

SPECIFICATION

Title of Invention

MIXED CEMENT

5

Technical Field

[0001]

The present invention relates to a mixed cement to which coal ash is added.

10

Background Art

[0002]

The amount of coal ash produced increases as the power generation amount increases in a coal-fired power plant. Most of coal ash becomes industrial waste. However, it is difficult to secure a landfill site for industrial waste, and environmental regulations are strengthened. Therefore, the efficient use of coal ash is required. Coal ash produced from a coal-fired power plant is roughly divided into fly ash and clinker ash. Fly ash refers to fine powder ash that is collected by a dust collector in coal ash generated when coal is burned in a coal-fired power plant. Clinker ash refers to ash obtained by crushing massive coal ash, which falls to a water tank in the bottom of a boiler in a red-heat state, by a crusher. Fly ash accounts for about 90% of coal ash.

[0003]

From the viewpoint of efficiently using coal ash, a fly ash cement to which fly ash is added as an admixture is manufactured and commercially available. The quality of a part
5 of fly ash used as an admixture of cement is defined in JIS A6201 "Fly Ash for Use in Concrete". In this specification, coal ash refers to fly ash.

[0004]

Coal ash contains pozzolan in which silicon dioxide (SiO_2)
10 and aluminum oxide (Al_2O_3) are major components. Pozzolan in coal ash slowly reacts (pozzolanic reaction) with calcium hydroxide ($\text{Ca}(\text{OH})_2$) produced by a hydration reaction of cement to produce a hydrate, which contributes to strength development of a long-term material age of a cured product. On the other
15 hand, in order to compensate for strength development of a short-term material age of a cured product, as a strength improver, a composition containing a reaction product obtained by reacting glycerin with formaldehyde, or a composition containing a specific amount of one or more compounds selected
20 from the group consisting of mannose, galactose, talose, ribose, and erythrose is disclosed (Patent Literature Nos. 1 and 2).

Prior art Literature

Patent Literature

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[0005]

[Patent Literature No. 1] Japanese Laid-open Patent
Publication No. 2014-189417A

[Patent Literature No. 2] Japanese Laid-open Patent
5 Publication No. 2014-237577A

Summary of Invention

Problem to be solved

[0006]

10 For a mixed cement in which coal ash is used as an admixture,
the coal ash itself has substantially no hydraulicity in a
short-term material age. Therefore, short-term strength
development at a material age of 3 days deteriorates. Even in
a case where a strength improver of the related art is used in
15 order to compensate for short-term strength development, an
effect of improving short-term strength development may not be
sufficiently obtained depending on components which are
contained in coal ash used as an admixture or the mixing amount
of coal ash.

20 [0007]

Therefore, an object of the present invention is to provide
a mixed cement that contains coal ash and in which short-term
strength development is high while maintaining properties as
an admixture of coal ash.

25

Solution to Problems

[0008]

The present inventors performed a thorough investigation in order to achieve the object, focused on the content of silica (SiO₂) and a mass ratio (SiO₂/Al₂O₃) of silica (SiO₂) to alumina (Al₂O₃) in pozzolan contained in coal ash, and found that, in a mixed cement in which the SiO₂ content and the mass ratio SiO₂/Al₂O₃ are in specific ranges, short-term strength development is high while maintaining properties of the coal ash as an admixture, thereby completing the present invention. That is, the present invention is as follows.

[0009]

[1] A mixed cement comprising: 20 ~ 40 mass% of coal ash and 60 ~ 80 mass% of Portland cement with respect to the total amount of the coal ash and the Portland cement,

wherein a SiO₂ content is 55 ~ 60 mass% and a mass ratio SiO₂/Al₂O₃ is 2.3 or higher and 2.7 or lower in the coal ash; and

100 mg/kg or higher and 300 mg/kg or lower of trialkanolamine which has three linear alkanol groups having 3 or less carbon atoms.

[2] The mixed cement according to [1],
in which the trialkanolamine is triethanolamine.

[3] The mixed cement according to [1] or [2],
in which the sum of the SiO₂ content and an Al₂O₃ content

in the coal ash is 70 ~ 82 mass%.

[4] The mixed cement according to any one of [1] to [3],
in which a Fe_2O_3 content in the coal ash is 5.0 ~ 8.0 mass%.

[5] The mixed cement according to any one of [1] to [4],
5 in which a mass ratio (the amount of Fe in a crystal
phase/the amount of Fe in the coal ash) of an iron content in
a crystal phase of the coal ash to an iron content in the coal
ash is 0.10 ~ 0.17.

[6] The mixed cement according to any one of [1] to [5],
10 in which an insoluble residue (insol) content in the coal
ash is 75 ~ 87 mass%.

[7] The mixed cement according to any one of [1] to [6],
in which a Blaine specific surface area of the coal ash
is 2500 ~ 4000 cm^2/g .

[8] The mixed cement according to any one of [1] to [7],
15 in which a content of the coal ash is 25 ~ 35 mass% and a content
of the Portland cement is 65 ~ 75 mass%.

Effects of Invention

20 [0010]

According to the present invention, it is possible to
provide a mixed cement that contains coal ash and in which
short-term strength development is high while maintaining
properties as an admixture of coal ash.

25

Mode for carrying out the Invention

[0011]

Hereinafter, the present invention will be described.

A mixed cement composition according to one embodiment of
5 the present invention contains 20 ~ 40 mass% of coal ash and
60 ~ 80 mass% of Portland cement with respect to the total amount
of the coal ash and the Portland cement, in which a SiO_2 content
is 55 ~ 60 mass% or lower and a mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 2.3 ~
2.7 or lower in the coal ash, and 100 mg/kg or higher and 300
10 mg/kg or lower of trialkanolamine which has three linear alkanol
groups having 3 or less carbon atoms is added.

[0012]

[Coal Ash]

In the coal ash, the SiO_2 content is 55 ~ 60 mass%, and
15 the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 2.3 ~ 2.7. It is preferable that
the coal ash is produced from a coal-fired power plant.

