

DESCRIPTION

HARDENING ACCELERATOR FOR HYDRAULIC MATERIALS, CEMENT COMPOSITION, AND HARDENED SUBSTANCE

Technical Field

[0001]

The present invention relates to a hardening accelerator for a hydraulic material, a cement composition containing the accelerator, and a hardened body.

Background Art

[0002]

A hydraulic material such as cement used in civil engineering and construction fields typically hardens by being mixed with water and left to stand still for a predetermined period. The hardening rate of the hydraulic material can also be affected by the ratio of a material and water, the ambient environmental temperature, and the curing method, but by using an admixture that accelerates hardening, namely, a hardening accelerator, the time required for the hydraulic material to harden can be shortened.

[0003]

Shortening the time required for the hydraulic material to harden leads to improved productivity at a worksite. For example, a concrete hardened body used in a

precast method for reinforced concrete buildings and the like, can generally be obtained by pouring a cement composition into a mold, allowing the cement composition to be left to stand still for a predetermined period, and then further curing the cement composition by steam curing and the like to obtain a hardened body, but by using a hardening accelerator, the time required to reach an initial strength necessary for demolding can be shortened, so that the hardened body can be efficiently produced.

[0004]

After pouring the cement composition, "compaction" is usually performed using a vibrator or the like to distribute the cement composition evenly within the mold, but when the fluidity of the cement composition immediately after pouring decreases, the compaction requires a lot of effort and time, resulting in reduced productivity.

[0005]

Regarding the hardening accelerator, for example, Patent Literature 1 discloses a hardening accelerator for a hydraulic material, containing predetermined amounts of an inorganic sulfate, calcium sulfoaluminate, and an inorganic hydroxide. Patent Literature 2 discloses a cement admixture containing calcium sulfoaluminate having a Blaine specific surface area value of 4000 cm²/g or more, and one or two or more selected from the group consisting of a

formate, an acetate, and a lactate.

Citation List

Patent Literatures

[0006]

Patent Literature 1: JP 2014-19618 A

Patent Literature 2: JP 2010-235399 A

Summary of Invention

Technical Problem

[0007]

However, the hydraulic material using the hardening accelerator as described above loses fluidity immediately after being kneaded with water, and thus requires effort and time for compaction after pouring, which leads to concerns about reduced productivity.

[0008]

From the above, an object of the present invention is to provide a hardening accelerator for a hydraulic material capable of improving the fluidity retention, the coagulability, and initial strength development of a hydraulic material.

Solution to Problem

[0009]

As a result of intensive studies to solve the problems as described above, the present inventors have found that the problems can be solved by a hardening accelerator for a hydraulic material, containing calcium formate, an inorganic calcium compound, and an inorganic sulfate excluding calcium sulfate in a predetermined ratio, leading to the present invention. That is, the present invention is as follows.

[0010]

[1] A hardening accelerator for a hydraulic material, containing 20.0 to 80.0 mass% of calcium formate, 15.0 to 70.0 mass% of an inorganic calcium compound, and 0.5 to 30.0 mass% of an inorganic sulfate excluding calcium sulfate.

[2] The hardening accelerator for a hydraulic material described in [1], in which the inorganic calcium compound is one or more selected from the group consisting of calcium sulfate, calcium hydroxide, calcium carbonate, and calcium oxide.

[3] The hardening accelerator for a hydraulic material described in [1] or [2], in which the inorganic sulfate is one or more selected from the group consisting of a sulfate, a thiosulfate, a sulfite, a bisulfite, a pyrosulfate, and a pyrobisulfite.

[4] The hardening accelerator for a hydraulic material

described in any one of [1] to [3], further containing 4.5 to 65.0 mass% of calcium sulfoaluminate.

[5] A cement composition containing the hardening accelerator for a hydraulic material described in any one of [1] to [4], and cement.

[6] The cement composition described in [5], in which a content of the hardening accelerator for a hydraulic material is 0.5 to 10 mass%.

[7] A hardened body obtained by hardening the cement composition described in [5] or [6].

[8] A method for producing a hardened body, including hardening a cement composition containing the hardening accelerator for a hydraulic material described in any one of [1] to [4], cement, and water by steam curing at a maximum temperature of 40 to 80°C for 2 to 8 hours.

Advantageous Effects of Invention

[0011]

According to the present invention, it is possible to provide a hardening accelerator for a hydraulic material capable of improving the fluidity retention, the coagulability, and initial strength development of a hydraulic material.

Description of Embodiments

[0012]

Hereinafter, an embodiment of the present invention (present embodiment) will be described in detail, but the present invention is not limited to the embodiment. In the present invention, a "hydraulic material" refers to a material that hardens by being kneaded with water, and a "hardened body" refers to one obtained by hardening cement paste, mortar, concrete, or the like. Note that "%" and "part(s)" in the present description are on a mass basis unless otherwise specified.

[0013]

[Hardening accelerator for hydraulic material]

A hardening accelerator for a hydraulic material according to the present embodiment contains 20.0 to 80.0 mass% of calcium formate, 15.0 to 70.0 mass% of an inorganic calcium compound, and 0.5 to 30.0 mass% of an inorganic sulfate excluding calcium sulfate. The hardening accelerator for a hydraulic material not only accelerates hardening of a hydraulic material when the hydraulic material hardens by being kneaded with water, but in some cases, the hardening accelerator for a hydraulic material itself may also harden while accelerating the hardening.

