powder may be agglomerated should be taken into account.

Then a second measurement is carried out with ultrasounds (without emptying the tank). The pump speed is set at 2500 rpm, the stirring at 1000 rpm, ultrasounds are emitted at 100% (30 watts). This regime is maintained for 3 minutes, then the initial parameters are used again: pump speed 2000 rpm, stirrer speed 800 rpm, absence of ultrasounds. At the end of 10 s (to remove any possible air bubbles), a measurement is made for 30 s (30000 images analyzed). This second measurement corresponds to a de-agglomerated powder by ultrasonic dispersion.

Each measurement is repeated at least twice to verify the stability of the results. The device is calibrated before each work session by means of a standard sample (Sifraço C10 silica) for which the size distribution curve is known. All the measurements given in the description and the reported ranges correspond to the values obtained with ultrasounds.

Example 2: method of direct visualization by scanning electron microscopy

For powders with a strong tendency to agglomerate, the technique of direct visualization by scanning electron microscopy is used (with measurement and counting of the particles on the obtained image). Each sample of powder is optionally dried by passing it through a drying oven at a temperature less than 50°C, or under vacuum or by lyophilization. Then two alternative methods to prepare the sample are used: preparation on adhesive tape to globally observe the powder (agglomeration effect, etc.) and preparation in suspension to individually characterize the particles (size, shape, surface aspect, etc.)

In the preparation on adhesive tape, a metal block is taken and a double-sided self-adhesive conductive patch or double-sided self adhesive conductive tape is placed on its upper surface. Using a spatula, the powder to be examined is sprinkled on this

surface, paying attention to the electrostatic effects during the sampling and sprinkling. The surface equipped with the double-sided adhesive tape may equally be applied on the powder to be examined. The excess powder not retained by the adhesive tape is removed by tapping the block, the upper side is maintained vertically,
 5 on a hard surface. Optionally, the sample is lightly blown with a dry air spray to remove any particles that are badly fixed, and metallization is carried out.

A graphite block is used to prepare the suspension. It is cleaned with ethanol, the surface is polished with a polishing paste (for example PIKAL). Approximately 10 cm³ of the suspension liquid, in this case ethanol, is introduced in a beaker. The
 10 powder to be observed is gradually added, the beaker being placed in an ultrasonic tank (in order to obtain low opacity of the suspension). Application of ultrasounds is continued once introduction of the powder is complete. Then a few drops of the suspension are sampled and placed on the graphite block. The sampling is carried out using a micropipette or spatula. In order to avoid sedimentation phenomena, the
 15 sampling is carried out as rapidly as possible, without stopping stirring the suspension. The liquid is then evaporated, optionally by placing the block under an infra-red lamp. The deposited film must be very fine not showing any accumulation, it must be scarcely visible to the naked eye. Otherwise, the sample cannot be used. The insufficiently retained excess powder on the surface is removed by tapping the block,
 20 the upper surface is maintained vertically, on a hard surface. Optionally, the sample is lightly blown with a dry air spray to remove the particles that are badly, and metallization is carried out.

Metallization is carried out by spraying a flow of molten metal (or carbon) under vacuum. The SEM measurement itself is carried out in a conventional manner
 25 known to a person skilled in the art.

Example 3: Measurement method of the Specific BET surface area

The specific surface area of the different powders is measured as follows. A sample of powder of the following mass is taken: 0.1 to 0.2 g for an estimated specific
 30 surface area of more than 30 m²/g; 0.3 g for an estimated specific surface area of 10-30 m²/g; 1 g for an estimated specific surface area of 3-10 m²/g; 1.5 g for an estimated specific surface area of 2-3 m²/g; 2 g for an estimated specific surface area of 1.5-2 m²/g; 3 g for an estimated specific surface area of 1-1.5 m²/g.

