

DESCRIPTION

Title of Invention : CEMENT COMPOSITION FOR HIGH-TEMPERATURE ENVIRONMENT AND CONCRETE FOR HIGH-TEMPERATURE ENVIRONMENT

[Technical Field]

[0001] The present invention relates to a cement composition for high temperature environment and a concrete for high temperature environment that can be used in regions with high temperatures.

[Background Art]

[0002] In regions with high temperatures such as the tropical and subtropical zones, concretes are often required to have properties as indicated in (i) and (ii) below:

(i) concretes have temperature increase therein of 70°C or lower; and

(ii) it is possible to secure the workability on concretes for a certain period of time even under high temperatures.

Conventional concretes for high temperature environment that satisfy the required properties include concretes (hereinafter referred to as "conventional concretes") containing cement that contains 65 to 75% by mass of blast furnace slag powder, a super-retarding water reducing agent and a high-range water reducing agent.

However, although the conventional concretes have advantages such as preferable strength development and low hydration heat, the conventional concretes have a defect of high autogenous

shrinkage strain. When the autogenous shrinkage strain is high, the concrete may easily develop cracks resulting in decreased durability. Thus, there is a need for a concrete having decreased autogenous shrinkage strain and comparable strength development and temperature increase compared to the conventional concretes.

[0003] A few means for reducing the autogenous shrinkage strain of concretes have been proposed so far, which include, for example, the following:

the method for producing a mortar/concrete disclosed in PTL 1 is one in which powder formed of fine particles containing silicon dioxide as a main component and zirconium oxide as one of the components is blended to a mortar/concrete; and

a hydraulic composition disclosed in PTL 2 is a composition for concrete comprising, relative to 100 parts by mass of a calciumsulfoaluminate composition containing 3 to 60% by weight of calciumsulfoaluminate ($3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4$) and 1 to 40% by weight of anhydrous gypsum, 0.1 to 3.0 parts by mass of lithium carbonate having a specific surface area of 1000 to 4000 cm^2/g .

[0004] However, either of the above means lacks practicality because of using expensive materials such as zirconium oxide and calciumsulfoaluminate. Thus, there is a need for a concrete having decreased autogenous shrinkage strain and equivalent temperature increase and strength development compared to the conventional concretes without using expensive materials.

[Citation List]

[Patent Literature]

[0005]

[PTL 1] Japanese Patent Application Publication No. 2004-203733

[PTL 2] Japanese Patent Application Publication No. 2002-097051

[Summary of Invention]

[Technical Problem]

[0006] Therefore, an object of the present invention is to provide a concrete for high temperature environment that is made of materials that are widely used in the field of concretes without using expensive materials and has decreased autogenous shrinkage strain and equivalent temperature increase and strength development compared to conventional concretes and a cement composition for high temperature environment used for production of the concrete for high temperature environment.

[Solution to Problem]

[0007] The inventors of the present invention exhaustively studied cement compositions and concretes that may achieve the above object and found that a cement composition containing a fly ash that satisfies certain conditions and a concrete produced with the cement composition can achieve the above object, thereby completing the present invention.

Namely, the present invention pertains to a cement composition for high temperature environment and a concrete for high temperature environment having the configurations indicated below.

[0008] [1] A cement composition for high temperature environment, containing at least: fly ash satisfying all conditions (1) to (4) below; and Portland cement:

(1) the fly ash has a Blaine specific surface area of 2500 to 6000 cm²/g;

(2) the fly ash has a mass reduction rate of 5% by mass or less after heating at 975 ± 25°C for 15 minutes;

(3) the fly ash has a SiO₂ content of 50% by mass or more; and

(4) the fly ash has a mass ratio $(\text{Na}_2\text{O} + 0.658 \times \text{K}_2\text{O}) / (\text{MgO} + \text{SO}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5 + \text{MnO})$ of 0.2 to 1.0, (where the units for the chemical formulae in the above formula are % by mass),

wherein a content of the fly ash is 15 to 55% by mass with the sum of the fly ash and the Portland cement being 100% by mass.

[2] The cement composition for high temperature environment according to [1], wherein the fly ash further satisfies condition (5) below:

(5) quartz in the fly ash has a lattice volume of 113.5 to 114.5 Å³, (where the lattice volume is determined by the Rietveld analysis).

[3] The cement composition for high temperature environment according to [1] or [2], further comprising blast furnace slag powder,

wherein a content of the blast furnace slag powder is 50% by mass or less with the sum of the Portland cement, the fly ash and the blast furnace slag powder being 100% by mass.

[4] The cement composition for high temperature environment according to any of [1] to [3], further comprising one or more types

of gypsum selected from anhydrous gypsum, hemihydrate gypsum and dihydrate gypsum,

wherein a content of the gypsum in terms of SO_3 is 2.5% by mass or less with the sum of the Portland cement, the fly ash, the blast furnace slag powder and the gypsum being 100% by mass.

[5] A concrete for high temperature environment containing: the cement composition for high temperature environment according to any of [1] to [4]; a water reducing agent (R1) indicated below; a water reducing agent (R2) other than the water reducing agent (R1); a fine aggregate; a coarse aggregate; and water:

water reducing agent (R1): one or more types of water reducing agents selected from a super-retarding water reducing agent, a retarding water reducing agent, a retarding AE water reducing agent and a retarding high-performance AE water reducing agent.

[6] The concrete for high temperature environment according to [5], which is used under an environment with an environmental temperature (temperature surrounding the concrete) of 25°C or above.

[Advantageous Effects of Invention]

[0009] The concrete for high temperature environment produced with the cement composition for high temperature environment of the present invention has decreased autogenous shrinkage strain and equivalent temperature increase and strength development compared to conventional concretes.

[Brief Description of Drawings]

[0010]

[Fig. 1]

Fig. 1 is a view illustrating a simplified adiabatic test container to which a concrete is placed. The numerical values are in mm.

[Fig. 2]

Fig. 2(a) illustrates a support steel that supports an embedded strain gauge, and Fig. 2(b) illustrates attachment of the support steel to a simplified adiabatic test container.