[0014]

(Calcium formate)

The hardening accelerator for a hydraulic material

contains calcium formate in an amount of 20.0 to 80.0 mass%, preferably 30.0 to 70.0 mass%, and more preferably 40.0 to 65.0 mass%. When the content ratio of the calcium formate is less than 20.0 mass%, the fluidity retention, the coagulability, and the initial strength development of the hydraulic material may not be improved, and when the content ratio thereof is more than 80.0 mass%, the fluidity retention, the coagulability, and the initial strength development may not be improved.

[0015]

(Inorganic calcium compound)

The hardening accelerator for a hydraulic material contains an inorganic calcium compound in an amount of 15.0 to 70.0 mass%, preferably 18.0 to 60.0 mass%, and more preferably 20.0 to 40.0 mass%. When the content ratio of the inorganic calcium compound is less than 15.0 mass%, the fluidity retention, the coagulability, and the initial strength development of the hydraulic material may not be improved, and when the content ratio thereof is more than 70.0 mass%, the fluidity retention, the coagulability, and the initial strength development of the hydraulic material may not be improved.

[0016]

In the present embodiment, the inorganic calcium compound is preferably one or more selected from the group

consisting of calcium sulfate, calcium hydroxide, calcium carbonate, and calcium oxide. When two or more inorganic calcium compounds are used, the total of the respective content ratios is taken as the content ratio of the inorganic calcium compound. In the present embodiment, from the viewpoint of initial strength development, it is preferable to use calcium sulfate, calcium hydroxide and/or calcium oxide, and calcium sulfate is more preferable. When calcium sulfate is used, it is more preferably anhydrous.

[0017]

(Inorganic sulfate)

The hardening accelerator for a hydraulic material contains an inorganic sulfate excluding calcium sulfate in an amount of 0.5 to 30.0 mass%, preferably 1.0 to 25.0 mass%, and more preferably 3.0 to 15.0 mass%. When the content ratio of the inorganic sulfate excluding calcium sulfate is out of the range of 0.5 to 30.0 mass%, the fluidity retention, the coagulability, and the initial strength development of the hydraulic material may not be improved.

[0018]

In the present embodiment, the inorganic sulfate is preferably one or more selected from the group consisting of a sulfate, a thiosulfate, a sulfite, a bisulfite, a

pyrosulfate, and a pyrobisulfite. When two or more inorganic sulfates are used, the total of the respective content ratios is taken as the content ratio of the inorganic sulfate. As an inorganic substance that forms a salt, an alkali metal and an alkaline earth metal are preferable. In the present embodiment, from the viewpoint of initial strength development, it is preferable to use a sulfate and/or a thiosulfate, sodium sulfate, aluminum sulfate, sodium thiosulfate, and potassium alum are more preferable, from the viewpoint of initial strength development, sodium sulfate and aluminum sulfate are further preferable, and among these, from the viewpoint of fluidity retention, sodium sulfate is still more preferable. When sodium sulfate is used, it is more preferably anhydrous.

[0019]

The hardening accelerator for a hydraulic material according to the present embodiment further contains calcium sulfoaluminate in an amount of preferably 4.5 to 65.0 mass%, more preferably 15.0 to 60.0 mass%, and further preferably 30.0 to 50.0 mass%. When the content ratio of the calcium sulfoaluminate is within the above range, the fluidity retention and the initial strength development of the hydraulic material can be further improved.

The calcium sulfoaluminate is a general term for

hydraulic substances and hydrated salts represented by the chemical formula $x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{CaSO}_4 \cdot m\text{H}_2\text{O}$ (x , y , and z are positive real numbers other than 0, and m is 0 or a positive real number), and examples thereof include AFt phase represented by ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), AFm phase represented by monosulfate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$), and those in which the AFt phase and the AFm phase coexist in addition to hauynite ($3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$). The calcium sulfoaluminate may be amorphous. A part of Al_2O_3 may be substituted with a trace amount of Fe_2O_3 , SiO_2 , or the like, and a part of CaSO_4 may be substituted with $\text{Ca}(\text{OH})_2$, CaCO_3 , or the like. Note that, in the present invention, in the chemical formula $x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{CaSO}_4 \cdot m\text{H}_2\text{O}$, since the fluidity of the hydraulic material cannot be maintained, and the strength at the time of hardening may be lowered due to a phase transition, z cannot be set to 0.

[0020]

The calcium sulfoaluminate can be produced by blending a calcia raw material such as lime, a sulfate raw material such as gypsum, alumina raw material such as bauxite (aluminum hydroxide), and the like, as raw materials, in a predetermined ratio, for example, a molar ratio of $\text{CaO} : \text{CaSO}_4 : \text{Al}_2\text{O}_3 = 3 : 3 : 1$, firing the mixture at about $1,500^\circ\text{C}$ using a kiln or the like, and pulverizing

the mixture. It is acceptable to add silicon dioxide or the like to the once-fired material, perform a heat treatment, and pulverize the mixture.

