(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 February 2007 (01.02.2007)

PCT

(10) International Publication Number
WO 2007/013803 A2

(51) International Patent Classification:
C04B 14/10 (2006.01)

(21) International Application Number:
PCT/NL2006/000387

(22) International Filing Date: 26 July 2006 (26.07.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
05076741.7 28 July 2005 (28.07.2005) EP

(71) Applicant *(for all designated States except US)*: **ZOCO-INNOVATIONS B.V.** [NL/NL]; Kerkstraat 7A, NL-5328 AA Rossum (NL).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **EERLAND, Dick** [NL/NL]; Stationsweg 2, NL-4191 KK Geldermalsen (NL).

(74) Agent: **PLAGGENBORG, Menko, Bernard**; Octrooibureau Los en Stigter B.V., Weteringschans 96, NL-1017 XS Amsterdam (NL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2007/013803 A2

(54) Title: A CONCRETE AND METHOD FOR MAKING SAME

(57) Abstract: The invention relates to a concrete, comprising a hydraulic binder, water, an aggregate, a mineral admixture and a chemical admixture acting as a superplasticiser, characterized in that said mineral admixture comprises comprises colloidal silica, and clay with a blain value in the range of from 2000 to 8000 cm2/g. The invention also relates to a method for obtaining such a concrete, comprising a first step of mixing the dry compounds and a final step of adding the water. According to another embodiment the method comprises adding a part of the total amount of water added, after mixing some of the dry compounds and in a later step adding the rest of the water.

A concrete and method for making same

The present invention relates to a concrete. More in particular, the invention relates to a concrete, comprising a hydraulic binder, water, an aggregate, a mineral admixture and a chemical admixture acting as a superplasticiser. Futhermore, the invention relates to a method for making a concrete.

Such concrete is generally known. For example, US 5,932,000 relates to a method for the preparation of a hardening composition, i.e. concrete. According to said publication, the silica added to the composition needs to fulfil some strict requirements. The particle size distribution is a very important parameter.

Although the concrete obtained according to said publication, provides advantageous results, there still exists a need for an improved concrete. More in particular there exists a need for a concrete that can be made easily, simply and at low costs.

Therefore, according to a first object the present invention aims at providing an improved concrete.

According to another object, the present invention aims at providing a concrete that can be made with relatively cheap compounds.

More in general, the present invention has as an object to provide a concrete with a desirable compressive strength and flexural strength.

So as to obtain at least one of the above identified objects, the present invention provides a concrete as mentioned in the preamble and that is characterized by the measures identified in claim 1.

According to the present invention, said concrete has an impressive compressive strength. A compressive strength of well above 100 N/mm2, is easily obtainable.

Preferred embodiments of the concrete according to the invention are subject of the dependent claims 2 to 10.

The colloidal silica that can be used in accordance with the present invention, is generally known in the art and does not need to fulfil special requirements regarding particle size distribution, like the material known from US 5,932,000. Hence, the materials from which the concrete according to the present invantion is made, are much cheaper. The properties of the concrete obtained with the starting materials according to the present invention are nevertheless strongly improved.

The blain value of the clay can be determined with an automatical blain value device, for example the Blain-Star ZEB 1330, manufactured by Wasagchemie Synthen GmbH, Germany.

According to the invention, it is especially preferred that the blain value of the clay is in the range of from 3000 to 7000 cm2/g, preferably from 3300 to 6000 cm2/g, more preferably from 4000 to 5000 cm2/g. If the blain value is within these limits, the compressive strength can be improved further.

It is preferred that the condensed silica fume and the precipitated silica have a blain value of 50 to 200 m2/g.

As a further preference, the concrete comprises a superplasticiser, also known as water reducing agent. Preferably, said superplasticizer is comprised of a sulphonated formaldehyde comprising resin, for example a sulphonated naphtalene formaldehyde condensate, or a poly-carboxylate compound, that is in the dry form. The use of such plasticizers is well-known in the art of concrete manufacture. Reference is made to WO 91/12214 and EP 692 465. Examples of superplasticisers that can be used in the present invention are disclosed in those publications, incorporated herein by reference.

