

DESCRIPTION

Title of Invention

HARDENING AGENT FOR READY-MIXED SHIPPED
 RAPID-HARDENING CONCRETE, READY-MIXED SHIPPED
 RAPID-HARDENING CONCRETE MATERIAL, READY-MIXED SHIPPED
 RAPID-HARDENING CONCRETE COMPOSITION, AND METHOD FOR
 PREPARING SAME

Technical Field

[0001]

The present invention relates to a hardening initiator for a ready-mixed shipping type rapid-hardening concrete, a ready-mixed shipping type rapid-hardening concrete material, a ready-mixed shipping type rapid-hardening concrete composition, and a method for preparing the same.

Background Art

[0002]

In the worldwide viewpoint, the production volume of cements is being increased, and the infrastructure constructions are being promoted rapidly. In particular, the building spree is still continuing in China and the south-eastern Asia. Among the infrastructure constructions, the road construction holds a prominent position. The roads are demanded to be liberated promptly for the service in both new construction and maintenance, and therefore as a material used therefor, a material enabling the service in the initial stage is demanded. One of the examples thereof is a rapid-hardening concrete.

[0003]

As the demanded capabilities of the rapid-hardening concrete, the usable time is also an important capability. In consideration of the period of time for the production of a ready-mixed concrete in ready-mixed concrete plant, the delivery to the construction site, and the construction, and the period of time for washing an agitator vehicle for the delivery of the ready-mixed concrete, the usable time is desirably at least 120 minutes or more, and 180 minutes or more when possible. However, the securement of the long usable time leads to the delay of the hardening time, and thus the demanded strength of an early age material cannot

be satisfied. Accordingly, the ordinary techniques are difficult to satisfy the necessary strength exhibition of an early age material while securing the sufficient usable time.

[0004]

It is the current actual situation that a rapid-hardening concrete is prepared in a construction site. For a construction with a small cast amount, a rapid-hardening concrete is kneaded with a mixer having a capacity of approximately from 0.1 to 0.2 m³, and the preparation and the casting of the rapid-hardening concrete are performed by a labor-intensive manner. In this operation, the large human resources and the large worker hour increase the cost, and the available supply volume of the rapid-hardening concrete is limited. Furthermore, in a construction with a large cast amount, a rapid-hardening concrete is continuously supplied by using a concrete mobile vehicle. In this operation, however, the concrete mobile vehicle is necessarily arranged, and in addition, the worker hour is increased since a fine aggregate and a coarse aggregate with a water content having been managed to a certain value in advance are packed in a flexible bag container and delivered to the construction site, and a rapid-hardening cement is packed in a flexible bag container, delivered to the site, and prepared therein, resulting in considerable increase of the cost of the rapid-hardening concrete. Moreover, there is a limitation in the arrangement of the concrete mobile vehicle.

[0005]

The development of a rapid-hardening concrete that can be shipped from a ready-mixed concrete plant is strongly demanded in these days. The shipment of a rapid-hardening concrete from a ready-mixed concrete plant enables the supply of a large amount of a rapid-hardening concrete to a construction site by utilizing the existing kneading equipments and delivery systems.

[0006]

For imparting rapid-hardening properties to a portland cement, the addition of a calcium aluminate thereto and the combination use of a gypsum compound have been considered since old times by Spackman in the U.S. (see, for example, PTL 1). The utilization of a mixture of an amorphous calcium aluminate and a gypsum compound as a rapid hardener has been known (see, for example, PTLs 2 and 3).

[0007]

PTLs 4 to 8 describe a rapid-setting concrete, in which a rapid-hardening concrete is shipped from a ready-mixed concrete plant, and after reaching a construction site, a rapid-setting agent is added thereto.

[0008]

Furthermore, PTLs 9 to 11 describe a rapid-setting concrete, in which a setting retarding agent and calcium hydroxide are added to a ready-mixed concrete along with β -naphthalenesulfonic acid in advance, and after reaching a construction site, a rapid-setting agent is added thereto.

[0009]

PTLs 12 and 13 describe a method for producing a rapid-hardening concrete, in which a setting retarding agent formed of an oxycarboxylic acid or a salt thereof and lithium carbonate is added to a base concrete in kneading or immediately after kneading, and a rapid hardener containing $\text{CaO} \cdot \text{Al}_2\text{O}_3$ crystals as a major component is added to the kneaded base concrete at the time of construction.

Citation List

Patent Literatures

[0010]

PTL 1: U.S. Patent No. 903,019

PTL 2: JP 48-1024 A

PTL 3: JP 04-97932 A

PTL 4: JP 2000-264712 A

PTL 5: JP 2000-327394 A

PTL 6: JP 2001-213655 A

PTL 7: JP 2001-253753 A

PTL 8: JP 2002-037654 A

PTL 9: JP 11-24074 A

PTL 10: JP 2002-321958 A

PTL 11: JP 2002-321959 A

PTL 12: JP 2007-045654 A

PTL 13: JP 2012-139897 A

Summary of Invention

Technical Problem

[0011]

However, even though only the rapid hardener techniques of PTLs 1 to 3 are applied, a rapid-hardening concrete capable of being shipped as a ready-mixed concrete cannot be prepared. Specifically, the ordinary rapid-hardening concrete uses a rapid hardener and a retarding agent used in combination, in addition to a portland cement, and in the case where the strength exhibition is demanded for an early age material, the usable time is necessarily set to 60 minutes or less. In this case, the shipment from a ready-mixed concrete plant is practically impossible. For achieving the shipment from a ready-mixed concrete plant, on the other hand, in the case where the usable time is set to 120 minutes or more by adding a retarding agent in a larger amount, the strength exhibition of an early age material is impossible. Furthermore, in the practical construction, there is a possibility that unexpected accidents including interruptions of the construction due to traffic jams and problems in the construction frequently occur. In the case where a ready-mixed shipping type rapid-hardening concrete is to be considered, it is important to ensure such a long usable time that covers all the aforementioned risks.

[0012]

Accordingly, the usable time is necessarily at least 120 minutes even in a construction site with a short delivery time, and even more in the case where the traffic volume is large, or the delivery distance is long, the usable time is desirably 180 minutes or more. As described herein, the reason why the ready-mixed shipping type rapid-hardening concrete has not been achieved is that the securement of the long usable time and the strength exhibition in a short period of time are in a trade-off relationship and are considerably difficult to achieve simultaneously.

