

Specification

Title of the Invention Cement Composition

Field of the Invention

[0001]

The present invention relates to a new cement composition. More specifically, the present invention relates to a new cement composition, comprising a cement clinker producible with baking at a lower temperature than general cement clinkers, and having good strength development characteristic both in the initial period and the medium to long-term period.

Background Art

[0002]

The cement industry has been a typical mass production and mass consumption industry and is required to save resources and energy. For example, the production of general Portland cements clinker, the most mass produced cement clinker, requires baking raw materials with predetermined chemical compositions at 1450 degree Celsius to 1550 degree Celsius; and the baking is the most energy consuming process. Therefore, the reduction in the baking temperature results in energy saving. For reducing the baking temperature of clinker, a cement clinker with an increased content of C_4AF ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$), one of the major mineral component of Portland cement clinker, has been developed (Patent Document 1: JP 2012-224504A).

[0003]

In relation to the present global environmental issues, the effective utilization of wastes and various by-products has been an important issue. With the characteristics of the cement industry and cement manufacturing factory, wastes and by-products can be safely and effectively used as the raw materials and fuels for the production of cement clinkers. Wastes and by-products have a high Al_2O_3 content in general. The above cement clinker with an increased amount of C_4AF contains a larger amount of Al_2O_3 than usual Portland cement clinkers and therefore is suitable for the use of wastes and by-products. In this respect, the cement clinker according to Patent Document 1 is superior.

[0004]

When Portland cement clinkers are simply crushed and mixed with water, they rapidly begin to stiffen and lose the fluidity. This is because C_3A , one of the major Portland cement components, reacts rapidly with water and generates hydrates precipitating on the particle surface. For elongating the fast setting period, gypsum has been added, for example, during the finishing grinding process. The above Portland cement clinker with the increased C_4AF content is added with gypsum of $2.0 \pm 0.2\%$ in SO_3 reduction to adjust the setting period, (for example, Patent Document 1: JP 2012-224504A).

Prior Art Document

Patent Document

[0005]

[Patent Document 1] JP 2012-224504A

Summary of the Invention

Problem to be Solved by the Invention

[0006]

The cement clinker according to Patent Document 1 can be baked at a relatively lower temperature and consumes a relatively larger amount of Al_2O_3 -containing wastes. However, in comparison with general Portland cements clinkers having a total amount of C_3A and C_4AF of about 20% or less, it has a slightly lower medium to long-term strength at about 28 days of age. Further, for shortening the construction cycle, it has been demanded to improve the initial strength up to about 7 days of age, corresponding to the formwork removal. Thus, the cement composition, baked at the relatively lower temperature and having consumed a large amount of Al_2O_3 -containing wastes, is demanded to have a good strength development characteristic at the initial and the medium to long-term periods.

Means for Solving the Problem

[0007]

The present inventors have worked diligently to solve the above problem. From the above low-temperature baked cement clinker, the inventors have found a new cement composition having the same fresh properties as general cement clinkers and superior initial and medium to long-term strength development characteristics to general cement clinkers. Here, "fresh properties" refer to the fluidity of mortar before hardening and the setting property of cement. The setting property is evaluated specifically by the initial period until setting begins and the period until setting is complete.

[0008]

The cement composition according to the invention comprises a cement clinker having a total amount of C_3A and C_4AF of 22% or more, a C_3S content of 60% or more, both according to Bogue's formulas, and an iron modulus ($\text{I.M.} = \text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$) of 1.3 or less, and gypsum. The cement composition is characterized in that the SO_3 content is 2.3 to 3.3 mass% relative to the total amount of cement clinker and gypsum. The SO_3 content is adjustable by the SO_3 content in the cement clinker itself and the content of gypsum added to the cement clinker.

Advantageous Effect of the Invention

[0009]

The cement composition according to the present invention comprises the cement clinker producible with the low-temperature baking and having absorbed a large content of wastes, has a fresh properties equivalent to general Portland cements, and has a good initial

strength development characteristic and also a medium to long-term strength development characteristic both equivalent to or better than general Portland cements.

Brief Description of the Drawing

[0010]

[Fig. 1] A characteristic diagram showing the XRD patterns of the cement compositions of the

Embodiments and comparative examples.