A 3 cm³ or 9 cm³ cell is used depending on the volume of the sample. The

measurement cell assembly is weighed (cell + glass rod). Then the sample is added to the cell: the product must not be at less than one millimeter from the top of the opening of the cell. The assembly is weighed (cell + glass rod + sample). The measurement cell is placed on a degassing unit and the sample is degassed. Degassing parameters are 30 min/45°C for Portland cement, gypsum, pozzolans; 3 h/200°C for slags, silica fumes, fly ash, high-alumina cement, limestone; and 4 h/300°C for the control alumina. The cell is rapidly closed with a stopper after degassing. The assembly is weighed and the result noted. All weighing is carried out without the stopper. The mass of the sample is obtained by subtracting the mass of the cell from the mass of the cell + degassed sample.

The analysis of the sample is then carried out after placing it on the measurement unit. The analyzer is the Beckman Coulter SA 3100. The measurement is based on the adsorption of nitrogen by the sample at a given temperature, in this case the temperature of liquid nitrogen i.e. – 196°C. The apparatus measures the pressure of the reference cell in which the adsorbate is at its saturation vapor pressure and that of the sample cell in which known volumes of adsorbate are injected. The resulting curve of these measurements is the adsorption isotherm. In the measurement process, it is necessary to know the dead space of the cell: a measurement of this volume is therefore carried out with helium before the analysis.

The previously calculated mass of the sample is entered as a parameter. The specific BET surface is determined by the software by linear regression from the experimental curve. The obtained reproducibility standard deviation from 10 measurements on a silica with a 21.4 m²/g specific surface area is 0.07. The obtained reproducibility standard deviation from 10 measurements on a cement of with a 0.9 m²/g specific surface area is 0.02. A control is carried out every two weeks on a reference product. Twice a year, a control is carried out with the reference alumina supplied by the manufacturer.

Example 4: the raw materials used

The following materials are more particularly used in the following:

- larger particle size range: Cassis 10-20 aggregates and Cassis 6-10 aggregates (supplier Lafarge);
- medium particle size range: Honfleur sand (supplier Lafarge);
- cement: HTS CPA CEM1 52.5 PEMS Le Teil cement: 0.84 m²/g BET or

St Pierre La Cour CPA CEMI 52.5 R cement: 0.89 m²/g BET (supplier Lafarge);

- fine particle size range: fly ash (also denoted FA hereafter) Sundance: 1.52 m²/g BET (supplier Lafarge), Superpozz: 1.96 m²/g BET (supplier Lafarge) or Cordemais: 4.14 m²/g BET (supplier Surschiste); limestone powder (also denoted FC hereafter) Mikhart: 4.66 m²/g BET (supplier Provençale SA) or BL200: 0.7 m²/g BET (supplier Omya);
- ultrafine particle size range: silica fumes (also denoted SF hereafter) Elkem 971U; 21.52 m²/g BET.

The particle-size distribution profile of the materials used (as determined by laser particle-size analyses for particles with a mean size less than 200 µm and by video particle-size analyses for particles with a mean size greater than 200 µm) is represented in **Figures 1a to 1d** and highlights the compartmentalization of the materials into separate particle size ranges.

In the examples that follow, an admixture, Prémia 180, is also used as plasticizer or superplasticizer.

Example 5: concrete formulations according to the invention

The photograph in **Figure 2** provides a convenient diagrammatic visualization of a dry mortar according to the invention and a dry mortar of the standard B25 type. The proportion of cement is observed to be reduced by approximately 80% in the dry mortar according to the invention, and the quantity of binder (cement, fine and ultrafine ranges) is approximately 40% greater in the dry mortar according to the invention, compared to the standard mortar. The quantity of water is reduced, and a new ultrafine range appears.

The formulations that follow are formulations of concrete compositions according to the invention, based on fly ash. The materials used are those described in Example 4. Each number corresponds to the mass of material used (in kg) to prepare 1 m³ of concrete.

