

DESCRIPTION

Title of Invention:

GROUND-IMPROVING MATERIAL SLURRY, GROUND-IMPROVING MATERIAL CURED PRODUCT, AND GROUND IMPROVEMENT METHOD

Technical Field

[0001]

The present invention relates to a ground-improving material slurry, a ground-improving material hardened product, and a ground improvement method.

Background Art

[0002]

As one type of ground improvement method, there is known a chemical injection method in which a hardenable chemical is injected into the ground. Further, various ground grouting materials for use in this construction method are known. The chemical injection method using a ground grouting material is different from a method such as a jet grouting method in which the ground is improved while being disturbed by a high-pressure jet, and has advantages such that the improvement can be achieved without disturbing the ground as much as possible, and the equipment is compact. Therefore, it has many achievements.

[0003]

So far, various ground grouting materials have been known in the art. For example, there is known a technique in which specific two liquids (one of the two liquids contains cement) are mixed to form a mixture, and the mixture is injected into the ground as a ground grouting material.

[0004]

As an example, PTL 1 describes a ground grouting agent of a two-liquid type of a quick hardening agent-containing slurry and a cement slurry. Here, the quick hardening agent-containing slurry contains calcium aluminate containing SiO_2 and MgO as chemical components and having a content molar ratio of Al_2O_3 to MgO ($\text{Al}_2\text{O}_3/\text{MgO}$) of 17 to 60 and a content molar ratio of SiO_2 to MgO (SiO_2/MgO) of 2.0 to 7.5, gypsum, a carbonate of an alkali metal, sodium aluminate, a setting retarder, and water. The cement slurry contains cement and water.

[0005]

As another example, PTL 2 describes that an aqueous slurry A and an aqueous slurry B are mixed to form a ground grouting material. Here, the aqueous slurry A contains 100 parts by mass of calcium aluminate, 20 to 300 parts by mass of a gypsum, 0.5 to 15 parts by mass of one or more selected from the group consisting of a carbonate, a hydrogen carbonate, and a sulfate of an alkali metal, 0.5 to 15 parts by mass of sodium aluminate, and 0.1 to 10 parts by mass of a setting retarder. Further, the aqueous slurry B contains 100 to 2200 parts by mass of cement with respect to 100 parts by mass of calcium aluminate in the aqueous slurry A.

[0006]

The ground grouting material of the two-liquid type as described in the above Patent Documents is usually designed with the intention that each liquid has sufficient fluidity before mixing of the two liquids, but that hardening proceeds rapidly after mixing of the two liquids. Therefore, in the two-liquid type ground grouting material, at least one of the two liquids tends to be gelled or hardened in a relatively short time before being mixed with the other liquid.

PTL 3 describes a two-liquid type ground grouting material containing liquid A, which is a mixed slurry of powder material A containing calcium aluminate and a carboxylate and water, and liquid B, which is a mixed slurry of powder material B containing cement and water, which provides a new two-liquid type ground grouting material that exhibits a ground improvement effect quickly immediately after ground injection and can ensure a sufficient usable time before ground injection, in which the gel time measured by a specific procedure by mixing the liquid A and the liquid B is 1 second or more and 30 seconds or less. However, these patents do not describe a ground-improving material having an effect of preventing rusting of metallic members required to have durability, such as concrete reinforcing bars and rock bolts used in a tunnel structure.

Citation List

Patent Literature

[0007]

PTL 1: JP 2017-154948 A

PTL 2: JP 2014-109012 A

PTL 3: WO 2020/121738 A1

Summary of Invention

Technical Problem

[0008]

As a result of studies, the present inventors have found that the ground-improving material described in PTL 3 has room for improvement in that the ground-improving material can improve good penetration property and enhancement of initial strength in a well-balanced manner and can impart an effect of preventing rusting of a metallic member existing in the ground.

[0009]

In view of the above, an object of the present invention is to provide a ground-improving material slurry that exhibits good penetration property when injected into the ground, that provides a good initial strength enhancing effect, and that is capable of imparting an effect of preventing rusting of metallic members existing in the ground.

Solution to Problem

[0010]

As a result of intensive research, the present inventors have found that a ground-improving material slurry containing specific calcium aluminate, gypsum, and cement, having a specific amount of chlorine, and exhibiting a specific oxidation-reduction potential exhibits good penetration property and an initial strength enhancing effect, and can impart an effect of preventing rusting of a metallic member, thereby completing the present invention.

That is, the present invention is as follows.

[0011]

[1] A ground-improving material slurry containing calcium aluminate having a percentage of glass content of 70% or more, a $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio of 1.0 to 2.7, and an impurity content of 15% by mass or less, gypsum, and cement in water, in which a total amount of chlorine contained in the calcium aluminate, the gypsum, and the cement is 20 ppm to 2000 ppm, and an oxidation-reduction potential of the ground-improving material slurry is -0.4 to 0.1 V.

[2] The ground-improving material slurry as set forth in [1], further containing a setting modifier.

[3] The ground-improving material slurry as set forth in [1] or [2], further containing alum.