Means for Carrying out the Invention

[0011]

The contents of C_3A , C_4AF , C_3S , and C_2S in the present invention are determined by the Bogue's formulas. The Bogue's formulas have been used together with various indexes and moduli for calculating the approximate chemical composition regarding the major components of cement clinkers from major chemical analysis values and have been well known in the field. For reference, the calculation of contents of minerals in cement clinker by the Bogue's formulas is described below. The unit for components such as CaO is mass%, and the unit for the contents of C_3S , etc. is samely mass%. In addition to the main components comprising CaO , SiO_2 , Al_2O_3 and Fe_2O_3 , cement clinkers also contain small contents of MgO , K_2O and other components, and the Bogue's formulas calculate without taking the small contents into account. As a result, the total content of the C_3S and C_4AF is sometimes less than 100%.

C_3S content = $(4.07 \times CaO) - (7.60 \times SiO_2) - (6.72 \times Al_2O_3) - (1.43 \times Fe_2O_3)$

C_2S content = $(2.87 \times SiO_2) - (0.754 \times C_3S)$

C_3A content = $(2.65 \times Al_2O_3) - (1.69 \times Fe_2O_3)$

C_4AF content = $3.04 \times Fe_2O_3$.

[0012]

The iron modulus (I.M.) is calculated from the major chemical analysis values, along with hydraulic modulus (H.M.), silica modulus (S.M.), activity index (A.I.) and lime saturation degree (L.S.D.). The iron modulus has been used for clinker production management, along with other moduli and indexes and has been well known to those in the industry. For reference, the calculation of iron modulus, etc., is described below. In the calculation of the iron modulus (I.M.), hydraulic modulus (H.M.), etc., the unit for components such as CaO is mass%.

Hydraulic modulus (H.M.) = $CaO / (SiO_2 + Al_2O_3 + Fe_2O_3)$

Silica modulus (S.M.) = $SiO_2 / (Al_2O_3 + Fe_2O_3)$

Iron modulus (I.M.) = Al_2O_3 / Fe_2O_3

Activity index (A.I.) = SiO_2 / Al_2O_3

Lime saturation degree (LSD) = $CaO / (2.8 \times SiO_2 + 1.2 \times Al_2O_3 + 0.65 \times Fe_2O_3)$.

The values of " CaO ", " SiO_2 ", " Al_2O_3 ", and " Fe_2O_3 " in the formulas can be measured according to JIS R 5202 "Chemical Analysis of Portland Cement" and JIS R 5204 "X-ray Fluorescence Analysis of Cement", etc.

[0013]

In the cement clinker according to the invention, the total content of C_3A and C_4AF is 22% or more. If the total content falls below 22%, it becomes difficult to obtain cement clinker with good properties such as strength development characteristics with the relatively lower temperature baking. As described later, the content of C_3S in the cement clinker according to the invention is 60% or more. Therefore, the total content of C_3A and C_4AF is limited up to 40%. The total content of C_3A and C_4AF is preferably 28% or less, and more preferably 27% or less. In this specification, the unit for C_2S , C_3S , C_3A , and C_4AF is mass%.

[0014]

The content of C_3S is very important in the invention for the strength development characteristics of the cement composition (hereinafter simply referred to as "cement"). If the content of C_3S falls below 60%, with the total content of C_3A and C_4AF , the content of C_2S , and the iron modulus, etc. within the specified range, good strength development characteristics cannot be obtained. It is preferable that the content of C_3S is 61% or more.

[0015]

The content of C_2S is not particularly limited, but it is important for the fluidity and initial strength development of the cement. When the content is 8% or more, the fluidity is good, and when it is 11% or less, sufficient initial strength development characteristic is obtained. For the good fluidity and good initial strength development characteristic, the C_2S content is preferably 8-10% and, in particular, 9-10%.

[0016]

The cement clinker according to the invention should have the iron modulus (I.M.) up to 1.3. If the iron modulus exceeds 1.3, the cement clinker, satisfying other requirements, has not sufficient strength development characteristic (more specifically, mortar strength development characteristic, and so on). Furthermore, if the iron modulus exceeds 1.3, the period from the setting of cement to the end of setting becomes generally too long, so the iron modulus should be 1.3 or less. The more preferable range of the iron modulus is 1.0 to 1.3.

[0017]

The hydraulic modulus and silica modulus are not particularly limited. In order to achieve a good balance of various physical properties, the hydraulic modulus is preferably 1.8 to 2.2, and is particularly preferably 1.9 to 2.1. The silica modulus is preferably 1.0 to 2.0, and is particularly preferably 1.1 to 1.7.