In a case where coal ash is used as an admixture of cement,
it was found that, although the mechanism thereof is not clear,
the content of SiO_2 as one of major components of pozzolan and
20 the mass ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of the major components (SiO_2 and
 Al_2O_3) of pozzolan contribute to, for example, short-term
strength development at a material age of 3 days.

It is known that pozzolan in coal ash slowly reacts
(pozzolanic reaction) with calcium hydroxide ($\text{Ca}(\text{OH})_2$) produced
25 by a hydration reaction of cement, to produce a hydrate, which

contributes to strength development of a long-term material age of a cured product.

For the mixed cement of the present disclosure, it is presumed that a hydration reaction of the Portland cement is promoted due to a chelate effect of trialkanolamine which has three linear alkanol groups having 3 or less carbon atoms.

Therefore, in a relatively early stage, a pozzolanic reaction between calcium hydroxide (Ca(OH)_2) produced by the hydration reaction of the Portland cement and the pozzolan components

(Al_2O_3 , SiO_2) in the coal ash occurs, and short-term strength development is improved. In addition, it is presumed that, in

a case where cations (for example, calcium ions (Ca^{2+}) or aluminum ions (Al^{3+})) in the Portland cement are masked due to the chelate effect of the trialkanolamine, cations in the pozzolan component

(SiO_2 , Al_2O_3) of the coal ash are likely to be reactive in order to maintain the equilibrium state of the hydration reaction of the mixed cement. For the mixed cement of the present disclosure,

it is presumed that, due to the chelate effect of the

trialkanolamine, the hydration reaction of the Portland cement

is promoted in an early stage, and the pozzolanic reaction

between the produced calcium hydroxide (Ca(OH)_2) and the

pozzolan components (Al_2O_3 , SiO_2) in the coal ash is also promoted in an early stage, which further contributes to improvement of short-term strength development.

In this specification, the chemical compositions of SiO_2 ,

Al_2O_3 , Fe_2O_3 , and the like in the coal ash refer to values measured according to JIS R5204 "Chemical Analysis Method of Cement by X-Ray Fluorescence".

[0013]

5 The SiO_2 content in the coal ash is 55 ~ 60 mass%, preferably 55.0 ~ 59.5 mass%, and still more preferably 55.0 ~ 59.0 mass%. In a case where the SiO_2 content in the coal ash is lower than 55.0 mass%, the content of SiO_2 as one of the pozzolan components in the coal ash is excessively low, and the mixed cement
10 containing the coal ash may not exhibit desired long-term strength development. In a case where the SiO_2 content in the coal ash is higher than 60.0 mass%, the SiO_2 content in the coal ash is excessively high. Therefore, the Al_2O_3 content is relatively low, and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is higher than 2.7.
15 The SiO_2 content in the coal ash correlates to the contents of other components in the coal ash, for example, Al_2O_3 , Fe_2O_3 , CaO , or MgO . In a case where the SiO_2 content in the coal ash increases, the contents of the other components tend to decrease.

[0014]

20 The mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the coal ash is 2.3 ~ 2.7 and preferably 2.30 ~ 2.65. In a case where the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the coal ash is higher than 2.7, the content of silica (SiO_2) in the coal ash is high, and the content of alumina (Al_2O_3) is low. Therefore, even in a case where calcium ions or aluminum
25 ions in the mixed cement are masked due to the chelate effect

of the trialkanolamine, the amount of aluminum ions in the pozzolan components of the coal ash is low. Thus, the pozzolanic reaction is not promoted in an early stage, and it is difficult to improve short-term strength development.

5 [0015]

The sum of the SiO_2 content and the Al_2O_3 content in the coal ash is preferably 70 ~ 82 mass%, more preferably 72.0 ~ 82.0 mass%, and still more preferably 75.0 ~ 81.5 mass%. In a case where the sum of the SiO_2 content and the Al_2O_3 content in
10 the coal ash contained in the mixed cement is 70 ~ 82 mass%, the slow pozzolanic reaction contributing to long-term strength development is promoted and the hydration reaction of the Portland cement is also promoted due to the chelate effect of the trialkanolamine. In a case where cations in the Portland
15 cement of the mixed cement are masked due to the chelate effect of the trialkanolamine, cations in the pozzolan component (SiO_2 , Al_2O_3) of the coal ash are likely to be reactive in order to maintain the equilibrium state of the hydration reaction of the mixed cement. In the mixed cement, it is presumed that, in a
20 relatively early stage, the pozzolan components (Al_2O_3 , SiO_2) in the coal ash react with calcium hydroxide ($\text{Ca}(\text{OH})_2$) produced by the hydration reaction of the Portland cement, and the pozzolanic reaction is promoted, which contributes to improvement of short-term strength development.

25 [0016]

In the coal ash, the Fe_2O_3 content is preferably 5.0 ~ 8.0 mass% and more preferably 5.1 ~ 7.9 mass%. The mechanism in which the Fe_2O_3 content in the coal ash contributes to short-term strength development is not clear but is presumed to be as follows.

5 In a case where the Fe_2O_3 content in the coal ash is 5.0 ~ 8.0 mass%, the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is likely to be 2.3 ~ 2.7 due to the relationship between the SiO_2 content in the coal ash and the contents of components other than SiO_2 in the coal ash, for example, Al_2O_3 , Fe_2O_3 , CaO , or MgO . Therefore, the mass ratio
10 $\text{SiO}_2/\text{Al}_2\text{O}_3$ is likely to be in a preferable range contributing to short-term strength development.

[0017]

A mass ratio (amount of Fe in crystal phase/amount of Fe in coal ash) of an iron content in a crystal phase (amount of
15 Fe in crystal phase) of the coal ash to an iron content in the coal ash (amount of Fe in coal ash) is preferably 0.10 ~ 0.17 and more preferably 0.110 ~ 0.170. The mass ratio (amount of Fe in crystal phase/amount of Fe in coal ash) of the iron content in the crystal phase of the coal ash to the iron content in the
20 coal ash is an index indicating a mass ratio of the amount of the crystal phase to the amount of an amorphous phase in the coal ash. In this specification, the amount of Fe in the crystal phase is obtained by a method of measuring the amounts (mass%) of the crystal phase and the amorphous phase in the coal ash
25 described below in Examples, and refers to the amount of Fe in

the crystal phase calculated in consideration of the total amount G_{total} (mass%) of the amorphous phase containing unburned carbon. In this specification, "the amount of Fe in the crystal phase calculated in consideration of the total amount G_{total} (mass%) of the amorphous phase containing unburned carbon" will also be referred to as "the amount of Fe in the crystal phase".

