LIQUID ADMIXTURE FOR CEMENT, CEMENT COMPOSITION, CEMENT HARDENED BODY, AND METHOD FOR PRODUCING CEMENT HARDENED BODY

Technical Field

[0001]

The present invention relates to a liquid admixture for cement, a cement composition containing the admixture, a hardened cement body thereof, and a method for producing the hardened cement body. The present invention relates especially to a liquid admixture for cement containing microorganisms that generate carbon dioxide through metabolism, a cement composition containing the admixture, a hardened cement body that is a hardened product thereof, and a method for producing the hardened cement body.

Background Art

[0002]

Hardened cement products such as concrete and mortar develop cracks over time. When water and oxygen penetrate through these cracks, rust forms on the surface of the reinforcing bars, and the concrete around the rusted reinforcing bars peels off, resulting in deterioration.

[0003]

Patent Document 1 (JP-B-6716331) discloses that aerobic microorganisms are added to a cement admixture,

so that the oxygen in the resulting hardened cement products is consumed by these aerobic microorganisms, thereby suppressing corrosion of steel materials in the hardened cement products and that when damages such as cracks occurs in the hardened cement products, carbon dioxide emitted by the aerobic microorganisms can be expected to produce a crack-closing effect.

[0004]

Apart from the problem of time-dependent cracking in hardened cement products described above, concrete structures used in sewer systems—such as sewer pipes installed in sewage facilities—suffer from a separate problem in which the concrete undergoes premature corrosion caused by sulfuric acid produced by sulfur-oxidizing bacteria.

[0005]

Patent Document 2 (JP-A-2016-525879), Patent Document 3 (JP-B-3044669), and Patent Document 4 (JP-B-3320074) disclose the addition of a growth inhibitory agent that inhibits the activity of microorganisms producing sulfuric acid (sulfur-oxidizing bacteria) to cement compositions. This growth inhibitory agent enables the corrosion of hardened cement products such as concrete to be suppressed even in the presence of microorganisms producing sulfuric acid.

Prior Art Document

Patent Document

[0006]

Patent Document 1 JP-B-6716331

Patent Document 2 JP-A-2016-525879

Patent Document 3 JP-B-3044669

Patent Document 4 JP-B-3320074

Summary of Invention

Problem to be solved by the Invention

[0007]

According to the invention disclosed in Patent Document 1 (JP-B-6716331), cracks generated in a hardened cement body are closed, and corrosion of steel materials within the hardened cement body is suppressed. As described above, the growth inhibitory agents of Patent Documents 2 to 4 (JP-A-2016-525879, JP-B-3044669, and JP-B-3320074) enable corrosion in hardened cement product such as concrete to be suppressed even in the presence of microorganisms that produce sulfuric acid.

[0008]

However, although techniques for self-repair of concrete and techniques for imparting sulfuric-acid resistance to concrete have each been known in the prior art, no technique has been available that provides both functionalities.

[0009]

Accordingly, the present inventors attempted to prepare concrete by adding commercially available "antimicrobial agents" to concrete compositions containing commercially available "microbial agents" that have the function of automatically repairing cracks. However, the resulting concrete did not exhibit the self-repairing effect. It was considered that this was due to the antimicrobial agent suppressing the activity of the microorganisms contained in the microbial agent.

[0010]

However, further investigation by the present inventors revealed that the inhibition of the activity of the microorganisms was not caused by the antimicrobial agent itself, but rather by a finely powdered dispersant that had been added to the antimicrobial agent to improve the dispersibility of the admixture. However, simply removing the finely powdered dispersant would deteriorate the dispersibility of the admixture, creating a risk that the activity of the antimicrobial agent and the microorganisms would vary within the hardened cement body.

[0011]

In view of the above-described problems, an object of the present invention is to provide an admixture capable of imparting both crack self-repairing properties and resistance to sulfuric acid deterioration uniformly throughout an entire cement-based material, a cement

composition containing the admixture, and a hardened body thereof as well as a method for producing a cement-based material containing the admixture.

Means for Solving the Problem

[0012]

The present inventors have conducted extensive studies to achieve the above-mentioned object. As a result, the present inventors have found that, by adding water as a dispersant instead of the finely powdered dispersant, inhibition of the activity of aerobic microorganisms by the finely powdered dispersant can be avoided, and the aerobic microorganisms and the growth-inhibitory agent that inhibits the activity of sulfur-oxidizing bacteria can be uniformly dispersed throughout an entire cement-based material. Accordingly, the present inventors have completed the present invention.

[0013]

That is, it has been found that the object of the present invention can be achieved by a liquid admixture for cement comprising a first component comprising microorganisms that generate carbon dioxide through metabolism and a second component comprising a proliferation inhibitor of bacteria having the capability to oxidize sulfur.

[0014]

It is preferable that the second component be different from the first component, both first component and second component be liquid, and the admixture be a two-component admixture in which the first component and the second component are separately mixed into a cement directly before use.

[0015]

Furthermore, it is preferable that the microorganisms be selected from *Bacillus* bacteria having alkali resistance. It is particularly preferable that the *Bacillus* bacteria having alkali resistance be *Bacillus subtilis var. natto*, and biotin be further comprised as a coenzyme.