[4] The ground-improving material slurry as set forth in any of [1] to [3], further containing an additive, in which the additive is at least one selected from the group consisting of a sulfate excluding gypsum, a sulfite, and a thiosulfate.

[5] The ground-improving material slurry as set forth in [4], in which the sulfate is at least one selected from the group consisting of ferrous sulfate and ferric sulfate, the thiosulfate is at least one selected from the group consisting of sodium thiosulfate and calcium thiosulfate, and the sulfite is at least one selected from the group consisting of sodium sulfite and calcium sulfite.

[6] The ground-improving material slurry as set forth in [4] or [5], in which the additive contains the thiosulfate, the sulfite, and boron, and when a content of the thiosulfate in the additive is X (% by mass) and a content of the sulfite in the additive is Y (% by mass), X and Y satisfy $10 \leq X/Y \leq 100$.

[7] The ground-improving material slurry as set forth in [6], in which a content of the boron measured in accordance with JIS K 0102 is 0.01 mg/L or more and 5.0 mg/L or less.

[8] A ground-improving material hardened product containing a hardened product of the ground-improving material slurry as set forth in any of [1] to [7].

[9] A ground improvement method including improving a ground with the ground-improving material slurry as set forth in any of [1] to [7].

Advantageous Effects of Invention

[0012]

According to the present invention, it is possible to provide a ground-improving material slurry that exhibits good penetration property when injected into the ground, that provides a good initial strength enhancing effect, and that is capable of imparting an effect of preventing rusting of metallic members existing in the ground.

Description of Embodiments

[0013]

Hereinafter, embodiments of the present invention will be described in detail.

In the description herein, as to a value that may vary depending on temperature conditions, a value under a condition of 20°C is adopted, unless otherwise specified.

[0014]

The ground-improving material slurry of the present embodiment contains calcium aluminate, gypsum, and cement in water. Preferably, the ground-improving material slurry further contains a setting modifier and the like. More preferably, the ground-improving material slurry further contains alum and the like. Still more preferably, the ground-improving material slurry further contains an additive. The components and properties of the ground-improving material slurry will be described below.

[0015]

[Calcium Aluminate]

In the technical field of hydraulic materials, calcium aluminate is a general term for substances containing aluminum oxide (Al_2O_3) and calcium oxide (CaO) as main components and having hydration activity. Here, the term “main component” means that the total content of aluminum oxide and calcium oxide in the entire calcium aluminate is, for example, 50% by mass or more, preferably 70% by mass or more, and more preferably 90% by mass or more.

[0016]

Typically, calcium aluminate can be obtained by mixing aluminum oxide and calcium oxide (in some cases, silica (SiO_2) or the like) to form a mixture, firing and/or melting the mixture, and then cooling the mixture. For firing and melting, a rotary kiln, an electric furnace, or the like can be used. Examples of the CaO raw material include calcium carbonate such as limestone and shells, calcium hydroxide such as slaked lime, and calcium oxide such as quick lime. Examples of the Al_2O_3 raw material include bauxite, industrial by-products called aluminum residual ash, and aluminum powder.

[0017]

As the calcium aluminate, either crystalline or amorphous calcium aluminate can be used. From the viewpoint of further enhancing the hardenability after injection into the ground, an amorphous material, for example, amorphous calcium aluminate produced by rapid cooling after melting is preferable.

[0018]

The $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio in the calcium aluminate is preferably 1.0 to 2.7, and more preferably 1.7 to 2.5. By appropriately adjusting this molar ratio, the initial strength of the hardened product can be increased, and a ground

improvement effect can be obtained at an early stage.

[0019]

The content percentage of an impurity (components other than CaO and Al₂O₃) in the calcium aluminate is preferably 15% by mass or less, and more preferably 10% by mass or less. When the content of the impurity is 15% by mass or less, the initial strength of the hardened product is increased, and a ground improvement effect is easily obtained at an earlier stage. Here, typical examples of the impurity include silicon oxide, magnesium oxide, and sulfur oxide. In addition, examples of the impurity include organic substances, alkali metal oxides, alkaline earth metal oxides, titanium oxide, iron oxide, alkali metal halides, alkaline earth metal halides, alkali metal sulfates, and substances obtained by substituting or solid-dissolving these in a part of CaO or Al₂O₃. Needless to say, the impurities are not limited to these.

The content percentage of the impurities in the calcium aluminate can be determined by measurement using fluorescent X-ray analysis.

[0020]

The percentage of glass content of calcium aluminate is preferably 70% or more, and more preferably 90% or more, in terms of reaction activity. By making this value appropriate, it is easy to obtain a ground improvement effect at an earlier stage. For the percentage of glass content, the main peak area S of the crystalline mineral of the measurement sample is measured in advance by the powder X-ray diffraction method, and then the sample is heated at 1000°C for 2 hours, and then slowly cooled at a cooling rate of (1 to 10°C)/min. The main peak area S0 of the crystalline mineral after heating by the powder X-ray diffraction method is obtained, and the percentage of glass content χ is calculated using the following equation using the values of S0 and S.

$$\text{Percentage of glass content } \chi (\%) = 100 \times (1 - S/S0)$$

[0021]

The particle size of the calcium aluminate is preferably a Blaine specific surface area value (JIS R 5201) of 3000 cm²/g or more, and more preferably 5000 cm²/g or more, from the viewpoint of initial strength developing property. The upper limit is, for example, 9000 cm²/g or less. By appropriately increasing this value, the initial strength of the hardened product is increased, and a ground improvement effect is easily obtained at an earlier stage.