In a case where the amount of Fe in the crystal phase/the amount of Fe in the coal ash is 0.10 ~ 0.17, the iron content in the crystal phase is relatively low. In other words, it is presumed that the amount of the crystal phase not contributing to the pozzolanic reaction in the coal ash is relatively low, and the amount of the amorphous phase containing alumina (Al_2O_3) and silica (SiO_2) contributing to the pozzolanic reaction is relatively high. In a case where the amount of Fe in the crystal phase/the amount of Fe in the coal ash is higher than 0.17, it is presumed that the content of the crystal phase in the coal ash increases, and the amount of the amorphous phase which is likely to contribute to the pozzolanic reaction decreases. Examples of the crystal phase in the coal ash contain quartz or cristobalite (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), hematite (Fe_2O_3), and magnetite (Fe_3O_4).

In a case where the mass ratio of the amount of Fe in the crystal phase to the amount of Fe in the coal ash, which is the index indicating the amount of the crystal phase and the amount of the amorphous phase in the coal ash, is 0.17 or lower, the

amount of the crystal phase in the coal ash is low, and the amount of the amorphous phase in the coal ash is relatively high. It is presumed that, in a case where the mass ratio of the amount of Fe in the crystal phase of the coal ash to the amount of Fe in the coal ash is 0.17 or lower in the mixed cement, due to the chelate effect of the trialkanolamine, the hydration reaction of the Portland cement is promoted to produce calcium hydroxide (Ca(OH)_2) in a relatively early stage, the pozzolanic reaction between the produced calcium hydroxide (Ca(OH)_2) and the pozzolan components (Al_2O_3 , SiO_2) contained in the amorphous phase occurs, and short-term strength development is improved. Further, it is presumed that, in a case where cations in the Portland cement of the mixed cement are masked due to the chelate effect of the trialkanolamine, cations in the pozzolan component (SiO_2 , Al_2O_3) of the coal ash are likely to be reactive in order to maintain the equilibrium state of the hydration reaction of the mixed cement, and the reactivity of the pozzolanic reaction, which occurs relatively slowly, is promoted in an early stage, which contributes to improvement of short-term strength development. Regarding the mass ratio of the amount of Fe in the crystal phase to the amount of Fe in the coal ash which is the index indicating the amount of the crystal phase and the amount of the amorphous phase in the coal ash, the amount of the crystal phase in the coal ash decreases and the amount of the amorphous phase in the coal ash increases as the numerical

value decreases. In other words, the amount of the pozzolan components (Al_2O_3 , SiO_2) in the coal ash increases, and the pozzolanic reaction is more likely to occur. Typically, the mass ratio of the amount of Fe in the crystal phase of the coal ash to the amount of Fe in the coal ash is 0.10 or higher.

[0018]

In the coal ash, the insoluble residue (insol) content is preferably 75 ~ 87 mass% and more preferably 75.5 ~ 86.5 mass%. It is presumed that the insoluble residues in the coal ash contain a crystal phase and an amorphous phase (glassy phase) constituting silicic acid or a silicate. The mechanism to contribute to short-term strength development of the insoluble residue (insol) content in the coal ash contained in the mixed cement is not clear. In a case where the insoluble residue (insol) content in the coal ash contained in the mixed cement is 75.0 ~ 87.0 mass%, the amount of the amorphous phase in the pozzolan components (Al_2O_3 , SiO_2), which are contained in the coal ash and contribute to the pozzolanic reaction, is relatively high. The mixed cement contains, the coal ash in which the SiO_2 content and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ are in the preferable ranges, and the trialkanolamine. As a result, it is presumed that the slow pozzolanic reaction contributing to long-term strength development is promoted, the pozzolan components (Al_2O_3 , SiO_2) in the coal ash react with calcium hydroxide ($\text{Ca}(\text{OH})_2$) produced by the hydration reaction of the Portland cement in a relatively

early stage, the pozzolanic reaction is promoted, and short-term strength development is improved.

In this specification, the insoluble residue content in the coal ash is a value measured by a method described in JIS
5 R5202 "Methods for Chemical Analysis of Cements".

[0019]

The Blaine specific surface area of the coal ash is preferably 2500 ~ 4000 cm²/g, more preferably 2600 cm²/g or higher, still more preferably 2700 cm²/g or higher, and even still more
10 preferably 2800 ~ 4000 cm²/g.

In a case where the Blaine specific surface area of the coal ash is high, the activity increases. The pozzolan components (Al₂O₃, SiO₂) in the coal ash are likely to react with calcium hydroxide (Ca(OH)₂) produced by the hydration reaction of the
15 Portland cement in a relatively early stage. In a case where the Blaine specific surface area of the coal ash is 2500 ~ 4000 cm²/g, the coal ash and the Portland cement can be uniformly mixed with each other, and the chelate effect of the trialkanolamine also affect the Portland cement and alumina (Al₂O₃) as the
20 pozzolan component in the coal ash. As a result, the pozzolanic reaction progresses in a relatively early stage, and short-term strength development can be improved.

In this specification, the Blaine specific surface area of the coal ash refers to a value measured according to JIS R5201
25 "Physical Testing Methods for Cement".

[0020]

The amount of the coal ash in the mixed cement is preferably 20 ~ 40 mass% and more preferably 25 ~ 35 mass% with respect to the total amount of the coal ash and the Portland cement.

5 In a case where the amount of the coal ash in the mixed cement is lower than 20 mass% with respect to the total amount of the coal ash and the Portland cement, the amount of the coal ash is excessively low, and the coal ash cannot be efficiently used.