An advantage of the concrete according to the present invention is that the total amount of water can be reduced. As a matter of fact, the strength of concrete after hardening is improved when the amount of water is reduced.

According to a further preferred embodiment, the concrete comprises one or more of Portland cement and blast furnace slag cement as hydraulic binder. The use of a blast

furnace slag cement partially or completely replacing Portland cement is known in the art. In case of complete replacement, said slag is activated by alkali. For example, sodium hydroxide or sodium carbonate can be used as alkaline activators for said ground blast furnace slags. The blast furnace slag cement and Portland cement are commonly interchangeable. However, if a pigmented concrete is required, the use of white Portland cement is advisable, since blast furnace slag cement has a greyish colour.

According to a further preferred embodiment, the concrete comprises one or more of natural aggregates, recycled aggregates, industrial metal slag aggregates and light weight aggregates, all in the range of 0-4 mm and/or 4-10 mm as aggregate. The amount of the aggregates, not being the light weight aggregates, should be in the range of from 200-450%, based on 100% hydraulic binder. In case light weight aggregates are used, the amount by volume of the light weight aggregates should be comparable with the amount by volume of the aggregates not being the light weight aggregates, if those had been added. As a matter of fact, light weight aggregates are aggregates having a specific density of less than 2000 kg/m3.

Furthermore it is preferred that the concrete has a water : binder ratio of from 0,15-0,45, preferably from 0,20-0,40, still more preferably from 0,24-0,35. Using this amount of water, in combination with the use of a superplasticiser as indicated above, and preferably in an amount of from 2-10%, based on 100% hydraulic binder, yields an improved concrete.

As known in the art, it may be required to add reinforcing fibers or a reinforcing net to the composition from which the concrete is made. These fibers will especially improve the tensile strength of the concrete.

So as to obtain a concrete, having strongly improved strength, compared to the concrete known in the state of the art, it is preferred that said concrete is comprised of:

Hydraulic binder	100%
Mineral admixture	10 - 35%
Superplasticiser	2 - 10%
Aggregates	200 - 450%
Water	15 - 45%

preferably:

Hydraulic binder	100%
Mineral admixture	11 - 30%
Superplasticiser	3 - 7%
Aggregates	220 - 400%
Water	20 - 40%

more preferably:

Hydraulic binder	100%
Mineral admixture	12 - 28%
Superplasticiser	3,5 - 6%
Aggregates	250 - 350%
Water	23 - 36%

wherein all percentages are based on 100% hydraulic binder; with the proviso that if light weight aggregates are used, the amount by volume of light weight aggregates should be comparable with the amount by volume of the aggregates not being the light weight aggregates, if those had been added. However, the invention is not limited to the above identified ranges.

According to a first embodiment of a method for making a concrete from dry compounds and water, according to the present invention it comprises a first step of mixing the dry compounds and a final step of adding the water. After the water has been added, the mixture can be hardened. This method is completely novel and provides the advantage that the mixture can be prefabricated in the dry form. Only at the site, water should be added. Hence, transport is made much

easier and cheaper than known in the art, since no wet transport is required according to the present invention.

Preferably, said method according to the first embodiment comprises the steps of:

(a) mixing a hydraulic binder, a clay, a chemical admixture, and a colloidal silica;
(b) adding water;
(c) mixing said mixture obtained in step (b) and hardening same.

If the concrete to be obtained should be coloured, it is especially preferred that a pigment is added during or after any of steps a) - b). If a light colour of the concrete is required, it is preferred that as hydraulic binder, white Portland cement is used.

