

HIGH EARLY STRENGTH AGENT FOR CEMENTS, HIGH EARLY STRENGTH CEMENT USING THE SAME, AND METHOD FOR PRODUCING HIGH EARLY STRENGTH CONCRETE

TECHNICAL FIELD

[0001] The present invention relates mainly to a cement composition used in civil engineering and constructions, a cement hardened body using the same, and a method for producing thereof.

BACKGROUND ART

[0002] Concrete products are produced by pouring a mixture of cement, aggregate, water, and admixture into a form, appropriately curing, and deforming. During this produce, it is important to develop a high strength at an early stage of age in order to improve productivity, that is, to improve the turnover of the forms. Improving the turnover of the forms leads to reduce in the number of the required expensive forms. For increasing the initial strength, it is known to use high early strength cement, decrease the water/cement ratio of concrete with a water reducing agent, and perform a steam curing process.

[0003] In recent years, shorten steam curing methods, and furthermore, no required steam curing methods has been demanded, due to higher energy cost incurred by the use of steam. In addition, further shorten curing process has been also demanded for the requirement of higher productivity, for example, it may be necessary to develop higher strength at curing time of 16 hours during producing concrete products. Curing process normally includes some complicated processes, such as a heating work process with steam, and it would not be a practical method, even if such process is attempted to be changed for improvement of the initial strength. Therefore, the market seeks a method for easily producing a concrete product having higher initial strength without changing the process, from the viewpoint of producing cost.

[0004] It is disclosed that admixtures for increasing the strength mainly include compositions with such as quicklime, gypsum, and alkali metal sulfate, and a combination of a specific compound such as glycerin and an alkali metal sulfate (see Patent Documents 1 to 4). Furthermore, it is reported that nitrate or carboxylic acid has been used as a curing accelerator, but only a few reports have mentioned the combination of these curing accelerating components (Patent Documents 5 to 7). Furthermore, a curing accelerator containing chlorine such as sodium chloride or calcium

chloride is also known, but such accelerator is unpreferably used, because it would be a factor of deterioration of concrete, such as steel corrosion or salt damage.

[0005] In addition, it is reported that an aqueous solution containing nitrate can promote an elution of calcium hydroxide in a cement hardened body (Non-Patent Document 1). When nitrate is used as a curing accelerator, the formation of calcium hydroxide, which is a hydration product of cement, might not proceed sufficiently, and the strength property might not be developed for a long term. Therefore, it is preferable that adjusting the concentration of calcium in the aqueous solution containing nitrate to a certain value or more in order to maintain the formation of calcium hydroxide, but too much high concentration of the calcium results in a poor storability of the liquid, because the salt of calcium precipitates in the solution.

[0006] A curing accelerator containing a nitrate and a carboxylic acid has been disclosed, but the conventional accelerator is used in the form of solid (Patent Document 8), and its concentration has not been studied (Patent Document 9).

CITATION LIST

Patent Literature

[0007]

Patent Document 1: Japanese Patent Application Laid-open Publication No. 2001-294460A

Patent Document 2: Japanese Patent Application Laid-open Publication No. 2011-153068A

Patent Document 3: Japanese Patent Application Laid-open Publication No. 2000-233959A

Patent Document 4: Japanese Patent Application Laid-open Publication No. 2008-519752A

Patent Document 5: Japanese Patent Application Laid-open Publication No. H02-279546A

Patent Document 6: Japanese Patent Application Laid-open Publication No. 2000-516191A

Patent Document 7: Japanese Patent Application Laid-open Publication No. 2010-132547A

Patent Document 8: Japanese Patent Application Laid-open Publication No. 2002-220267A

Patent Document 9: Japanese Patent Publication No. 5140215B2

[0008]

Non-Patent Literature

Non-Patent Document 1: Cement Science and Concrete Technology Vol. 61 (2008), pp. 262 - 269

SUMMARY OF INVENTION

Technical Problem

[0009] As a result of studies of the above-mentioned problems and demands, the present inventors has found a high early strength agent obtained by dissolving nitric acid and a salt thereof, and a carboxylic acid and a salt thereof in water in a specific blending range, which can maintain a storability of a liquid and a strength developability for a long term, and have completed the present invention.

Solution to Problem

[0010] The present invention can provide the below embodiments.