[Description of Embodiments]

[0011] First, the cement composition for high temperature environment of the present invention is described.

1. Cement composition for high temperature environment

The cement composition for high temperature environment of the present invention contains at least fly ash and Portland cement, wherein the content of the fly ash is 15 to 55% by mass with the sum of the fly ash and the Portland cement being 100% by mass. When the content of the fly ash is less than 15% by mass, the concrete for high temperature environment may have high autogenous shrinkage strain and temperature increase, and when the content is above 55% by mass, the concrete for high temperature environment may have decreased strength development. The content of the fly ash is preferably above 30% by mass and 53% by mass or less, and more preferably 30.5 to 50% by mass.

The Portland cement may be one or more types selected from ordinary Portland cement, high-early-strength Portland cement, moderate-heat Portland cement and low-heat Portland cement defined in Japanese Industrial Standard (hereinafter referred to as "JIS")

R 5210 (Portland cement). Among these, the Portland cement is preferably ordinary Portland cement and/or high-early-strength Portland cement in view of improving the strength development or the like of the concrete for high temperature environment.

[0012] The fly ash satisfies all conditions: (1) the fly ash has a Blaine specific surface area of 2500 to 6000 cm²/g; (2) the fly ash has a mass reduction rate of 5% by mass or less after heating at 975 ± 25°C for 15 minutes; (3) the fly ash has a SiO₂ content of 50% by mass or more; and (4) the fly ash has a mass ratio (Na₂O + 0.658 × K₂O) / (MgO + SO₃ + TiO₂ + P₂O₅ + MnO) of 0.2 to 1.0, (where the units for the chemical formulae in the above formula are % by mass).

When the fly ash has a Blaine specific surface area of less than 2500 cm²/g, the concrete for high temperature environment may have decreased strength development, and when the Blaine specific surface area is above 6000 cm²/g, the concrete for high temperature environment may have increased autogenous shrinkage strain and temperature increase and it is difficult to obtain the fly ash having a Blaine specific surface area of above 6000 cm²/g. The Blaine specific surface area is preferably 2700 to 5000 cm²/g and more preferably 2900 to 4000 cm²/g.

When the fly ash has a mass reduction rate of above 5% by mass after heating at 975 ± 25°C for 15 minutes, the concrete for high temperature environment may have decreased strength development. The mass reduction rate is preferably 1.0 to 4.5% by mass and more

preferably 1.5 to 4.0% by mass in view of availability and the strength development.

When the fly ash has a SiO_2 content of less than 50% by mass, the concrete for high temperature environment may have decreased strength development. The SiO_2 content is preferably 51 to 70% by mass and more preferably 52 to 65% by mass in view of availability and the strength development.

When the mass ratio $(\text{Na}_2\text{O} + 0.658 \times \text{K}_2\text{O}) / (\text{MgO} + \text{SO}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5 + \text{MnO})$ in the fly ash is less than 0.2, the concrete for high temperature environment may have decreased strength development when an environmental temperature (temperature surrounding the concrete) is increased (such as 27°C or above), and when the mass ratio is above 1.0, the concrete for high temperature environment may have increased autogenous shrinkage strain and temperature increase when an environmental temperature is increased (such as 27°C or above). The ratio is preferably 0.25 to 0.8, more preferably 0.28 to 0.7 and still more preferably 0.3 to 0.6.

[0013] Fly ash generally contains 5 to 25% by mass of quartz, and quartz in the fly ash used for the present invention has a lattice volume of preferably 113.5 to 114.5 Å³ as determined by the Rietveld analysis. When quartz has a lattice volume within the above range, autogenous shrinkage strain and temperature increase may be further suppressed when the environmental temperature of the concrete for high temperature environment is increased (such as 27°C or above). The lattice volume of quartz is more preferably 113.6 to 114.4 Å³

and still more preferably 113.7 to 114.3 Å³.

The Rietveld analysis of quartz in the fly ash may be based on the X-ray diffraction diagram of the fly ash using, for example, an analytical software (Topas ver. 2.1) manufactured by Bruker and the crystallographic structural data (ICDD number) of 331161 (Quartz).

[0014] In order to improve fluidity and suppress autogenous shrinkage strain of the concrete for high temperature environment, the fly ash preferably has a compacted density as measured and calculated according to the measurement method described hereinbelow of 1.0 to 1.5 cm³/g, more preferably 1.05 to 1.45 cm³/g and still more preferably 1.1 to 1.4 cm³/g.

[Measurement method of compacted density]

On a powder tester PT-D manufactured by Hosokawa Micron Corporation, a 100-cm³ cup is filled with fly ash while tapping the cup 180 times in 180 seconds, and then the mass of the compacted fly ash in the cup is measured to calculate the compacted density.

[0015] The cement composition for high temperature environment of the present invention may further contain blast furnace slag powder. The blast furnace slag powder may increase a long-term strength development of the concrete for high temperature environment.

When the cement composition for high temperature environment of the present invention contains blast furnace slag powder, the content of the blast furnace slag powder is preferably 50% by mass or less and more preferably 45% by mass or less with the sum of

the fly ash, the Portland cement and the blast furnace slag powder being 100% by mass. When the blast furnace slag powder is above 50% by mass, an effect of improving a long-term strength development of the concrete for high temperature environment may decrease and autogenous shrinkage strain may increase.

The blast furnace slag powder preferably has a Blaine specific surface area of 3000 to 6000 cm²/g and more preferably 3300 to 5000 cm²/g in view of improving the strength development and suppressing temperature increase of the concrete for high temperature environment.

[0016] The cement composition for high temperature environment of the present invention may further contain one or more types of gypsum selected from anhydrous gypsum, hemihydrate gypsum and dihydrate gypsum. The gypsum may increase the strength development of the concrete for high temperature environment.

When the cement composition for high temperature environment of the present invention contains gypsum, the content of gypsum in terms of SO₃ is 2.5% by mass or less with the sum of the fly ash, the Portland cement, the blast furnace slag powder and the gypsum being 100% by mass. When the content of gypsum in terms of SO₃ is above 2.5% by mass, the concrete for high temperature environment may have increased autogenous shrinkage strain and temperature increase. The content of gypsum in terms of SO₃ is more preferably 2.2% by mass or less, still more preferably 2.0% by mass or less and particularly preferably 1.6% by mass or less.