[0013]

Even though such a long usable time is set that allows the agitation in a ready-mixed concrete plant, the period of time of the delivery to a construction site with an agitator vehicle and the casting thereof, the period of time required for washing, and all the accidents including interruptions of the construction due to traffic jams and problems in the construction, a rapid-hardening concrete capable of rapidly exhibiting the strength after casting is strongly demanded.

[0014]

The techniques of PTLs 4 to 8 are those used for the pre-lining of tunnels,

in which the rapid setting agent applied is an alkali aluminate, aluminum sulfate, sodium silicate, or the like, and the working time cannot be secured after the addition of the rapid setting agent. In the guidance of Japan Society of Civil Engineers, as the definition of a rapid setting agent, the quality standard of the rapid setting agent is defined in the spray concrete guide (plan). According to the guide, the start of the setting time is 5 minutes or less, and the end thereof is 15 minutes or less. Therefore, a usable time of 15 minutes or more cannot be secured by using the rapid setting agent.

[0015]

The techniques of PTLs 9 to 11 also use a rapid setting agent, and thus a usable time of 15 minutes or more cannot be secured after the addition of the rapid setting agent.

[0016]

The techniques of PTLs 12 and 13 require the addition of a large amount of rapid hardener after reaching a construction site, and thus have poor practical applicability. Specifically, from 10 to 60 parts of a rapid hardener is added to from 40 to 90 parts of a silicate cement. The cement is kneaded in an agitator track after the post-addition of a large amount of the rapid hardener, and therefore the ready-mixed concrete can be delivered only in an amount of only $\frac{3}{8}$ (37.5% by volume) or less in capacity with respect to the drum capacity of the agitator.

[0017]

Furthermore, the exhibition of a good initial strength even at a low temperature (for example, approximately 5°C) is effective for the enhancement of the workability, but the ordinary literatures do not refer to the initial strength at a low temperature.

[0018]

In consideration of the above, an object of the present invention is to provide a ready-mixed shipping type rapid-hardening concrete composition that is excellent in the strength exhibition in the initial stage even in a low temperature environment while ensuring a sufficient usable time. Furthermore, another object thereof is to provide a hardening initiator for a ready-mixed shipping type rapid-hardening concrete that is capable of favorably exhibiting the effects of the ready-mixed shipping type rapid-hardening concrete composition. Moreover, still another object thereof is to provide a method for preparing a ready-mixed

shipping type rapid-hardening concrete composition for producing the ready-mixed shipping type rapid-hardening concrete composition.

Solution to Problem

[0019]

As a result of the various efforts accumulated by the present inventors for solving the problems, it has been found that a rapid-hardening concrete that ensures a sufficient usable time, and is excellent in the initial strength exhibition even in a low temperature environment can be prepared in such a manner that a concrete prepared with a combination of a particular rapid hardener and a particular retarder is prepared in a ready-mixed concrete plant, and after the delivery to a construction site, a particular hardening initiator is added and mixed therein, and thus the present invention has been completed. Accordingly, the present invention is as follows.

[0020]

[1] A hardening initiator for a ready-mixed shipping type rapid-hardening concrete, to be added to a composition containing a cement, a rapid hardener, and a retarder, the hardening initiator providing a hardening initiator-containing composition obtained after 30 minutes from addition of the hardening initiator to the composition under condition of 5°C, a liquid phase obtained through solid-liquid separation of the hardening initiator-containing composition having an aluminum ion concentration that is 1.1 times or more an aluminum ion concentration of a liquid phase obtained through solid-liquid separation of a hardening initiator-non-containing composition obtained by not adding the hardening initiator to the composition under condition of 5°C.

[2] The hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to the item [1], wherein the hardening initiator contains a calcium aluminate based compound.

[3] The hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to the item [2], wherein the hardening initiator further contains a gypsum compound.

[4] The hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to the item [2] or [3], wherein the calcium aluminate based compound contains CaO in a range of from 30 to 60% by mass, Al₂O₃ in a range of from 30 to 60% by mass, and SiO₂ in a range of from 1 to 18%

by mass.

[5] The hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to any one of the items [2] to [4], wherein the calcium aluminate based compound has a degree of amorphousness of 70% or more.

[0021]

[6] A two-component type ready-mixed shipping type rapid-hardening concrete including: a material A containing a cement, a rapid hardener, and a retarder; and a material B containing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to any one of the items [1] to [5].

[7] A ready-mixed shipping type rapid-hardening concrete composition containing a material A containing a cement, a rapid hardener, and a retarder, having added thereto and mixed therewith a material B containing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to any one of the items [1] to [5].

[8] The ready-mixed shipping type rapid-hardening concrete composition according to the item [7], wherein the hardening initiator contains a calcium aluminate based compound and a gypsum compound.

[9] The ready-mixed shipping type rapid-hardening concrete composition according to the item [8], wherein the calcium aluminate based compound contains a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ based compound, and the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ based compound has a degree of amorphousness of 70% or more and contains SiO_2 in a range of from 1 to 18% by mass.

[10] The ready-mixed shipping type rapid-hardening concrete composition according to any one of the items [7] to [9], wherein the retarder contains an oxycarboxylic acid, or a mixture of a carbonate salt of an alkali metal except for lithium and an oxycarboxylic acid.

[11] The ready-mixed shipping type rapid-hardening concrete composition according to any one of the items [7] to [10], wherein the composition has a content of the hardening initiator for a ready-mixed shipping type rapid-hardening concrete of from 0.5 to 7 parts by mass per 100 parts by mass in total of the cement and the rapid hardener.

[0022]

[12] A method for preparing a ready-mixed shipping type rapid-hardening concrete, including in this order: kneading at least a cement, a

rapid hardener, and a retarder with kneading water in a kneading vessel; and further mixing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to any one of the items [1] to [5].

[13] The method for preparing a ready-mixed shipping type rapid-hardening concrete according to the item [12], wherein a base concrete containing at least the cement, the rapid hardener, the retarder, the aggregate, and the kneading water has a volume of 40% or more of an inner capacity of the kneading vessel.