[0011] (1) A high early strength agent for cement, comprising:

30% by mass or more and 60% by mass or less of nitric acid or a salt thereof;

0.1% by mass or more and 10% by mass or less of a carboxylic acid or a salt thereof; and

water, and

wherein a concentration of calcium element in the high early strength agent is in the range of 5% by mass or more and 20% by mass or less.

[0012] (2) The high early strength agent for cements according to (1), further comprising alcohol amine or glycerin.

[0013] (3) High early strength cement containing 0.1 to 10 parts by mass of the high early strength agent according (1) or (2) with respect to 100 parts by mass of the cement.

[0014] (4) A method for producing a high early strength concrete characterized in that post-adding the high early strength agent according to (1) or (2) into a fresh concrete in an agitator car.

[0015] (5) A method for producing concrete characterized in that applying or spraying 100 to 600 g/m² of the high early strength agent according to (1) or (2) on a concrete surface before curing.

Advantageous Effects of Invention

[0016] The high early strength agent for cements according to an embodiment of the present invention can provide higher initial strength developability, higher fluidity and higher storage stability as compared with the conventional agents.

DESCRIPTION of EMBODIMENTS

[0017] The present invention will be described as the below in detail. Parts and percentages (%) referred to herein show standard weight (mass), unless otherwise specified. The term "concrete" referred to herein collectively means cement paste, mortar, and cement concrete. A cement hardened body referred to herein collectively means concrete secondary products and concrete structures produced from cement paste, mortar or concrete, or further compounded with such as reinforcing.

[0018] A numerical range referred to herein includes its upper limit value and its lower limit value, unless otherwise specified.

[0019] The nitric acid and a salt thereof used in an embodiment of the present invention may be either an anhydride or a hydrate. Nitrates may include salts of alkali metals, alkaline earth metals and aluminum. Two or more of these may be used in combination. Among of them, nitric acid, sodium nitrate, magnesium nitrate, potassium nitrate, calcium nitrate, and aluminum nitrate may be preferably used, and sodium nitrate and calcium nitrate may be more preferably used, from the viewpoint of higher strength developability. Calcium nitrate and sodium nitrate may be furthermore preferably used in combination.

[0020] The content of the nitric acid and a salt thereof in the high early strength agent for cements according to an embodiment of the present invention may preferably be in the range of 30% or more to 60% or less, more preferably in the range of 40% or more to 50% or less in terms of an anhydride. If the content of the nitric acid and a salt thereof is less than 30%, the higher strength developability might not be obtained, and if it exceeds 60%, the slump might be lowered or the long-term strength might be lowered.

[0021] The carboxylic acid and a salt thereof used in an embodiment of the present invention collectively refers to an organic compound having a carboxyl group and a salt thereof. Such carboxylic acids may include monocarboxylic acids such as formic acid, acetic acid and propionic acid, dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, maleic acid, fumaric acid and

phthalic acid, tricarboxylic acids such as trimellitic acid and tricarballic acid, oxymonocarboxylic acids such as hydroxybutyric acid, lactic acid and salicylic acid, oxydicarboxylic acids such as malic acid, aminocarboxylic acids such as aspartic acid and glutamic acid, aminopolycarboxylic acid such as ethylenediaminetetraacetic acid (EDTA) and trans-1,2-diaminocyclohexane tetraacetic acid (CyDTA). The carboxylic acid salt may include a salt of an alkali metal and an alkaline earth metal and any of the carboxylic acids as mentioned the above. Two or more of these may be used in combination. Among the carboxylic acids and a salt thereof, formic acid, sodium formate, calcium formate, sodium acetate, sodium oxalate, sodium lactate, and sodium aspartate may be preferably used, and among of them, formic acid, sodium formate, and calcium formate may be more preferably used, from the viewpoint of the higher strength developability. Formic acid and sodium formate may be further preferably used in combination.

[0022] The content of the carboxylic acid and a salt thereof in the high early strength agent for cements according to an embodiment of the present invention may preferably be in the range of 0.1% or more to 10% or less, more preferably in the range of 2% or more to 7% or less. If the content of the carboxylic acid and a salt thereof is less than 0.1%, the higher strength developability might not be obtained, and if it exceeds 10%, the long-term strength might be lowered.