[0021]

The Blaine specific surface area value (hereinafter, also simply referred to as "Blaine value") of the calcium sulfoaluminate is preferably 1,000 to 6,000 cm²/g, more preferably 2,000 to 4,000 cm²/g, and further preferably 2,200 to 3,800 cm²/g.

In the present invention, the Blaine specific surface area value is measured in accordance with the specific surface area test described in JIS R 5201:2015 "Physical testing methods for cement".

[0022]

[Cement composition]

A cement composition according to the present embodiment contains the hardening accelerator for a hydraulic material and cement.

[0023]

The cement is not particularly limited, but examples thereof include various types of Portland cement such as ordinary, rapid-hardening, ultra-rapid-hardening, low-heat, and moderate-heat, various types of mixed cement obtained by mixing blast furnace slag, fly ash, silica fume, or the like with these Portland cements, environmentally friendly

cements (eco cements) produced using urban waste incineration ash or sewage sludge incineration ash as a raw material, commercially available fine-particle cements, and white cement, and It is also possible to use various types of cement in a finely powdered form. It is also possible to use those which are adjusted by increasing or decreasing the amount of components (such as gypsum) normally used in cement. Furthermore, a combination of two or more of these can also be used. From the viewpoint of enhancing the initial strength development, it is preferable to select ordinary Portland cement or rapid-hardening Portland cement, but even when blast furnace cement or fly ash cement having a low initial strength development is used, early demolding is possible.

[0024]

In the cement used in the present invention, from the viewpoint of production costs and strength development, the Blaine specific surface area value of the cement is preferably 2,500 cm²/g to 7,000 cm²/g, more preferably 2,750 cm²/g to 6,000 cm²/g, and further preferably 3,000 cm²/g to 4,500 cm²/g.

[0025]

The content of the hardening accelerator for a hydraulic material in the cement composition is preferably 0.5 to 10 mass%, more preferably 1.0 to 9.0 mass%, and

further preferably 2.5 to 8.0 mass%. When the content of the hardening accelerator for a hydraulic material in the cement composition is within the above range, the fluidity retention, the coagulability, and the initial strength development of the hydraulic material can be further improved.

[0026]

The flow value of the cement composition before pouring is preferably 160 to 230, more preferably 170 to 220, and further preferably 190 to 200. When the flow value of the cement composition is within the above range, pouring and compaction are easily performed, and workability is improved. The change rate of the flow value (flow change rate) after 1 hour from kneading of the cement composition is preferably less than 20%, more preferably less than 15%, and further preferably less than 10%. When the flow change rate of the cement composition is within the above range, even when pouring is performed after 1 hour from kneading of the cement composition, pouring and compaction are easily performed, and workability is improved.

Note that, in the present invention, the flow value can be measured in accordance with the method specified in JIS R 5201:2015 "Physical testing methods for cement". The flow change rate can be determined by calculating a value

of (flow value after 1 hour from kneading)/(flow value immediately after kneading) × 100 (%) and then subtracting the value from 100%.

[0027]

The cement composition preferably contains an aggregate. As the aggregate to be used, the same fine aggregate or coarse aggregate as that used in ordinary cement mortar or concrete can be used. That is, river sand, river gravel, mountain sand, mountain gravel, crushed stone, crushed sand, limestone aggregate, lime sand, silica sand, colored sand, artificial aggregate, blast furnace slag aggregate, sea sand, sea gravel, artificial lightweight aggregate, heavy weight aggregate, and the like can be used, and combinations of these are also possible.

[0028]

The content ratio of the aggregate is preferably 40 parts by mass or more and 250 parts by mass or less, more preferably 50 parts by mass or more and 230 parts by mass or less, and further preferably 60 parts by mass or more and 200 parts by mass or less, with respect to 100 parts by mass of the cement in the cement composition. When the content ratio of the aggregate is within the above range, the fluidity retention and the initial strength development of the hydraulic material can be further improved.

[0029]

The cement composition can contain an alkali metal carbonate. When the cement composition contains an alkali metal carbonate, the fluidity retention and the initial strength development are easily improved. Examples of the alkali metal carbonate include sodium carbonate, potassium carbonate, lithium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, and lithium hydrogen carbonate, and combinations of these are also possible.

[0030]

The content ratio of the alkali metal carbonate is preferably 1 to 6 parts by mass and more preferably 2 to 5 parts by mass in terms of solid content with respect to 100 parts by mass of the cement in the cement composition. When the content ratio of the alkali metal carbonate is within the above range, the fluidity retention and the initial strength development are easily improved.

[0031]

The cement composition can contain siliceous fine powder. When the cement composition contains siliceous fine powder, the fluidity retention and the initial strength development are easily improved. Examples of the siliceous fine powder include latent hydraulic substances such as granulated blast-furnace slag fine powder, and pozzolanic substances such as fly ash and silica fume, and among them, silica fume is preferable. The type of the

silica fume is not limited, but from the viewpoint of fluidity, it is more preferable to use silica fume containing 10% or less of ZrO_2 as an impurity or acid silica fume. The acid silica fume refers to silica fume in which a supernatant liquid when 1 g of silica fume is added to 100 cc of pure water and stirred shows an acidity with a pH of 5.0 or less.

[0032]

The fineness of the siliceous fine powder is not particularly limited, but usually, the granulated blast-furnace slag fine powder and the fly ash have a Blaine value in a range of 3,000 cm^2/g or more and 9,000 cm^2/g or less, and the silica fume has a BET specific surface area in a range of 20,000 cm^2/g or more and 300,000 cm^2/g or less.