In a case where the amount of the coal ash in the mixed cement
10 is higher than 40 mass% with respect to the total amount of the coal ash and the Portland cement, the amount of the coal ash which has substantially no hydraulicity in a short-term material age is excessively high, and the short-term strength development of the mixed cement deteriorates. The mixed cement contains 100
15 mg/kg ~ 300 mg/kg of the trialkanolamine and 20 ~ 40 mass% of the coal ash with respect to the total amount of the coal ash and the Portland cement. In the coal ash, the SiO_2 content is 55 ~ 60 mass%, and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 2.3 ~ 2.7. Such configuration can contribute to improve, short-term strength
20 development.

[0021]

[Portland Cement]

The kind of the Portland cement in the mixed cement is not particularly limited. Examples of the Portland cement are
25 normal Portland cement, high early strength Portland cement,

moderate heat Portland cement, and low-heat Portland cement.

[0022]

The content of the Portland cement in the mixed cement is 60 ~ 80 mass% and preferably 65 ~ 75 mass% with respect to the total amount of the coal ash and the Portland cement. In a case where the content of the Portland cement is lower than 60 mass% with respect to the total amount of the coal ash and the Portland cement, the amount of the cement is low, and thus a cured product having a desired strength cannot be obtained. In a case where the content of the Portland cement is higher than 80 mass%, the amount of the coal ash in the mixed cement is low, and the coal ash cannot be efficiently used.

[0023]

[Trialkanolamine]

The content of the trialkanolamine which has three linear alkanol groups having 3 or less carbon atoms in the mixed cement is 100 ~ 300 mg/kg and preferably 150 ~ 250 mg/kg with respect to the total amount of the coal ash and the Portland cement. It is presumed that, due to the chelate effect of the Portland cement, the trialkanolamine promotes the hydration reaction of the Portland cement to produce calcium hydroxide (Ca(OH)_2) in a relatively early stage, and the chelate effect of the trialkanolamine also affects alumina (Al_2O_3) as the pozzolan component in the coal ash. It is also presumed that, calcium hydroxide (Ca(OH)_2) produced by the hydration reaction of the

Portland cement and the pozzolan components (Al_2O_3 , SiO_2) in the coal ash are more likely to react with each other, the pozzolanic reaction progresses in a relatively early stage, and short-term strength development can be improved. In a case where the content of the trialkanolamine is 100 mg/kg or lower with respect to the total amount of the coal ash and the Portland cement, the chelate effect of the trialkanolamine is excessively low, the hydration reaction of the Portland cement occurs slowly, and short-term strength development may not be improved. In a case where the content of the trialkanolamine is higher than 300 mg/kg with respect to the total amount of the coal ash and the Portland cement, the chelate effect corresponding to the content is not obtained, and the hydration reaction of the Portland cement cannot be further promoted.

[0024]

The trialkanolamine has three linear alkanol groups having 3 or less carbon atoms, and specific examples thereof are trimethanolamine, triethanolamine, and tripropanolamine. Among these, triethanolamine is preferable. For the Portland cement containing no coal ash, in a case where triisopropanolamine is used among triisopropanolamine and triethanolamine, short-term strength (for example, mortar strength) at a material age of 3 days may be improved.

On the other hand, in the mixed cement containing 20 ~ 40 mass% of the coal ash, in a case where triethanolamine is used,

an effect of improving short-term strength is higher than that of a case where triisopropanolamine is used. The mechanism to contribute to short-term strength development of the mixed cement containing the coal ash is not clear but is presumed to be as follows: the hydration reaction of the Portland cement is promoted to produce calcium hydroxide (Ca(OH)_2) due to the appropriate chelate effect of the triethanolamine at a rate at which the reaction with the pozzolan components (Al_2O_3 , SiO_2) in the coal ash is likely to occur.

10 [0025]

[Manufacturing of Mixed Cement]

The mixed cement can be manufactured by a method comprising: mixing 20 ~ 40 mass% of coal ash and 60 ~ 80 mass% of Portland cement with respect to the total amount of the coal ash and the Portland cement, in which a SiO_2 content is 55 ~ 60 mass% and a mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 2.3 ~ 2.7 in the coal ash; and further adding 100 ~ 300 mg/kg of trialkanolamine which has three linear alkanol groups having 3 or less carbon atoms.

[0026]

20 The mixed cement can be used as a mixed cement composition by adding an admixture in addition to the coal ash and the Portland cement. Examples of the admixture are blast furnace slag powder, limestone powder, quartz powder, and gypsum.

Examples

25 [0027]

Next, the present invention will be described in more detail with Examples but is not limited to the Examples.

[0028]

Analysis of Coal Ash

5 Coal ashes of Examples 1 to 9 were analyzed. The chemical composition of the coal ash were analyzed according to JIS R5204 "Chemical Analysis Method of Cement by X-Ray Fluorescence". Based on the results of the analysis of the chemical composition of the coal ash, the total amount of silica (SiO_2) and alumina
10 (Al_2O_3) in the coal ash, and the mass ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of silica to alumina were calculated.

The amounts of boron (B) and fluorine (F) in the coal ash of each of Examples 1 to 9 were measured based on the Japan Cement Association standard test method (JCAS I-53).

15 In addition, the ignition loss (ig. loss) and the insoluble residue (insol) content in the coal ash is a value measured by a method described in JIS R5202 "Methods for Chemical Analysis of Cements". In addition, the Blaine specific surface area of the coal ash was measured according to JIS R5201 "Physical
20 Testing Methods for Cement". The results are shown in Table 1.

[0029]

In addition, when measured by a method described below, the amounts of amorphous phases in the coal ashes according to Examples 1 to 6 were in a range of 66.7 mass% or higher and 68.2
25 mass% or lower, respectively. The amounts of amorphous phases

in the coal ashes of Examples 7 to 9 were in a range of 60.5 mass% or higher and 61.9 mass% or lower, respectively. The amounts (mass%) of amorphous phases in the coal ashes of Examples 1 to 9 are shown in Table 1. In Table 1, the amount G_{FA} of an amorphous phase in the coal ash refers to a value obtained by subtracting the amount (mass%) of unburned carbon in the coal ash from the amount G_{total} (mass%) of an amorphous phase in the coal ash obtained by Rietveld analysis. A method of measuring the amounts (mass%) of a crystal phase and an amorphous phase in the coal ash will be described.