[0023] The content of calcium (Ca) element contained in the high early strength agent for cements according to an embodiment of the present invention is preferably in the range of 5% or more to 20% or less, more preferably in the range of 8% or more to 15% or less. If the content of the calcium element is less than 5%, the long-term strength developability might be lowered, and if it exceeds 20%, the storage stability of the liquid might be worse. For incorporating the calcium element into the high early strength agent, a calcium salt may be used as a raw material, for example, the calcium salt of the nitric acid or the carboxylic acid as described above may be used, the other calcium salts may be also used, and the both of them may be used. Such calcium salt is not particularly limited as long as it is a water-soluble salt. A calcium salt having low water solubility may be also used, as long as it reacts and dissolves with the nitric acid and a salt thereof and the carboxylic acid and a salt thereof contained in the high early strength agent according to an embodiment of the present invention. Such calcium salt may include calcium hydroxide.

[0024] The method of determining the content of the calcium element is not particularly

limited as long as it is a general quantitative analysis method, for example, an atomic absorption photometer can be used for the determination.

[0025] The high early strength agent for cements according to an embodiment of the present invention contains water as an essential component. The agent contains the nitric acid or a salt thereof and the carboxylic acid or a salt thereof, or the nitric acid or a salt thereof and the carboxylic acid or a salt thereof with another calcium salt, and water as the remainder.

[0026] The content of water in the high early strength agent for cements according to an embodiment of the present invention may preferably be from 25% or more to 60% or less, more preferably from 30% or more to 55% or less. If the content of water is less than 25%, the materials might be separated, if it exceeds 60%, a high early strength might be insufficient.

[0027] The high early strength agent for cements according to an embodiment of the present invention may contain an alcohol amine. Alcohol amine is used for the purpose of improving an initial strength of the cement compositions. The alcohol amine is not particularly limited, as long as it can be dissolved in the high early strength agent. Alcohol amine is an organic compound having a structure $>N-R-OH$ in the structural formula. Here, R is usually an atomic group called an alkyl group or an aryl group, and R has a linear alkylene group such as methylene group, ethylene group, n-propylene group, an alkylene group having a branched structure such as isopropylene group, and an aryl group having an aromatic ring such as a phenyl group and a benzyl group. R may be bonded to a nitrogen atom at two or more positions, and a part or all of R may have a cyclic structure. R may be bonded to a plurality of hydroxyl groups. R may have an element other than carbon and hydrogen, such as sulfur, fluorine, chlorine, oxygen, in a part of the alkyl group. R may be bonded to a plurality of hydroxyl groups.

[0028] Alcohol amines may include ethanolamine, diethanolamine, diisopropanolamine, triethanolamine, N-methyldiethanolamine, N,N-dimethylethanolamine, N,N-dibutylethanolamine, N-(2-aminoethyl)ethanolamine, boron trifluoride triethanolamine, and derivatives thereof. One or more of these may be used.

[0029] Among the alcohol amines, monoethanolamine, diethanolamine, triethanolamine, and diisopropanolamine may be preferably used, and diethanolamine may be more preferably used, from the viewpoint of a fluidity improvement. The content

of the alcohol amine contained in the high early strength agent for cements may preferably be in the range of 1% to 15%, more preferably in the range of 5% to 10%. If the content of the alcohol amine is less than 1%, the improvement of the initial strength might be small, and if it exceeds 15%, the fluidity might be lowered.

[0030] The high early strength agent for cements according to an embodiment of the present invention may contain glycerin. The glycerin is used for the purpose of improving the initial strength of the cement compositions. The glycerin used in the present invention is a compound represented by the chemical formula $C_3H_8O_3$, chemical name 1,2,3-propanetriol or glycerol. The content of the glycerin contained in the high early strength agent for cements may preferably be in the range of 1% to 10%, more preferably in the range of 3% to 7%. If the content of the glycerin is less than 1%, the improvement of the early strength might be small, and if it exceeds 10%, the long-term strength might be lowered.

[0031] The content of chlorine in the high early strength agent for cements according to an embodiment of the present invention may preferably be 0.1% or less. Such content is required for suppression of steel corrosion or salt damage, which is a factor of deteriorating concrete. For maintaining the content of the chlorine in 0.1% or less, the use of the chlorine-containing materials should be avoided in the production of the high early strength agent. Water is generally most likely to contain chlorine among the above-mentioned raw materials, but such content will rarely incur a problem unless it is seawater.

[0032] The high early strength cement can be produced by blending the high early strength agent according to an embodiment of the present invention into a cement. The content of the high early strength agent may be preferably 0.05 to 12 parts, more preferably 0.1 to 10 parts, more preferably 0.5 to 10 parts, furthermore preferably 0.7 to 7 parts, and most preferably 1 to 5 parts, with respect to 100 parts of the cement. If the content of the high early strength agent is less than 0.5 parts, the improvement of the strength developability might be small, and if it exceeds 10 parts, the slump might be lowered or the long-term strength developability might be lowered.