[0016]

Furthermore, it is more preferable that the *Bacillus* bacteria having alkali resistance be *Bacillus pumilus*.

[0017]

It is preferable that the proliferation inhibitor of the bacteria having the capability to oxidize sulfur be selected from the group consisting of nickel, nickel compounds, tungsten, tungsten compounds, dicarboxylate compounds, and mixtures thereof.

[0018]

Furthermore, the object of the present invention can also be achieved by a cement composition comprising the liquid admixture for cement of the present invention and

cement, and a hardened cement body obtained by curing this cement composition.

[0019]

In addition, the object of the present invention can also be achieved by a method for producing a hardened cement body, comprising:

a mixing step of adding a liquid admixture for cement comprising a first component containing microorganisms that generate carbon dioxide through metabolism and a second component containing a proliferation inhibitor of bacteria having sulfur-oxidizing capability to a cement or a ready-mix concrete comprising a cement, and mixing them to yield a cement composition; or, when the liquid admixture for cement is a two-component admixture, separately adding a liquid first component containing microorganisms that generate carbon dioxide through metabolism and a liquid second component containing a proliferation inhibitor of bacteria having sulfur-oxidizing capability to a cement or a ready-mix concrete comprising a cement, and mixing them to yield a cement composition; and

a curing step of curing the cement composition to obtain a hardened cement body.

Effects of Invention

[0020]

According to the present invention, because a finely powdered dispersant is not added, the activity of microorganisms that generate carbon dioxide through metabolism is not inhibited by such fine particles. Furthermore, since an admixture is prepared as a liquid admixture, mixing the liquid admixture with cement improves the dispersibility of microorganisms that generate carbon dioxide through metabolism and a proliferation inhibitor of bacteria having sulfur-oxidizing capability, thereby enabling these components to be uniformly dispersed throughout the hardened product of the resulting cement composition.

[0021]

Accordingly, it becomes possible to impart crack self-repairing properties and resistance to sulfuric acid deterioration uniformly throughout the entire hardened product of a cement composition.

Brief Description of Drawings

[0022]

[Fig. 1]

Fig. 1 is a flow chart showing a method for producing a hardened cement body of the present invention.

[Fig. 2]

Fig. 2 is a schematic view showing a mold used to form a hardened cement body for a water leak test in Examples (Test 1).

[Fig. 3]

Fig. 3 is a schematic view showing a compression tester B used to obtain a cracked sample of a hardened cement body for the water leak test in Examples (Test 1).

[Fig. 4]

Fig. 4 is a schematic view for illustrating the water leak test in Examples (Test 1).

[Fig. 5]

Fig. 5 is a graph showing the results of the water leak test in Examples (Test 1).

[Fig. 6]

Fig. 6 is a flow chart showing the procedure for preparing a cracked sample of a hardened cement body for a water leak test in Examples (Test 2).

[Fig. 7]

Fig. 7 is a schematic view illustrating the water leak test related to Test 2 of Examples.

[Fig. 8]

Fig. 8 is a graph showing the results of the water leak test in Test 2 of Examples.

Mode for carrying out the Invention

[0023]

<Liquid admixture for cement>

The liquid admixture for cement of the present invention comprises a first component containing microorganisms that generate carbon dioxide through

metabolism and a second component containing a proliferation inhibitor for bacteria having a capability to oxidize sulfur .

[0024]

The microorganisms contained in the first component that generate carbon dioxide through metabolism are microorganisms that metabolize a nutrient source, either directly or indirectly, to produce carbon dioxide. These microorganisms metabolize the organic carbon source described later, either in the presence or absence of oxygen, thereby generating carbon dioxide.

[0025]

The mechanism of self-repair of a hardened cement body by these microorganisms is as follows:

this carbon dioxide is reacted with water to generate carbonate ions, and these carbonate ions are reacted with calcium ions derived from calcium hydroxide in a hardened cement body to deposit calcium carbonate, which fills cracks in the hardened cement body.

[0026]

As the microorganisms, one or more can be selected and used from obligately (strictly) anaerobic microorganisms, facultative anaerobic microorganisms, obligately aerobic microorganisms, and microaerophilic microorganisms, and the selected one or more species can be used. From the viewpoint, as described later, the microorganisms consume oxygen in the hardened cement

body, and thereby preventing the corrosion of steel materials disposed in this hardened product, facultative anaerobic microorganisms, obligately aerobic microorganisms, microaerophilic microorganisms are preferable, and obligately aerobic microorganisms are particularly preferable .

[0027]

Furthermore, from the viewpoint of oxygen consumption, the microorganisms are preferably microorganisms of *Bacillus*. Since the microorganisms that generate carbon dioxide through metabolism are mixed into an alkaline environment of the cement composition, *Bacillus* bacteria having alkali resistance are particularly preferably, .