[0018]

Method for manufacturing the cement clinker according to the invention are not particularly limited. With preparing and mixing known cement (clinker) raw materials in a predetermined ratio and then baking them by a known method (e.g., in an SP kiln or an NSP kiln), the cement clinker according to the present invention is obtained.

[0019]

The preparation and mixing of the cement raw materials is carried out according to known methods. For example, the compositions of wastes, by-products and other raw materials

(such as limestone, quicklime, slaked lime, etc. as the CaO source, silica sand, etc. as the SiO₂ source, clay, etc. as the Al₂O₃ source, an iron source, and so on) are measured in advance, the mixing ratio of the raw materials is calculated such that the composition of the cement clinker satisfies the specified conditions, and then the raw materials are mixed in the mixing ratio.

[0020]

The raw materials of the cement clinker according to the invention are those used in the production of general Portland cement clinkers. It is preferable in the invention to use raw materials including wastes and by-products.

[0021]

It is preferable in the invention to use wastes and by-products for their effective use in the manufacture of the cement clinker. Examples of usable wastes and by-products include: blast furnace slag, steel slag, nonferrous metal slag, coal ash, sewage sludge, water purification sludge, paper manufacturing sludge, construction earth wastes, wasted casting sand, soot, incinerated fly ash, melted fly ash, chlorine bypass dust, wood chips, waste clay, slag, waste tires, shells, urban wastes, and its incinerated ash. Some of these materials are used as both a cement ingredient and a heat energy source.

[0022]

The cement clinker according to the invention contains a relatively larger amount of C₃A and C₄AF including aluminum. As a result, in comparison with general cement clinkers, a larger amounts of wastes and by-products having a high aluminum content is usable.

[0023]

The cement clinker according to the invention is made into cement in the same way as general cement clinkers, with grinding it together with gypsum, or with mixing gypsum to ground cement clinker. The produced cement may be ordinary Portland cement, early-strength Portland cement, ultra-early-strength Portland cement, etc. In addition, the cement clinker according to the invention may be used as a component of various blended cements and of solidifiers such as soil solidifiers.

[0024]

Dihydrate gypsum, hemihydrate gypsum, anhydrite gypsum, and so on can be used as the gypsum source without any particular restrictions. They have been known as gypsum source suitable for cement production. According to the invention, gypsum is added such that the content of SO₃ in the total of the cement clinker and the added gypsum is 2.3 to 3.3 mass%. If the content of SO₃ in them is less than 2.3 mass%, or more than 3.3 mass%, the resultant strength development characteristic is poor. For example, in Comparative Example 1 (SO₃ content of 2.17%) in Table 3, the compressive strength of the mortar at the first day is low. In Comparative Examples 2 and 3, where the SO₃ content exceeds 3.3%, the compressive strength of the mortar is low in the initial period from the first to the seventh day, and also the long-term compressive strength at the 28th day is low. Preferably, the SO₃ content should be 2.3% to 3.2%. From the perspective of strength development, it is particularly desirable to have an SO₃ content of 2.3% to 2.7%. Embodiment 1 in Table 3 (SO₃ content: 2.54%) has a higher SO₃

content than Comparative Example 1 but has higher compressive strength than Comparative Example 1 always from the first day 1 to 28th day. In addition, Embodiment 1 has always a higher mortar compressive strength than Embodiment 2 and Comparative Examples 2, 3 (all with SO₃ contents above 2.7%). In other words, when the content of SO₃ is between 2.3 and 2.7 mass%, the compressive strength of the mortar is exceptionally high. In this specification, when a range is indicated such as 2.3 to 2.7 mass%, it means, for example, 2.3 mass% or more and 2.7 mass% or less.

[0025]

The cement composition according to the invention may include one or more of limestone, fly ash, blast furnace slag, and siliceous material. In this case, the total content of limestone, blast furnace slag, fly ash, and siliceous material is 10% or less of the total cement composition.

[0026]

It is preferable that the powder fineness of the cement clinker, gypsum, limestone, and other mixing materials is adjusted so that the cement composition has a Blaine specific surface area of 2800 to 4500 cm²/g.

[0027]

Regarding the grinding to prepare the powder fineness, known methods can be used without restriction. The cement clinker and other components may be ground separately and then mixed, or the components may be mixed together and then ground. Ball mills, vertical mills, etc. are usable as the grinding machine.