Formula FA1

Larger range	Cassis 6-10	953.70
Medium range	Honfleur sand	953.70

Cement	HTS 52.5 LT	74.20
Fine range	FA Superpozz	353.80
Ultrafine range	SF Elkem 971U	31.79
Plasticizer	Prémia 180	6.00
Water		100.00

Formula FA 2

Larger range	Cassis 10-20	676.20
	Cassis 6-10	350.22
Medium range	Honfleur sand	874.77
Cement	HTS 52.5 LT	72.21
Fine range	FA Superpozz	354.06
Ultrafine range	SF Elkem 971U	30.95
Plasticizer	Prémia 180	4.54
Water		100.00

Formula FA 3

Larger range	Cassis 6-10	953.85
Medium range	Honfleur sand	953.85
Cement	HTS 52.5 LT	74.20
Fine range	FA Cordemais	374.95
Ultrafine range	SF Elkem 971U	31.79
Plasticizer	Prémia 180	12.00
Water		110.00

Formula FA 4

Larger range	Cassis 6-10	953.70
Medium range	Honfleur sand	953.70
Cement	HTS 52.5 LT	74.20
Fine range	FA Sundance	296.00
Ultrafine range	SF Elkem 971U	31.80
Plasticizer	Prémia 180	6.00
Water		100.00

Formula FA 5

Larger range	Cassis 10-20	663.15
	Cassis 6-10	343.38
Medium range	Honfleur sand	857.93
Cement	HTS 52.5 LT	70.19
Fine range	FA Sundance	336.49
Ultrafine range	SF Elkem 971U	30.08
Plasticizer	Prémia 180	6.00
Water		100.00

Formula FA 6

Larger range	Cassis 6-10	953.70
Medium range	Honfleur sand	953.70
Cement	SPLC 52.5 R	74.20
Fine range	FA Superpozz	353.80
Ultrafine range	SF Elkem 971U	31.79
Plasticizer	Prémia 180	6.00
Water		100.00

Formula FA 7

Larger range	Cassis 6-10	953.70
Medium range	Honfleur sand	953.70
Cement	HTS 52.5 LT	73.50
Fine range	FA Superpozz	350.30
Ultrafine range	SF Elkem 971U	31.10
Plasticizer	Prémia 180	10.00
Water		103.50

Formula FA 8

Larger range	Cassis 6-10	954.00
Medium range	Honfleur sand	954.00
Cement	HTS 52.5 LT	102.00
Fine range	FA Superpozz	329.00

Ultrafine range	SF Elkem 971U	32.00
Plasticizer	Prémia 180	3.50
Water		130.00

5

The following formulations are formulations of concrete compositions according to the invention, based on limestone powder or limestone filler.

Formula FC1

Larger range	Cassis 6-10	950.00
Medium range	Honfleur sand	950.00
Cement	HTS 52.5 LT	70.00
Fine range	FC Mikhart 1	90.00
	FC BL200	304.00
Ultrafine range	SF Elkem 971U	30.00
Plasticizer	Prémia 180	8.00
Water		100.00

Formula FC2

Larger range	Cassis 10-20	661.84
	Cassis 6-10	342.54
Medium range	Honfleur sand	855.84
Cement	HTS 52.5 LT	70.02
Fine range	FC Mikhart 1	100.03
	FC BL200	336.78
Ultrafine range	SF Elkem 971U	30.01
Plasticizer	Prémia 180	7.07
Water		100.00

Formula FC3

Larger range	Cassis 10-20	661.84
	Cassis 6-10	342.54
Medium range	Honfleur sand	855.82
Cement	HTS 52.5 LT	70.02

Fine range	FC BL200	436.50
Ultrafine range	SF Elkem 971U	30.01
Plasticizer	Prémia 180	7.07
Water		100.00