[0028]

Examples of the species of *Bacillus* include *B. acidiceler, B. acidicola, B. acidiproducens, B. acidocaldarius, B. acidoterrestris, B. aeolius, B. aerius, B. aerophilus, B. agaradhaerens, B. agri, B. aidingensis, B. akibai, B. alcalophilus, B. algicola, B. alginolyticus, B. alkalidiazotrophicus, B. alkalinitrilicus, B. alkalisediminis, B. alkalitelluris, B. altitudinis, B. alveayuensis, B. alvei, B. amyloliquefaciens, B. amylolyticus, B. andreesenii, B. aneurinilyticus, B. anthracis, B. aquimaris, B. arenosi, B. arseniciselenatis, B. arsenicus, B. aurantiacus, B. arvi, B. aryabhattai, B. asahii, B. atrophaeus, B.*

axarquiensis, B. azotofixans, B. azotoformans, B. badius, B. barbaricus, B. bataviensis, B. beijingensis, B. benzoevorans, B. beringensis, B. berkeleyi, B. beveridgei, B. bogoriensis, B. boroniphilus, B. borstelensis, B. brevis Migula, B. butanolivorans, B. canaveralius, B. carboniphilus, B. cecembensis, B. cellulosilyticus, B. centrosporus, B. cereus, B. chagannorensis, B. chitinolyticus, B. chondroitinus, B. choshinensis, B. chungangensis, B. cibi, B. circulans, B. clarkii, B. clausii, B. coagulans, B. coahuilensis, B. cohnii, B. composti, B. curdlanolyticus, B. cycloheptanicus, B. cytotoxicus, B. daliensis, B. decisifrondis, B. decolorationis, B. deserti, B. dipsosauri, B. drentensis, B. edaphicus, B. ehimensis, B. eiseniae, B. enclensis, B. endophyticus, B. endoradicis, B. farraginis, B. fastidiosus, B. fengqiuensis, B. firmus, B. flexus, B. foraminis, B. fordii, B. formosus, B. fortis, B. fumarioli, B. funiculus, B. fusiformis, B. galactophilus, B. galactosidilyticus, B. galliciensis, B. gelatini, B. gibsonii, B. ginsengi, B. ginsengihumi, B. ginsengisoli, B. globisporus, B. glucanolyticus, B. gordonae, B. gottheilii, B. graminis, B. halmapalus, B. haloalkaliphilus, B. halochares, B. halodenitrificans, B. halodurans, B. halophilus, B. halosaccharovorans, B. hemicellulosilyticus, B. hemicentroti, B. herbersteinensis, B. horikoshii, B. horneckiae, B. horti, B. huizhouensis, B. humi, B. hwajinpoensis, B. idriensis,

B. indicus, B. infantis, B. infernus, B. insolitus, B. invictae, B. iranensis, B. isabeliae, B. isronensis, B. jeotgali, B. kaustophilus, B. kobensis, B. kochii, B. kokeshiiformis, B. koreensis, B. korlensis, B. kribbensis, B. krulwichiae, B. laevolacticus, B. larvae, B. laterosporus, B. lautus, B. lehensis, B. lentimorbus, B. lentus, B. licheniformis, B. ligniniphilus, B. litoralis, B. locisalis, B. luciferensis, B. luteolus, B. luteus, B. macauensis, B. macerans, B. macquariensis, B. macyae, B. malacitensis, B. mannanilyticus, B. marinus, B. marisflavi, B. marismortui, B. marmarensis, B. massiliensis, B. megaterium, B. mesonae, B. methanolicus, B. methylotrophicus, B. migulanus, B. mojavensis, B. mucilaginosus, B. muralis, B. murimartini, B. mycoides, B. naganoensis, B. nanhaiensis, B. nanhaiisediminis, B. nealsonii, B. neidei, B. neizhouensis, B. niabensis, B. niacini, B. novalis, B. oceanisediminis, B. odysseyi, B. okhensis, B. okuhidensis, B. oleronius, B. oryzaecorticis, B. oshimensis, B. pabuli, B. pakistanensis, B. pallidus, B. pallidus, B. panacisoli, B. panaciterrae, B. pantothenticus, B. parabrevis, B. paraflexus, B. pasteurii, B. patagoniensis, B. peoriae, B. persepolensis, B. persicus, B. pervagus, B. plakortidis, B. pocheonensis, B. polygoni, B. polymyxa, B. popilliae, B. pseudalcaliphilu, B. pseudofirmus, B. pseudomycoides, B. psychrodurans, B. psychrophilus, B. psychrosaccharolyticus, B. psychrotolerans, B.

pulvifaciens, B. pumilus, B. purgationiresistens, B. pycnus, B. qingdaonensis, B. qingshengii, B. reuszeri, B. rhizosphaerae, B. rigui, B. ruris, B. safensis, B. salarius, B. salexigens, B. saliphilus, B. schlegelii, B. sediminis, B. selenatarsenatis, B. selenitireducens, B. seohaeanensis, B. shacheensis, B. shackletonii, B. siamensis, B. silvestris, B. simplex, B. siralis, B. smithii, B. soli, B. solimangrovi, B. solisalsi, B. songklensis, B. sonorensis, B. sphaericus, B. sporothermodurans, B. stearothermophilus, B. stratosphericus, B. subterraneus, B. subtilis, B. taeanensis, B. tequilensis, B. thermantarcticus, B. thermoaerophilus, B. thermoamylovorans, B. thermocatenulatus, B. thermocloacae, B. thermocopriae, B. thermodenitrificans, B. thermoglucosidasius, B. thermolactis, B. thermoleovorans, B. thermophilus, B. thermoruber, B. thermosphaericus, B. thiaminolyticus, B. thioparans, B. thuringiensis, B. tianshenii, B. trypoxylicola, B. tusciae, B. validus, B. vallismortis, B. vedderi, B. velezensis, B. vietnamensis, B. vireti, B. vulcani, B. wakoensis, B. weihenstephanensis, B. xiamenensis, B. xiaoxiensis, B. zhanjiangensis.