[0028]

The cement composition according to the invention is usable as Portland cement, and in particular, one according to JIS standard. Portland cement includes ordinary Portland cement, early-strength Portland cement, and ultra-early-strength Portland cement. In addition to Portland cement, it can also be used as a component of various blended cements and a solidifier such as a soil solidifier.

Embodiments

[0029]

The present invention will be described in detail with reference to embodiments; however, the present invention is not limited to the embodiments.

[0030]

Industrial raw materials containing wastes were mixed so that a general Portland cement clinker (C1) and a cement clinker according to the invention (C2) are resultant after baking. The cement clinker C1 was baked at 1450 degree Celsius, and the cement clinker C2 was baked at 1350 degree Celsius. The baking temperatures, the mineral compositions, and the moduli of the cement clinkers are shown in Table 1.

[0031]

To the general cement clinker (C1), gypsum equivalent to 2.2 mass% SO₃ was added,

and then mixed and ground to a Blaine specific surface area of $3200 \pm 50 \text{ cm}^2/\text{g}$ (Reference Example). Five types of cement compositions were produced by adding gypsum to cement clinker (C2): one having SO_3 content of 2.0% (Comparative Example 1); 2.5% (Embodiment 1), 3.0% (Embodiment 2); 3.5% (Comparative Example 2); and 4.0% (Comparative Example 3). The chemical compositions of the cement compositions are shown in Table 2.

[0032]

The cement clinkers were made to cements as above, the compressive strengths of the mortars at specified age were measured for evaluating the strength development characteristics. For evaluating the fresh properties, the setting periods of the cements and the mortar fluidities were measured. The results are shown in Table 3.

- (1) The chemical compositions of raw materials, cement clinkers, and cement compositions: measured by the X-ray fluorescence analysis in accordance with JIS R 5204.
- (2) Mortar compressive strength: measured in accordance with JIS R 5201.
- (3) Setting period of cement: measured in accordance with JIS R 5201.
In Table 4, times such as 2:00 mean 2 hours and 0 minutes and so on.
- (4) Mortar flow: measured in accordance with JIS R 5201.

[0033]

[Table 1]

Cement Clinker	Baked at (°C)	Mineral Composition according to Bogue's Formulas (%)					Moduli and Index of Clinker		
		C ₃ S	C ₂ S	C ₃ A	C ₄ AF	C ₃ A+ C ₄ AF	H.M.	S.M.	I.M.
C1	1450	61.5	12.3	9.7	8.9	18.6	2.19	2.42	1.88
C2	1350	61.4	11.0	7.2	15.9	23.1	2.05	1.77	1.15

[0034]

[Table 2]

	Cement Clinker	Chemical Composition of Cement (%)												
		SO ₃	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	SrO	Cl
Ref.	C1	2.21	20.46	5.53	2.94	65.03	1.55	0.31	0.44	0.35	0.25	0.06	0.04	0.01
Emb.1	C2	2.54	19.41	5.78	5.15	62.95	2.07	0.28	0.35	0.28	0.17	0.07	0.04	0.01
Emb.2	C2	3.10	19.28	5.76	5.15	62.41	2.05	0.27	0.35	0.27	0.17	0.07	0.04	0.01
Comp.1	C2	2.17	19.57	5.85	5.30	63.13	2.09	0.27	0.35	0.28	0.17	0.07	0.04	0.01
Comp.2	C2	3.55	19.09	5.71	5.09	62.18	2.03	0.27	0.34	0.27	0.17	0.07	0.04	0.01
Comp.3	C2	4.09	18.87	5.65	5.04	61.88	2.01	0.26	0.34	0.26	0.17	0.07	0.04	0.01

[0035]

[Table 3]

	SO ₃ Content (%)	Mortar Compression (N/mm ²)				Setting Period		Mortar Flow (mm)
		1st Day	3rd Day	7th Day	28th Day	Start	End	
Ref.	2.21	13.4	29.4	46.2	61.8	2:00	3:15	160.4
Emb.1	2.54	16.4	34.5	46.3	65.5	1:45	3:35	174.2
Emb.2	3.10	14.3	32.8	46.1	60.1	2:00	3:45	170.2
Comp.1	2.17	12.6	32.0	45.5	62.5	2:00	3:50	178.8
Comp.2	3.55	12.3	31.0	42.4	57.0	1:55	3:50	171.1
Comp.3	4.09	10.3	24.3	40.5	55.4	2:00	3:55	162.9

[0036]

Reference Example shows the results of ordinary cement composition baked at a standard temperature. Therefore, the results of the embodiments and comparative examples are discussed in reference to the results of Reference Example.