[0030]

(Measurement of Amounts (mass%) of Crystal Phase and Amorphous Phase in Coal Ash)

The amount (mass%) of a crystal phase and the amount of an amorphous phase in the coal ash were measured by Rietveld analysis using an internal standard material by a powder X-ray diffractometer. As the powder X-ray diffractometer, D8 Advance (manufactured by Bruker AXS GmbH) was used. Measurement conditions, the internal standard material, and Rietveld analysis conditions were as described below.

Measurement Conditions

X-ray bulb: Cu

Tube voltage: 40 kV

Tube current: 40 mA

Measurement range of diffraction angle 2θ : start angle=5°,

end angle=70°/75°

* In a case where rutile type titanium dioxide was added as the internal standard material and the end angle was 70°, a peak shape of the titanium dioxide at about 70° was not able to
5 be correctly obtained. Therefore, the end angle was set as 75° for a sample to which the titanium dioxide was added.

Step width: 0.025°/step

Measurement time: 60 sec/step

Internal standard material: rutile type titanium dioxide

10 Rietveld Analysis Conditions

Rietveld analysis software: TOPAS Ver. 4.2 (manufactured by Bruker AXS GmbH)

Zero-point correction: not performed

Correction of height of sample surface: performed

15 Analysis target mineral: quartz, mullite (3:2), anhydride, limestone, magnetite, hematite, and titanium dioxide (only a sample added as an internal standard material)

Preferred orientation function of hematite phase:
assuming that preferred orientation of the hematite phase
20 appears on a diffraction line of the (110) plane at a diffraction angle 2θ of about 35.5, refinement was performed using a March-Dollase function with an initial coefficient value as 1. Regarding the magnetite phase, it was assumed that preferred orientation did not appear.

[0031]

The measurement procedure of the crystal phase such as magnetite or hematite and the amorphous phase in the coal ash was as described below.

5 (i) As the internal standard material, coal ash (sample 1) to which 20 mass% of rutile type titanium dioxide was added, and coal ash (sample 2) to which no internal standard material was added were prepared.

 (ii) The coal ash (sample 2) to which no internal standard
10 material was added was measured by a powder X-ray diffractometer. Fitting between the obtained power X-ray diffraction pattern of the coal ash (sample 2) and each of theoretical profiles of quartz, mullite, anhydrite, limestone, magnetite, and hematite as the analysis target minerals was performed to quantitatively
15 analyze the respective analysis target minerals in the coal ash. Next, the amounts (mass%) of the respective analysis target minerals were calculated by the analysis software. Regarding magnetite and hematite, the amounts (mass%) of magnetite and hematite in the coal ash were obtained from only the coal ash
20 (sample 2) to which no internal standard material was added.

 The reason why the sample 2 to which no internal standard material was added was used for the quantitative analysis of magnetite and hematite is that peaks of magnetite and hematite at a diffraction angle 2θ = around $35.5^\circ \sim 35.6^\circ$ or less are close
25 to a peak of rutile type titanium dioxide at a diffraction angle

2θ = around 36.1° . In particular, the reason is as follows. In a case where rutile type titanium dioxide having a small particle diameter and a small crystallite size is used as the internal standard material, peak broadening occurs, and the vicinity of the bottom of the peak of rutile titanium dioxide at a diffraction angle $2\theta = 36.1^\circ$ overlaps with the peaks of magnetite and hematite. In particular, in a case where the content of magnetite or hematite is low, there is a large effect on the value determined by the quantitative analysis.

(iii) The coal ash (sample 1) to which rutile type titanium dioxide was added as the internal standard material was measured by a powder X-ray diffractometer. Fitting between the obtained powder X-ray diffraction pattern of the coal ash (sample 1) and each of theoretical profiles of quartz, mullite, anhydrite, limestone, hematite, magnetite, and titanium dioxide as the analysis target minerals was performed to quantitatively analyze the respective analysis target minerals in the coal ash (sample 1) to which the internal standard material was added. Next, the amounts (mass%) of the respective analysis target minerals were calculated by the analysis software.

(iv) Based on the value determined by the quantitative analysis of rutile type titanium dioxide of the sample 1, the total amount G_{total} (mass%) of the amorphous phase including unburned carbon was calculated from the following Expression (A).

Total Amount G_{total} of Amorphous

$$\text{Phase} = 100 \times (Y - X) / \{Y \times (100 - X) / 100\} \quad (A)$$

In Expression (A), X represents the addition amount (20 mass%) of the internal standard material, and Y represents the value (%) determined by the Rietveld analysis of rutile type titanium dioxide.

(v) The total amount of the amorphous phase was quantitatively analyzed based on the content (mass%) of the crystal phase of the analysis target minerals in the sample 1. Next, the content of the crystal phase in consideration of the total amount of the amorphous phase was calculated from the following Expression (2) based on the contents (mass%) of the analysis target minerals of the sample 2.

$$\text{Crystal Phase (in consideration of Total Amount } G_{total} \text{ of Amorphous Phase)} = \text{Crystal Phase (Analysis Value of Sample 2)} \times (100 - G_{total}) / 100 \quad (B)$$

In Expression (B), G_{total} represents the total amount (%) of the amorphous phase determined by the quantitative analysis from Expression (A) based on the analysis value of the sample 1.

(vi) According to the following Expression (1), the content (mass%) of unburned carbon in the coal ash was subtracted from the total amount G_{total} (mass%) of the amorphous phase calculated from Expression (A), and the obtained value was set as the amount G_{FA} (mass%) of the amorphous phase in the coal ash.

As the content (mass%) of the unburned carbon in the coal ash, an ignition loss measured according to JIS A6201 "Fly Ash for Use in Concrete" was obtained.

Amount G_{FA} (mass%) of Amorphous Phase in Coal Ash=Total
5 Amount G_{total} (mass%) of Amorphous Phase obtained by Rietveld
Analysis-Content (mass%) of Unburned Carbon (1)

[0032]

A mass ratio (amount of Fe in crystal phase/amount of Fe
in coal ash) of an iron content in a crystal phase of the coal
10 ash to an iron content in the coal ash of each of Examples 1
to 9 was calculated as follows.