[0033] The high early strength agent for cements according to an embodiment of the present invention can be sprayed on the concrete surface before curing for the purpose of a higher crack resistance. The content to be sprayed on the concrete surface is not particularly limited, but it may preferably be 50 to 800 g/m², more preferably 100 to 600

g/m², furthermore preferably 200 to 500 g/m². If the content is outside the above range, the crack resistance effect might be insufficient.

[0034] The cement mentioned herein may include any portland cements such as normal, high early strength, moderate heat, and super high early strength, which are generally commercially available, and any cements mixed with fly ash and blast furnace slag to each portland cement. They may be used in the form of fine powder.

[0035] The concrete used in an embodiment of the present invention may include cements and aggregates. The aggregates may be preferably those having low water absorption and high aggregate strength.

[0036] For fine aggregates, river sand, mountain sand, lime sand, and quartz sand may be used, and for coarse aggregates river gravel, mountain gravel, and lime gravel may be used.

[0037] The content of water used for the concrete may preferably be 30% or more, more preferably 33 to 55%, from the view of the strength developability. If the content of water is less than 30%, cement concrete might be insufficiently mixed.

[0038] The nitric acid and a salt thereof and the carboxylic acid and a salt thereof used in an embodiment of the present invention individually works as a high early strength agent. However, the present inventor found a remarkable effect that each of the component exhibits a synergistic effect, higher fluidity, and higher strength developability, when they are blended with water in the appropriate rate for the high early strength agent, compared with the case where they are individually used. The mechanism of the effect of the high early strength agent for cements according to an embodiment of the present invention is, without being bound to a specific theory, considered that nitrate ions and carboxylate ions supplied from the raw material synergistically promote elution of the cement components and hydration reaction.

[0039] The embodiment are used in the form of liquid blended with water as a solvent, thereby, the promoting effect will be higher as compared with the case where the nitrate or carboxylate is used in the form of a solid. As the reason for this, it is considered that the form of liquid can be blended into the cement easier than the form of solid, and an endothermic reaction occurs when the nitrate is dissolved in water. When the nitrate in the form of solid is added to the concrete, the temperature of the concrete might decrease

and the reaction might be suppressed.

[0040] For this reason, the high early strength agent according to an embodiment of the present invention can be widely used, for a example, in an on-site striking concrete, which is particularly difficult to control. For an example, a high early strength concrete can be properly produced after transporting the concrete to the on-site by an agitator car and adding the high early strength agent into the concrete just before putting it at the site, because the concrete and the high early strength agent can be blended without segregation.

[0041] Further, the concentration of the calcium element in the high early strength agent according to an embodiment of the present invention is within a certain range, therefore, elution of calcium hydroxide caused by hydration of the cement is suppressed, and the long-term strength developability can be also maintained.

EXAMPLES

[0042] Hereinafter, the present invention will be described in detail based on examples.

[0043] [Experiment 1]

Nitric acid and a salt thereof, carboxylic acid and a salt thereof and, optionally, calcium salt were added to water and stirred for 4 hours to prepare various types of high early strength agents for cements in the form of liquid, as shown in Tables 1 and 2. The prepared high early strength agents were added to concretes and evaluated.

[0044] Concrete (the basic blend range: 145 kg/m³ of water, 440 kg/m³ of cement, 2.5 kg/m³ of water reducing agent, 39.4% of s/a, and 4.5% of air) was blended with the high early strength agents for cements with the blend range as shown in Tables 1 and 2 under the environment of 20 °C, and the slumps of the concrete were measured. 13.2 kg/m³ (equivalent to 3 parts to 100 parts cement) of the high early strength agent was weighed and added to the cement. Thereafter, the concrete was filled into a form, kept at 20 °C, deformed from the form after 8 hours, and the compression strength of the cement was measured. The results are shown in Tables 1 and 2.

[0045] The following examples were also conducted: no adding the high early strength agent for cements, and adding each of the nitrate and carboxylate in the form of solid alone or in combination.