[0033]

The content ratio of the siliceous fine powder is preferably 1 to 20 parts by mass, more preferably 2 to 15 parts by mass, and further preferably 3 to 12 parts by mass, with respect to 100 parts by mass of the cement in the cement composition. When the content ratio of the siliceous fine powder is the lower limit value or more, the fluidity retention and the initial strength development are easily improved. When the content ratio of the siliceous fine powder is the upper limit value or less, the fluidity

retention is more easily improved.

[0034]

The cement composition can also contain a defoaming agent as long as it does not adversely affect the performance. The defoaming agent is used to suppress the amount of air that is entrained during mixing. The type of the defoaming agent is not particularly limited as long as it does not significantly adversely affect the strength characteristics of the hardened mortar, and both a liquid form and a powder form can be used. Examples thereof include polyether-based defoaming agents, polyhydric alcohol-based defoaming agents such as esterified products of polyhydric alcohols and alkyl ethers, alkyl phosphate-based defoaming agents, and silicone-based defoaming agents.

[0035]

The content ratio of the defoaming agent is preferably 0.002 to 0.5 parts by mass, more preferably 0.005 to 0.45 parts by mass, and further preferably 0.01 to 0.4 parts by mass, with respect to 100 parts by mass of the cement in the cement composition. When the content ratio of the defoaming agent is the lower limit value or more, the defoaming effect can be sufficiently exhibited, and when the content ratio of the defoaming agent is the upper limit value or less, the fluidity retention is easily

improved.

[0036]

For the cement composition, as long as the performance is not adversely affected, one or two or more of admixtures such as gas foaming substances, water-reducing agents, AE agents, rust inhibitors, water repellents, antibacterial agents, colorants, antifreeze agents, limestone fine powder, cooled-down blast-furnace slag fine powder, sewage sludge incineration ash or its molten slag, urban waste incineration ash or its molten slag, and pulp sludge incineration ash, thickeners, shrinkage-reducing agents, polymers, clay minerals such as bentonite and sepiolite, and anionic exchangers such as hydrotalcite, and the like can be used as long as they do not substantially inhibit the objects of the present invention.

[0037]

[Hardened body]

A hardened body according to the present embodiment is obtained by hardening a cement composition. The hardened body is usually produced by kneading a cement composition with water, whereby the cement, which is a hydraulic material, undergoes a hydration reaction and hardens. The amount of water to be mixed is not particularly limited, but is preferably 10 to 70 parts by

mass, more preferably 14 to 65 parts by mass, and further preferably 16 parts by mass to 60 parts by mass, with respect to 100 parts by mass of the cement composition. When the amount of water to be mixed is within the above range, the initial strength development of the hydraulic material is easily improved.

[0038]

The hardened body is obtained by kneading a cement composition with water and leaving the kneaded product to stand still so as to harden the kneaded product, but the hardened body can be more efficiently obtained by filling (pouring) the kneaded product in a mold after kneading, or directly pouring, spraying, or applying the kneaded product to a construction site.

[0039]

The compressive strength of the hardened body depends on the type of cement to be used, but is preferably 10.5 to 15.0 N/mm², more preferably 11.0 to 14.0 N/mm², and further preferably 12.0 to 13.0 N/mm², 6 hours after pouring. The compressive strength at the material age of 7 days is preferably 40.0 to 50.0 N/mm², more preferably 41.0 to 48.0 N/mm², and further preferably 42.0 to 46.0 N/mm².

Note that, in the present invention, the compressive strength can be measured in accordance with the method specified in JIS R 5201:2015 "Physical testing methods for

cement".

[0040]

[Method for producing hardened body]

A method for producing a hardened body according to the present embodiment is a method of hardening a cement composition containing a hardening accelerator for a hydraulic material, cement, and water by steam curing at a maximum temperature of 40 to 80°C for 2 to 8 hours. The method for producing a hardened body preferably includes a kneading step of kneading a hardening accelerator for a hydraulic material, cement, and water, a pouring step of filling the kneaded cement composition in a mold, and a curing step of curing the cement composition filled in the mold, in this order.

[0041]

The kneading method in the kneading step is not particularly limited, and each of the materials may be mixed at the time of construction, or some or all of the materials may be mixed in advance. As a mixing device, any existing device such as a tilting drum mixer, an omni mixer, a Henschel mixer, a V-type mixer, a ProShear mixer, and a Nauta mixer can be used.

[0042]

The pouring method in the pouring step can be performed by a known method. The temperature of the cement

composition at the time of pouring is preferably 0 to 50°C and more preferably 10 to 40°C. When the temperature of the cement composition at the time of pouring is within the above range, the hardened body can be easily demolded at an early stage.

[0043]

The method for producing a hardened body preferably further includes a compaction step after the pouring step. As the compaction method, a known method can be used, but from the viewpoint of workability, it is preferable to use a vibrator. Since the cement composition containing the hardening accelerator for a hydraulic material of the present invention maintains favorable fluidity immediately before pouring, compaction can be easily performed, the cement composition can be uniformly distributed in the mold, and air bubbles mixed at the time of pouring or the like can be removed.