[0037]

Embodiments 1 and 2, according to the present invention, have SO₃ contents of 2.3 to 3.3 mass%. Embodiment 1 had a superior compressive strength after the first day, the third day, and the 28th day and a superior mortar flow to those of Reference Example. The compressive strength after the 7th day were substantially the same between Embodiment 1 and Reference Example. Embodiment 2 had a superior compressive strength after the first day and the third day and a superior mortar flow to those of Reference Example. Embodiment 2 and Reference example had substantially the same compressive strength after the 7th day and the 28th day. Embodiments 1 and 2 satisfied the setting period required to Portland cement.

[0038]

In comparison with Reference Example, the mortar flow of Comparative Examples 1 to 3 showed good results, the setting properties also met the quality standards for ordinary Portland cement, and the fresh properties were better than before. However, in Comparative example 1 with the SO₃ content under 2.3%, the compressive strengths after 1st day and 7th days were inferior to Reference Example. In Comparative example 2 with the SO₃ content over 3.3%, the compressive strengths after 1st, 7th day, and 28th days were inferior to Reference Example. In Comparative example 3 with further more SO₃ content, the compressive strengths were always inferior to Reference Example.

[0039]

When the SO₃ content was 2.3 to 3.3 mass%, high mortar compressive strength was obtained at the initial age, and particularly high mortar compressive strength was obtained when the SO₃ content was 2.3 to 2.7 mass%. The inventors have speculated the following mechanism for this. The gypsum in the cement composition reacted with C₃A and C₄AF and water and produced calcium sulphaaluminate hydrates such as ettringite (3CaO · Al₂O₃ · 3CaSO₄ · 12H₂O) and monosulphate (3CaO · Al₂O₃ · CaSO₄ · 12H₂O). Fig. 1 shows the XRD patterns of Embodiments 1 and 2, and Comparative Examples 1 to 3, at the third day, in the range of 2

$\sin(\theta) = 9$ to 10 degrees.

[0040]

In Embodiments 1 and 2, and Comparative Examples 1 to 3, peaks of ettringite were confirmed, and the peak intensity increased as the SO_3 content increased. On the other hand, the monosulfate peaks were confirmed in Embodiments 1 and 2, and in Comparative Example 1.

The monosulfate peak was prominently high in Embodiment 1. Thus, the SO_3 content caused changes in the ratio of ettringite and monosulfate in calcium sulfoaluminate hydrates.

[0041]

In Table 3, when the gypsum content was increased from Comparative Example 1 to Comparative Example 3, the initial compressive strength of the mortar decreased. However, when the SO_3 content was 2.3 to 3.3 mass%, the compressive strength increased exceptionally. The improvement in compressive strength of the mortar was particularly prominent when the SO_3 content was 2.3 to 2.7 mass%. When considering how the formation of calcium sulfoaluminate hydrates changed the strength development characteristic, when only ettringite was formed, the strength development characteristic was not high. On the contrary, when both ettringite and monosulfate were formed, the strength development characteristic improved. Furthermore, when SO_3 content was 2.3 to 2.7 mass%, monosulfate was prominently generated, and as a result, the ratio between of ettringite and monosulfate was suited for the better strength development characteristic.

[0042]

As described above, the cement composition according to the invention has no adverse effect on the fresh properties, compared to general Portland cement compositions, and has initial and medium to long-term strength development characteristics equivalent to or better than general Portland cement compositions.

What is claimed is:

1. A cement composition comprising a cement clinker having a total content of C_3A and C_4AF of 22% or more, a C_3S content of 60% or more, both according to Bogue's formulas, and an iron modulus ($I.M. = Al_2O_3/Fe_2O_3$) of 1.3 or less, and gypsum, characterized in that the SO_3 content is 2.3 to 3.3 mass% relative to the total amount of cement clinker and gypsum.
2. The cement composition according to claim 1 further including one or more of a group consisting of blast furnace slag, siliceous admixture, fly ash, and limestone.
3. The cement composition according to claim 1, characterized in that the SO_3 content is 2.3 to 2.7 mass% relative to the total amount of cement clinker and gypsum.