(i) The amount of Fe in the coal ash was calculated by
converting a measured value 1 of the iron content (iron oxide
(III): Fe_2O_3) in terms of oxides which is measured according to
15 JIS R5204 "Chemical Analysis Method of Cement by X-Ray
Fluorescence" into the iron content obtained from the following
Expression (2).

Iron Content in Coal Ash (Amount of Fe in Coal
Ash)=Measured Value 1 $\times$ 2Fe/ Fe_2O_3 (111.6/159.7) (mass%)
20 (2)

(ii) The iron content in the crystal phase of the coal ash
was calculated from the following Expression (3) based on a
measured value 2 and a measured value 3, the measured value 2
being the content (mass%) of hematite in the crystal phase that
25 was calculated in consideration of the total amount G_{total} (mass%)

of the amorphous phase containing unburned carbon in the coal ash, and the measured value 3 being the content (mass%) of magnetite in the crystal phase that was calculated in consideration of the total amount G_{total} (mass%) of the amorphous phase containing unburned carbon in the coal ash.

Iron Content (Amount of Fe) in Crystal Phase in consideration of Total Amount G_{total} of Amorphous Phase including Unburned Carbon in Coal Ash= $[\text{Measured Value } 2 \times \{2\text{Fe}/\text{Fe}_2\text{O}_3 (111.6/159.7)\}] + [\text{Measured Value } 3 \times \{3\text{Fe}/\text{Fe}_3\text{O}_4 (167.4/231.5)\}]$

(3)

(iii) Based on the iron content in the coal ash (the amount of Fe in the coal ash) obtained from Expression (2) and the iron content in the crystal phase (the amount of Fe in the crystal phase) obtained from Expression (3) in consideration of the total amount G_{total} of the amorphous phase containing unburned carbon in the coal ash, the mass ratio (amount of Fe in crystal phase/amount of Fe in coal ash) of the amount of Fe in the crystal phase, which was calculated in consideration of the total amount G_{total} of the amorphous phase containing unburned carbon, to the amount of Fe in the coal ash was obtained. The results are shown in Tables 1 and 2.

[0033]

[Table 1]

	Chemical Analysis Value (mass%)													Chemical Analysis Value (ppm)		Amount of Fe in Crystal Phases/Amount of Fe in Coal Ash	*Amount G _{FA} of Amorphous Phase (mass%)	Calculated Value		Blaine Specific Surface Area
	ig. loss	insol	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	B	F			SiO ₂ /Al ₂ O ₃	SiO ₂ +Al ₂ O ₃ (mass%)	
Example 1	5.26	86.35	57.27	23.55	5.26	3.20	0.96	0.46	0.30	1.36	1.33	0.40	0.06	176	101	0.145	68.2	2.43	80.82	3620
Example 2	6.21	83.71	56.74	22.69	5.10	3.39	1.36	0.34	0.26	1.22	1.36	0.30	0.04	404	73	0.168	68.1	2.50	79.43	3410
Example 3	5.02	85.68	58.99	22.44	5.73	2.47	1.36	0.51	0.71	1.11	1.24	0.28	0.06	226	95	0.133	67.7	2.63	81.43	3540
Example 4	3.05	83.75	58.60	22.23	7.89	2.24	1.58	0.38	0.70	1.65	1.11	0.27	0.05	514	95	0.119	67.4	2.64	80.83	3140
Example 5	3.50	80.35	57.79	23.69	7.00	1.86	1.75	0.00	0.63	1.71	1.19	0.29	0.04	496	113	0.125	66.7	2.44	81.48	3270
Example 6	3.16	75.87	55.14	23.61	7.82	2.67	2.07	0.00	0.86	1.97	1.05	0.34	0.05	777	123	0.113	67.8	2.34	78.75	2860
Example 7	1.75	90.13	65.89	21.63	4.40	1.84	1.06	0.03	0.42	1.09	1.09	0.28	0.04	102	216	0.187	61.3	3.05	87.52	3060
Example 8	3.10	91.23	63.93	21.85	4.65	1.99	0.84	0.05	0.65	1.12	1.11	0.34	0.06	125	102	0.188	60.5	2.93	85.78	3040
Example 9	3.22	92.46	64.39	22.22	4.20	1.35	0.64	0.02	0.46	1.40	1.14	0.26	0.05	49	108	0.214	61.9	2.90	86.61	3260

*: "Amount G_{FA} of Amorphous Phase (mass%)" refers to a value obtained by subtracting the amount (mass%) of unburned carbon in the coal ash from the amount G_{total} (mass%) of an amorphous phase in the coal ash obtained by Rietveld analysis.

[0034]

(Examples 1 to 8 and Comparative Examples 1 to 6)

Mixed cements were manufactured at mixing ratios shown in Table 2 using normal Portland cement, Examples 1 to 9, and one
5 additive selective from the group consisting of triethanolamine (TEA), triisopropanolamine (TIPA), and diethylene glycol (DEG). The content of the coal ash is the mixing ratio with respect to 100 mass% of the total amount of the coal ash and the normal Portland cement. In addition, the addition amount of one
10 additive selective from the group consisting of triethanolamine (TEA), triisopropanolamine (TIPA), and diethylene glycol (DEG) is the addition amount (mg/kg) with respect to 1000 kg of the total amount of the coal ash and the normal Portland cement. Regarding each of the coal ashes contained in the mixed cements,
15 Table 2 shows the chemical compositions (mass%) of silica (SiO_2) and alumina (Al_2O_3), the mass ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of silica to alumina, the chemical composition (mass%) of Fe_2O_3 , the mass ratio of the amount of Fe in the crystal phase calculated in consideration of the total amount G_{total} of the amorphous phase
20 containing unburned carbon to the amount of Fe in the coal ash, and the Blaine specific surface area (cm^2/g).