[0022]

Specific examples of the calcium aluminate can include alumina cement. That is, a commercially available alumina cement or the like may be used as the calcium aluminate raw material.

Specific examples of the alumina cement can include alumina cement No. 1 and alumina cement No. 2. These can be purchased from Denka Company Limited or AGC Inc.

[0023]

The ground-improving material slurry may contain only one type of calcium aluminate, or may contain two or more types of calcium aluminates having different properties/physical properties or the like. The amount of calcium aluminate in the powder of the ground-improving material slurry is, for example, 5% by mass or more and 80% by mass or less, preferably 10% by mass or more and 75% by mass or less, and more preferably 15% by mass or more and 70% by mass or less. By appropriately adjusting the amount of calcium aluminate, the balance between the speed of hardening and the initial strength is improved. Further, it is easier to obtain a ground improvement effect at an early stage.

[0024]

[Gypsum]

By containing gypsum, the ground-improving material slurry can be easily designed to have a long usable time, and the operability is improved.

[0025]

The gypsum that can be used is not particularly limited. It is also possible to use different types of gypsum in combination. Examples of the gypsum include hemihydrate gypsum and anhydrous gypsum. Anhydrous gypsum is preferable in terms of strength developing property. Specific examples of anhydrous gypsum include anhydrous gypsum produced as a by-product of hydrofluoric acid and natural anhydrous gypsum.

[0026]

The particle size of the gypsum is preferably $3000\text{ cm}^2/\text{g}$ or more, and more preferably $5000\text{ cm}^2/\text{g}$ or more in terms of a Blaine specific surface area value from the viewpoint of initial strength developing property. On the other hand, from the viewpoint of longer usable time, this value is preferably $30000\text{ cm}^2/\text{g}$ or less, and more preferably $20000\text{ cm}^2/\text{g}$ or less.

[0027]

The amount of gypsum in the ground-improving material slurry is 5% by

mass or more and 80% by mass or less, preferably 10% by mass or more and 75% by mass or less, and more preferably 15% by mass or more and 70% by mass or less. As another viewpoint, the amount of gypsum relative to calcium aluminate in the ground-improving material slurry is preferably 50% by mass or more and 250% by mass or less, and more preferably 70% by mass or more and 200% by mass or less with respect to 100% by mass of calcium aluminate. By appropriately increasing the amount of gypsum, a long usable time can be obtained. On the other hand, by appropriately decreasing the amount of gypsum, the initial strength of the hardened product can be increased. That is, the ground improvement effect is easily obtained at an earlier stage.

[0028]

[Cement]

The cement that can be used is not particularly limited. Specific examples thereof include various Portland cements such as normal, high-early strength, ultra high-early strength, low-heat, and moderate-heat; various mixed cements obtained by mixing blast furnace slag, fly ash, or silica with these Portland cements; filler cements obtained by mixing limestone powder, gypsum, or slowly cooled blast furnace slag fine powder with these Portland cements; Portland cements such as environmentally friendly cements (eco-cements) produced using municipal waste incineration ash or sewage sludge incineration ash as a raw material; commercially available cement-based solidification materials; and commercially available fine particle cements. (In addition, alumina cement, which means calcium aluminate, is preferably excluded from the cement herein).

[0029]

Various cements and various mixed cements may be used in the form of fine powder. In addition, those prepared by increasing or decreasing the amount of components (for example, gypsum and the like) usually used in cement can also be used. The cement may be used alone or in combination of two or more thereof. Among these, blast furnace cement is preferable because of its low hexavalent chromium content.

[0030]

The amount of cement in the ground-improving material slurry is 10% by mass or more and 60% by mass or less, preferably 15% by mass or more and 40% by mass or less, and more preferably 20% by mass or more and 35% by mass or less.

[0031]

[Setting Modifier]

The setting modifier may be contained for the purpose of, for example, adjusting the usable time and the hardenability. In particular, the setting modifier may be contained in advance or may be added at the time of preparation.

[0032]

Examples of the setting modifier include inorganic salts such as aluminates such as sodium aluminate and potassium aluminate; carbonates such as sodium carbonate and potassium carbonate; oxycarboxylic acids or salts thereof; hydroxides such as sodium hydroxide and potassium hydroxide; aluminum sulfate; iron (III) sulfate; silicates such as sodium silicate and potassium silicate; phosphates such as sodium phosphate, calcium phosphate, and magnesium phosphate; and borates such as lithium borate and sodium borate; and saccharides.