[0044]

As the curing method used in the curing step, from the viewpoint of improving productivity, it is preferable to use steam curing using a curing chamber, a heating sheet, or the like. The steam curing is usually performed by raising the temperature of surrounding atmosphere of a target and maintaining a constant temperature while maintaining a moderate humidity. As steam curing

conditions, it is preferable that the maximum temperature is 40 to 80°C and the curing time is 2 to 8 hours, it is more preferable that the maximum temperature is 40 to 75°C and the curing time is 2.5 to 7.5 hours, and it is further preferable that the maximum temperature is 45 to 60°C and the curing time is 3 to 7 hours. When steam curing is performed with the maximum temperature of the atmosphere around the cement composition during steam curing set within the above range and the curing time set within the above range, the hardened body can be easily demolded at an early stage.

[0045]

The relative humidity around the cement composition during steam curing is preferably 50% RH or more, more preferably 75% RH or more, and further preferably 90% RH or more. The upper limit is not limited, but may be 100% RH. When the relative humidity around the cement composition during steam curing is within the above range, the hardened body can be easily demolded at an early stage.

[0046]

The curing step preferably includes a pre-curing step. As pre-curing conditions, it is preferable to keep the temperature constant at a temperature of 10 to 50°C for about 1 to 3 hours. When the curing step includes the pre-curing step, the temperature inside the poured cement

composition can be made uniform, and it is easy to prevent thermal cracks due to the temperature difference between the inside and the outside.

[0047]

The curing step preferably includes a heating step. As the heating method, a known method can be used, heating is preferably performed at a temperature increase rate of 10 to 30°C/hr, heating is more preferably performed at a temperature increase rate of 12 to 28°C/hr, and heating is further preferably performed at a temperature increase rate of 15 to 25°C. When the temperature increase rate in the heating step is within the above range, hardening can be accelerated while preventing thermal cracks due to a sudden increase in temperature of the cement composition.

[0048]

The curing step preferably includes a temperature maintaining step. As the temperature maintaining method, a known method can be used, and a constant temperature is maintained preferably in a temperature range of 40 to 80°C for 1 to 8 hours, more preferably in a temperature range of 40 to 75°C for 1 to 6 hours, and further preferably in a temperature range of 45 to 65°C for 2.5 to 5 hours. By maintaining a constant temperature within the above numerical range in the temperature maintaining step, the poured cement composition can be uniformly hardened, and it

is easy to enable early demolding.

[0049]

The method for producing a hardened body preferably includes a natural cooling step after the curing step. In the natural cooling step, the hardened body obtained in the curing step is naturally cooled under a normal temperature atmosphere. The cooling time is not particularly limited, but as long as the hardened body can be cooled to a temperature that allows the hardened body to be easily demolded, the cooling time is sufficient to be about 0.5 to 2 hours. By including the natural cooling step after the curing step, thermal cracks of the hardened body can be prevented.

Examples

[0050]

Hereinafter, the present invention will be further described based on experimental examples, but the present invention is not limited thereto.

[0051]

<Experimental Example 1>

A mortar having a water/cement ratio of 45% and a cement/aggregate ratio of 1 : 2.5 (mass ratio) was prepared using the following materials. A water-reducing agent was added to the obtained mortar in the ratio shown in Table 1,

and the mixture was kneaded so that the mixing amount of the hardening accelerator for a hydraulic material having the composition shown in Table 1 was the ratio shown in Table 1, thereby preparing a cement composition. The flow value of the obtained cement composition was measured, and the flow change rate was calculated. The initial setting time was also measured. Both are also shown in Table 1.

The prepared cement composition was filled in a mold having a dimension of $4 \times 4 \times 16$ cm, and then steam curing was performed to obtain a hardened body. As the steam curing conditions, pre-curing was performed at 20°C for 1 hour, followed by a temperature increase at a rate of 20°C/hr for 1.5 hours, a temperature retention at 50°C for 3 hours, and natural cooling for 0.5 hours. The compressive strength of the obtained hardened body was measured. The results are also shown in Table 1.

[0052]

(Materials used)

Cement: ordinary Portland cement (commercially available product), Blaine specific surface area: 3,200 cm²/g, specific gravity: 3.15 g/cm³

Water: tap water

Aggregate: river sand sourced from Himekawa River system in Niigata Prefecture

Water-reducing agent: polycarboxylic acid-based

high-performance water-reducing agent (commercially available product)

Calcium formate: reagent

Calcium sulfate (inorganic calcium compound): reagent

Sodium sulfate (inorganic sulfate): anhydrous, reagent

[0053]

(Measurement items)

Flow change rate: In accordance with the method specified in JIS R 5201:2015 "Physical testing methods for cement", the flow values of the cement composition immediately after kneading and after 1 hour from kneading were measured. The flow values immediately after kneading were all about 200. Using each measured flow value, the flow change rate was calculated as $(\text{flow change rate}) = 1 - (\text{flow value after 1 hour from kneading})/(\text{immediately after kneading}) \times 100$.

Initial setting time: In accordance with the method specified in JIS A 1147:2019 "Method of test for time of setting of concrete mixtures by penetration resistance", the time at which the penetration resistance value was 3.5 N/mm² was defined as the initial setting time.