The gypsum is preferably anhydrous gypsum or dihydrate gypsum

in view of improving the strength development of the concrete for high temperature environment. The gypsum preferably has a Blaine specific surface area of 3000 to 15000 cm²/g and more preferably 3500 to 13000 cm²/g in order to improve the strength development and suppress temperature increase.

[0017] The cement composition for high temperature environment of the present invention may contain, as an optional constituent, limestone powder, quartz powder, silica fume or the like.

[0018] The concrete for high temperature environment of the present invention is hereinafter described.

The concrete for high temperature environment of the present invention contains the cement composition for high temperature environment, a water reducing agent (R1), a water reducing agent (R2) other than the water reducing agent (R1), a fine aggregate, a coarse aggregate and water.

The unit quantity of the cement composition for high temperature environment is preferably unit quantity 200 to 550 kg per 1 m³ of the concrete. When the unit quantity is within the range, the strength development, fluidity, workability and the like may be preferable. The unit quantity is more preferably 220 to 520 kg per 1 m³ of the concrete and still more preferably 250 to 480 kg per 1 m³ of the concrete.

[0019] Constituents of the concrete for high temperature environment other than the cement composition for high temperature environment are hereinafter described.

2. Water reducing agent (R1)

The water reducing agent (R1) used for the present invention is one or more types of water reducing agent selected from a super-retarding water reducing agent, a retarding water reducing agent, a retarding AE water reducing agent and a retarding high-performance AE water reducing agent. The retarding water reducing agent, the retarding AE water reducing agent and the retarding high-performance AE water reducing agent are those defined in JIS A 6204 (Chemical admixtures for concrete). The super-retarding water reducing agent used for the present invention refers to a water reducing agent that has a higher difference (interval of retarded time) of the initial times and/or ending times of the concrete for high temperature environment than the retarding water reducing agent defined by JIS A 6204 (Chemical admixtures for concrete).

The water reducing agent (R1) may contain any water reducing component without particular limitation and examples thereof include one or more types selected from ligninsulfonic acid, naphthalenesulfonic acid-formaldehyde condensates, melaminesulfonic acid-formaldehyde condensates and salts thereof. The water reducing agent (R1) may further contain, in addition to the water reducing component, one or more types of retarder selected from citric acid, tartaric acid, sucrose and the like.

The water reducing agent (R1) used for the present invention is preferably a super-retarding water reducing agent or a retarding water reducing agent and more preferably a super-retarding water reducing agent. Specifically, the super-retarding water reducing

agent may be MasterPozzolith (registered trademark) No. 89 manufactured by BASF SE or MasterPozzolith (registered trademark) 138R manufactured by BASF SE.

The amount of the water reducing agent (R1) added is preferably 0.1 to 1 part by mass ($B \times 0.1$ to 1%) relative to 100 parts by mass of the cement composition for high temperature environment. When the amount of addition is within the above range, the workability and the strength development over a medium to long term of the concrete are preferable. The amount of addition is more preferably 0.3 to 0.8 parts by mass ($B \times 0.3$ to 0.8%) relative to 100 parts by mass of the cement composition for high temperature environment.

[0020] 3. Water reducing agent (R2)

The water reducing agent (R2) used for the present invention is a water reducing agent other than the water reducing agent (R1), and may specifically be one or more types selected from a standard type water reducing agent, a standard type AE water reducing agent, a high-range water reducing agent and a standard type high-performance AE water reducing agent defined in JIS A 6204 (Chemical admixtures for concrete). Among these, the water reducing agent (R2) is preferably a high-range water reducing agent.

When the water reducing agent (R2) is represented by a water reducing component thereof, one or more types selected from polycarboxylic acid, naphthalenesulfonic acid-formaldehyde condensates, melaminesulfonic acid formaldehyde condensates,

ligninsulfonic acid and salts thereof may be mentioned.

The amount of the water reducing agent (R2) added is preferably 0.1 to 4 parts by mass ($B \times 0.1$ to 4%) relative to 100 parts by mass of the cement composition for high temperature environment. When the amount of addition is within the above range, the workability and the strength development over a medium to long term of the concrete are preferable. The amount of addition is more preferably 0.3 to 3 parts by mass ($B \times 0.3$ to 3%) and still more preferably 0.5 to 2 parts by mass ($B \times 0.5$ to 2%) relative to 100 parts by mass of the cement composition for high temperature environment.

[0021] 4. Fine aggregate

The fine aggregate used for the present invention may be one or more types selected from river sand, mountain sand, land sand, sea sand, crushed sand, silica sand, slag fine aggregate and lightweight fine aggregate. The fine aggregate may be natural aggregate or recycled aggregate.

The unit quantity of the fine aggregate is preferably 600 to 900 kg per 1 m³ of the concrete. When the unit quantity is within the above range, the concrete for high temperature environment may have preferable fluidity, workability and the like. The unit quantity is more preferably 650 to 850 kg per 1 m³ of the concrete.

[0022] 5. Coarse aggregate

The coarse aggregate used for the present invention may be one or more types selected from gravel, crushed stone, slag coarse

aggregate and lightweight coarse aggregate. The coarse aggregate may be, similar to the fine aggregate, natural aggregate or recycled aggregate.

The unit quantity of the coarse aggregate is preferably 900 to 1130 kg per 1 m³ of the concrete. When the unit quantity is within the above range, the concrete for high temperature environment may have preferable fluidity and workability. The unit quantity is more preferably 950 to 1080 kg per 1 m³ of the concrete.

[0023] 6. Water

Water used for the present invention may be one that does not have an adverse impact on the strength, fluidity or the like of the concrete for high temperature environment, and may include, for example, tap water, treated sewage, supernatant of fresh concrete and the like.

The unit quantity of water is preferably 100 to 200 kg per 1 m³ of the concrete. When the unit quantity is within the above range, the concrete for high temperature environment may have preferable fluidity, workability and the like. The unit quantity is more preferably 130 to 180 kg per 1 m³ of the concrete.