[0046] <Materials used>

Nitric acid and a salt thereof: [A] concentrated nitric acid, [B] sodium nitrate, [C] magnesium nitrate, [D] potassium nitrate, [E] calcium nitrate, [F] aluminum nitrate, (all: commercially available products)

Carboxylic acid and a salt thereof: [a] formic acid, [b] sodium formate, [c] calcium formate, [d] sodium acetate, [e] sodium oxalate, [f] sodium lactate, [g] sodium aspartate (all: commercially available products)

Salt for adjusting calcium concentration: calcium hydroxide

Water: industrial water

Cement: normal portland cement, commercial available product, Blaine value 3,200 cm²/g, Specific gravity 3.15

Fine aggregate: made in Himakawa, Niigata Prefecture, Japan, 5 mm under, density 2.62 g/cm³

Coarse aggregate: made in Himakawa, Niigata Prefecture, Japan, 25 mm under, density 2.64 g/cm³

Water reducing agent: naphthalene sulfonic acid, trade name "Mighty 150", manufactured by Kao Corporation

[0047] <Measurement method>

Slump: in accordance with JIS A 1101

Compression strength: in accordance with JIS A 1108

The concrete was sealed and cured at 20 °C until age of 24 hours, and thereafter was cured in water at 20 °C. The concentration of calcium element was calculated by an atomic absorption photometer.

[0048] [Table 1]

Experiment No.	High early strength agents for cements (Composition Range)					(Analysis Value)	Slump (cm)	Compression strength (N/mm ²)			Remarks
	Nitric acid and a salt thereof		Carboxylic acid and a salt thereof		Calcium Hydroxide	Calcium element concentration					
	type	(%)	type	(%)	(%)	(%)		8 hours	7 days	28 days	
1-1	—	—	a	5.0	20.4	11	15	6.2	47.6	54.2	Comparative Example
1-2	A	45.0	a	5.0	20.4	11	14	13.5	51.5	62.6	Example
1-3	B	45.0	a	5.0	20.4	11	12	12.2	49.2	62.0	Example
1-4	C	45.0	a	5.0	20.4	11	11	11.8	48.8	61.6	Example
1-5	D	45.0	a	5.0	20.4	11	10	10.0	47.3	58.1	Example
1-6	E	25.0	a	5.0	9.1	11	13	6.6	47.5	60.1	Comparative Example
1-7	E	30.0	a	5.0	6.8	11	12	8.6	48.6	61.9	Example
1-8	E	40.0	a	5.0	2.3	11	11	12.5	50.1	62.3	Example
1-9	E	45.0	a	5.0	0	11	10	14.0	52.0	63.3	Example
1-9'	B E	10.0 35.0	a	5.0	4.6	11	11	16.3	53.0	63.0	Example
1-9''	B E	20.0 25.0	a	5.0	9.1	11	11	16.1	53.8	63.4	Example
1-9'''	B E	30.0 15.0	a	5.0	13.5	11	11	15.1	52.8	63.3	Example
1-10	E	50.0	a	5.0	1.5	13	9	14.2	50.3	61.1	Example
1-11	E	60.0	a	5.0	0.6	15	7	13.9	50.0	60.9	Example
1-12	E	65.0	a	5.0	0	16	5	13.5	48.1	57.5	Comparative Example
1-13	F	45.0	a	5.0	20.4	11	13	9.0	47.7	59.9	Example

[0049] [Table 2]