[0033]

As the setting modifier, a commercially available product may be used. Examples of the commercially available product include Denka Setter D-100 and D-300 manufactured by Denka Company Limited.

[0034]

When the ground-improving material slurry contains a setting modifier, the amount of the setting modifier may be appropriately adjusted based on the desired usable time, hardenability, and the like. To be specific, it is preferable that the amount of the setting modifier is used so as to be, for example, 0.0005% by mass or more and 2% by mass or less, preferably 0.001% by mass or more and 1.5% by mass or less, and more preferably 0.002% by mass or more and 1% by mass or less, in all the components of the ground-improving material slurry except water. That is, when the setting modifier is included in advance, it is preferable that the amount of the setting modifier with respect to the entire ground-improving material slurry is about the above-described amount. Further, when the setting modifier is separately prepared, it is preferable that the amount of the setting modifier in the entire mixture of the ground-improving material slurry and the setting modifier is about the above-described amount.

[0035]

[Alum]

The ground-improving material slurry preferably contains alum. As a finding of the present inventors, it is possible to further accelerate hardening by

containing alum. In addition, it is possible to obtain a ground improvement effect more quickly.

[0036]

The alum that can be used is not particularly limited. Examples thereof include various alum such as potassium alum, chromium alum, and iron alum. Alunite can also be used. Here, the alunite is a natural product having a composition range of $[(K, Na)(Al, Fe)_3(SO_4)_2(OH)_6]$. In addition, raw alunite powder obtained by pulverizing alunite, calcined alunite powder obtained by calcining alunite at a temperature of 800°C or lower and pulverizing the calcined alunite, and the like can also be used. As the alum, generally commercially available potassium alum or calcined alunite powder is preferably used. The alum may contain an anhydrous salt or water of crystallization, and any of them can be used as it is.

[0037]

The amount of alum in the ground-improving material slurry is, for example, 0.3 parts by mass or more and 10 parts by mass or less, and preferably 0.5 parts by mass or more and 5 parts by mass or less with respect to 100 parts by mass of cement. By using a moderately large amount of alum, the hardening can be made faster. In addition, by using a moderately small amount of alum, it is possible to suppress unintended change over time (for example, a decrease in fluidity or hardening).

[0038]

[Additive]

The additive is at least one selected from the group consisting of a sulfate other than gypsum, a sulfite, and a thiosulfate. The amount of these additives in the ground-improving material slurry (the total amount when a plurality of additives are used) is 0.0001% by mass or more and 10% by mass or less, preferably 0.001% by mass or more and 8% by mass or less, and more preferably 0.01% by mass or more and 5% by mass or less.

The additive may be composed of a liquid composition containing a sulfate excluding gypsum.

Further, the additive may be composed of a liquid composition containing a thiosulfate, a sulfite, and boron. Thereby, dispersibility in the cement is enhanced. The liquid additive may be composed of an aqueous solution containing these components and water.

[0039]

The solid content concentration of the liquid additive can be appropriately changed depending on the purpose. The lower limit of the solid content concentration of the additive is, for example, 10% by mass or more, preferably 20% by mass or more, and more preferably 30% by mass or more. According to this, the effect of the additive can be sufficiently obtained. On the other hand, the upper limit of the solid content concentration of the additive is, for example, 60% by mass or less, preferably 50% by mass or less, and more preferably 45% by mass or less. According to this, the liquid stability of the additive can be enhanced.

[0040]

The sulfate may include at least one selected from the group consisting of ferrous sulfate and ferric sulfate. These may be used alone or in combination of two or more thereof. As a result, the rusting of the reinforcing bar can be suppressed, and the bleeding of the hardened body is reduced.

[0041]

The thiosulfate may include at least one selected from the group consisting of sodium thiosulfate and calcium thiosulfate. These may be used alone or in combination of two or more thereof. As a result, the rusting of the reinforcing bar can be suppressed, and the bleeding of the hardened body is reduced.

[0042]

The sulfite may include at least one selected from the group consisting of sodium sulfite and calcium sulfite. These may be used alone or in combination of two or more thereof. As a result, bleeding of the hardened body is decreased.

[0043]

The additive contains a thiosulfate, a sulfite, and boron, and the content of the thiosulfate in the additive is X (% by mass) and the content of the sulfite is Y (% by mass). In the additive, X and Y may be configured so as to satisfy, for example, $10 \leq X/Y \leq 100$, preferably $15 \leq X/Y \leq 70$, and more preferably $20 \leq X/Y \leq 50$. Within the above range, it is possible to achieve a balance between the suppression of the rusting of the reinforcing bar and the decrease in the bleeding rate.

[0044]

One of the methods for measuring the contents of sulfite and thiosulfate in the additive is as follows.

(1) First, 10 mL of a sample solution containing additives is put into a

measuring flask using a whole pipette, and the total amount is made into 500 mL by adding with water, and these are plugged and mixed to obtain a mixture.

(2) Subsequently, about 100 mL of water is put into a 300 mL conical beaker, and 20 mL of the mixture of (1) is added using a whole pipette to obtain a sample. Two such samples are prepared.