Compressive strength: In accordance with the method specified in JIS R 5201:2015 "Physical testing methods for

cement”, the compressive strengths of the hardened body at the material age of 6 hours after the end of steam curing (immediately after demolding) and at the material age of 7 days were measured.

[0054]

[Table 1]

Table 1

No.	Hardening accelerator for hydraulic material				Cement (parts by mass)	Water-reducing agent (parts by mass)	Flow change rate (%)	Initial setting time (min)	Compressive strength (N/mm ²)		Remarks
	Calcium formate (mass%)	Calcium sulfate (mass%)	Sodium sulfate (mass%)	Mixing amount (parts by mass)					Immediately after demolding	7 days	
1-1	0	0	0	0	100	0.006	25.3	455	8.1	40.1	Reference Example
1-2	60.0	35.0	5.0	5	95	0.006	6.0	283	14.2	43.4	Example
1-3	55.0	25.0	20.0	5	95	0.006	6.8	294	13.4	43.1	Example
1-4	50.0	40.0	10.0	5	95	0.006	7.8	287	12.9	41.2	Example
1-5	80.0	15.0	5.0	5	95	0.006	5.0	295	14.3	42.9	Example
1-6	35.0	45.0	20.0	5	95	0.006	6.5	304	12.4	41.9	Example
1-7	30.0	65.0	5.0	5	95	0.006	10.7	297	14.1	43.5	Example
1-8	60.0	20.0	20.0	5	95	0.006	9.8	285	14.1	42.9	Example
1-9	40.0	35.0	25.0	5	95	0.006	8.8	289	13.4	42.1	Example
1-10	60.0	39.0	1.0	5	95	0.006	9.7	285	14.4	44.7	Example
1-11	15.0	55.0	30.0	5	95	0.006	23.5	378	8.5	40.4	Comparative Example
1-12	84.5	15.0	0.5	5	95	0.006	20.4	355	9.0	40.2	Comparative Example
1-13	65.0	5.0	30.0	5	95	0.006	24.1	410	8.3	40.8	Comparative Example
1-14	20.0	75.0	5.0	5	95	0.006	25.0	412	8.5	40.7	Comparative Example
1-15	60.4	39.5	0.1	5	95	0.008	24.5	435	8.4	40.1	Comparative Example
1-16	40.0	25.0	35.0	5	95	0.006	23.0	423	9.4	40.0	Comparative Example

[0055]

From the results shown in Table 1, it was confirmed that by using the hardening accelerator for a hydraulic material containing calcium formate, an inorganic calcium compound, and an inorganic sulfate excluding calcium sulfate in a predetermined ratio, the fluidity retention, the coagulability, and the initial strength development of the cement composition can be improved.

[0056]

<Experimental Example 2>

A mortar, a cement composition, and a hardened body were prepared in the same manner as in Experimental Example 1, except that calcium hydroxide, calcium carbonate, and calcium oxide were used in the ratio shown in Table 2 in addition to calcium sulfate as the inorganic calcium compound contained in the hardening accelerator for a hydraulic material, and the flow change rate, the initial setting time, and the compressive strength were measured. The results are also shown in Table 2.

[0057]

(Inorganic calcium compound)

Calcium hydroxide: reagent

Calcium carbonate: reagent

Calcium oxide: reagent

[0058]

[Table 2]

Table 2

No.	Hardening accelerator for hydraulic material							Cement Mixing amount (parts by mass)	Water- reducing agent (parts by mass)	Flow change rate (%)	Initial setting time (min)	Compressive strength (N/mm ²)		Remarks
	Calcium formate (mass%)	Inorganic calcium compound (mass%)				Sodium sulfate (mass%)	Mixing amount (parts by mass)					Immediately after demolding	7 days	
		Calcium sulfate	Calcium hydroxide	Calcium carbonate	Calcium oxide									
1-1	0	0	0	0	0	0	0	100	0.006	25.3	455	8.1	40.1	Reference Example
1-2	60.0	35.0	0	0	0	5.0	5	95	0.006	6.0	283	14.2	43.4	Example
2-1	60.0	0	35.0	0	0	5.0	5	95	0.006	8.4	298	12.1	42.9	Example
2-2	60.0	0	0	35.0	0	5.0	5	95	0.006	6.2	308	11.5	43.5	Example
2-3	60.0	0	0	0	35.0	5.0	5	95	0.006	8.5	284	13.5	42.7	Example
2-4	60.0	17.5	17.5	0	0	5.0	5	95	0.006	9.1	294	13.2	43.0	Example
2-5	60.0	17.5	0	0	17.5	5.0	5	95	0.006	9.4	275	14.0	43.9	Example

[0059]

From the results shown in Table 2, it was confirmed that by using calcium sulfate, calcium hydroxide, calcium carbonate, and calcium oxide as the inorganic calcium compound contained in the hardening accelerator for a hydraulic material, the fluidity retention, the coagulability, and the initial strength development of the cement composition can be improved. In particular, it was confirmed that in the case of containing calcium sulfate, the initial strength development of the cement composition can be particularly improved.

[0060]

<Experimental Example 3>

A mortar, a cement composition, and a hardened body

were prepared in the same manner as in Experimental Example 1, except that aluminum sulfate, potassium alum, and sodium thiosulfate were used in the ratio shown in Table 3 in addition to sodium sulfate as the inorganic sulfate contained in the hardening accelerator for a hydraulic material, and the flow change rate, the initial setting time, and the compressive strength were measured. The results are also shown in Table 3.