Example 6: concrete performances according to the invention

5 The performances of the concretes according to the invention are evaluated on the following points.

- 10 - Compressive strength. This is measured by producing cylindrical test specimens with a diameter of 70, 110 or 160 mm and a slenderness ratio of 2, rectifying the latter according to the NF P18-406 standard, then loading them up to failure. As regards the loading, the protocol involves surrounding each sample with two or three layers of cellophane tape, centering it on the lower plate of a press using a centering template (mechanical testing machine with a force-control capacity of 3000 kN, conforming with the standards NF P18-411 and 412), to be configured for

15 a force control of 1 MPa/s, carrying out the loading up to failure according to the NF P18-406 standard and noting the value of the load at the failure point. The strength value is then deduced by dividing the force by the section of the test specimen.
- 20 - Shrinkage. This is measured on test specimens produced conforming with the NF P 196-1 standard using prismatic moulds with 4x4x16 or 7x7x28 or 10x10x40 dimensions (in cm). Uniform drying is ensured by arranging the test specimens horizontally on two supports having a linear contact with the test specimens. Measurement pegs conforming with the NF P 15-433 standard are anchored in each test specimen. The test specimens are

25 removed from the moulds, then measurements are carried out using a retractometer (initially, then at each chosen time). Throughout the entire period of the experiment, the room in which the test specimens are stored is maintained at a temperature of $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and at a relative humidity of $50\% \pm 5\%$.
- 30 - Durability (measurement of water porosity and gas permeability). The latter is evaluated according to the AFGC test or Association Française de Genie Civil (see Scientific and Technical Document, 2004: "Conception

des bétons pour une duration de vie donnée des ouvrages”) [« Design of concretes for a given structure’s service life »].

These performances are occasionally compared in what follows to those of a standard B25 concrete (control) with the following composition:

5	Cassis 10-20 Aggregates	655.00 kg/m ³
	Cassis 6-10 Aggregates	339.00 kg/m ³
	Honfleur Sand 0-4	847.00 kg/m ³
	SPLC CEMI 52.5 Cement	237.00 kg/m ³
	MEAC BL 200 Filler	95.00 kg/ m ³
10	Chrysoplast 209 Admixture	0.77 kg/m ³
	Water	164.00 kg/m ³

It should be noted that the concrete chosen as the control concrete has exceptionally high performances compared to the standard B25. Therefore a concrete that has slightly lower performances than those of this control may still be judged
15 entirely satisfactory.

The result of the compressive strength measurements is shown in Table 1 below: it shows in particular that numerous formulations among those in Example 5 make it possible to obtain a compressive strength greater than or equal to 4 MPa after 16 hours and greater than or equal to 25 or even 30 MPa after 28 days.

20

Table 1 - compressive strength (in MPa) up to 28 days

	Time: 16 hours	Time: 24 hours	Time: 28 days
Control	10.3	15.2	43
FA 1 (1)	3.83	6.00	34.37
FA 2 (2)		6.03	36.75
FA 3 (1)		3.79	
FA 5 (2)		4.1	39.03
FA 6 (1)	5.61	8.13	
FC1 (1)	4.89	6.28	
FC2 (2)		8.30	43.10
FC3 (2)	4.67	6.63	38.07

(1): experiment carried out on a test specimen 70 mm diameter, for a slenderness ratio factor of 2;

(2): experiment carried out on a test specimen 110 mm diameter, for a slenderness ratio factor of 2.

5 The control is tested on a test specimen 110 mm diameter, for a slenderness ratio factor of 2.

10 Another separate experiment is carried out on another batch of cement, to monitor the compressive strength of certain samples on the longer term. The results are given in Table 2, and indicate that, over time, certain formulations acquire a mechanical strength similar to that of very good quality B25 concrete, or even better.