(3) To one sample of (2), 5 mL of 20% acetic acid is added and mixed.

(4) To the other sample of (2), 5 mL of 20% acetic acid and 5 mL of 37% formalin are added and mixed, and allowed to stand for 2 to 3 minutes.

(5) Using a starch solution as an indicator, the sample of (3) is titrated with an N/10 iodine solution, and the addition amount thereof is defined as A mL. Similarly, the sample of (4) is titrated, and the addition amount thereof is defined as B mL.

(6) The contents of sulfite and thiosulfate in the additive is calculated based on the following equations.

$$\cdot \text{Na}_2\text{S}_2\text{O}_3: \text{w/w}\% = B \times f \times 3.953 \div \text{specific gravity}$$

$$\cdot \text{Na}_2\text{SO}_3: \text{w/w}\% = (A - B) \times f \times 1.576 \div \text{specific gravity}$$

$$\cdot f: \text{N/10 iodine solution factor}$$

[0045]

The lower limit of the content of boron in the additive is, for example, 0.01 mg/L or more, preferably 0.05 mg/L or more, and more preferably 0.1 mg/L or more. As a result, the initial strength is increased and bleeding is reduced. On the other hand, the upper limit of the content of boron is, for example, 5.0 mg/L or less, preferably 3.0 mg/L or less, and more preferably 1.0 mg/L or less. As a result, the environmental load can be reduced.

[0046]

The content of boron may be measured by ICP emission spectrometry in accordance with JIS K 0102.

[0047]

In the present embodiment, it is possible to control the content of the sulfite, X/Y, and the boron content in the additive by appropriately selecting, for example, the type and blending amount of each component contained in the additive, and the method for preparing the additive. Among these, for example, addition of a sulfite as a sulfite ion source, addition of an appropriate amount of water, and the like are exemplified as elements for setting the content of the sulfite, X/Y, and the boron content in the additive to desired numerical ranges.

[0048]

[Water]

As described above, the ground-improving material slurry is a slurry in which calcium aluminate, gypsum, and cement are mixed with water and additives as appropriate. The amount of water when the calcium aluminate, the gypsum, and the cement are mixed with water to form a ground-improving material slurry may be adjusted as appropriate depending on the desired fluidity, pumpability with a pump, injectability into the ground, and the like. The amount of water can be adjusted to, for example, 10% by mass or more and 95% by mass or less, and preferably 50% by mass or more and 90% by mass or less, in the entire ground-improving material slurry.

[0049]

The solid content concentration of the ground-improving material slurry is 10% by mass or more and 80% by mass or less, preferably 15% by mass or more and 50% by mass or less, and more preferably 20% by mass or more and 40% by mass or less.

[0050]

[Method for Producing Ground-Improving Material Slurry]

The method for producing the ground-improving material slurry is not particularly limited. Calcium aluminate, gypsum, and cement may be put into water and mixed to prepare the ground-improving material slurry. When the ground-improving material slurry contains a setting modifier, it is preferable to obtain the ground-improving material slurry in the order of first putting the setting modifier into water and then putting the other components into water, from the viewpoint of production stability, prevention of unintentional coagulation or gelling, and the like. In addition, when alum is used, alum may be included in the powder components (solid contents) in the ground-improving material slurry in advance, or alum may be added as a separate material during the preparation. Further, when the additives are used, it is preferable to obtain the ground-improving material slurry in the order that the additives are first put into water and then the other components are put into water. For the mixing, various mixers known in this technical field can be used.

[0051]

As long as the effects of the present invention are not excessively impaired, the ground-improving material slurry may contain components other than calcium

aluminate, gypsum, cement, water, setting modifiers, alum, sulfates, thiosulfates, sulfites, and boron. Examples of the “other components” include carbonates, heavy metal carbonates, calcium hydroxide, magnesium hydroxide, and alkali hydroxides.

[0052]

In the present invention, it has been found that the amount of chlorine in calcium aluminate, gypsum, and cement contained in the ground-improving material slurry affects the strength (initial good strength enhancing effect), the penetration property, and the effect of preventing rusting. That is, the amount of chlorine contained in the ground-improving material slurry is preferably 20 to 2000 ppm, more preferably 50 to 1500 ppm, still more preferably 90 to 1000 ppm, and even more preferably 90 to 500 ppm. The amount of chlorine contained in the ground-improving material slurry can be adjusted, for example, by adding a chlorine-containing admixture when preparing the ground-improving material slurry. In addition, the amount of chlorine can be measured by the method described in Examples described later. If the amount of chlorine contained in the ground-improving material slurry is less than 20 ppm, the strength of the ground-improving material slurry may be reduced (in particular, the initial strength enhancing effect may not be obtained), and rusting may be promoted. On the other hand, if the amount of chlorine is more than 2000 ppm, rusting may be promoted. In addition, penetration property may be reduced.