[0029]

Among others, *Bacillus* bacteria having alkali resistance are preferably *B. pumilus*. This is because spores of *B. pumilus* have resistance to UV exposure, γ-ray irradiation, dryness, hydrogen peroxide, chemical

disinfection, and other stresses, and are highly resistant to environmental stress, so that they can germinate and metabolize even after being retained in the hardened cement body for a long period. It is particularly preferable that the *Bacillus* bacteria having alkali resistance be *Bacillus subtilis var. natto*, and that biotin be further contained as a coenzyme.

[0030]

The term microorganisms as used herein means bacteria, yeast, fungi, protists, protozoa, and others.

[0031]

The microorganisms that generate carbon dioxide through metabolism may be an in-house cultured item or a commercial item. Examples of the commercial item include purely cultured *Bacillus subtilis var. natto*, volume: 50 ml (available from Miyagino Natto Seizosho).

[0032]

The proliferation inhibitor of bacteria having sulfur-oxidizing capability that is contained in the second component may be any substance, provided that it is capable of inhibiting the proliferation of bacteria having sulfur-oxidizing capability.

[0033]

Examples of the bacteria having a capability to oxidize sulfur and influencing the corrosion of the hardened cement body in sewer environments include sulfur-oxidizing bacteria *Acidithiobacillus albertensis*,

Acidithiobacillus thiooxidans, *Halothiobacillus neapolitanus*, *Thiomonas sp.*, *Acidithiobacillus ferrooxidans*. The bacteria having a capability to oxidize sulfur are not limited to sulfur-oxidizing bacteria, and also include bacteria such as iron-oxidizing bacteria (*Acidithiobacillus ferrooxidans*) that can oxidize sulfur compounds.

[0034]

Examples of the proliferation inhibitor of the bacteria having sulfur-oxidizing capability include nickel, tungsten, lead, zinc, cobalt, tin, compounds thereof, hydroxy acid compounds, and dicarboxylate compounds.

[0035]

The proliferation inhibitor of the bacteria having sulfur-oxidizing capability is preferably selected from the group consisting of nickel, nickel compounds, tungsten, tungsten compounds, dicarboxylate compounds, and mixtures thereof, from the viewpoint of maintaining the activity of the microorganisms that generate carbon dioxide through metabolism.

[0036]

Nickel and tungsten are provided as finely powdered metals (with an oxidation number of zero).

[0037]

Examples of the nickel compounds include water-soluble nickel compounds besides nickel oxides, nickel

phthalocyanine powder, nickel phthalocyanine derivative powder. The nickel phthalocyanine powder is powder of a compound in which unsubstituted phthalocyanine skeletons are coordinated with nickel atoms.

[0038]

The nickel phthalocyanine derivative powder is powder of a compound having one or more substituent atoms or one or more substituent atoms other than hydrogen atoms on benzene rings of nickel phthalocyanine skeleton molecules. The nickel phthalocyanine derivative powder is generally water-insoluble, and is scarcely soluble in acid.

[0039]

The substituent atom(s) or the substituent(s) of the nickel phthalocyanine derivative are as described in JP-B-3320074. Specific examples include halogen atoms; substituted or unsubstituted alkyl groups; substituted or unsubstituted alkoxy groups; substituted or unsubstituted thioalkoxy groups; alkyl group-substituted amino groups; carbocyclic aromatic amino groups; mono- or disubstituted amino groups; substituted or unsubstituted aryloxy groups; substituted or unsubstituted arylthio groups; and substituted or unsubstituted aromatic ring groups.

[0040]

Examples of the water-soluble nickel compounds include nickel sulfate, nickel nitrate, and nickel

chloride. These compounds are present as sparingly soluble nickel hydroxide in the hardened cement body.

[0041]

Examples of the tungsten compounds include alkali metal salts of tungstic acid, alkali metal hydrated salts of tungstic acid, tungsten (VI) oxide (WO_3), and tungsten (VI) oxide hydrate. Specific examples of the tungsten compounds include $W_{28}O_{58}$, Na_2WO_4, $CaWO_4$, $CaWO_4 \cdot H_2O$, $CaWO_4 \cdot 2H_2O$, and $5(NH_4)_2O \cdot 12WO_3 \cdot nH_2O$ (n = 0 to 5).

[0042]

The dicarboxylate compounds can be provided in the form of alkali metal salts of oxalic acid, succinic acid, malonic acid, glutaric acid, maleic acid, fumaric acid, citraconic acid, mesaconic acid, and itaconic acid.