[0024] 7. Optional constituent

The concrete for high temperature environment of the present invention may contain, in addition to the above prerequisite constituents, an expansion material and/or a shrinkage reducing agent in order to suppress shrinkage and cracking. In order to improve the workability and secure a flowing time of the concrete for high temperature environment, the concrete for high temperature

environment may also contain a retarder in addition to the water reducing agent (R1) and the water reducing agent (R2). In order to suppress excess air entrainment in the concrete for high temperature environment, the concrete for high temperature environment may also contain an air controlling agent.

Examples

[0025] The present invention is hereinafter specifically described by way of Examples which do not limit the present invention.

1. Materials

Materials used in the tests are indicated in Table 1. Properties of fly ashes (FAs) used in the tests are indicated in Table 2. FAs 1 to 5 in Table 2 satisfy all conditions (1) to (4), while FAs 6 to 10 do not satisfy any of conditions (1) to (4).

The conditions of X-ray diffraction (XRD) measurement and the conditions of Rietveld analysis used for determining the lattice volume of quartz in fly ashes are indicated below.

(a) Conditions of X-ray diffraction measurement

X-ray diffraction was measured on an X-ray diffractometer (D8 Advance) manufactured by Bruker under the following conditions: target: $\text{CuK}\alpha$, tube voltage: 35 kV, tube current: 350 mA, scanning range: 10° to 60° (2θ), step width: 0.0234° and scanning speed: $0.13^\circ/\text{s}$.

(b) Rietveld analysis conditions

Rietveld analysis was carried out with an analytical software

(Topas ver. 2.1) manufactured by Bruker. The crystallographic structural data (ICDD number) used was 331161 (Quartz).

The compacted density of FAs 2 to 4 indicated in Table 2 was measured according to the measurement method of the compacted density described above.

[0026]

[Table 1]

Material	Symbol	Type/brand	Density (g/cm ³)	Remarks
Water	W	Tap water	1.00	Tap water at Kawara machi, Tagawa gun, Fukuoka, Japan
Cement composition (B)	C	Ordinary Portland cement	3.16	Manufactured by Taiheiyo Cement Corporation (product from Kamiiso Plant)
	FA	Fly ash	-	Properties are indicated in Table 2.
	BS	Blast furnace slag powder	2.89	Blaine specific surface area: 4300 cm ² /g
	GG	Dihydrate gypsum	2.23	Blaine specific surface area: 10000 cm ² /g
Fine aggregate	S1	Crushed sand/product of Malaysia	2.60	F.M.: 3.48, water absorption: 1.29%, content of fine particles: 10.4%
	S2	Natural sand/ product of Malaysia	2.61	F.M.: 2.48, water absorption: 1.07%, content of fine particles: 0.8%
Coarse aggregate	G	Crushed granite/product of Indonesia	2.64	Water absorption: 0.71%, solid content: 59.7%, F.M.: 6.62

Chemical admixture	R1	MasterPozzolith 138R	-	Super-retarding water reducing agent (ligninsulfonic acid-based), registered trade mark, manufactured by BASF SE
	R2	MasterRheobuild 1000	-	High-range water reducing agent (naphthalenesulfonic acid-based), registered trade mark, manufactured by BASF SE
	AF	MasterAir 400	-	Air controlling agent, registered trade mark, manufactured by BASF SE

Note: The density of the fine aggregate and the coarse aggregate is the density in saturated surface-dry condition.

[0027]

[Table 2]

Fly ash	Blaine specific surface area (cm ² /g)	Mass reduction rate (% by mass)	SiO ₂ content (% by mass)	Mass ratio	Lattice volume (Å ³)	Compacted density (cm ³ /g)
FA 1	3750	3.1	57.3	0.38	114.8	–
FA 2	3660	3.4	54.8	0.34	114.1	1.40
FA 3	3340	2.2	63.1	0.53	113.7	1.21
FA 4	3120	3.7	58.3	0.68	114.3	0.94
FA 5	3500	2.7	51.3	0.64	113.2	–
FA 6	2300	2.9	53.3	0.63	113.9	–
FA 7	3160	7.2	53.8	0.6	114.2	–
FA 8	3360	4.2	46.8	0.58	114.3	–
FA 9	3310	3.2	59.5	0.17	113.9	–
FA 10	3480	3.8	60.9	1.78	114.7	–

Note: Mass ratio represents the mass ratio of $(\text{Na}_2\text{O} + 0.658 \times \text{K}_2\text{O}) / (\text{MgO} + \text{SO}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5 + \text{MnO})$.

[0028] 2. Production of cement compositions for high temperature environment

Fly ash (FA), cement (C) and optional blast furnace slag powder (BS) and gypsum powder (GG) were mixed according to the formulations of the cement compositions indicated in Table 3 to produce the cement compositions.

In Table 3:

(i) Examples 1 to 16 are cement compositions for high temperature environment of the present invention in which the content of the fly ash is in the range of 15 to 55% by mass with the sum of the fly ash (FAs 1 to 5) satisfying all conditions (1) to (4) and Portland cement being 100% by mass;

(ii) Comparative Examples 1, 2 and 10 are cement compositions without fly ash;

(iii) Comparative Examples 3 to 9 are cement compositions containing FAs 6 to 10 which do not satisfy any of the conditions (1) to (4); and

(iv) Comparative Examples 11 and 12 are cement compositions in which the content of the fly ash is outside of the range of 15 to 55% by mass.