[0053]

Further, from the viewpoint of contributing to good penetration property and prevention of rusting of reinforcing bars in the ground-improving material slurry, the oxidation-reduction potential of the ground-improving material slurry is preferably -0.4 to 0.1 V, and more preferably -0.3 to -0.1 V. The oxidation-reduction potential can be measured by using an oxidation-reduction potential (ORP) meter. In order to set the oxidation-reduction potential to -0.4 to 0.1 V, it is possible to adjust the potential by bubbling oxygen into the slurry or the like. When the oxidation-reduction potential is less than -0.4 V or greater than 0.1 V, a stable oxide film cannot be formed on the surface of the reinforcing bar, and there is a possibility that rust generation is promoted and rusting of the reinforcing bar cannot be prevented. In addition, penetration property may be reduced.

[0054]

As the ground-improving material slurry, a hardened product thereof can

be obtained. In other words, a ground-improving material hardened product containing the hardened product of the ground-improving material slurry of the present invention described above can be obtained. Thus, the ground can be improved. Further, it is possible to provide a ground improvement method for improving the ground by the ground-improving material slurry of the present invention described above.

[0055]

As described above, the ground-improving material slurry may be a one-liquid type or may be, for example, a two-liquid type. In the case of the two-liquid type, for example, two liquids of material A containing calcium aluminate and gypsum in water or an aqueous solution and material B containing cement in water or an aqueous solution may be separately prepared and mixed to form a ground-improving material slurry.

[0056]

In the case of the two-liquid type, more specifically, the ground-improving material slurry is a two-liquid type ground-improving material slurry composed of a combination of material A containing calcium aluminate having a percentage of glass content of 70% or more, a $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio of 1.0 to 2.7, and an impurity content of 15% by mass or less, and gypsum in water or an aqueous solution, and material B containing cement in water or an aqueous solution, wherein a total amount of chlorine contained in the calcium aluminate, the gypsum, and the cement is 20 ppm to 2000 ppm, and an oxidation-reduction potential of the ground-improving material slurry when the material A and the material B are mixed is -0.4 to 0.1 V.

[0057]

The method for mixing the material A and the material B and the specific procedure for improving the ground with the material A and the material B are not particularly limited, and various methods known in the technical field of ground improvement can be applied. For example, (i) a so-called two shot system in which the material A and the material B are merged and mixed at the front end of a double pipe and injected into the ground, (ii) a so-called 1.5 shot system in which the material A and the material B are mixed and injected on the way from an injection pump to an injection pipe, and (iii) a one shot system in which the material A and the material B are mixed in a mixing tank such as a mixer can be employed. When these methods are carried out, a known injection pump or the

like can be used.

[0058]

In other words, (1) the material A and the material B may be mixed to form a mixture before ground grouting and the mixture may be grouted into the ground, or (2) the material A and the material B may be separately pressure-fed and mixed in the ground at the moment of grouting into the ground or after ground grouting.

[0059]

The mixing ratio of the material A and the material B may be appropriately adjusted depending on the desired hardening speed, pumpability, and the like. The mixing ratio of the material A to the material B is typically about 20:80 to 80:20, and preferably about 30:70 to 70:30 in terms of a volume ratio.

[0060]

In addition, in the case of the one-liquid type, the slurry may be injected into the ground as it is by a known method.

[0061]

Although the embodiments of the present invention have been described above, these are merely examples of the present invention, and various configurations other than those described above can be employed. In addition, the present invention is not limited to the above-described embodiments, and modifications, improvements, and the like within a range in which the object of the present invention can be achieved are included in the present invention.

Examples

[0062]

Embodiments of the present invention will be described in detail based on Examples and Comparative Examples. However, the present invention is not limited to Examples.

[0063]

[Experimental Example 1]

(Preparation of Ground-Improving Material Slurry)

First, calcium aluminate, gypsum, cement, and potassium alum were mixed using a ProShear mixer (WB type, manufactured by Pacific Machinery & Engineering Co., Ltd.). Thereafter, a setting modifier (Denka Setter D-100, manufactured by Denka Company Limited) and the above-described mixture were put into water in this order and sufficiently kneaded to obtain a ground-improving

material slurry. The amount of each component in the ground-improving material slurry is as described in Table 1. As for the amount of chlorine, the amounts of chlorine in calcium aluminate, gypsum, and cement were measured, and the deficient amount was adjusted by adding a chlorine-containing admixture (material name: sodium chloride) at the time of mixing the powders. The ORP of the prepared ground-improving material slurry was adjusted by bubbling with oxygen.

[0064]

As the gypsum, natural anhydrous gypsum having a Blaine specific surface area value of 5,000 cm²/g was used.

As the cement, ordinary Portland cement (manufactured by Denka Company Limited) was used in Experiment Nos. 1-1 to 1-5, 1-7 to 1-12, 1-14, and 2-1 to 2-9, and trial cement (cement prepared by using various commercially available pure chemicals for adjustment of mixed raw materials and chemical components of cement plants and using anhydrous gypsum as the pure chemical for adjustment of the amount of SO₃, amount of chlorine of 1.5 ppm, and Blaine value of 3,450 cm²/g) was used in Experiment Nos. 1-6 and 1-13.