[14] The method for preparing a ready-mixed shipping type rapid-hardening concrete according to the item [12] or [13], wherein a kind and an amount of the hardening initiator for a ready-mixed shipping type rapid-hardening concrete are determined to ensure a usable time of 15 minutes or more after mixing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete.

[15] The method for preparing a ready-mixed shipping type rapid-hardening concrete according to any one of the items [12] to [14], wherein the retarder is used in an amount of from 0.3 to 5 parts by mass per 100 parts by mass in total of the cement and the rapid hardener.

Advantageous Effects of Invention

[0023]

According to the present invention, a ready-mixed shipping type rapid-hardening concrete composition that is excellent in the strength exhibition in the initial stage even in a low temperature environment while ensuring a sufficient usable time can be provided. Furthermore, a hardening initiator for a ready-mixed shipping type rapid-hardening concrete that is capable of favorably exhibiting the effects of the ready-mixed shipping type rapid-hardening concrete composition can be provided. Moreover, a method for preparing a ready-mixed shipping type rapid-hardening concrete composition for producing the ready-mixed shipping type rapid-hardening concrete composition can be provided.

In consideration of the aforementioned effects, the present invention can be applied particularly favorably to the civil engineering and construction fields.

Description of Embodiments

[0024]

Embodiments of the present invention will be described in detail below, but the present invention is not limited to the embodiments. In the description herein, the "part" and "percentage" are based on mass unless otherwise indicated. In the description herein, the "composition" collectively means a cement composition, a mortar composition, and a concrete composition.

[0025]

[1] Hardening Initiator for Ready-mixed Shipping type Rapid-hardening Concrete

The hardening initiator for a ready-mixed shipping type rapid-hardening concrete (which may be referred simply to as a "hardening initiator") is a hardening initiator that is to be added to a composition containing a cement, a rapid hardener, and a retarder, and in a liquid phase obtained through solid-liquid separation of a hardening initiator-containing composition obtained after 30 minutes from addition of the hardening initiator to the composition under condition of 5°C, the aluminum ion concentration ($X_{5^{\circ}\text{C}}$) is 1.1 times ($X_{5^{\circ}\text{C}}/Y_{5^{\circ}\text{C}} = 1.1$) or more the aluminum ion concentration ($Y_{5^{\circ}\text{C}}$) in a liquid phase obtained through solid-liquid separation of a hardening initiator-non-containing composition obtained by not adding the hardening initiator to the composition under condition of 5°C.

The hardening initiator-containing composition and the hardening initiator-non-containing composition are the same as each other except for the presence or absence of the hardening initiator. The amount of the hardening initiator added in this case is preferably approximately from 0.5 to 7 parts by mass per 100 parts by mass in total of the cement and the rapid hardener.

[0026]

The value $X_{5^{\circ}\text{C}}/Y_{5^{\circ}\text{C}}$ above means the elution rate of aluminum ion, which largely influence the enhancement of the initial strength, and with a large value thereof, a relatively large amount of aluminum ion can exist in the initial stage, and the ettringite formation in the initial stage becomes prominent, facilitating the strength exhibition. Accordingly, with a value $X_{5^{\circ}\text{C}}/Y_{5^{\circ}\text{C}}$ of less than 1.1, the strength exhibition in the initial stage in a low temperature environment at 5°C is difficult to achieve, which makes difficult the production of the ready-mixed shipping type rapid-hardening concrete composition. The value $X_{5^{\circ}\text{C}}/Y_{5^{\circ}\text{C}}$ is preferably from 1.2 to 4.0. The aluminum ion concentration in a liquid phase can be measured by the inductively coupled plasma atomic emission spectroscopy

(ICP-AES) or the like as described in the examples, and the value $X_{5^{\circ}\text{C}}/Y_{5^{\circ}\text{C}}$ can be calculated from the measured values thereof.

For achieving a value $X_{5^{\circ}\text{C}}/Y_{5^{\circ}\text{C}}$ of 1.1 or more, for example, it suffices that a component that accelerates the ettringite formation, such as a calcium aluminate based compound, is added, and furthermore, it suffices that gypsum or the like is added to the hardening initiator from the standpoint of the long-term strength exhibition.

[0027]

Similarly, the aluminum ion concentration ($X_{20^{\circ}\text{C}}$) in a liquid phase obtained through solid-liquid separation of a hardening initiator-containing composition obtained after 30 minutes from addition of the hardening initiator to the composition under condition of 20°C is preferably 1.2 times ($X_{20^{\circ}\text{C}}/Y_{20^{\circ}\text{C}} = 1.2$) or more, and more preferably from 1.2 to 4.0 times, the aluminum ion concentration ($Y_{20^{\circ}\text{C}}$) in a liquid phase obtained through solid-liquid separation of a hardening initiator-non-containing composition obtained by not adding the hardening initiator to the composition under condition of 20°C .

With a value $X_{20^{\circ}\text{C}}/Y_{20^{\circ}\text{C}}$ of 1.2 times or more, the ettringite formation in the initial stage can become prominent, facilitating the strength exhibition.

[0028]

The value $X_{5^{\circ}\text{C}}/X_{20^{\circ}\text{C}}$ is preferably 0.65 or more, and more preferably 0.75 or more. The upper limit thereof is practically 1. With a value $X_{5^{\circ}\text{C}}/X_{20^{\circ}\text{C}}$ of 0.65 or more, the hardening initiator for a ready-mixed shipping type rapid-hardening concrete can exhibit the function thereof with less fluctuation between a low temperature and a high temperature, and thus can be used substantially without the consideration of the working temperature.

[0029]

The components and the like will be described below.

In an embodiment relating to the hardening initiator for a ready-mixed shipping type rapid-hardening concrete of the present invention, the hardening initiator for a ready-mixed shipping type rapid-hardening concrete means such a material that again invokes the hydration hardening of a rapid-hardening concrete having been retarded by adding a large amount of the retarder described later thereto (i.e., a concrete where the hydration hardening thereof is substantially stopped therewith). Specific examples thereof include a calcium aluminate based compound.