[0029]

[Table 3]

	Cement composition				
	Type of FA	FA (% by mass)	C (% by mass)	BS (% by mass)	GG (% by mass)
Ex. 1	FA 1	30.5	69.5	–	–
Ex. 2	FA 2	30.5	69.5	–	–
Ex. 3	FA 3	30.5	69.5	–	–
Ex. 4	FA 4	30.5	69.5	–	–
Ex. 5	FA 5	30.5	69.5	–	–
Ex. 6	FA 1	21.4	48.6	28.7	1.3
Ex. 7	FA 2	21.4	48.6	28.7	1.3
Ex. 8	FA 3	21.4	48.6	28.7	1.3
Ex. 9	FA 4	21.4	48.6	28.7	1.3
Ex. 10	FA 5	21.4	48.6	28.7	1.3
Ex. 11	FA 2	25.0	75.0	–	–
Ex. 12	FA 2	45.0	55.0	–	–
Ex. 13	FA 2	18.3	41.7	38.3	1.7
Ex. 14	FA 2	16.8	38.2	43.1	1.9
Ex. 15	FA 2	15.3	34.7	47.8	2.2
Ex. 16	FA 2	12.2	27.8	57.4	2.6
Comp. Ex. 1	–	–	35.0	62.2	2.8
Comp. Ex. 2	–	–	25.0	71.8	3.2
Comp. Ex. 3	FA 6	30.5	69.5	–	–
Comp. Ex. 4	FA 7	30.5	69.5	–	–
Comp. Ex. 5	FA 8	30.5	69.5	–	–
Comp. Ex. 6	FA 9	30.5	69.5	–	–
Comp. Ex. 7	FA 10	30.5	69.5	–	–
Comp. Ex. 8	FA 9	21.4	48.6	28.7	1.3

Comp. Ex. 9	FA 10	21.4	48.6	28.7	1.3
Comp. Ex. 10	-	-	100	-	-
Comp. Ex. 11	FA 2	10.0	90	-	-
Comp. Ex. 12	FA 2	60.0	40	-	-

[0030] 2. Formulations of concretes

The formulations of concretes used for the tests are indicated in Table 4.

[0031]

[Table 4]

Concrete No.	W/B (%)	s/a (%)	Unit quantity (kg/m³)					R2	R1	AF
			W	B	S1	S2	G	(B × %)		
1	40	40	165	413	278	418	1057	1.35	0.5	0.01
2			165	413	278	419	1059	1.15		
3			165	413	278	418	1057	1.35	-	
4			165	412	281	424	1072	0.875	0.5	
5			165	412	281	423	1070	0.775		
6	50	42	165	331	438	315	1064	1.45	0.5	0.01
7			165	330	438	315	1064	1.3		
8			165	330	441	317	1070	1.05		
9			165	330	440	316	1069	1.1		
10	60	44	165	276	328	494	1059	1.40	0.5	0.01
11			165	276	328	494	1061	1.05		
12			165	275	331	498	1068	0.95		
13			165	275	330	497	1067	0.875		

Note: B (cement composition) represents the total mass of fly ash, cement, blast furnace slag powder and dihydrate gypsum.

Note: W/B = 40%, W/B = 50% and W/B = 60% represent S1:S2 = 40:60, S1:S2 = 58:42 and S1:S2 = 32:68, respectively.

The ratios of S1:S2 are all in volume ratio.

[0032] 3. Test method

The tests indicated in Table 5 were carried out according to the test methods in JIS and the like indicated in Table 5.

[0033]

[Table 5]

Test	Test method	Remarks
Slump	JIS A 1101	Target value: 12 ± 2.5 cm
Air content	JIS A 1118	Target value: 2.0% or less
Concrete temperature	-	Target value: $27 \pm 2.0^{\circ}\text{C}$
Autogenous shrinkage strain and simplified adiabatic temperature increase	Method described in paragraph [0037]	- Specimen: $400 \times 400 \times 400$ mm - Insulating material: Foamed polystyrene having a thickness of 200 mm - Embedded strain gauge (product number: KM-100BT) was placed at the centre of the specimen.
Compressive strength	JIS A 1108	- Curing condition: Formwork was removed at the material age of 1 day and the material was cured in water at 27°C. - Test material age: 28, 56 and 91 days ($n = 3$)

[0034] 4. Test for fresh properties of concrete

(1) Test method

For mixing and kneading concrete, a coarse aggregate, a fine

aggregate and a cement composition indicated in Table 3 were added to a forced pan-shaped mixer having a nominal volume of 55 L in a test room adjusted to an environmental temperature of 27°C which is a test standard in Singapore. The content was dry-mixed for 20 seconds and then water, a water reducing agent and an air controlling agent were added and kneaded for 60 seconds. After scraping off the concrete in the mixer, the concrete was again kneaded for 60 seconds, discharged from the mixer and immediately measured for the slump and air content of concrete and temperature of (fresh) concrete. As typical examples, test results for concrete Nos. 1 to 5 containing cement compositions of Examples 1 to 4, Examples 6 to 9 and Comparative Examples 1 and 2 are indicated in Table 6.

[0035]

[Table 6]

Concrete No.	Type of B	Type of FA	Slump (cm)	Air content (%)	Temperature of concrete (°C)
1	Ex. 1	FA 1	14.4	1.4	29.0
	Ex. 2	FA 2	15.9	1.4	29.0
	Ex. 3	FA 3	15.7	1.5	29.0
	Ex. 4	FA 4	15.3	1.3	29.0
2	Ex. 6	FA 1	15.5	1.5	29.0
	Ex. 7	FA 2	16.7	1.4	28.5
	Ex. 8	FA 3	16.4	1.5	28.5
	Ex. 9	FA 4	16.0	1.4	28.5

3	Ex. 3	FA 3	3.0	1.4	29.0
4	Comp. Ex. 1	–	14.7	1.6	28.5
5	Comp. Ex. 2	–	16.5	1.6	28.5

[0036] (2) Evaluation of test results

As indicated in Table 6, concretes for high temperature environment of the present invention containing cement compositions for high temperature environment (Examples 1 to 4 and Examples 6 to 9) of the present invention had almost equivalent fresh properties to those of conventional concretes (Comparative Examples 1 and 2) without fly ash, and thus had equivalent applicability of concrete.

Meanwhile, concrete (No. 3) that did not contain a super-retarding water reducing agent (R1) had a slump as small as 3.0 cm and thus had poor applicability.

[0037] 5. Tests for autogenous shrinkage strain, simplified adiabatic temperature increase and compressive strength

(1) Test method

A container for the simplified adiabatic test used for the test of the simplified adiabatic temperature increase has, as illustrated in Fig. 1, an inner space of 400 mm long, 400 mm wide and 400 mm high and made of a foamed polystyrene insulating material having a thickness of 200 mm and a concrete panel having a thickness of 12 mm for facilitating removal after the test.