Experiment No.	High early strength agents for cements (Composition Range)					(Analysis Value)	Slump (cm)	Compression strength (N/mm ²)			Remarks
	Nitric acid and a salt thereof		Carboxylic acid and a salt thereof		Calcium Hydroxide	Calcium element concentration					
	Type	(%)	Type	(%)	(%)	(%)		8 hours	7 days	28 days	
1-14	E	45.0	—	—	0	11	5	6.8	47.1	56.2	Comparative Example
1-15	E	45.0	a	0.05	0	11	5	8.1	49.9	59.7	Comparative Example
1-16	E	45.0	a	0.1	0	11	7	9.9	50.2	61.5	Example
1-17	E	45.0	a	2.0	0	11	9	11.8	51.1	63.0	Example
1-18	E	45.0	a	7.0	0	11	11	12.4	50.1	62.2	Example
1-19	E	45.0	a	10.0	0	11	12	12.3	49.7	60.4	Example
1-20	E	45.0	a	12.0	0	11	14	12.2	47.6	58.0	Comparative Example
1-20'	E	45.0	a b	5.0 1.0	0	11	14	14.3	52.1	61.9	Example
1-20''	E	45.0	a b	5.0 3.0	0	11	14	15.9	53.9	62.8	Example
1-20'''	E	45.0	a b	5.0 5.0	0	11	13	15.7	53.6	62.7	Example
1-21	E	45.0	b	5.0	0	11	13	10.5	48.1	59.6	Example
1-22	E	45.0	c	5.0	0	12.5	10	13.5	51.0	62.5	Example
1-23	E	45.0	d	5.0	3.7	13	11	13.2	50.6	61.1	Example
1-24	E	45.0	e	5.0	0	11	12	13.5	49.7	59.4	Example
1-25	E	45.0	f	5.0	0	11	13	9.3	47.5	58.2	Example
1-26	E	45.0	g	5.0	0	11	13	9.2	48.8	59.7	Example
1-27	A	45	a	5.0	6	3	10	13.3	45.2	50.2	Comparative Example
1-28	A	45	a	5.0	9	5	10	13.5	49.7	58.9	Example
1-29	A	45	a	5.0	15	8	10	13.7	50.5	60.4	Example
1-30	E	45	a	5.0	7.4	15	10	13.5	51.0	63.2	Example
1-31	E	45	a	5.0	16.7	20	10	13.1	50.0	61.5	Example
1-32	E	45	a	5.0	25.9	25	Solids precipitate in solution				Comparative Example

1-33	None	10	6.0	47.5	58.0	Comparative Example
1-34	Calcium nitrate	11	8.0	47.2	55.1	Comparative Example
1-35	Sodium formate	13	9.2	43.1	48.1	Comparative Example
1-36	Calcium nitrate : Sodium formate = 9:1	7	9.6	42.4	47.7	Comparative Example

[0050] As shown in Tables 1 and 2, when the concentration of the nitric acid and a salt thereof is 30% to 60% and the concentration of the carboxylic acid and a salt thereof is 0.1 to 10%, the initial strength was improved and the influences in the slump and the long-term strength were also small. It is also understood that when the calcium element concentration is 5% to 20%, the long-term strength developability could be maintained and the storage stability of the liquid was also good. For the use of the nitric acid and a salt thereof, calcium nitrate is particularly preferable, and the combination of calcium nitrate and sodium nitrate is more preferable. For the use of the carboxylic acids and a salt thereof, formic acid is particularly preferable, and the combination of formic acid and sodium formate is more preferable.

[0051] It is understood that the use of the high early strength agent for cement according to an embodiment of the present invention leads to improve the initial strength and develop the strength required for deforming, resulting in shortening the required cure time and improving in the productivity of concretes.

[0052] [Experiment 2]

For the composition of 45% of the calcium nitrate, 5% of the formic acid, and 11% of the calcium element concentration (Corresponding to Experiment No. 1-9 in Example 1), alcohol amine or glycerin was added to water and stirred for 4 hours to prepare various types and concentrations of the high early strength agents for cement shown in Table 3. And, the prepared high early strength agents for cement were added to concretes and evaluated.

[0053] Concrete (the basic blend range: 145 kg/m³ of water, 440 kg/m³ of cement, 2.5 kg/m³ of water reducing agent, 39.4% of s/a, and 4.5% of air), was blended with the high early strength agent for cement as shown in Table 3 under the environment of 20 °C, and the slumps of the concrete were measured. 13.2 kg/m³ (equivalent to 3 parts to 100 parts cement) of the high early strength agent for concretes was with water

weighed and added to the cement. Thereafter, the concrete was filled into a form, kept at 20 °C, deformed from the form after 8 hours, and the compression strength of the cement was measured. The results are shown in Table 3.

[0054] <Materials used>

Alcohol amine or glycerin: [α] monoethanolamine, [β] diethanolamine, [γ] triethanolamine, [Δ] diisopropanolamine, [ε] glycerin, and the other materials are the same as that of used in "Experiment 1".