Table 2 - compressive strength (in MPa) up to a time limit of 4 months

	1 month	2 months	3 months	4 months
Control	36.8	39.8	45.1	46.1
FA 2	32	44.9	49	53.9
FC3	32	39.8	45.1	44.8

15

The experiment comparing the shrinkage of a concrete according to the invention with that of a control B25 concrete has given the results that are compiled in **Figure 3**. The formula FA2 (x) is characterized by less shrinkage beyond two weeks compared to a standard formula. Therefore, a concrete of this type appears to be
20 appropriate for horizontal applications or massive structures.

As regards the durability study, the physical properties of the concretes formulated according to the invention are more favorable than those of a standard B25 concrete, due to lower water porosity (approximately 10% for a concrete formula FA2, approximately 17% for an ordinary B25 concrete, one day after mixing, and
25 respectively 8% and 14% 28 days after the mixing) and lower gas permeability (approximately $5 \times 10^{-16} \text{ m}^2$ for a concrete of formula FA2 versus $1.1 \times 10^{-15} \text{ m}^2$ for a standard B25 concrete, 28 days after mixing). Corrosion tests also show that the behavior is better compared to a normal B25 concrete.

CLAIMS

1. A mixture comprising in mass proportions:
 - from 0.4 to 4%, preferably from 0.8 to 1.7%, of materials in the
5 ultrafine particle size range, comprising particles with a D90 less than 1 μm and/or
with a specific BET surface area greater than 6 m^2/g ;
 - from 1 to 6%, preferably from 2 to 5%, of Portland cement;
 - from 8 to 25%, preferably from 12 to 21%, of fine particle size range
materials, comprising particles wherein the D10 and the D90 are from 1 μm to 100
10 μm and with a specific BET surface area less than 5 m^2/g , different from the cement;
 - from 25 to 50%, preferably from 30 to 42%, of medium particle size
range materials, comprising particles wherein the D10 and the D90 are from 100 μm
to 5 mm; and
 - from 25 to 55%, preferably from 35 to 47%, of larger particle size
15 range materials, comprising particles wherein the D10 is greater than 5 mm.

2. A binder premix comprising:
 - Portland cement;
 - a fine particle size range as defined in claim 1; and
 - 20 - an ultrafine particle size range as defined in claim 1;

wherein the mass proportion of Portland cement in the premix is less than 50%
and preferably from 5 to 35%, more preferably from 10 to 25%.

3. The binder premix according to claim 2, wherein the mass proportion
25 of the ultrafine particle size range in the premix is from 2 to 20%, preferably from 5 to
10%.

4. The binder premix according to claim 2 or 3, comprising in mass
proportions:
 - 30 - from 5 to 35%, preferably from 10 to 25%, of Portland cement;
 - from 60 to 90%, preferably from 65 to 85%, of materials in the fine
particle size range, and
 - from 2 to 20%, preferably from 5 to 10%, of materials in the ultrafine
particle size range.

- 35 5. The mixture or binder premix according to one of claims 1 to 4,
wherein the ultrafine particle size range comprises materials chosen from the group
comprising silica fumes, limestone powders, precipitated silicas, precipitated

carbonates, pyrogenated silicas, natural pozzolans, pumice stones, ground fly ash, ground hydrated or carbonated silicic hydraulic binder, and mixtures or co-grindings of the latter, in dried form or aqueous suspension.

5 6. The mixture or binder premix according to one of claims 1 to 5, wherein the mixture (Portland cement and fine particle size range) comprises:

- a first particle size sub-range, comprising particles wherein the D10 and the D90 are from 1 to 10 μm ; and

10 - a second particle size sub-range, comprising particles wherein the D10 and the D90 are from 10 to 100 μm ;

 and in which the first particle size sub-range comprises Portland cement.

15 7. The mixture or binder premix according to one of claims 1 to 5, wherein the mixture (Portland cement and fine particle size range) comprises particles wherein the D10 and the D90 are from 1 to 20 μm .

20 8. The mixture or binder premix according to one of claims 1 to 7, wherein the fine particle size range comprises one or more materials chosen from fly ash, pozzolans, limestone powders, siliceous powders, lime, calcium sulphate, slags.