[0030]

The "ready-mixed shipping type rapid-hardening concrete" referred in the present embodiment means such a concrete that is kneaded as a ready-mixed concrete in a ready-mixed concrete factory, a ready-mixed concrete plant, or the like, delivered with an agitator vehicle, shipped to a construction site, such as a civil engineering site or a building site, and hardened relatively rapidly after casting. The ready-mixed shipping type rapid-hardening concrete necessarily has a usable time from the shipment to the completion of the work of at least 120 minutes or more in relation to the delivery time, and desirably has a usable time of 180 minutes or more ensured in the case where the delivery distance is long. The present embodiment may be specialized to this application.

The "agitator vehicle" herein means such a cargo vehicle that is equipped with a mixing drum (i.e., a vessel for kneading) on the deck thereof, and is capable of delivering a ready-mixed concrete under agitation, and includes vehicles having a maximum load of from 2 to 11 ton while there is no large difference among them, which may be selected depending on the application.

[0031]

It is necessary to ensure the working time after the addition of the hardening initiator for a ready-mixed shipping type rapid-hardening concrete, and therefore the kind of the hardening initiator and the amount thereof added are necessarily selected to ensure a usable time of at least 15 minutes or more. From this standpoint, such rapid setting agents as sodium aluminate, aluminum sulfate, sodium silicate are necessarily prevented from being selected as the hardening initiator. These rapid setting agents exhibit the rapid setting phenomenon immediately after the addition thereof, and a usable time of 10 minutes or more is difficult to ensure. Accordingly, the amount of these rapid setting agents is preferably 30 parts or less per 100 parts of the hardening initiator for a ready-mixed shipping type rapid-hardening concrete, and it is more preferred that these rapid setting agents are not used.

[0032]

The hardening initiator for a ready-mixed shipping type rapid-hardening concrete may have, for example, a 300 μm sieve residue of 5% or less, and preferably has a 100 μm sieve residue of 10% or less.

[0033]

The hardening initiator according to the present invention preferably

contains a calcium aluminate based compound. In the present invention, while a calcium aluminate based compound is also used in the rapid hardener described later, the calcium aluminate based compound that is applied to the hardening initiator preferably has a $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio in a range of from 0.5 to 2.4. In the case where the $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio is 0.5 or more, the effect of improving the temperature dependency can be further sufficiently exhibited, and in the case where the molar ratio is 2.4 or less, the rapid hardening phenomenon can be suppressed when the hardening initiator is used as a slurry.

Within the aforementioned preferred range, a range of from 0.5 to 1.2 is more preferred, and a range of from 0.75 to 1.0 is further preferred, from the standpoint of the prolongation of the usable time. From the standpoint of the strength exhibition in the initial stage, a range of from 1.2 to 2.4 is more preferred, and a range of from 1.25 to 2.3 is further preferred.

[0034]

In the calcium aluminate based compound, it is preferred that CaO is in a range of from 30 to 60% by mass, Al_2O_3 is in a range of from 30 to 60% by mass, and SiO_2 is in a range of from 1 to 18% by mass, and it is more preferred that CaO is in a range of from 40 to 50% by mass, Al_2O_3 is in a range of from 40 to 50% by mass, and SiO_2 is in a range of from 3 to 10% by mass. In the case where CaO , Al_2O_3 , and SiO_2 are in the aforementioned ranges, the effect of improving the temperature dependency can be sufficiently exhibited, and the rapid hardening phenomenon can be suppressed when the hardening initiator is used as a slurry.

[0035]

The calcium aluminate based compound can be roughly classified into an amorphous calcium aluminate based compound and a crystalline calcium aluminate based compound, and an amorphous calcium aluminate based compound is preferably used from the standpoint of the long-term strength exhibition. From this standpoint, the degree of amorphousness thereof is preferably 70% or more, and more preferably 80% or more. The measurement method of the degree of amorphousness will be described later.

[0036]

In the hardening initiator for a ready-mixed shipping type rapid-hardening concrete, the amount of the calcium aluminate based compound is preferably 70% or more, and more preferably 80% or more, from the standpoint of the efficient exhibition of the effect thereof.

The presence of a substance other than the hardening initiator exemplified above (i.e., an additional component) may enhance the dispersibility of the hardening initiator or may facilitate the effect of the hardening initiator, and therefore the additional component that does not impair the effects of the present invention may be contained in a range of 30% or less.

[0037]

The hardening initiator of the present invention preferably contains gypsum in addition to any of the aforementioned components, and more preferably contains a calcium aluminate based compound and gypsum.

The gypsum used may be any of anhydrous gypsum, hemihydrate gypsum, and dihydrate gypsum. Natural gypsum, chemical gypsum, such as phosphoric acid by-product gypsum, stack gas desulfurized gypsum, and hydrofluoric acid by-product gypsum, and gypsum obtained through heat treatment of these kinds of gypsum may also be used. Among these, anhydrous gypsum and/or hemihydrate gypsum are preferred from the standpoint of the strength exhibition, anhydrous gypsum is preferably selected from the standpoint of the cost, and type II anhydrous gypsum and/or natural anhydrous gypsum are preferred. The granularity in terms of Blaine value of the gypsum is preferably 3,000 cm^2/g or more, and more preferably from 4,000 to 7,000 cm^2/g . In the case where the granularity is 3,000 cm^2/g or more, the initial strength exhibition can be favorably achieved.

[0038]

The amount of the gypsum used is preferably from 10 to 200 parts, more preferably from 15 to 150 parts, and further preferably from 90 to 130 parts, per 100 parts of the hardening initiator (preferably a calcium aluminate based compound). With the range, the long-term strength exhibition and the durability can be improved.

[0039]

The amount of the hardening initiator for a ready-mixed shipping type rapid-hardening concrete is not particularly limited, and is preferably from 0.5 to 7 parts, and more preferably from 1 to 5 parts, per 100 parts in total of the cement and the rapid hardener, which are described later. In the case where the amount thereof is from 0.5 to 7 parts, the strength exhibition of an early age material can be sufficient, and the usable time can be ensured. The hardening initiator may be formed in to a slurry, which may be then added to various base concretes or the

like. In this case, it is desirable from the standpoint of the strength exhibition that a part of the kneading water of the concrete mix is used for the slurry of the hardening initiator, and the corresponding amount of water is deducted from the base concrete.