[0035]

Mortar Strength

Regarding the mixed cement of each of Examples 1 to 8 and
25 Comparative Examples 1 to 6, mortar compressive strength (N/mm^2)

was measured at a material age of 3 days according to "11. Strength Test" of "JIS R5201 "Physical Testing Methods for Cement". The mortar compressive strength of a mortar specimen using the mixed cement of Comparative Example 6 in which the content of the coal ash at a material age of 3 days was 25 mass% was calculated as 1.00, and relative mortar strengths of Examples 1 to 8 and Comparative Examples 1 to 6 were calculated.

In addition, regarding some of Examples and Comparative Examples, mortar compressive strength (N/mm^2) was measured at a material age of 28 days and a material age of 91 days according to "11. Strength Test" of JIS R5201 "Physical Testing Methods for Cement". The mortar compressive strength of a mortar specimen using the mixed cement of Comparative Example 6 was 25 mass% after a material age of 28 days was calculated as 1.00, and relative mortar strengths of Examples 6 to 8 and Comparative Example 3 were calculated. In addition, the mortar compressive strength of a mortar specimen using the mixed cement of Comparative Example 6 at a material age of 91 days was calculated as 1.00, and relative mortar strengths of Examples 6 to 8 and Comparative Example 3 were calculated. The results are shown in Table 2.

[0036]

[Table 2]

	Coal Ash								Additive		Mortar Strength at Material Age of 3 days*			Mortar Strength at Material Age of 28 days**	Mortar Strength at Material Age of 91 days***
	Kind	SiO ₂ (mass%)	Al ₂ O ₃ (mass%)	SiO ₂ /Al ₂ O ₃	SiO ₂ +Al ₂ O ₃ (mass%)	Fe ₂ O ₃ (mass%)	Amount of Fe in Crystal Phase/Amount of Fe in Coal Ash	Blaine Specific Surface Area (cm ² /g)	Kind	Addition Amount (mg/kg)	Coal Ash Content 25 mass%	Coal Ash Content 30 mass%	Coal Ash Content 35 mass%	Coal Ash Content 25 mass%	Coal Ash Content 25 mass%
Example 1	Example 1	57.27	23.55	2.43	80.82	5.26	0.145	3620	TEA	200	1.17	1.09	1.01	-	-
Example 2	Example 2	56.74	22.69	2.50	79.43	5.10	0.168	3410	TEA	200	1.16	1.08	1.00	-	-
Example 3	Example 3	58.99	22.44	2.63	81.43	5.73	0.133	3540	TEA	200	1.15	1.07	0.99	-	-
Example 4	Example 4	58.60	22.23	2.64	80.83	7.89	0.119	3140	TEA	200	1.14	1.06	0.99	-	-
Example 5	Example 5	57.79	23.69	2.44	81.48	7.00	0.125	3270	TEA	200	1.16	1.10	1.01	-	-
Example 6	Example 6	55.14	23.61	2.34	78.75	7.82	0.113	2860	TEA	200	1.18	1.10	1.02	1.15	1.16
Example 7	Example 6	55.14	23.61	2.34	78.75	7.82	0.113	2860	TEA	100	1.16	1.08	0.98	1.15	1.16
Example 8	Example 6	55.14	23.61	2.34	78.75	7.82	0.113	2860	TEA	300	1.14	1.10	0.98	1.17	1.15
Comparative Example 1	Example 7	65.89	21.63	3.05	87.52	4.40	0.187	3060	TEA	200	1.11	1.04	0.96	-	-
Comparative Example 2	Example 8	63.93	21.85	2.93	85.78	4.65	0.188	3040	TEA	200	1.12	1.04	0.94	-	-
Comparative Example 3	Example 9	64.39	22.22	2.90	86.61	4.20	0.214	3260	TEA	200	1.11	1.04	0.95	1.09	1.09
Comparative Example 4	Example 6	55.14	23.61	2.34	78.75	7.82	0.113	2860	TIPA	200	1.05	0.97	0.88	-	-
Comparative Example 5	Example 6	55.14	23.61	2.34	78.75	7.82	0.113	2860	DEG	200	1.10	1.02	0.91	-	-
Comparative Example 6	Example 6	55.14	23.61	2.34	78.75	7.82	0.113	2860	-	0	1.00	0.95	0.83	1.00	1.00

*: The mortar compressive strength of a mortar specimen using the mixed cement of Comparative Example 6 (coal ash content: 25 mass%; additive amount 0 m/kg) at a material age of 3 days was 25 mass% was calculated as 1.00.

5 **: The mortar compressive strength of a mortar specimen using the mixed cement of Comparative Example 6 (coal ash content: 25 mass%; additive amount 0 m/kg) at a material age of 28 days was 25 mass% was calculated as 1.00.

***: The mortar compressive strength of a mortar specimen using the mixed cement of Comparative Example 6 (coal ash content: 25 mass%; additive amount 0 m/kg) at a material age of 91 days was 25 mass% was calculated as 1.00.

[0037]

As shown in Table 2, in the mixed cements of Examples 1 to 6 containing 25 mass% of the coal ash in which the SiO_2 content was 55 ~ 60 mass% and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 2.3 ~ 2.7, the mortar strengths at a material age of 3 days relative to the mortar strength of Comparative Example 6 (coal ash content: 25 mass%; additive: 0mg/kg) were 1.14 or higher, and short-term strength development was improved.

In addition, in the mixed cements of Examples 1 to 6 containing 30 mass% of the coal ash in which the SiO_2 content was 55 ~ 60 mass% and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 2.3 ~ 2.7, the mortar strengths at a material age of 3 days relative to the mortar strength of Comparative Example 6 (coal ash content: 25 mass%; additive: 0mg/kg) were 1.06 or higher, and it was found that short-term strength development was improved.

In the mixed cements of Examples 1 to 6 containing 35 mass% of the coal ash in which the SiO_2 content was 55 ~ 60 mass% and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 2.3 ~ 2.7, the mortar strengths at a material age of 3 days relative to the mortar strength of Comparative Example 6 (coal ash content: 25 mass%; additive: 0mg/kg) were 0.98 or higher, and short-term strength development was improved.

In addition, in the mixed cements of Examples 6 to 8 containing 25 mass% of the coal ash, the mortar strengths at a material age of 28 days and the mortar strengths at a material

age of 91 days relative to the mortar strengths of Comparative Example 6 (coal ash content: 25 mass%; additive: 0mg/kg) were 1.15 or higher, and the properties of the coal ashes in the mixed cements contributing to the long-term strength development were also maintained.