According to a second embodiment, the invention relates to a method for making a concrete according to the invention, comprising the steps of:

a) mixing the hydraulic binder and clay,
b) adding a part of the water, in an amount sufficient to obtain an adequately manageable mass;
c) mixing said chemical admixture with said mass obtained in b),
d) adding and mixing the colloidal silica and the rest of the water with the mixture obtained in step c),
e) mixing in the aggregates, and
f) hardening the mixture.

This following order of the steps for making the concrete yields a concrete having the improved characteristics.

If a concrete is required that has a preferred colour, a pigment may be added during or after any of steps (a)-(e). If a light colour of the concrete is required, it is preferred that as hydraulic binder, white Portland cement is used.

A man skilled in the art can easily determine the amount of water to be added during step (b). If the amount of water added in step (b) is too high, a very liquid mass will be obtained. If too little water is added, a sticky and not manageable mass will be obtained.

The pigment added, may be added as a dry compound, however it is possible to add the pigment as a dispersion in water. In that case, the amount of water incorporated in this dispersion may be detracted from the amount of water added in steps (b) and (d).

The invention will now be described by means of examples.

EXAMPLES

First embodiment

A dry mass of the following compounds was obtained by mixing the dry compounds (pbw = parts by weight):

Portland cement	100 pbw,
Kaolin clay	10 pbw,
Condensed silica fume	4.5 pbw,
Superplasticizer	3 pbw,
Sand (0 - 4 mm)	300 pbw.

A homogeneous mass was obtained. Then, water was added in a water : dry material ratio of 0.33 (w/c).

A pigment to be added may be in the form of a dry powder. However, improved results may be obtained when the pigment is added as a dispersion in water. For example, it may be added together with the water or thereafter. In that case the amount of water added is to be subtracted from the amount of the total water calculated.

In a second example, the normalised sand was replaced by recycling concrete with the same dimensional property values of 0 - 4 mm. The test results are indicated in the Table I, hereafter:

Table I:

		Age of test piece (days)		
Material	Property	1	7	28
Normalised sand 0-4 mm	Compression strength (N/mm2)	55	95	114.5
	Flexural strength (N/mm2)	7.5	12	15.5
Recycling concrete 0-4 mm	Compression strength (N/mm2)	27	68	90
	Flexural strength (N/mm2)	5.5	8	10.5

Second embodiment

In accordance with the method according to the second embodiment, as indicated above, a concrete test piece was made and tested. As a binder, ordinary Portland cement was used. The mineral admixture consisted of kaolin clay in an amount of 11%. Colloidal silica was added in an amount of 9%. Polycarboxylate compound, as a superplasticiser, was added in an amount of 4,2%. All above percentages are based on 100% ordinary Portland cement.

As aggregate, normalised sand in a range of 0 - 4 mm, was added in an amount of 300%. Finally, the water : binder ratio was 0,30.

In a second example, the normalised sand was replaced by recycling concrete with same dimensional property values of 0 - 4 mm. The test results are indicated in the following Table II:

Table II:

		Age of test piece (days)		
Material	Property	1	7	28
Normalised sand 0-4 mm	Compression strength (N/mm2)	30	65	75
	Flexural strength (N/mm2)	7	10	12
Recycling concrete 0-4 mm	Compression strength (N/mm2)	20	50	70
	Flexural strength (N/mm2)	5	8	10

It is clear that the results obtained by the methods according to both the first and the second embodiment of the present invention, are indications of a concrete that has impressively increased compression strength and flexural strength.

Furthermore, the concrete obtained by casting it in a mould with a smooth surface, has a very glassy, shiny and mirror like surface. Such concrete has never been made before. The concrete has a pore free surface. The sound when striking the concrete with a metal key and the look of the concrete, resemble that of a ceramic material. Even on the cast side, no pores or cracks are visible in the surface of the concrete.

Due to the surface of the concrete according to the present invention, it has a very high abrasion resistance, a low water absorption, a very high freeze-thaw resistance, an extremely good chemical resistance, a very high acid resistance, and a high fire resistance. Also, it has no explosion spalling.

Since the concrete, obtained with the present invention, is a self-compacting mass, it does not need compaction energy. It has self-compacting properties.