[0061]

(Inorganic sulfate)

Aluminum sulfate: reagent

Potassium alum: reagent

Sodium thiosulfate: reagent

[0062]

[Table 3]

Table 3

No.	Hardening accelerating agent for hydraulic material							Cement Mixing amount (parts by mass)	Water- reducing agent (parts by mass)	Flow change rate (%)	Initial setting time (min)	Compressive strength (N/mm ²)		Remarks
	Calcium formate (mass%)	Calcium sulfate (mass%)	Inorganic sulfate (mass%)				Mixing amount (parts by mass)					Immediately after demolding	7 days	
			Sodium sulfate	Aluminum sulfate	Potassium alum	Sodium thiosulfate								
1-1	0	0	0	0	0	0	0	100	0.006	25.3	455	8.1	40.1	Reference Example
1-2	60.0	35.0	5.0	0	0	0	5	95	0.006	6.0	283	14.2	43.4	Example
3-1	50.0	30.0	20.0	0	0	0	5	95	0.006	7.8	241	14.3	41.2	Example
3-2	50.0	30.0	0	20.0	0	0	5	95	0.006	11.2	243	14.8	44.3	Example
3-3	50.0	30.0	0	0	20.0	0	5	95	0.006	10.9	264	13.9	41.2	Example
3-4	50.0	30.0	0	0	0	20.0	5	95	0.006	9.4	275	13.2	40.5	Example

[0063]

From the results shown in Table 3, it was confirmed that by using sodium sulfate, aluminum sulfate, potassium alum, and sodium thiosulfate as the inorganic sulfate contained in the hardening accelerator for a hydraulic material, the fluidity retention, the coagulability, and the initial strength development of the cement composition can be improved. In particular, it was confirmed that in the case of containing sodium sulfate and aluminum sulfate, the initial strength development can be further improved, and particularly, in the case of containing sodium sulfate, the fluidity retention can also be further improved.

[0064]

<Experimental Example 4>

A mortar, a cement composition, and a hardened body were prepared in the same manner as in Experimental Example 1, except that calcium sulfoaluminate was further added to the hardening accelerator for a hydraulic material in the ratio shown in Table 4, and the flow change rate, the initial setting time, and the compressive strength were measured. The results are also shown in Table 4.

[0065]

(Calcium sulfoaluminate)

A sample product obtained by mixing primary reagent calcium carbonate, calcium sulfate dihydrate, and aluminum

hydroxide so that the molar ratio of $\text{CaO} : \text{CaSO}_4 : \text{Al}_2\text{O}_3$ is 4 : 3 : 1, firing the mixture at $1,400^\circ\text{C}$ for 2 hours, leaving the mixture to stand still at room temperature, and pulverizing the mixture until the Blaine specific surface area becomes $3,500 \text{ cm}^2/\text{g}$.

[0066]

[Table 4]

Table 4

No.	Hardening accelerator for hydraulic material					Cement (parts by mass)	Water- reducin g agent (parts by mass)	Flow change rate (%)	Initial setting time (min)	Compressive strength (N/mm ²)		Remarks
	Calcium sulfoaluminate (mass%)	Calcium formate (mass%)	Calcium sulfate (mass%)	Sodium sulfate (mass%)	Mixing amount (parts by mass)					Immediately after demolding	7 days	
1-1	0.0	0.0	0.0	0.0	0	100	0.006	25.3	455	8.1	40.1	Reference Example
1-2	0.0	60.0	35.0	5.0	5	95	0.006	6.0	283	14.2	43.4	Example
4-1	35.0	39.0	22.8	3.2	5	95	0.006	8.1	350	14.5	42.1	Example
4-2	20.0	48.0	28.0	4.0	5	95	0.006	9.2	313	14.9	42.9	Example
4-3	60.0	24.0	14.0	2.0	5	95	0.006	10.5	394	15.2	40.4	Example

[0067]

From the results shown in Table 4, it was confirmed that when the hardening accelerator for a hydraulic material further contains calcium sulfoaluminate, the initial strength development can be further improved.

[0068]

<Experimental Example 5>

A mortar, a cement composition, and a hardened body

were prepared in the same manner as in Experimental Example 1, except that mixing amount of the hardening accelerator for a hydraulic material was set to the ratio shown in Table 5, and the flow change rate, the initial setting time, and the compressive strength were measured. The results are also shown in Table 5.

[0069]

[Table 5]

Table 5

No.	Hardening accelerator for hydraulic material				Cement Mixing amount (parts by mass)	Water- reducing agent (parts by mass)	Flow change rate (%)	Initial setting time (min)	Compressive strength (N/mm ²)		Remarks
	Calcium formate (mass%)	Calcium sulfate (mass%)	Sodium sulfate (mass%)	Mixing amount (parts by mass)					Immediately after demolding	7 days	
1-1	0	0	0	0	100	0.006	25.3	455	8.1	40.1	Reference Example
1-2	60.0	35.0	5.0	5	95	0.006	6.0	283	14.2	43.4	Example
5-1	60.0	35.0	5.0	2	98	0.006	7.4	350	12.1	42.1	Example
5-2	60.0	35.0	5.0	8	92	0.006	9.1	223	15.8	45.6	Example
5-3	60.0	35.0	5.0	0.03	99.97	0.006	18.5	410	9.5	41.0	Example
5-4	60.0	35.0	5.0	20	80	0.003	28.5	164	16.0	38.5	Example

[0070]

From the results shown in Table 5, it was confirmed that by setting the mixing amount of the hardening accelerator for a hydraulic material to a predetermined range, the fluidity retention, the coagulability, and the initial strength development of the cement composition can be improved.