[0043]

The proliferation inhibitor of bacteria having sulfur-oxidizing capability is blended into the liquid admixture for cement at a content of 0.01% by mass or more, preferably 0.05% by mass or more, based on the total content of the cement composition from the viewpoint of resistance to sulfuric-acid deterioration.

[0044]

The proliferation inhibitor of the bacteria having sulfur-oxidizing capability is blended into the liquid admixture for cement in an amount of 100 mmol per 1 CFU of the microorganisms (mmol/CFU) or less, preferably 50 mmol/CFU or less, from the viewpoint of maintaining the

activity of the microorganisms that generate carbon dioxide through metabolism.

[0045]

The liquid admixture for cement of the present invention contains a liquid dispersant. The liquid dispersant may be any liquid capable of dispersing the first component and the second component in the liquid admixture for cement, and water can generally be used. For further improvement of dispersibility, however, it is preferable to add a non-ionic water-soluble polymer (such as polyvinylpyrrolidone) as an auxiliary agent. The amount of the liquid dispersant is 50 to 95 parts by mass, preferably 70 to 90 parts by mass, per 100 parts by mass of the total liquid admixture for cement.

[0046]

When the liquid admixture for cement of the present invention is a two-component admixture in which the second component is an agent different from the first component, and both first component and second component are liquid, the content of the liquid dispersant is 50 parts by mass or more and 90 parts by mass or less based on a total of 100 parts by mass of the first component, and is 50 parts by mass or more and 90 parts by mass or less, based on a total of 100 parts by mass of the second component.

[0047]

Furthermore, the liquid admixture for cement of the present invention does not contain any finely powdered dispersant. Examples of such finely powdered dispersant include blast furnace slag fine powder. In the present invention, the blast furnace slag fine powder refers to blast-furnace-slag fine powder having a specific surface area of 7000 cm^2/g or more, the specific surface area being determined by the specific surface area test in accordance with 8.1 of JIS R 5201.
This is because it is considered that if the fine powder (blast furnace slag fine powder) having such a large specific surface area —that is, the fine powder having a small particle size— was used as the dispersant, the fine powder was more likely to contact the above-mentioned microorganisms that generate carbon dioxide through metabolism, thereby inhibiting the self-repairing performance of the hardened cement body caused by these microorganisms.

[0048]

Accordingly, the liquid admixture for cement of the present invention may contain the above-mentioned blast furnace slag fine powder having the specific surface area of less than 7000 cm^2/g, or may likewise contain particles having a specific surface area of less than 7000 cm^2/g.

[0049]

The liquid admixture for cement of the present invention preferably contains a nutrient source for the above-mentioned microorganisms that generate carbon dioxide through metabolism (hereinafter referred to as a microorganism nutrient source).

[0050]

Examples of the microorganism nutrient source that may be used include one or more of organic carbon sources (for example, sugars, starch, and lipids); inorganic carbon sources (for example, sodium carbonate); organic nitrogen sources (for example, amino acids, peptides, and proteins); organic compounds other than organic carbon sources (for example, vitamins); inorganic nitrogen sources (for example, ammonium salts and nitrates); and inorganic nutrient sources (for example, P, S, K, and Na).

[0051]

The liquid admixture for cement of the present invention may be a one-part admixture in which the first component is mixed with the second component, or may be a two-part admixture in which the first component and the second component are prepared as separate agents.

[0052]

However, it is preferable that the admixture be a two-component admixture in which the second component is an agent different from the first component, both first component and second component are liquid, and the first

component and the second component are mixed into the cement separately immediately before use. This is because since the proliferation inhibitor of the microorganisms having sulfur-oxidizing capability very rarely inhibits the activity of the microorganisms that generate carbon dioxide through metabolism, preparing the admixture as a two-component system makes it possible to avoid the contact of the microorganisms with the proliferation inhibitor at high concentration, thereby improving the storage stability of the liquid admixture for cement.

[0053]

If the liquid admixture for cement of the present invention is a two-component admixture, the microorganism nutrient source is preferably contained in the first component from the viewpoint of improving the storage stability of the microorganisms that generate carbon dioxide through metabolism.

[0054]

<Cement composition>

A cement composition of the present invention comprises the liquid admixture for cement of the present invention and cement.

[0055]

The cement to be blended into the cement composition of the present invention may be any cement. For example, one or more of Portland cement (JIS R5210), mixed cement

(JIS R5211, R5212, and R5213), and eco-cement can be used.

[0056]

Since the liquid admixture for cement is as described above, its detailed description is omitted here.

[0057]

The cement composition of the present invention may optionally contain a fine aggregate (for example, sand) or a coarse aggregate (for example, gravel). The cement composition may also optionally contain admixtures such as an AE agent; a water-reducing agent (for example, an AE water-reducing agent, a water-reducing agent, and a high-performance AE water-reducing agent); a superplasticizer; a setting/curing modifier; an accelerator; an antirust agent; and a waterproofing agent.

[0058]

The cement composition of the present invention may contain powder such as silica fume, blast-furnace slag powder, fly ash, or rice husk ash, which undergo hydration reaction under alkaline conditions in cement. These particles have a specific surface area of less than 7000cm^2/g, preferably less than 5000cm^2/g.