A support steel including an embedded strain gauge with temperature measuring function as illustrated in Fig. 2(a) was installed upright at the centre of the inner space as illustrated in Fig. 2(b). The kneaded concretes of Examples and Comparative Examples described above were placed so as to be 3 separate layers using a vibrator on each layer, the container was then sealed with the concrete panel and the foamed polystyrene insulating material, and the autogenous shrinkage strain and the simplified adiabatic temperature increase of concrete at the material age of 28 days were measured in an environmental temperature of 27°C.

The compressive strength of concrete was measured according to JIS A 1108 "Method of test for compressive strength of concrete" as indicated in Table 5.

The test results are indicated in Table 7.

[0038]

[Table 7]

Test Example	Concrete No.	Type of B	Type of FA	Autogenous shrinkage strain ($\times 10^{-6}$)	Simplified adiabatic temperature increase (°C)	Compressive strength (MPa)		
						Material age 28 days	Material age 56 days	Material age 91 days
1	1	Ex. 1	FA 1	-150	35	56	62	70
2		Ex. 2	FA 2	-110	31	58	63	72
3		Ex. 3	FA 3	-105	31	58	62	71
4		Ex. 4	FA 4	-117	32	57	62	71
5		Ex. 5	FA 5	-155	35	56	63	71
6		Comp. Ex. 3	FA 6	-	-	50	55	67
7		Comp. Ex. 4	FA 7	-	-	50	55	66
8		Comp. Ex. 5	FA 8	-	-	48	54	65
9		Comp. Ex. 6	FA 9	-120	32	49	56	66
10		Comp. Ex. 7	FA 10	-208	43	60	66	74
11	2	Ex. 6	FA 1	-268	33	63	67	74
12		Ex. 7	FA 2	-230	28	66	71	78
13		Ex. 8	FA 3	-233	28	65	70	77
14		Ex. 9	FA 4	-240	29	65	69	77
15		Ex. 10	FA 5	-240	33	65	67	73
16		Comp. Ex. 8	FA 9	-229	29	52	58	68
17		Comp. Ex. 9	FA 10	-292	40	65	70	77
18	4	Comp. Ex. 1	-	-300	35	-	-	76

19	5	Comp. Ex. 2	-	-350	30	60	63	67
20	6	Ex. 1	FA 1	-175	31	39	46	50
21		Ex. 2	FA 2	-135	28	41	48	54
22		Ex. 3	FA 3	-136	28	41	48	53
23		Ex. 4	FA 4	-142	29	42	48	53
24		Ex. 5	FA 5	-180	32	39	45	51
25		Comp. Ex. 6	FA 9	-150	29	33	41	46
26		Comp. Ex. 7	FA 10	-250	38	43	52	55
27	7	Ex. 6	FA 1	-366	29	48	54	56
28		Ex. 7	FA 2	-330	24	50	57	61
29		Ex. 8	FA 3	-333	25	49	57	60
30		Ex. 9	FA 4	-340	25	49	56	59
31		Ex. 10	FA 5	-360	28	47	53	57
32		Comp. Ex. 8	FA 9	-332	24	36	44	49
33		Comp. Ex. 9	FA 10	-392	36	49	58	60
34	8	Comp. Ex. 1	-	-400	32	-	-	59
35	9	Comp. Ex. 2	-	-480	25	-	53	55
36	10	Ex. 1	FA 1	-20	25	31	39	41
37		Ex. 2	FA 2	-10	23	32	40	42
38	11	Ex. 7	FA 2	-80	23	39	45	48
39	12	Comp. Ex. 1	-	-150	27	-	-	-
40	13	Comp. Ex. 2	-	-160	23	-	42	44

[0039] (2) Evaluation of test results

(i) Autogenous shrinkage strain

From Table 7, the following can be found about the autogenous shrinkage strain of concrete. Namely:

(a) a concrete (Test Example 10) containing Comparative Example 7 that contained FA 10 having a mass ratio of $(\text{Na}_2\text{O} + 0.658 \text{ K}_2\text{O}) / (\text{MgO} + \text{SO}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5 + \text{MnO})$ as high as 1.78 had high autogenous shrinkage strain of -208×10^{-6} , while the concretes for high temperature environment (Test Examples 1 to 5) of the present invention containing the cement compositions for high temperature environment (Examples 1 to 5) of the present invention had low autogenous shrinkage strains of -105 to -155×10^{-6} . Similarly:

(b) a concrete (Test Example 17) had high autogenous shrinkage strain of -292×10^{-6} , while the concretes for high temperature environment (Test Examples 11 to 15) of the present invention had low autogenous shrinkage strains of -230 to -268×10^{-6} .

(c) A concrete (Test Example 26) had high autogenous shrinkage strain of -250×10^{-6} , while the concretes for high temperature environment (Test Examples 20 to 24) of the present invention had low autogenous shrinkage strains of -135 to -180×10^{-6} .

(d) A concrete (Test Example 33) had a high autogenous shrinkage strain of -392×10^{-6} , while the concretes for high temperature environment (Test Examples 27 to 31) of the present invention had low autogenous shrinkage strains of -330 to -366×10^{-6} .

The results are not affected by the ratio of water/cement composition (W/B).

Meanwhile, conventional concretes (Test Examples 18 and 19) containing cement compositions (Comparative Examples 1 and 2) that contained blast furnace slag without containing fly ash had autogenous shrinkage strains of -300×10^{-6} and -350×10^{-6} , respectively, which are higher than autogenous shrinkage strains of Test Examples 1 to 5 and 11 to 15.