 9. The mixture or premix according to one of claims 1 to 8, comprising:

- Portland cement and fly ash; or

- Portland cement and limestone powder; or

25 - Portland cement and slag; or

- Portland cement, fly ash and limestone powder; or

- Portland cement, fly ash and slag; or

- Portland cement, limestone powder and slag; or

- Portland cement, fly ash, limestone powder and slag.

30

 10. The mixture or pre-mix according to one of claims 1 to 9, comprising Portland cement and fly ash and not comprising slag.

35 11. The mixture or pre-mix according to one of claims 1 to 9, comprising Portland cement and slag and not comprising fly ash.

 12. The mixture or binder premix according to one of claims 1 to 11, further comprising:

- a plasticizer
- optionally an accelerator and/or an air-entraining agent and/or a thickening agent and/or a retarder.

5 13. The binder premix according to claim 12, wherein the proportion of plasticizer is from 0.05 to 3%, preferably from 0.2 to 0.5% expressed as a mass ratio of dry extract of plasticizer to the mass of binder premix.

10 14. A mixture comprising:

- a binder premix according to one of claims 2 to 13;
- a medium particle size range as defined in claim 1; and
- a larger particle size range as defined in claim 1.

15 15. The mixture according to claim 14, in mass proportions:

- from 10 to 35%, preferably from 15 to 25%, of binder premix;
- from 25 to 50%, preferably from 30 to 42%, of materials in the medium particle size range; and
- from 25 to 55%, preferably from 35 to 47%, of materials in the larger particle size range.

20 16. The mixture according to one of claims 1, 5 to 12, 14 or 15, wherein:

- the medium particle size range comprises sand and/or fine sand; and
- the larger particle size range comprises aggregates and/or gravel and/or pebbles and/or fine gravel.

25 17. The mixture according to one of claims 1, 5 to 12, 14 to 16, wherein the spacing coefficient of the skeleton by the binder is from 0.5 to 1.3, preferably from 0.7 to 1.0.

30 18. A composition of wet concrete, comprising:

- a mixture according to one of claims 1, 5 to 12, 14 to 17, mixed with
- water.

35 19. A composition of wet concrete, comprising:

- from 10 to 100 kg/m³, preferably from 20 to 40 kg/m³ of materials in the ultrafine particle size range as defined in claim 1;
- from 25 to 150 kg/m³, preferably from 50 to 120 kg/m³, more preferably, from 60 to 105 kg/m³, of Portland cement;

- from 200 to 600 kg/m³, preferably from 300 to 500 kg/m³ of materials in the fine particle size range as defined in claim 1;

- from 600 to 1200 kg/m³, preferably from 700 to 1000 kg/m³ of materials in the medium particle size range as defined in claim 1;

5 - from 600 to 1300 kg/m³, preferably from 800 to 1100 kg/m³ of materials in the larger particle size range as defined in claim 1; and

- optionally, a plasticizer.

20. The composition of wet concrete, according to claim 18 or 19
10 comprising:

- an accelerator and/or an air-entraining agent and/or a thickening agent and/or a retarder.

21. The composition of wet concrete, according to one of claims 18 to 20,
15 wherein the W/C ratio, where W designates the quantity of water and C the quantity of Portland cement, is from 1 to 2.5, preferably from 1.3 to 1.5.

22. The composition of wet concrete, according to one of claims 18 to 21,
wherein W/B ratio, where W designates the quantity of water and B the quantity of
20 materials in the mixture (Portland cement and fine particle size range), is from 0.1 to 0.45, preferably from 0.18 to 0.32.

23. The composition of wet concrete, according to one of claims 18 to 22,
from 60 to 180 l/m³, preferably from 80 to 150 l/m³, more preferably from 95 to 135
25 l/m³ of water.