[0055] [Table 3]

Experiment No.	Alcohol amine, or glycerin		Slump (cm)	Compression strength (N/mm ²)			Remarks
	Type	(%)		8 hours	7 days	28 days	
1-9	—	—	10	14.0	52.0	63.3	Example
2-1	α	8.0	8	14.5	52.2	62.9	Example
2-2	β	0.5	10	14.0	52.3	63.1	Example
2-3	β	1.0	10	14.5	52.6	62.6	Example
2-4	β	5.0	9	15.2	53.3	62.4	Example
2-5	β	8.0	9	16.2	54.1	62.0	Example
2-6	β	10.0	8	16.5	53.0	60.2	Example
2-7	β	15.0	7	16.7	51.7	59.0	Example
2-8	β	18.0	4	16.8	48.4	57.1	Example
2-9	γ	8.0	9	15.0	52.2	59.9	Example
2-10	Δ	8.0	9	14.7	52.1	58.5	Example
2-11	ε	0.5	10	14.1	51.7	62.7	Example
2-12	ε	1.0	10	14.7	51.6	62.6	Example
2-13	ε	3.0	10	15.3	51.4	62.1	Example
2-14	ε	5.0	9	15.8	50.9	60.8	Example
2-15	ε	7.0	9	16.3	50.3	59.1	Example
2-16	ε	10.0	9	16.5	48.0	57.7	Example
2-17	ε	12.0	8	16.6	46.9	52.2	Example

[0056] As shown in Table 3, when the ethanolamine or glycerin was added, the initial strength was improved. Among the ethanolamines, diethanolamine is preferable. It is also understood that the concentration of the ethanolamine is preferably in the range of 1 to 15% and the concentration of the glycerin in the range of 1 to 10% from the view of the fluidity and the strength developability.

[0057] [Experiment 3]

Concrete (the basic blend range: 145 kg/m³ of water, 440 kg/m³ of cement, 2.5 kg/m³ of water reducing agent, 39.4% of s/a, and 4.5% of air) was blended with some types of the high early strength agents for cement prepared in [Experiment 1] with the addition rate as shown in Table 4 under the environment of 20 °C, and the slump of the concrete were measured. The addition rate of the high early strength agent for cement was measured as a part with respect to 100 parts of cement. Thereafter, the concrete was filled into a form, kept at 20 °C., deformed from the form after 8 hours, and the compression strength of the cement was measured. The results are shown in Table 4.

[0058] The following examples were also conducted: no adding the high early strength agent for cement, and adding each of the nitrate and carboxylate alone.

[0059] <Materials used>

Same as the material used in "Experiment 1".

[0060] [Table 4]

Experiment No.	High early strength agents for cements		Slump (cm)	Compression strength (N/mm ²)			Remarks
	Type	Usage Content (Parts)		8 hours	7 days	28 days	
1-1	Ex No 1-1	3	15	6.2	47.6	54.2	Comparative Example
3-1	Ex No 1-1	5	15	7.4	46.2	55.2	Comparative Example
3-2	Ex No 1-1	10	15	8.9	44.2	50.1	Comparative Example
3-3	Ex No 1-9	0.05	10	6.4	47.7	58.2	Example
3-4	Ex No 1-9	0.1	10	8.0	48.0	58.9	Example
3-5	Ex No 1-9	1	10	10.7	48.9	60.2	Example
3-6	Ex No 1-9	3	10	12.2	49.2	62.0	Example
3-7	Ex No 1-9	5	9	13.2	48.5	60.0	Example
3-8	Ex No 1-9	10	7	13.6	47.8	59.1	Example
3-9	Ex No 1-9	12	4	13.7	47.5	58.2	Example
1-14	Ex No 1-14	3	5	11.8	48.8	61.6	Comparative Example
3-10	Ex No 1-14	5	4	11.9	47.4	55.3	Comparative Example
3-11	Ex No 1-14	10	2	12.3	46.5	50.2	Comparative Example
1-33	Non	—	10	6.0	47.5	58.0	Comparative Example

[0061] As shown in Table 4, even when the high early strength agent for cement according to an embodiment of the present invention is used with varied addition rate, the initial strength was improved. Further, it is also understood that the addition rate of the high early strength agent for cement is preferably 0.1 parts to 10 parts with respect to 100 parts of the cement, because fluctuation of the slump can be suppressed and the strength developability is better.

[0062] [Experiment 4]

Concrete (the basic blend range: 145 kg/m³ of water, 440 kg/m³ of cement, 2.5 kg/m³ of water reducing agent, 39.4% of s/a, and 4.5% of air), and post-added with the

high early strength agents for cement prepared in [Experiment 1] after 30 minutes, and the slump of the concrete were measured. 13.2 kg/m³ (equivalent to 3 parts to 100 parts cement) of the high early strength agent for concretes was weighed and post-added to the cement. Thereafter, the concrete was filled into a form, kept at 20 °C, deformed from the form after 8 hours, and the compression strength of the cement was measured. The results are shown in Table 5.