[0040] (ii) Simplified adiabatic temperature increase

From Table 7, the following can be found about the simplified adiabatic temperature increase of concrete. Namely:

(a) a concrete (Test Example 10) containing Comparative Example 7 that contained FA 10 having a mass ratio of $(\text{Na}_2\text{O} + 0.658 \times \text{K}_2\text{O}) / (\text{MgO} + \text{SO}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5 + \text{MnO})$ as high as 1.78 had high simplified adiabatic temperature increase of 43°C, while the concretes for high temperature environment (Test Examples 1 to 5) of the present invention containing the cement compositions for high temperature environment (Examples 1 to 5) of the present invention had low simplified adiabatic temperature increases of 31°C to 35°C. Similarly:

(b) a concrete (Test Example 17) had high simplified adiabatic temperature increase of 40°C, while the concretes for high temperature environment (Test Examples 11 to 15) of the present invention had low simplified adiabatic temperature increases of 28°C to 33°C.

(c) A concrete (Test Example 26) had high simplified adiabatic temperature increase of 38°C, while the concretes for high temperature environment (Test Examples 20 to 24) of the present invention had low simplified adiabatic temperature increases of 28°C to 32°C.

(d) A concrete (Test Example 33) had high simplified adiabatic temperature increase of 36°C, while the concretes for high temperature environment (Test Examples 27 to 31) of the present invention had low simplified adiabatic temperature increases of 24°C to 29°C.

The results are not affected by the ratio of water/cement composition.

[0041] (ii) Compressive strength

From Table 7, the following can be found about the compressive strength of concrete. Namely:

(a) a concrete (Test Example 6) containing Comparative Example 3 that contained FA 6 having a Blaine specific surface area of less than 2500 cm²/g, a concrete (Test Example 7) containing Comparative Example 4 that contained FA 7 having a mass reduction of above 5% by mass, a concrete (Test Example 8) containing Comparative Example 5 that contained FA 8 having a SiO₂ content of less than 50% by mass and a concrete (Test Example 9) containing Comparative Example 6 that contained FA 9 having a mass ratio of $(\text{Na}_2\text{O} + 0.658 \times \text{K}_2\text{O}) / (\text{MgO} + \text{SO}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5 + \text{MnO})$ of less than 0.2 had low compressive strengths at the material age of 28 days, 56 days and 91 days

respectively of 48 to 50 MPa, 54 to 56 MPa and 65 to 67 MPa, while the concretes for high temperature environment (Test Examples 1 to 5) of the present invention containing the cement compositions for high temperature environment (Examples 1 to 5) of the present invention had high compressive strength at the material age of 28 days, 56 days and 91 days respectively of 56 to 58 MPa, 62 to 63 MPa and 70 to 72 MPa. Similarly:

(b) a concrete (Test Example 16) had low compressive strength at the material age of 28 days, 56 days and 91 days respectively of 52 MPa, 58 MPa and 68 MPa, while the concretes for high temperature environment (Test Examples 11 to 15) of the present invention had high compressive strengths at the material age of 28 days, 56 days and 91 days respectively of 63 to 66 MPa, 67 to 71 MPa and 73 to 78 MPa.

(c) A concrete (Test Example 25) had low compressive strength at the material age of 28 days, 56 days and 91 days respectively of 33 MPa, 41 MPa and 46 MPa, while the concretes for high temperature environment (Test Examples 20 to 24) of the present invention had high compressive strengths at the material age of 28 days, 56 days and 91 days respectively of 39 to 42 MPa, 45 to 48 MPa and 50 to 54 MPa.

(d) A concrete (Test Example 32) had low compressive strength at the material age of 28 days, 56 days and 91 days respectively of 36 MPa, 44 MPa and 49 MPa, while the concretes for high temperature environment (Test Examples 27 to 31) of the present invention had high compressive strengths at the material age of 28 days, 56 days

and 91 days respectively of 47 to 50 MPa, 53 to 57 MPa and 57 to 61 MPa.

The results are not affected by the ratio of water/cement composition.

[0042] 6. Relationship between the content of fly ash and concrete properties

Concretes (Test Examples 41 to 45) containing cement compositions that had the contents of fly ash (FA 2) of 0% by mass (Comparative Example 10), 10% by mass (Comparative Example 11), 25% by mass (Example 11), 45% by mass (Example 12) and 60% by mass (Comparative Example 12) with the sum of the fly ash (FA 2) and Portland cement being 100% by mass were mixed and kneaded in the same manner as the test method of fresh properties of concrete described above and the concretes were measured for the autogenous shrinkage strain, simplified adiabatic temperature increase and compressive strength thereof in the same manner as described above. The results are indicated in Table 8 together with the results for Test Examples 2 (the content of the fly ash (FA 2) in the cement composition was 30.5% by mass), 18 and 19.

[0043]

[Table 8]

Test Example	Concrete No.	Type of B	Type of FA	Autogenous shrinkage strain ($\times 10^{-6}$)	Simplified adiabatic temperature increase ($^{\circ}\text{C}$)	Compressive strength (MPa)		
						Material age 28 days	Material age 56 days	Material age 91 days
41	1	Ex. 11	FA 2	-120	34	67	70	76
2		Ex. 2	FA 2	-110	31	58	63	72
42		Ex. 12	FA 2	-100	25	-	59	67
43		Comp. Ex. 10	-	-210	45	70	73	79
44		Comp. Ex. 11	FA 2	-185	42	70	74	80
45		Comp. Ex. 12	FA 2	-	-	-	50	55
18	4	Comp. Ex. 1	-	-300	35	-	-	76
19	5	Comp. Ex. 2	-	-350	30	60	63	67

[0044] Test Examples 43 and 44 which had low fly ash contents of 0% by mass and 10% by mass had high autogenous shrinkage strains of -210×10^{-6} and -185×10^{-6} , respectively, while the concretes (Test Examples 41, 2 and 42) containing cement compositions for high temperature environment (Examples 11, 2 and 12) of the present invention that had the contents of 25 to 45% by mass had low autogenous shrinkage strains of -100 to -120×10^{-6} .

Even when compared to conventional concretes (Test Examples 18 and 19), the concretes (Test Examples 41, 2 and 42) had low autogenous shrinkage strains and comparable compressive strength.