In addition, calcium carbonate and aluminum oxide were used as the raw materials for calcium aluminate. The molar ratio of CaO/Al₂O₃ was changed, and after melting at 1650°C, the cooling rate was adjusted to prepare calcium aluminate having a percentage of glass content shown in Table 1. The Blaine specific surface area value was 5,000 to 6,000 cm². In Experiment Nos. 1-5 and 1-12, silica sand, magnesium oxide, and sulfur oxide were added so that the impurity contents became the amounts shown in Table 1, and the mixture was fired.

Impurities of the calcium aluminate were silicon oxide, magnesium oxide, and sulfur oxide, which were measured by fluorescent X-ray analysis, and the total content (impurity content) was obtained.

[0065]

(Initial Strength)

The strength was measured in accordance with JIS R 5201. To be specific, using the composition of the ground-improving material slurry, a test piece of vertical 4 cm × horizontal 4 cm × height 16 cm was produced, and the compressive strength after 30 minutes, 1 hour, and 1 day from the preparation of the ground-improving material slurry was measured.

Then, the enhancing rate of the initial strength from the material age of 1 hour to the material age of 1 day was obtained from the following Formula 1.

[Formula 1]: Enhancing rate of compressive strength (times) = (compressive strength at material age of 1 day – compressive strength at material age of 1 hour)/compressive strength at material age of 1 hour

[0066]

(Measurement of Penetration Length)

Sand for measurement of penetration length was filled into a Japan Society of Civil Engineers standard vinyl bag having a diameter of 5 cm so as to form a 20 cm, 200 mL of the slurry immediately after the preparation of the ground-improving material slurry was poured from the upper surface of the vinyl bag and allowed to naturally penetrate, and the penetration length was measured. In addition, it is preferable that the penetration length is 20 cm or more. As the sand for measurement, a mixture (particle size adjustment product) of Himekawa sand and mined limestone sand manufactured by Denka Company Limited were used.

[0067]

(Chlorine Concentration)

The chlorine concentrations of calcium aluminate, gypsum, and cement were measured in accordance with JIS R 5202, respectively, and the total amount of chlorine was calculated.

[0068]

(Rusting Rate of Reinforcing Bar)

A round steel of ϕ 19 mm with an embedding depth of 18 cm was filled with ground-improving material slurry so that the cover thickness became 10 mm, and 20°C water curing was performed until the material age of 28 days, and then accelerated neutralization was performed for 12 weeks in an environment of 30°C, 60% relative humidity, and 5% carbon dioxide concentration. Further, during the accelerated neutralization test, the test piece was taken out every three weeks, and immersed in water for one day in a 20°C environment to perform the accelerated neutralization test. After completion of the test, the round steel was taken out, and the rust was removed by a 10% diammonium hydrogen citrate solution to measure the weight (m2) of the round steel after the test, and the rusting rate of the reinforcing bar due to the change from the weight (m1) of the round steel before the test was calculated by the following equation.

Rusting rate (%) of reinforcing bar = $[(m_1 - m_2)/m_1] \times 100$

[0069]

The composition of the ground-improving material slurry, the measurement/evaluation results, and the like are collectively shown in Table 1 and Table 2.

[0070]

Table 1

No.	Ground-improving material slurry						Type of calcium aluminate			Amount of chlorine (ppm)	Oxidation-reduction potential (V)	
	Calcium aluminate (g)	Gypsum (g)	Cement (g)	Setting modifier (g)	Potassium alum (g)	Water (g)	Percentage of glass content (%)	CaO/Al ₂ O ₃ molar ratio	Impurity content (%)			
1-1	37.5	37.5	300	0.375	6	879	97	2.2	2	100	-0.1	Example
1-2	37.5	37.5	300	0.375	6	879	70	2.2	2	100	-0.1	Example
1-3	37.5	37.5	300	0.375	6	879	97	1.0	2	100	-0.1	Example
1-4	37.5	37.5	300	0.375	6	879	97	2.7	2	100	-0.1	Example
1-5	37.5	37.5	300	0.375	6	879	97	2.2	15	100	-0.1	Example
1-6	37.5	37.5	300	0.375	6	879	97	2.2	2	20	-0.1	Example
1-7	37.5	37.5	300	0.375	6	879	97	2.2	2	2000	-0.1	Example
1-8	37.5	37.5	300	0.375	6	879	97	2.2	2	100	-0.4	Example
1-9	37.5	37.5	300	0.375	6	879	97	2.2	2	100	0.1	Example
1-10	37.5	37.5	300	0.375	6	879	60	2.2	2	100	-0.1	Comparative Example
1-11	37.5	37.5	300	0.375	6	879	97	3.1	2	100	-0.1	Comparative Example
1-12	37.5	37.5	300	0.375	6	879	97	2.2	20	100	-0.1	Comparative Example
1-13	37.5	37.5	300	0.375	6	879	97	2.2	2	10	-0.6	Comparative Example
1-14	37.5	37.5	300	0.375	6	879	97	2.2	2	3000	0.4	Comparative Example

[0071]