The invention is not limited to the examples as described above. A man skilled in the art is easily capable of making amendments to the invention as described above. Such amendments all fall within the scope of the present invention.

CLAIMS

1. A concrete, comprising a hydraulic binder, water, an aggregate, a mineral admixture and a chemical admixture acting as a superplasticiser, **characterized** in that said mineral admixture comprises:

- colloidal silica, and
- clay with a blain value in the range of from 2000 to 8000 cm^2/g.

2. A concrete in accordance with claim 1, **characterized** in that said clay is chosen from one or more of kaolin clay, metakaolin clay and montmorillonite clay.

3. A concrete in accordance with claim 1 or 2, **characterized** in that the blain value of the clay is in the range of from 3000 to 7000 cm^2/g, preferably from 3300-6000 cm^2/g, more preferably from 4000-5000 cm^2/g.

4. A concrete in accordance with claim 1, **characterized** in that said colloidal silica is comprised of at least one of condensed silica fume and precipitated silica.

5. A concrete in accordance with any preceding claim, **characterized** in that said colloidal silica has a blain value of 50 to 200 m^2/g.

6. A concrete in accordance with any preceding claim, **characterized** in that said superplasticiser is comprised of a sulphonated formaldehyde comprising resin or a polycarboxylate compound.

7. A concrete in accordance with any any preceding claim, **characterized** in that it comprises one or more of Portland cement and blast furnace slag cement as hydraulic binder

8. A concrete in accordance with any preceding claim, **characterized** in that it comprises one or more of natural aggregates, recycled aggregates, industrial metal slag aggregates and light weight aggregates, all in the range of 0-4 mm and 4-10 mm as aggregate.

9. A concrete in accordance with any preceding claim, **characterized** in that it has a water : binder ratio of

from 0,15-0,45, preferably from 0,20-0,40, more preferably 0,24-0,35.

10. A concrete in accordance with any any preceding claim, **characterized** in that it is comprised of:

Hydraulic binder	100%
Mineral admixture	10 - 35%
Superplasticiser	2 - 10%
Aggregates	200 - 450%
Water	15 - 45%

preferably:

Hydraulic binder	100%
Mineral admixture	11 - 30%
Superplasticiser	3 - 7%
Aggregates	220 - 400%
Water	20 - 40%

more preferably:

Hydraulic binder	100%
Mineral admixture	12 - 28%
Superplasticiser	3,5 - 6%
Aggregates	250 - 350%
Water	23 - 36%

wherein all percentages are based on 100% hydraulic binder; with the proviso that if light weight aggregates are used, the amount by volume of light weight aggregates should be comparable with the amount by volume of the aggregates not being the light weight aggregates, if those had been added.

11. A method for making a concrete from dry compounds and water, **characterized** in that it comprises a first step of mixing the dry compounds and a final step of adding the water.

12. A method according to claim 11 for making a concrete in accordance with claims 1 - 10, **characterized** in that it comprises the steps of:

(a) mixing a hydraulic binder, a clay, a chemical admixture, and a colloidal silica;

(b) adding water;

(c) mixing said mixture obtained in step (b) and hardening same.

13. A method according to claim 12, **characterized** in that a pigment is added during or after any of steps a) - b).

14. A method for making a concrete material in accordance with any of claims 1 - 10, **characterized** in that it comprises the steps of:

(a) mixing the hydraulic binder and clay,

(b) adding a part of the water, in an amount sufficient to obtain an adequately manageable mass;

(c) mixing said chemical admixture with said mass obtained in b),

(d) adding and mixing the colloidal silica and the rest of the water with the mixture obtained in step c),

(e) mixing in the aggregates, and

(f) hardening the mixture.

15. A method according to claim 14, **characterized** in that a pigment is added during or after any of steps a) - e).

16. A concrete with a shiny surface, obtainable by a method according to any of claims 11 - 15 in a mould with a smooth surface.