[0059]

Other admixtures such as polymers for mixing with cement and expansive additives, may also be further included.

[0060]

The cement composition of the present invention can be prepared, for example, by powder-mixing cement with other optional powder components, adding water, the liquid admixture for cement of the present invention, and other liquid components to this powder mixture, kneading the mixture to form paste, and mixing a fine aggregate and a coarse aggregate as needed.

[0061]

The cement composition of the present invention may be prepared by adding raw materials other than the liquid admixture for cement of the present invention and mixing and kneading them to obtain ready-mix concrete, then adding the liquid admixture for cement of the present invention to the ready-mix concrete, followed by mixing.

[0062]

<Hardened cement body>

The hardened cement body of the present invention can be obtained by applying the cement composition of the present invention to an object or by pouring the cement composition of the present invention into a mold, followed by curing for a predetermined period.

[0063]

<Method for producing hardened cement body>

Fig. 1 is a flow chart showing a method for producing the hardened cement body of the present invention. As shown in the figure, the method for producing the

hardened cement body of the present invention comprises a mixing step and a curing step.

[0064]

[Mixing step (S110)]

In this step, a liquid admixture for cement comprising a first component containing microorganisms that generate carbon dioxide through metabolism and a second component containing a proliferation inhibitor of bacteria having sulfur-oxidizing capability is added to a cement or a ready-mix concrete containing a cement, and mixed to obtain a cement composition.

[0065]

Since the microorganisms that generate carbon dioxide through metabolism, the proliferation inhibitor for sulfur-oxidizing bacteria, the liquid admixture for cement, the cement, and the cement composition have already been described above, their detailed descriptions are omitted here.

[0066]

The cement composition can be mixed by a well-known method. For example, mixing can be performed by powder-mixing the cement with the other powder components, adding water, the liquid admixture for cement of the present invention, and the liquid components after the powder mixing, and kneading the mixture.

[0067]

If the liquid admixture for cement of the present invention is added to ready-mix concrete containing cement, the liquid admixture of the present invention is added to ready-mix concrete that has been prepared by kneading all components except the liquid admixture. In this case, the liquid admixture of the present invention may be added to ready-mix concrete prepared in a batcher plant, or the liquid admixture of the present invention may be added through the charging port of an agitator car to ready-mix concrete loaded on the car.

[0068]

Alternatively, in this step, if the liquid admixture for cement is a two-component admixture, a liquid first component comprising the microorganisms that generate carbon dioxide through metabolism and a liquid second component comprising the proliferation inhibitor for sulfur-oxidizing bacteria are separately added to a cement or to a ready-mix concrete containing a cement, and then mixed to obtain the cement composition.

[0069]

In this case, the cement composition can be mixed, for example, by powder-mixing the cement with the other powder components, adding water and other liquid components after the powder mixing, separately adding the above-mentioned liquid first component and liquid second component, and then kneading the mixture

[0070]

When the liquid admixture is added to a ready-mix concrete containing a cement, the liquid first component and liquid second component are separately added to the ready-mix concrete that is free from the liquid admixture for cement of the present invention that is a two-component admixture and that has been prepared at a batcher plant or loaded in an agitator car.

[0071]

The thus obtained cement composition is suitably poured into a mold and compacted to be removed entrapped air. Compaction may be performed by striking the surface of the poured cement composition with a tamper, or by prodding the surface with a rod, or by applying vibration from a vibrator (the mixing step (S110) has been described above.).

[0072]

[Curing step (S120)]

In this step, the cement composition is cured to obtain the hardened product. The cement composition may be spread over a target object with a trowel and allowed to cure, or may be poured into a mold and cured. When the cement composition is fabricated into reinforced concrete, reinforcing bars are disposed in the mold beforehand.

[0073]

When the cement composition is poured into a mold, it is preferably compacted to remove entrapped air. Compaction is performed by striking the surface of the poured cement composition with a tamper, or by prodding the surface with a rod, or by applying vibration using a vibrator.

[0074]

The cement composition applied or poured into the mold is cured until the required compressive strength is obtained, thereby yielding the hardened cement body (the curing step (S120) has been described above.).

[0075]

As described above, according to the liquid admixture for cement of the present invention, the cement composition, the hardened cement body, and the method for producing a hardened cement body, no powdered dispersant is added; therefore, the powdered dispersant does not inhibit the activity of the microorganisms that generate carbon dioxide through metabolism. Because the admixture is prepared into a liquid admixture, mixing the admixture into cement improves the dispersibility of the microorganisms that generate carbon dioxide and the proliferation inhibitor for sulfur-oxidizing bacteria, enabling them to be uniformly dispersed throughout the hardened product obtained from the cement composition.

[0076]

Accordingly, the present invention enables imparting crack self-repairing properties and resistance to sulfuric acid deterioration uniformly to the entire hardened product of the cement composition. As a result, corrosion of the hardened cement body can be suppressed even in the presence of microorganisms that generate sulfuric acid in sewerage system facilities and others, and cracks can be self-repaired when they occur. This, in turn, reduces the maintenance cost and effort for the hardened cement body and extends its service life, thereby lowering the life-cycle cost, including both production and maintenance costs.