[0040]

[2] Ready-mixed Shipping type Rapid-hardening Concrete Material and Ready-mixed Shipping type Rapid-hardening Concrete Composition

An embodiment of the ready-mixed shipping type rapid-hardening concrete material of the present invention is a two-component type ready-mixed shipping type rapid-hardening concrete material including a material A containing a cement, a rapid hardener, and a retarder, and a material B containing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete described above.

An embodiment of the ready-mixed shipping type rapid-hardening concrete composition of the present invention includes the material A having added thereto and mixed therewith the material B.

[0041]

In the present embodiment, it is necessary in a ready-mixed concrete plant that a rapid hardener and a retarder are added and mixed in a cement in advance, and it is necessary that the hardening initiator is added and mixed therein after the delivery to a construction site. The usable time cannot be ensured if the hardening initiator is mixed in the ready-mixed concrete plant. Furthermore, if both the rapid hardener and the hardening initiator are added in the ready-mixed concrete factory, the usable time becomes extremely short, and the concrete is unavoidably discarded during the delivery. In the case where the hardening initiator is added in the ready-mixed concrete factory, and the rapid hardener is added in the construction site, the usable time after the addition of the rapid hardener becomes as extremely short as 10 minutes or less, disabling the construction. In the case where the rapid hardener and the hardening initiator are added in the construction site, the usable time is shortened, the compression strength becomes a low value, the wear resistance tends to be deteriorated, and furthermore only approximately 30% of the drum capacity of the agitator can be delivered. As described above, the addition timing of the rapid hardener and the hardening initiator is significantly important.

[0042]

In the present embodiment, accordingly, the two-component system including the material A containing a cement, a rapid hardener, and a retarder, and the material B containing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete is used, specifically, the material A and the material B are separately delivered from the ready-mixed concrete plant to the construction site, and then the components are mixed in the construction site, so as to provide the ready-mixed shipping type rapid-hardening concrete composition of the present embodiment. The components relating to the present embodiment will be described in detail below.

[0043]

(Cement)

The "cement" in the present embodiment is not particularly limited, and examples thereof include any type of cement, such as normal, early strength, moderate heat, and low heat portland cements defined in the Japanese Industrial Standard (JIS), various mixed cements obtained by mixing a blast furnace slag, a fly ash, or silica, an environment-conscious cement (eco-cement) produced from urban waste incineration ash or sewage sludge incineration ash, and a filler cement obtained by mixing with limestone powder, an air-cooled blast furnace slag, or the like, a sulfoaluminate cement, and an alumina cement, which are not defined in the Japanese Industrial Standard (JIS). Examples thereof further include a cement defined by the overseas standard EN197-2000 and any type of cement defined by the Chinese GB Standard. One kind or two or more kinds of these cements can be used.

[0044]

The constitutional compounds of a portland cement include alite ($3\text{CaO} \cdot \text{SiO}_2$), belite ($2\text{CaO} \cdot \text{SiO}_2$), aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$), and ferrite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$), and also include dihydrate gypsum (a part of which may be changed to hemihydrate gypsum in some cases) mixed therein. In the present embodiment, a cement that does not contain an admixture, such as a blast furnace slag, fly ash, silica, and limestone fine powder, is preferably selected from the standpoint of the strength exhibition, and among these, a cement having a large alite content and a high degree of fineness (i.e., a small particle size) is preferably selected. Examples of cements corresponding thereto include an early strength cement and a normal cement for the cements of Japan, and include PII52.5 and PII42.5 for the cements of China.

[0045]

(Rapid Hardener)

The rapid hardener of the present embodiment preferably contains a calcium aluminate based compound and a gypsum compound. The calcium aluminate based compound herein collectively means compound formed mainly of CaO and Al₂O₃, which are not particularly limited. Specific examples thereof include CaO·Al₂O₃, 12CaO·7Al₂O₃, 11CaO·7Al₂O₃·CaF₂, 3CaO·Al₂O₃, 3CaO·3Al₂O₃·CaSO₄, and an amorphous substance formed mainly of CaO and Al₂O₃ (such as CaO-Al₂O₃-SiO₂ based compound). Among these, the amorphous substance is preferably selected from the standpoint of the strength exhibition. However, the sulfoaluminate cement and the alumina cement defined by the Chinese GB Standard 20472-2006 are rapid-hardening cements by themselves, and may be used without the addition of the rapid hardener depending on the demanded initial strength exhibition.

[0046]

The degree of amorphousness in the present embodiment is defined as follows. The target substance is annealed at 1,000°C for 2 hours, and then gradually cooled at a cooling rate of 5°C per minute for crystallization. The crystallized substance is measured by the powder X-ray diffractometry, and the area S₀ of the main peak of the crystallized mineral is obtained. Subsequently, the degree of amorphousness X is obtained from the main peak area S of the crystal of the substance before annealing, according to the following expression.

$$X (\%) = 100 \times (1 - S/S_0)$$

[0047]

While the ordinary industrial materials contain impurities, such as SiO₂, MgO, Fe₂O₃, TiO₂, K₂O, and Na₂O, the impurities have an aspect of promoting the amorphization of the calcium aluminate based compound, and may exist with no problem, as far as the total amount thereof is 20% or less. Among these, SiO₂ preferably exist, and may be contained in a range of from 1 to 18% for providing amorphous calcium aluminate.

[0048]

Accordingly, it is preferred that the rapid hardener contains a CaO-Al₂O₃-SiO₂ based compound and a gypsum compound, and the

CaO-Al₂O₃-SiO₂ based compound has a degree of amorphousness of 70% or more and contains SiO₂ in a range of from 1 to 18% by mass. According to the embodiment, the sufficient usable time before the addition of the hardening initiator can be ensured, and the initial strength exhibition after the addition of the hardening initiator can be favorably improved. It is more preferred that the CaO-Al₂O₃-SiO₂ based compound has a degree of amorphousness of 80% or more and contains SiO₂ in a range of from 2 to 13% by mass.