[0045] 7. Relationship between the content of blast furnace slag powder and compressive strength of concrete

Concretes (Test Examples 46 to 49) containing cement compositions for high temperature environment of the present invention that had the contents of the blast furnace slag powder of 38.3% by mass (Example 13), 43.1% by mass (Example 14), 47.8% by mass (Example 15) and 57.4% by mass (Example 16) with the sum of the fly ash (FA 2), Portland cement and the blast furnace slag powder being 100% by mass were mixed and kneaded in the same manner as the test method of fresh properties of concrete described above and the concretes were measured for the compressive strength thereof in the same manner as described above. The results are indicated in Table 9 together with the results for Test Examples 2 (the content of the blast furnace slag powder in the cement composition was 0% by mass), 12 (the content of the blast furnace

slag powder in the cement composition was 28.7% by mass), 18 and 19.

[0046]

[Table 9]

Test Example	Concrete No.	Type of B	Type of FA	Compressive strength (MPa)		
				Material age 28 days	Material age 56 days	Material age 91 days
2	1	Ex. 2	FA 2	58	63	72
12	2	Ex. 7	FA 2	66	71	78
46		Ex. 13	FA 2	66	71	78
47		Ex. 14	FA 2	66	71	78
48		Ex. 15	FA 2	67	72	78
49		Ex. 16	FA 2	65	69	72
18	4	Comp. Ex. 1	—	—	—	76
19	5	Comp. Ex. 2	—	60	63	67

[0047] As indicated in Table 9, it is found that the concretes (Test Examples 12, 46 to 49) containing the cement compositions for high temperature environment of the present invention that contained appropriate amounts of the blast furnace slag powder and gypsum had improved strength development, particularly improved strength development at the material age of 28 days.

[0048] (Reference Example)

The concrete No. 6 (Test Example 50) containing the cement composition (Example 2) that contained FA 2 and the concrete No. 6 (Test Example 51) containing the cement composition (Comparative Example 7) that contained FA 10 were measured for the autogenous shrinkage strain, simplified adiabatic temperature increase and compressive strength at an environmental temperature of 20°C in the same manner as above except that mixing and kneading of concretes were carried out in a test room adjusted to 20°C. The results are indicated in Table 10.

The slump and air content of the concretes for Test Example 50 and Test Example 51 were 10.6 cm and 1.4% and 10.3 cm and air content of 1.4%, respectively.

[0049]

[Table 10]

Test Example	Concrete No.	Type of B	Type of FA	Autogenous shrinkage strain ($\times 10^{-6}$)	Simplified adiabatic temperature increase (°C)	Compressive strength (MPa)		
						Material age 28 days	Material age 56 days	Material age 91 days
50	6	Ex. 2	FA 2	-145	30	39	47	55
51		Comp. Ex. 7	FA 2	-160	33	40	49	55

[0050] Under an environmental temperature of 20°C, the autogenous shrinkage strain, simplified adiabatic temperature increase and compressive strength were comparable between the concrete (Test Example 50) containing the cement composition of

Example 2 and the concrete (Test Example 51) containing the cement composition of Comparative Example 7 as indicated in Table 10.

However, as indicated in Table 7, when the environmental temperature was as high as 27°C, there were big differences in the autogenous shrinkage strain and simplified adiabatic temperature increase between the concrete for high temperature environment (Test Example 21) of the present invention containing the cement composition of Example 2 and the concrete (Test Example 26) containing the cement composition of Comparative Example 7 which respectively correspond to Test Example 50 and Test Example 51, and Test Example 21 had low autogenous shrinkage strain and simplified adiabatic temperature increase compared to Test Example 26.

Therefore, according to the present invention, a concrete for high temperature environment having low autogenous shrinkage strain and temperature increase can be provided from the materials that are widely used in the field of concrete.

[Reference Signs List]

[0051]

- 1 Embedded strain gauge
- 2 Cover
- 3 Concrete panel
- 4 Support steel
- 5 Concrete
- 6 Foamed polystyrene

Claims

[Claim 1] A cement composition for high temperature environment, comprising at least: fly ash satisfying all conditions (1) to (4) below; and Portland cement:

(1) the fly ash has a Blaine specific surface area of 2500 to 6000 cm²/g;

(2) the fly ash has a mass reduction rate of 5% by mass or less after heating at 975 ± 25°C for 15 minutes;

(3) the fly ash has a SiO₂ content of 50% by mass or more; and

(4) the fly ash has a mass ratio $(\text{Na}_2\text{O} + 0.658 \times \text{K}_2\text{O}) / (\text{MgO} + \text{SO}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5 + \text{MnO})$ of 0.2 to 1.0, (where the units for the chemical formulae in the above formula are % by mass),

wherein a content of the fly ash is 15 to 55% by mass with the sum of the fly ash and the Portland cement being 100% by mass.

[Claim 2] The cement composition for high temperature environment according to claim 1, wherein the fly ash further satisfies condition (5) below:

(5) quartz in the fly ash has a lattice volume of 113.5 to 114.5 Å³, (where the lattice volume is determined by the Rietveld analysis).

[Claim 3] The cement composition for high temperature environment according to claim 1 or 2, further comprising blast furnace slag powder,

wherein a content of the blast furnace slag powder is 50% by mass or less with the sum of the Portland cement, the fly ash and the blast furnace slag powder being 100% by mass.

[Claim 4] The cement composition for high temperature environment according to any one of claims 1 to 3, further comprising one or more types of gypsum selected from anhydrous gypsum, hemihydrate

gypsum and dihydrate gypsum,

wherein a content of the gypsum in terms of SO_3 is 2.5% by mass or less with the sum of the Portland cement, the fly ash, the blast furnace slag powder and the gypsum being 100% by mass.

[Claim 5] A concrete for high temperature environment comprising: the cement composition for high temperature environment according to any one of claims 1 to 4; a water reducing agent (R1) indicated below; a water reducing agent (R2) other than the water reducing agent (R1); a fine aggregate; a coarse aggregate; and water,

water reducing agent (R1): one or more types of water reducing agents selected from a super-retarding water reducing agent, a retarding water reducing agent, a retarding AE water reducing agent and a retarding high-performance AE water reducing agent.

[Claim 6] The concrete for high temperature environment according to claim 5, which is used under an environment with an environmental temperature (temperature surrounding the concrete) of 25°C or above.