24. The composition of wet concrete, according to one of claims 18 to 23,
which is a self-placing concrete.

30 25. An object of hardened concrete of the composition according to one of claims 18 to 24.

26. The object of hardened concrete, comprising:

- from 10 to 100 kg/m³, preferably from 20 to 40 kg/m³ of materials in
35 the ultrafine particle size range as defined in claim 1;

- Portland cement hydrates in a quantity corresponding to a quantity of Portland cement from 25 to 150 kg/m³, preferably from 50 to 120 kg/m³, more preferably, from 60 to 105 kg/m³;

- from 200 to 600 kg/m³, preferably from 300 to 500 kg/m³ of materials in the fine particle size range as defined in claim 1;

- from 600 to 1200 kg/m³, preferably from 700 to 1000 kg/m³ of materials in the medium particle size range as defined in claim 1;

5 - from 600 to 1300 kg/m³, preferably from 800 to 1100 kg/m³ of materials in the larger particle size range as defined in claim 1.

27. The object of hardened concrete according to claim 26, wherein the spacing coefficient of the skeleton by the binder is from 0.5 to 1.3, preferably from
10 0.7 to 1.0.

28. The object of hardened concrete according to one of claims 25 to 27, having shrinkage less than 400 µm/m, preferably less than 200 µm/m, after 80 days.

15 29. A process for preparation of a composition of wet concrete comprising a step of:

- mixing a mixture as defined according to one of claims 1, 5 to 12, 14 to 17, with water,

20 30. A process for preparation of a composition of wet concrete comprising a step of:

- mixing a binder premix as defined in one of claims 2 to 13 with materials of the medium particle size range as defined in claim 1, materials of the larger particle size range materials as defined in claim 1 and water.

25 31. The process for preparation of a composition of wet concrete according to claim 29 or 30, wherein the quantity of Portland cement used is less than 150 kg/m³, preferably less than 120 kg/m³, and more preferably, comprised from 60 to 105 kg/m³.

30 32. A process for preparation of a composition of wet concrete comprising a step of mixing:

- from 10 to 100 kg/m³, preferably from 20 to 40 kg/m³, of materials in the ultrafine particle size range as defined in claim 1;

35 - from 25 to 150 kg/m³, preferably from 50 to 120 kg/m³, more preferably, from 60 to 105 kg/m³ of Portland cement;

- from 200 to 600 kg/m³, preferably from 300 to 500 kg/m³ of materials in the fine particle size range as defined in claim 1;

- from 600 to 1200 kg/m³, preferably from 700 to 1000 kg/m³ of materials in the medium particle size range as defined in claim 1;
- from 600 to 1300 kg/m³, preferably from 800 to 1100 kg/m³ of materials in the larger particle size range as defined in claim 1; and
- 5 - optionally, a plasticizer and/or an accelerator and/or an air-entraining agent and/or a thickening agent and/or a retarder; with
- water.

33. The process for preparation of a composition of wet concrete according
10 to one of claims 29 to 32, wherein the mixing is carried out at a W/C ratio, where W designates the quantity of water and C the quantity of Portland cement, from 1 to 2.5, preferably from 1.3 to 1.5.

34. The process for preparation of a composition of wet concrete according
15 to one of claims 29 to 33, wherein the mixing is carried out at a W/B ratio from 0.1 to 0.45, preferably from 0.18 to 0.32, where W designates the quantity of water and B the quantity of materials in the mixture (Portland cement and fine particle size range).

35. The process for preparation of a composition of wet concrete according
20 to one of claims 29 to 34, wherein the quantity of water used is from 60 to 180 l/m³, preferably from 80 to 150 l/m³, more preferably from 95 to 135 l/m³.

36. A process for preparation of a cast wet concrete, comprising a step of;
- casting a composition of wet concrete according to one of claims 18 to
25 24.

37. A process for production of an object of concrete, comprising a step of:
- hardening a composition of wet concrete according to one of claims 18
to 24.
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