[0049]

The calcium aluminate based compound is preferably controlled to have a Blaine specific surface area of from 4,000 to 9,000 cm²/g, and more preferably from 5,000 to 8,000 cm²/g, through a pulverization treatment. In the case where the degree of fineness (i.e., the Blaine specific surface area) of the calcium aluminate based compound is from 4,000 to 9,000 cm²/g, the sufficient rapid hardening properties can be readily obtained, and the strength exhibition at a low temperature can also be readily obtained.

[0050]

The rapid hardener of the present embodiment is preferably controlled to have a Blaine specific surface area of from 4,000 to 9,000 cm²/g, and more preferably from 5,000 to 8,000 cm²/g, through a pulverization treatment. In the case where the degree of fineness (i.e., the Blaine specific surface area) of the rapid hardener is from 4,000 to 9,000 cm²/g, the sufficient ultrarapid hardening properties can be readily obtained, and the strength exhibition at a low temperature can also be readily obtained.

[0051]

The amount of the rapid hardener used is preferably from 10 to 35 parts, more preferably from 15 to 30 parts, and further preferably from 20 to 25 parts, per 100 parts in total of the cement and the rapid hardener. In the case where the amount thereof is from 10 to 35 parts, the good initial strength exhibition can be readily obtained, and the decrease of the long-term strength can be readily prevented from occurring.

[0052]

(Retarder)

The retarder used in the present embodiment has a function of retarding the rapid-hardening concrete shipped as a ready-mixed concrete (i.e., substantially terminating the hydration hardening), and avoids accidental rapid

hardening in the ready-mixed concrete plant and accidental rapid hardening in the delivery with an agitator vehicle. Examples of the retarder include an oxycarboxylic acid or a salt thereof, a combination use thereof with a carbonate salt of an alkali metal, a sugar, and boric acid. The combination use of an oxycarboxylic acid and a carbonate salt of an alkali metal is preferred due to the large effect of retarding the rapid-hardening concrete and the good strength exhibition after the addition of the hardening initiator. The carbonate salt of an alkali metal is preferably a carbonate salt of an alkali metal other than lithium. It is necessary that a sufficient usable time is ensured for the base concrete, a certain usable time is ensured even after the addition of the hardening initiator, and good strength exhibition is ensured, and in these standpoints, the use of lithium carbonate is not preferred.

[0053]

The retarder preferably contains an oxycarboxylic acid, or a mixture of a carbonate salt of an alkali metal other than lithium and an oxycarboxylic acid, and more preferably contains a mixture of a carbonate salt of an alkali metal other than lithium and an oxycarboxylic acid. The mixing ratio of the carbonate salt of an alkali metal other than lithium and the oxycarboxylic acid in terms of (carbonate salt of alkali metal other than lithium)/(oxycarboxylic acid) is preferably from 10/90 to 90/10, and more preferably from 20/80 to 80/20.

[0054]

Examples of the oxycarboxylic acid or a salt thereof include citric acid, gluconic acid, tartaric acid, and malic acid, and examples of the salt thereof include a sodium salt, a potassium salt, a calcium salt, and a magnesium salt. These may be used alone or as a combination of two or more kinds thereof.

[0055]

The amount of the retarder used is preferably from 0.3 to 5 parts, and more preferably from 0.3 to 4.5 parts, per 100 parts in total of the cement and the rapid hardener. In the case where the amount thereof is from 0.3 to 5 parts, a sufficient working time can be readily ensured in addition to the delivery time to the construction site. Furthermore, the hydration hardening can be readily again invoked by the addition of the hardening initiator.

[0056]

(Gypsum)

The gypsum compound used in the present embodiment may be any of

anhydrous, hemihydrate, and dihydrate gypsum. Among these, anhydrous gypsum and/or hemihydrate gypsum are preferred from the standpoint of the strength exhibition, anhydrous gypsum is preferably selected from the standpoint of the cost, and type II anhydrous gypsum and/or natural anhydrous gypsum are preferred. The granularity in terms of Blaine value of the gypsum is preferably 3,000 cm²/g or more, and more preferably from 4,000 to 7,000 cm²/g. In the case where the granularity is 3,000 cm²/g, the initial strength exhibition can be favorably achieved.

[0057]

The amount of the gypsum compound used is preferably from 10 to 200 parts, more preferably from 15 to 150 parts, and further preferably from 20 to 130 parts, per 100 parts of the calcium aluminate based compound (preferably the calcium aluminate compound used as the rapid hardener). With the range, the strength exhibition can be favorably achieved.

[0058]

In the present embodiment, in addition to the rapid hardener, the retarder, and the hardening initiator described above, one kind or two or more kinds of an expanding agent, a water reducing agent, an AE water reducing agent, a high-performance water reducing agent, a slag, such as air-cooled blast furnace slag fine powder and air-cooled blast furnace slag fine powder, an admixture, such as limestone fine powder, silica fume and fly ash, a defoaming agent, a thickening agent, a rust inhibiting agent, an antifreezing agent, a contraction reducing agent, a polymer, a clay mineral, such as bentonite, and an anion exchanger, such as hydrotalcite, may be used in such a range that does not impair the object of the present invention.

[0059]

[3] Method for preparing Ready-mixed Shipping type Rapid-hardening Concrete

An embodiment of the method for preparing a ready-mixed shipping type rapid-hardening concrete of the present invention includes in this order: kneading at least a cement, a rapid hardener, and a retarder with kneading water in a kneading vessel; and further mixing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete, for example, in a construction site.

[0060]

In the step of kneading, a base concrete containing at least the cement, the

rapid hardener, the retarder, an aggregate, and the kneading water preferably has a volume of 40% (% by volume) or more, and more preferably 50% by volume or more, of the inner capacity of the kneading vessel.

The kneading vessel herein may be, for example, a vessel capable of retaining a ready-mixed concrete under agitation mounted on a vehicle for delivering a ready-mixed concrete, such as a drum of an agitator vehicle.

[0061]

The kind and the mixed amount of the hardening initiator for a ready-mixed shipping type rapid-hardening concrete are preferably determined to ensure a usable time of 10 minutes or more, and preferably 15 minutes or more, after mixing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete.