[0071]

<Experimental Example 6>

A mortar, a cement composition, and a hardened body were prepared in the same manner as in Experimental Example 1, except that blast furnace cement and fly ash cement were used as the cement used in the cement composition, and the flow change rate, the initial setting time, and the compressive strength were measured. The results are also shown in Table 6.

[0072]

(Cement)

Blast furnace B type cement: commercially available product, Blaine specific surface area: 3,200 cm²/g, specific gravity: 3.15 g/cm³

Blast furnace C type cement: commercially available product, Blaine specific surface area: 3,500 cm²/g, specific gravity: 3.15 g/cm³

Fly ash cement B type: commercially available product, Blaine specific surface area: 3,200 cm²/g, specific gravity: 3.15 g/cm³

[0073]

[Table 6]

Table 6

No.	Hardening accelerator for hydraulic material				Cement (parts by mass)	Cement type	Water-reducing agent (parts by mass)	Flow change rate (%)	Initial setting time (min)	Compressive strength (N/mm ²)		Remarks
	Calcium formate (mass%)	Calcium sulfate (mass%)	Sodium sulfate (mass%)	Mixing amount (parts by mass)						Immediately after demolding	7 days	

1-1	0	0	0	0	100	Ordinary Portland cement	0.006	25.3	455	8.1	40.1	Reference Example
1-2	60.0	35.0	5.0	5	95	Ordinary Portland cement	0.006	6.0	283	14.2	43.4	Example
6-1	0	0	0	0	100	Blast furnace cement B type	0.006	26.1	634	6.5	38.7	Reference Example
6-2	60.0	35.0	5.0	5	95	Blast furnace cement B type	0.006	6.5	456	10.4	41.5	Example
6-3	0	0	0	0	100	Blast furnace cement C type	0.006	28.3	785	4.2	33.5	Reference Example
6-4	60.0	35.0	5.0	5	95	Blast furnace cement C type	0.006	9.1	564	8.5	36.8	Example
6-5	0	0	0	0	100	Fly ash cement B type	0.006	27.5	656	4.1	28.4	Reference Example
6-6	60.0	35.0	5.0	5	95	Fly ash cement B type	0.006	8.5	473	8.1	30.4	Example

[0074]

From the results shown in Table 6, it was confirmed that even when blast furnace cement or fly ash cement is used as the cement used in the cement composition, the fluidity retention, the coagulability, and the initial strength development of the cement composition can be improved.

[0075]

From the above results, it was confirmed that the hardening accelerator for a hydraulic material of the

present invention contains calcium formate, an inorganic calcium compound, and an inorganic sulfate in a predetermined ratio, thereby making it possible to improve the fluidity retention, the coagulability, and the initial strength development of the cement composition.

Industrial Applicability

[0076]

The hardening accelerator for a hydraulic material of the present invention contains calcium formate, an inorganic calcium compound, and an inorganic sulfate excluding calcium sulfate in a predetermined ratio, thereby making it possible to improve the fluidity retention, the coagulability, and the initial strength development of the hydraulic material. Therefore, it can be widely applied to civil engineering and construction fields, such as a concrete hardened body used in the precast method.

CLAIMS

[Claim 1]

A hardening accelerator for a hydraulic material, comprising 20.0 to 80.0 mass% of calcium formate, 15.0 to 70.0 mass% of an inorganic calcium compound, and 0.5 to 30.0 mass% of an inorganic sulfate excluding calcium sulfate.

[Claim 2]

The hardening accelerator for a hydraulic material according to claim 1, wherein the inorganic calcium compound is one or more selected from the group consisting of calcium sulfate, calcium hydroxide, calcium carbonate, and calcium oxide.

[Claim 3]

The hardening accelerator for a hydraulic material according to claim 1 or 2, wherein the inorganic sulfate is one or more selected from the group consisting of a sulfate, a thiosulfate, a sulfite, a bisulfite, a pyrosulfate, and a pyrobisulfite.

[Claim 4]

The hardening accelerator for a hydraulic material according to claim 1 or 2, further comprising 4.5 to 65.0 mass% of calcium sulfoaluminate.

[Claim 5]

A cement composition comprising the hardening

accelerator for a hydraulic material according to claim 1 or 2, and cement.

[Claim 6]

The cement composition according to claim 5, wherein a content of the hardening accelerator for a hydraulic material is 0.5 to 10 mass%.

[Claim 7]

A hardened body obtained by hardening the cement composition according to claim 5.

[Claim 8]

A method for producing a hardened body, comprising hardening a cement composition containing the hardening accelerator for a hydraulic material according to claim 1 and cement by steam curing at a maximum temperature of 40 to 80°C for 2 to 8 hours.