[0063] The following examples were also conducted: no adding the high early strength agent for cement, and adding each of the nitrate and a salt thereof and carboxylate and a salt thereof alone.

[0064] <Materials used>

Same as the material used in "Experiment 1".

[0065] [Table 5]

Experiment No.	High early strength agents for cements		Slump (cm)	Compression strength (N/mm ²)			Remarks
	Type	Timing of Adding		8 hours	7 days	28 days	
1-1	Ex No 1-1	At Concrete Mixture	15	6.2	47.6	54.2	Comparative Example
4-1	Ex No 1-1	After 30 min. of concrete mixture	14	6.1	47.7	57.4	Comparative Example
1-9	Ex No 1-9	At Concrete Mixture	10	14.0	52.0	63.3	Example
4-2	Ex No 1-9	After 30 min. of concrete mixture	9	13.9	51.8	62.7	Example
1-14	Ex No 1-14	At Concrete Mixture	5	6.8	47.1	56.2	Comparative Example
4-3	Ex No 1-14	After 30 min. of concrete mixture	4	6.4	44.9	54.1	Comparative Example
1-33	Non	At Concrete Mixture	10	6.0	47.5	58.0	Comparative Example
4-4	Non	After 30 min. of concrete mixture	9	5.7	47.0	58.0	Comparative Example
1-34	Calcium nitrate	At Concrete Mixture	11	8.0	47.2	55.1	Comparative Example
4-5	Calcium nitrate	After 30 min. of concrete mixture	9	6.3	41.3	48.9	Comparative Example
1-35	Sodium formate	At Concrete Mixture	13	9.2	43.1	48.1	Comparative Example
4-6	Sodium formate	After 30 min. of concrete mixture	10	6.5	39.7	46.2	Comparative Example

[0066] As shown in Table 5, the high early strength agent for cement according to an embodiment of the present invention exhibited the same degree of slump and the strength developability regardless of the timing of addition of the high early strength agent. Such good property should be effective, when the high early strength agents can be post-added into an agitator car on the site after carrying pre-mixed concrete to the site.

[0067] [Experiment 5]

Concrete (the basic range: 145 kg/m³ of water, 440 kg/m³ of cement, 2.5 kg/m³ of water reducing agent, 39.4% of s/a, and 4.5% of air), and a concrete board with a height of 20 cm, a length of 2 m, and a width of 2 m was placed. The concrete surface was finished after the placement, 200 g/m³ of the high early strength agent for cement

of Experiment 1-9 was sprayed. Thereafter, the concrete surface was observed at age of 28 days. Crack resistance was evaluated. The results are shown in Table 6. The meanings of the marks are as follows.

- No cracks
- + 1 or 2 cracks
- ++ 3 to 5 cracks
- +++ 6 or more cracks

[0068] <Materials used>

Same as the material used in "Experiment 1".

[0069] [Table 6]

Experiment No.	Sprayed Amount of high early strength agents for cements (g/m ²)	Cracks Occurrence	Remarks
5-1	0	++	Comparative Example
5-2	50	+	Example
5-3	100	-	Example
5-4	200	-	Example
5-5	400	-	Example
5-6	800	+	Example

[0070] As shown in Table 6, spraying the high early strength agent for cement according to an embodiment of the present invention on the concrete surface can significantly prevent from the occurrence of cracks.

INDUSTRIAL APPLICABILITY

[0071] The high early strength agent for cement according to an embodiment of the present invention is superior in an initial strength developability, fluidity and storage stability as compared with the conventional agents, and suitable for the civil engineering and construction field utilizing concrete.

CLAIM

1. A high early strength agent for cement, comprising:
30% by mass or more and 60% by mass or less of nitric acid or a salt thereof;
0.1% by mass or more and 10% by mass or less of a carboxylic acid or a salt thereof; and
water, and
wherein a concentration of calcium element in the high early strength agent is in the range of 5% by mass or more and 20% by mass or less.
2. The high early strength agent according to Claim 1 further comprising alcohol amine or glycerin.
3. High early strength cement containing 0.1 to 10 parts by mass of the high early strength agent according Claim 1 or 2 with respect to 100 parts by mass of cement.
4. A method for producing a high early strength concrete characterized in that post-adding the high early strength agent according to Claim 1 or 2 into a fresh concrete in an agitator car.
5. A method for producing a concrete characterized in that applying or spraying 100 to 600 g/m² of the high early strength agent according to Claim 1 or 2 on a concrete surface before curing.