[0062]

As described above, the hardening initiator for a ready-mixed shipping type rapid-hardening concrete of the present embodiment is preferably used as an admixture that is added to a ready-mixed concrete after the casting operation, which has been kneaded and then shipped to a construction site. Similarly, the ready-mixed shipping type rapid-hardening concrete material of the embodiment is preferably used as an admixture that is added thereto after the casting operation as similar to the hardening initiator. With the use thereof, the usable time can be, for example, 120 minutes or more, and preferably 180 minutes or more.

Examples

[0063]

The present invention will be described in more detail with reference to experimental examples below, but the present invention is not limited thereto.

[0064]

(Experimental Example 1)

A rapid-hardening concrete was prepared by kneading 380 kg/m³ of a cement and 120 kg/m³ of a rapid hardener, at a water/binder ratio of 32%, s/a of 42%, and an air amount of 2.0±1.5% by volume, in a kneading vessel. At this time, 1.5 parts of a retarder was mixed in 100 parts of the binder formed of the cement and the rapid hardener, and the volume after kneading was 85% of the inner capacity of the kneading vessel, so as to prevent the hydration hardening

from occurring for 24 hours or more (material A). Assuming the delivery time to the construction site and the occurrence of the waiting time after reaching the construction site, after 120 minutes, 5 parts of various types of a hardening initiator (material B) shown in Table 1 below was added to 100 parts of the binder (i.e., the ready-mixed shipping type rapid-hardening concrete composition). The usable time after the addition of the hardening initiator was measured, and the compression strength after 6 hours from the addition of the hardening initiator (i.e., after 8 hours from the completion of kneading) was measured. The temperature of the series of tests was 5°C or 20°C.

[0065]

Separately, 76 parts of the cement obtained by removing the fine aggregate and the coarse aggregate from the aforementioned concrete formulation, 24 parts of the rapid hardener, 32 parts of water, and 1.5 parts of the retarder were kneaded to prepare a cement paste at 5°C or 20°C. After 120 minutes from the preparation of the cement paste at 5°C or 20°C, the hardening initiators A and B each were added thereto in an amount of 5 parts per 100 parts in total of the cement and the rapid hardener, and after 30 minutes from the addition of the hardening initiator, a liquid phase was obtained through solid-liquid separation by filtering under reduced pressure, with which the aluminum ion concentration was compared to the case with no hardening initiator added. The results are shown in Table 1.

The s/a is the fine aggregate ratio, which is the value in terms of percentage of the absolute volume ratio of the amount of the fine aggregate with respect to the total aggregate amount in the concrete.

[0066]

<Materials Used>

(1) Hardening Initiators A and B

Hardening initiator A: calcium hydroxide, commercially available product, 300 µm sieve residue: less than 1%, 100 µm sieve residue: 5%

Hardening initiator B: a calcium aluminate based compound, containing 47% of CaO, 53% of Al₂O₃, and 0% of SiO₂, Blaine specific surface area: 5,000 cm²/g, degree of amorphousness: 85%

[0067]

(2) Rapid Hardener

Rapid hardener A: a mixture of the same amounts of a CaO-Al₂O₃-SiO₂

based calcium aluminate based compound and anhydrous gypsum, the CaO-Al₂O₃-SiO₂ based calcium aluminate based compound containing 43% of CaO, 44% of Al₂O₃, 10% of SiO₂, 3% of others, density: Blaine specific surface area: 5,000 cm²/g, degree of amorphousness: 90%

[0068]

(3) Retarder

Retarder 1: a mixture of 75 parts of first class reagent potassium carbonate and 25 parts of first class reagent citric acid

[0069]

(4) Others

Cement: a commercially available normal portland cement (produced by Denka Co., Ltd., density: 3.15 g/cm³)

Anhydrous gypsum: type II anhydrous gypsum, pH 3.0, Blaine specific surface area: 5,000 cm²/g

Water: tap water

Fine aggregate: natural river sand

Coarse aggregate: crushed stone

[0070]

<Measurement Methods>

Usable time: The start time of setting was measured according to JIS A1147, and designated as the usable time.

Compression strength: The compression strength was measured according to JIS A1108.

[0071]

Aluminum ion concentration in liquid phase: The liquid phase collected was analyzed by ICP-AES. The magnifications assuming that the case with no hardening initiator added is 1.0 (1.0 time) are shown in Table 1.

[0072]

Table 1

Experiment No.	Hardening initiator	Test temperature (°C)	Usable time (min)	Aluminum ion concentration in liquid phase	Compression strength (N/mm ²)		Note
					6 hours	1 day	
1-1	A	5	24 hours or more	0.8 time	unmeasurable due to no hardening	unmeasurable due to no hardening	Comparative Example
1-2	B	5	71	1.2 times	27.8	40.7	Example
1-3	none	5	24 hours or more	1.0 time	unmeasurable due to no hardening	unmeasurable due to no hardening	Comparative Example
1-4	A	20	73	1.5 times	31.4	48.2	Comparative Example
1-5	B	20	68	1.5 times	33.4	50.9	Example
1-6	none	20	24 hours or more	1.0 time	unmeasurable due to no hardening	unmeasurable due to no hardening	Comparative Example

[0073]

It is understood from Table 1 that in the case where the aluminum ion concentration in the liquid phase after 30 minutes from the addition of the hardening initiator is 1.2 times or more the case with no hardening initiator added, the certain usable time is obtained, and good 6-hour strength and 1-day strength are obtained. In addition, the use of the calcium aluminate based compound can reduce the temperature dependency to provide excellent strength exhibition in a low temperature environment.

[0074]

(Experimental Example 2)

The same procedure was performed as in Experimental Example 1 except that the hardening initiator B was used as the hardening initiator, and anhydrous gypsum was mixed in the amount shown in the following table per 100 parts of the hardening initiator B. The results are shown in Table 2.

The anhydrous gypsum used was type II anhydrous gypsum produced in Thailand prepared to have a Blaine specific surface area of 5,000 cm²/g.

[0075]

Table 2

Experiment No.	Hardening initiator	Amount of anhydrous gypsum	Test temperature (°C)	Usable time (min)	Aluminum ion concentration in liquid phase	Compression strength (N/mm ²)			Note
						6 hours	1 day	28 days	
2-1	B	120 parts	5	98	2.5 times	27.0	46.1	57.6	Example
2-2	B	100 parts	5	90	2.1 times	27.1	44.6	54.3	Example
1-2	B	none	5	71	1.2 times	27.8	40.7	49.8	Example

[0076]

It is understood from Table 2 that in the case where anhydrous gypsum is added to the hardening initiator, the compression strength exhibition at a material age of 1 day or later is improved.