[0077]

In addition, extending the service life of the hardened cement body can also simultaneously provide an effect of reducing environmental burden.

Examples

[0078]

Although the present invention will be described hereinafter with reference to specific Examples, the present invention is not limited to these Examples.

[0079]

<1. Water leak confirmation test of concrete (hardened cement body)>

Hardened cement bodies were fabricated from cement compositions containing admixtures for cement comprising

microorganisms that generate carbon dioxide through metabolism and proliferation inhibitors of the bacteria having the capability to oxidize sulfur. Water leak tests were performed on these hardened cement bodies to confirm their self-repairing performance.

[0080]

1-1. Test 1

First, the results of the water leak test on hardened cement bodies fabricated from cement compositions containing powdered admixtures for cement, in which finely powdered dispersants (furnace slag fine powder) were used instead of liquid admixtures for cement, are described below.

[0081]

i) Preparation of cement compositions of Comparative Examples 1 to 2 and Reference Example 1

Ordinary Portland cement, a microorganism preparation (CHA-PLA, available from Basilisk Contracting BV), and a proliferation inhibitor 1 (Super Antimicrobial Agent, available from HAZAMA ANDO KOGYO CO., LTD.) were added and dry-mixed. The microorganism preparation was added based on the total mixture, that is, in an amount of 5 kg per 1 m^3 of the mixed powder of the ordinary Portland cement, the microorganism preparation, and Proliferation Inhibitor 1.

[0082]

Water (underground water) was mixed with this mixed powder to prepare a cement paste. A fine aggregate 1, a fine aggregate 2, and a coarse aggregate were further kneaded into the paste to obtain the cement composition of Comparative Example 1 having the blend 30-18-20N.

[0083]

Next, the raw materials were mixed and kneaded in the same composition and blending manner as in Comparative Example 1, except that the proliferation inhibitor 1 was replaced with the proliferation inhibitor 2 (Celeb Antimicrobial Agent, available from HAZAMA ANDO KOGYO CO., LTD.). This yielded the cement composition of Comparative Example 2.

[0084]

Raw materials were mixed and kneaded in the same blending manner as in Comparative Example 1, except that no proliferation inhibitor was added. This yielded a cement composition of Reference Example 1, which had the same composition as Comparative Example 1 except for the absence of a proliferation inhibitor.

[0085]

The compositions of the proliferation inhibitors 1 and 2 are shown in Table 1 below.

[0086]

[Table 1]

Component	Blending percentage (% by mass)	
	Super Antimicrobial Agent	Celeb Antimicrobial Agent
Nickel compound	7.5	-

Metal compound of dicarboxylic acid	-	7.5
Tungsten compound	7.5	7.5
Blast furnace slag fine powder	85.0	85.0

[0087]

ii) Fabrication of cracked samples of hardened cement bodies for water leak test

Fig. 2 is a schematic view showing a mold for forming a hardened cement body for a water leak test in Examples (Test 1). As shown, three molds A were prepared by sealing the bottom of a polyvinyl chloride pipe a having an inner diameter of w100 mm and a height of h80 mm with an acrylic plate b. The gap between the polyvinyl chloride pipe and the acrylic plate was filled with a caulking material c.

[0088]

From the open top of each mold A, the cement compositions of Comparative Examples 1 and 2 and Reference Example 1 were each poured into the corresponding polyvinyl chloride pipe a in a single layer. The compositions were tamped with a rod as appropriate, and the mold A was vibrated to remove entrapped air. Thereafter, the top surface was leveled and smoothed with a trowel.

[0089]

The cement compositions filled in the molds A were air-cured at room temperature for 28 days, thereby

yielding the hardened cement bodies of Comparative Examples 1 and 2 and Reference Example 1.

[0090]

After 28 days, the acrylic plate of each mold A was removed, and, as shown in Figure 3, a load was applied to the hardened cement body Z from both sides in the width direction using a compression testing machine B to forcibly generate a crack 12 in the hardened body Z. The crack width of the hardened body Z, measured with a crack gauge, was 0.4 mm for the hardened bodies of Reference Example 1 and Comparative Example 2, and 0.35 mm for the hardened body of Comparative Example 1.

[0091]

iii) Water leak test (evaluation of self-repairing performance)

Next, as shown in Figure 4, a mold a′ and a mold a″ having the same diameter as the mold a were connected to the upper and lower ends of the mold a, respectively, using a caulking material. A constricted portion d, having a smaller diameter than the mold a″ , was provided at the lower part of the mold a″ . The bottom surface of the constricted portion d was open, and a container f was arranged below the constricted portion d.

[0092]

A hole e having a diameter of around 10 mm was provided on the side surface of the mold a′ at a

position 50 mm above the joint between the mold a′ and the mold a.

[0093]

The hole e is provided to maintain a constant water head pressure on the hardened product Z in the mold a by allowing water poured from the mold a′ to be discharged through the hole e.

[0094]

Water was poured into the mold a′ from above at a rate such that the water level in the mold a′ remained constant at the height of the hole e; that is, water was poured so that the water introduced into the mold a′ was discharged through the hole e, thereby maintaining a constant water head pressure on the hardened product Z in the mold a. The leaked water g passing through the crack 12 in the hardened product Z was collected in the container f, and the amount of water leaked per day was measured. The results are shown in Fig. 5. In Fig. 5, the ordinate axis represents the amount of water leaked on each day (ml/day) from the start date to the end date of the water-leak test, and the abscissa axis represents the test day (day).