Table 2

No.	Compressive strength (N/mm ²)			Enhancing rate of compressive strength	Penetration length (cm)	Rusting rate of reinforcing bar (%)
	30 min	1 hr	1 day			
1-1	0.051	0.085	2.512	28.6	>20	37
1-2	0.021	0.035	2.107	59.2	>20	43
1-3	0.022	0.036	2.097	57.3	>20	42
1-4	0.066	0.103	2.546	23.7	>20	35
1-5	0.019	0.031	2.089	66.4	>20	45
1-6	0.012	0.022	1.923	86.4	>20	45
1-7	0.082	0.123	2.643	20.5	>20	40
1-8	0.051	0.074	2.364	30.9	>20	38
1-9	0.052	0.081	2.487	29.7	>20	37
1-10	0.000	0.004	0.622	154.5	>20	64
1-11	0.111	0.168	2.787	15.6	5	34
1-12	0.000	0.008	0.811	100.4	>20	67
1-13	0.000	0.011	0.958	86.1	>20	61
1-14	0.122	0.171	2.811	15.4	9	52

[0072]

A ground-improving material slurry containing specific calcium aluminate, gypsum, and cement, having a specific amount of chlorine, and exhibiting a specific oxidation-reduction potential has good penetration property and initial strength (for example, 1-day strength), and can suppress rusting of reinforcing bars existing in the ground. In other words, it was confirmed that the material exhibited favorable performance as a ground grouting material. In Experiment Nos. 1-10, 1-12, and 1-13, the enhancing rate of the initial strength is very high, but the compressive strength at 1 day of the material age itself is very small, and thus it cannot be said that these are preferable.

[0073]

[Experimental Example 2]

A ground-improving material slurry was prepared with the mix proportion shown in Table 3. The preparation method was the same as that in Experimental Example 1, except that the additives were first mixed with water so as to be 0.002% in the ground-improving material slurry, and the amount of chlorine and the oxidation-reduction potential were adjusted to 100 ppm and -0.1 V, respectively. As the calcium aluminate, calcium aluminate having a percentage of glass content of 97%, a $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio of 2.2, and an impurity content of 2% was used.

[0074]

(Bleeding Rate)

The bleeding rate was measured in accordance with JIS A 1123.

[0075]

(Rusting Rate of Reinforcing Bar)

The same test as in Experimental Example 1 was performed to measure the rusting rate of the reinforcing bars.

[0076]

The composition of the ground-improving material slurry, the same measurement and evaluation results as in Experimental Example 1, and the like are collectively shown in Table 3.

[0078]

The ground-improving material slurry containing the specific additives can reduce the bleeding rate and further suppress the rusting of reinforcing bars existing in the ground. In other words, it was confirmed that the slurry exhibited more preferable performances as a ground grouting material.

Industrial Applicability

[0079]

According to the present invention, there is provided a ground-improving material slurry which exhibits good penetration property and an initial strength enhancing effect and can impart an effect of preventing rusting of reinforcing bars existing in the ground, and the ground-improving material slurry can be suitably used mainly in the civil engineering field.

CLAIMS

[Claim 1]

A ground-improving material slurry comprising calcium aluminate having a percentage of glass content of 70% or more, a $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio of 1.0 to 2.7, and an impurity content of 15% by mass or less, gypsum, and cement in water, wherein a total amount of chlorine contained in the calcium aluminate, the gypsum, and the cement is 20 ppm to 2000 ppm, and an oxidation-reduction potential of the ground-improving material slurry is -0.4 to 0.1 V.

[Claim 2]

The ground-improving material slurry according to claim 1, further comprising a setting modifier.

[Claim 3]

The ground-improving material slurry according to claim 1 or 2, further comprising alum.

[Claim 4]

The ground-improving material slurry according to any one of claims 1 to 3, further comprising an additive, wherein the additive is at least one selected from the group consisting of a sulfate excluding gypsum, a sulfite, and a thiosulfate.

[Claim 5]

The ground-improving material slurry according to claim 4, wherein the sulfate is at least one selected from the group consisting of ferrous sulfate and ferric sulfate, the thiosulfate is at least one selected from the group consisting of sodium thiosulfate and calcium thiosulfate, and the sulfite is at least one selected from the group consisting of sodium sulfite and calcium sulfite.

[Claim 6]

The ground-improving material slurry according to claim 4 or 5, wherein the additive contains the thiosulfate, the sulfite, and boron, and when a content of the thiosulfate in the additive is X (% by mass) and a content of the sulfite in the additive is Y (% by mass), X and Y satisfy $10 \leq X/Y \leq 100$.

[Claim 7]

The ground-improving material slurry according to claim 6, wherein a content of the boron measured in accordance with JIS K 0102 is 0.01 mg/L or more and 5.0 mg/L or less.

[Claim 8]

A ground-improving material hardened product comprising a hardened product of the ground-improving material slurry according to any one of claims 1 to 7.

[Claim 9]

A ground improvement method comprising improving a ground with the ground-improving material slurry according to any one of claims 1 to 7.