[0077]

(Experimental Example 3)

The same procedure was performed as in Experimental Example 2 except that the chemical composition of the calcium aluminate based compound as the hardening initiator B was formulated as shown in the following table, and the hardening initiator B was as a slurry having a water/hardening initiator ratio 0.3 (provided that 1 part of the retarder was added to 100 parts of the hardening initiator B). The results are shown in Table 3.

The chemical composition was confirmed by JIS R5202 "Methods for chemical analysis of portland cements".

[0078]

Table 3

Experiment No.	Chemical composition of calcium aluminate based compound (part)			Test temperature (°C)	Usable time of hardening initiator slurry (min)	Usable time (min)	Aluminum ion concentration in liquid phase	Compression strength		Note
	CaO	Al ₂ O ₃	SiO ₂					after 6 hours (N/mm ²)	5°C	
2-1	47	53	0	5	-	98	2.5 times	27.0		Example
3-1	47	53	0	5	15	98	2.7 times	24.0		Example
3-2	46	53	1	5	30	120	2.5 times	22.0		Example
3-3	30	60	10	5	120	150	2.1 times	21.0		Example
3-4	60	30	10	5	20	70	2.7 times	27.0		Example
3-5	39	43	18	5	60	200	1.8 times	23.0		Example

[0079]

It is understood from Table 3 that in the case where the chemical composition of the calcium aluminate based compound is appropriately change, the effect of improving the temperature dependency can be sufficiently exhibited, and the rapid hardening phenomenon can be suppressed when the hardening initiator is used as a slurry.

Industrial Applicability

[0080]

The ready-mixed shipping type rapid-hardening concrete composition of the present invention is excellent in strength exhibition in the initial stage in a low temperature environment while ensuring a sufficient usable time, and therefore is favorably used particularly in the civil engineering and construction fields.

CLAIMS

[Claim 1]

A hardening initiator for a ready-mixed shipping type rapid-hardening concrete, to be added to a composition containing a cement, a rapid hardener, and a retarder, the hardening initiator providing a hardening initiator-containing composition obtained after 30 minutes from addition of the hardening initiator to the composition under condition of 5°C, a liquid phase obtained through solid-liquid separation of the hardening initiator-containing composition having an aluminum ion concentration ($X_{5^{\circ}\text{C}}$) that is 1.1 times or more an aluminum ion concentration ($Y_{5^{\circ}\text{C}}$) of a liquid phase obtained through solid-liquid separation of a hardening initiator-non-containing composition obtained by not adding the hardening initiator to the composition under condition of 5°C, wherein the hardening initiator comprises a calcium aluminate based compound in the amount of 70% or more by mass, or a calcium aluminate based compound and gypsum, wherein the gypsum is used in an amount of from 10 to 200 parts by mass per 100 parts by mass of the calcium aluminate based compound, wherein the hardening initiator providing a hardening initiator-containing composition obtained after 30 minutes from addition of the hardening initiator to the composition under condition of 20°C, a liquid phase obtained through solid-liquid separation of the hardening initiator-containing composition having an aluminum ion concentration ($X_{20^{\circ}\text{C}}$), wherein the value of $X_{5^{\circ}\text{C}}/X_{20^{\circ}\text{C}}$ is 0.65 or more.

[Claim 2]

The hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to claim 1, wherein the calcium aluminate based compound contains CaO in a range of from 30 to 60% by mass, Al_2O_3 in a range of from 30 to 60% by mass, and SiO_2 in a range of from 1 to 18% by mass.

[Claim 3]

The hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to claim 1 or 2, wherein the calcium aluminate based compound has a degree of amorphousness of 70% or more.

[Claim 4]

A two-component type ready-mixed shipping type rapid-hardening concrete comprising: a material A containing a cement, a rapid hardener, and a

retarder; and a material B containing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to any one of claims 1 to 3.

[Claim 5]

A ready-mixed shipping type rapid-hardening concrete composition comprising a material A containing a cement, a rapid hardener, and a retarder, having added thereto and mixed therewith a material B containing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to any one of claims 1 to 3.

[Claim 6]

The ready-mixed shipping type rapid-hardening concrete composition according to claim 5, wherein the hardening initiator contains a calcium aluminate based compound and a gypsum compound.

[Claim 7]

The ready-mixed shipping type rapid-hardening concrete composition according to claim 6, wherein the calcium aluminate based compound contains a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ based compound, and the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ based compound has a degree of amorphousness of 70% or more and contains SiO_2 in a range of from 1 to 18% by mass.

[Claim 8]

The ready-mixed shipping type rapid-hardening concrete composition according to any one of claims 5 to 7, wherein the retarder contains an oxycarboxylic acid, or a mixture of a carbonate salt of an alkali metal except for lithium and an oxycarboxylic acid.

[Claim 9]

The ready-mixed shipping type rapid-hardening concrete composition according to any one of claims 5 to 8, wherein the composition has a content of the hardening initiator for a ready-mixed shipping type rapid-hardening concrete of from 0.5 to 7 parts by mass per 100 parts by mass in total of the cement and the rapid hardener.

[Claim 10]

A method for preparing a ready-mixed shipping type rapid-hardening concrete, comprising in this order: kneading at least a cement, a rapid hardener, and a retarder with kneading water in a kneading vessel; and further mixing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete according to any one of claims 1 to 3.

[Claim 11]

The method for preparing a ready-mixed shipping type rapid-hardening concrete according to claim 10, wherein a kind and an amount of the hardening initiator for a ready-mixed shipping type rapid-hardening concrete are determined to ensure a usable time of 15 minutes or more after mixing the hardening initiator for a ready-mixed shipping type rapid-hardening concrete.

[Claim 12]

The method for preparing a ready-mixed shipping type rapid-hardening concrete according to claim 10 or 11, wherein the retarder is used in an amount of from 0.3 to 5 parts by mass per 100 parts by mass in total of the cement and the rapid hardener.