[0038]

Further, for the mixed cements of Examples 1 to 8 using the coal ash in which the SiO_2 content and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ were in the above-described ranges, the addition amount of triethanolamine (TEA) was 200 mg/kg, and the mass ratio of the amount of Fe in the crystal phase, which was calculated in consideration of the total amount G_{total} of the amorphous phase containing unburned carbon, to the amount of Fe in the coal ash was in a range of 0.10 to 0.17, the mortar strengths of all the cases where the coal ash contents were 25 mass%, 30 mass%, and 35 mass% at a material age of 3 days relative to the mortar strength of Comparative Example 6 (the content of the coal ash: 25 mass%; the additive: 0mg/kg) were higher than those of the cases where the coal ash contents in the mixed cements of Comparative Examples 1 to 5 were 25 mass%, 30 mass%, and 35 mass%, and short-term strength development was improved. As shown in Table 1, for the coal ashes of Examples 1 to 6 in which the mass ratio of the amount of Fe in the crystal phase, which was calculated in consideration of the total amount G_{total} of the amorphous phase containing unburned carbon, to the amount of

Fe in the coal ash was in a range of 0.10 to 0.17, the amounts G_{FA} of the amorphous phase were higher than those of Examples 7 and 8 in which the mass ratio of the amount of Fe in the crystal phase, which was calculated in consideration of the total amount G_{total} of the amorphous phase containing unburned carbon, to the amount of Fe in the coal ash was higher than 0.17.

[0039]

On the other hand, as shown in Table 2, for the mixed cements of Comparative Examples 1 to 3 using the coal ashes in which the SiO_2 content was higher than 60 mass% and the mass ratio SiO_2/Al_2O_3 was higher than 2.7, the mortar strengths of all the cases where the coal ash contents were 25 mass%, 30 mass%, and 35 mass% at a material age of 3 days relative to the mortar strength of Comparative Example 6 (coal ash content: 25 mass%; additive: 0mg/kg) were lower than 1.14, lower than 1.06, and lower than 0.98, respectively, and short-term strength development was not improved compared to the mixed cements of Examples 1 to 6.

In addition, in the mixed cement of Comparative Example 3 containing 25 mass% of the coal ash, the mortar strength at a material age of 28 days and the mortar strength at a material age of 91 days relative to the mortar strength of Comparative Example 6 (coal ash content: 25 mass%; additive: 0mg/kg) were 1.09, and the properties of the coal ash in the mixed cement contributing to the long-term strength development were

maintained. However, long-term strength development was slightly lower than those of Examples 6 to 8.

[0040]

As shown in Comparative Examples 4 and 5 of Table 2, even
5 in a case where the coal ash in which the SiO_2 content was 55 ~ 60 mass% or lower and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 2.3 ~ 2.7 was used, when triisopropanolamine (TIPA) or diethylene glycol (DEG) was used as the additive, the chelate effect of the additive on the normal Portland cement was not appropriate. As a result,
10 in the mixed cements of Comparative Examples 4 and 5, the mortar strengths of all the cases where the coal ash contents were 25 mass%, 30 mass%, and 35 mass% at a material age of 3 days relative to the mortar strength of Comparative Example 6 (coal ash content: 25 mass%; additive: 0mg/kg) were lower than 1.14, lower
15 than 1.06, and lower than 0.98, respectively, and short-term strength development was not improved compared to the mixed cements of Examples 1 to 6.

[0041]

As shown in Comparative Example 6 of Table 2, even in a
20 case where the coal ash the SiO_2 content was 55 ~ 60 mass% or lower and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 2.3 or higher and 2.7 or lower, when no additives was used, the mortar strength at a material age of 3 days relative to the mortar strength of Comparative Example 6 (the content of the coal ash: 25 mass%;
25 the additive: 0mg/kg) decreased as the coal ash content increased

to 25 mass%, 30 mass%, and 35 mass%. The coal ash itself has substantially no hydraulicity for a short material age.

Therefore, it is presumed that, as the coal ash content increased, the relative mortar strength at a material age of 3 days

5 deteriorated.

Industrial Applicability

[0042]

According to the present invention, coal ash, which is increasingly produced as the power generation amount increases
10 in a coal-fired power plant, can be efficiently used, and a mixed cement which has high short-term strength development and contains coal ash having specific components can be provided.

CLAIMS

1. A mixed cement comprising: 20 ~ 40 mass% of coal ash
and 60 ~ 80 mass% of Portland cement with respect to the total
5 amount of the coal ash and the Portland cement,

wherein a SiO_2 content is 55 ~ 60 mass% or lower and a mass
ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 2.3 ~ 2.7 or lower in the coal ash; and
100 ~ 300 mg/kg of trialkanolamine which has three linear
alkanol groups having 3 or less carbon atoms.

10

2. The mixed cement according to claim 1,
wherein the trialkanolamine is triethanolamine.

3. The mixed cement according to claim 1 or 2,
15 wherein the sum of the SiO_2 content and an Al_2O_3 content
in the coal ash is 70 ~ 82 mass%.

4. The mixed cement according to any one of claims 1 to
3,
20 wherein a Fe_2O_3 content in the coal ash is 5.0 ~ 8.0 mass%.

5. The mixed cement according to any one of claims 1 to
4,
wherein a mass ratio (the amount of Fe in a crystal
25 phase/the amount of Fe in the coal ash) of an iron content in

a crystal phase of the coal ash to an iron content in the coal ash is 0.10 ~ 0.17.

6. The mixed cement according to any one of claims 1 to 5, 5,

wherein an insoluble residue (insol) content in the coal ash is 75 ~ 87 mass%.

7. The mixed cement according to any one of claims 1 to 10 6,

wherein a Blaine specific surface area of the coal ash is 2500 ~ 4000 cm²/g.

8. The mixed cement according to any one of claims 1 to 15 7, wherein a content of the coal ash is 25 ~ 35 mass% and a content of the Portland cement is 65 ~ 75 mass%.