[0095]

As shown in the figure, although the water leak from the hardened cement body of Reference Example 1, to which only the microorganism preparation had been added, stopped around Day 40 from the start of the test, the

water leaks from the hardened cement bodies of Comparative Examples 1 and 2 did not stop even after approximately 45 days had passed from the test start. Moreover, the amounts of water leaked on the final test date, March 14, were still very large—namely, about 40% of the amounts leaked at the beginning of the test.

[0096]

It is considered that this is because the activity of the microorganisms in the microorganism preparation was inhibited by the finely powdered dispersant (blast-furnace slag fine powder) contained in the proliferation inhibitors 3 and 4 included in the cement compositions of Comparative Examples 1 and 2, resulting in a deterioration of the self-repairing performance.

[0097]

1-2. Test 2

The following describes the results of a water-leak test conducted on hardened cement bodies fabricated from cement compositions in which liquid admixtures for cement containing liquid dispersants were used in place of the finely powdered dispersant.

[0098]

i) Preparation of cement compositions of Examples 1 to 4, Reference Example 2, and Comparative Examples 3 to 4

Ordinary Portland cement (manufactured by UBE Cement Corporation), fine aggregate (Kakegawa sand; product

name: “Sand,” manufactured by Abekawa Development Co., Ltd.), and coarse aggregate (Saotome crushed stone; product name: “Crushed Stone,” manufactured by Satome Mining Co., Ltd.) were mixed at the unit cement amounts shown in Table 2. The mixture was dry-mixed in a mixer for 15 seconds to obtain a dry-mixed concrete. Various admixtures and water were then added in the amounts shown in Table 2, followed by mixing in the mixer for 30 seconds. After scraping off the materials adhering to the inner wall and blades of the mixer, the mixture was further mixed for 90 seconds and discharged from the mixer, thereby obtaining the cement compositions of Examples 1–4, Reference Example 2, and Comparative Examples 3–4.

[0099]

The blending conditions for these cement compositions are as follows.

[0100]

Water-to-cement ratio: 55%; fine aggregate percentage: 43.5%; target slump value: 12.5 ± 2.5 cm; target air content: 4.5 ± 0.5%.

[0101]

Among the admixtures, a culture solution of Bacillus subtilis var. natto was used, which was prepared as follows. A 100-μL portion of Bacillus subtilis var. natto (available from Miyagino Natto Seizosho) was inoculated into a test tube containing 5 mL of liquid medium, and

the test tube was subjected to shaking culture in a warm bath at 37°C at 100 rpm for 24 hours.

[0102]

[Table 2]

Case		cement content				Admixture (based on the cement content)				Admixture (based on the total mixture)		
Category	Identification	Water W (kg/m^3)	Cement C (kg/m^3)	Fine aggregate S (kg/m^3)	Coarse aggregate G (kg/m^3)	AE water-reducing agent*1 (CX)	AE agent*2 (CX)	defoaming agent*3 (CX)	Culture solution of *Bacillus subtilis var. natto* (first component) (WX)	CHA-PLA*4 (second component) (based on the total mixture)	Antimicrobial Agent S*5 (second component) (based on the total mixture)	Antimicrobial Agent C*6 (second component) (based on the total mixture)
Reference Example 2	Base	165	300	779	1038	0.25%	2A	-	-	-	-	-
Comparative Example 3	CHA-PLA	165	300	779	1038	0.20%	2A	2T	-	5	-	-
Example 1	CHA-PLA, Antimicrobial Agent S	165	300	779	1038	0.20%	2A	2T	-	5	0.6	-
Example 2	CHA-PLA, Antimicrobial Agent C	165	300	779	1038	0.20%	2A	2T	-	5	-	0.6
Comparative Example 4	*Bacillus subtilis var. natto*	165	300	779	1038	0.20%	2A	6T	5%	-	-	-
Example 3	*Bacillus subtilis var. natto* Antimicrobial Agent S	165	300	779	1038	0.20%	2A	6T	5%	-	0.6	-
Example 4	*Bacillus subtilis var. natto* Antimicrobial Agent C	165	300	779	1038	0.20%	2A	6T	5%	-	-	0.6

*1: Master Pozzolith No. 70, available from Pozzolith Solutions Ltd. *2: MasterAir 101, available from Pozzolith Solutions Ltd.

*3: MasterAir 404, available from Pozzolith Solutions Ltd.

*4: CHA-PLA, microorganism preparation available from Basilisk Contracting BV

*5: Mixed powder in which nickel sulfate hexahydrate and sodium tungstate dihydrate are mixed at a mass ratio of 4:5

*6: Mixed powder in which sodium tartrate dihydrate and sodium tungstate dihydrate are mixed at a mass ratio of 3:2

[0103]

Table 3 shows the fresh properties of the cement compositions of Examples 1 to 4, Reference Example 2, and Comparative Examples 3 and 4, as well as the compressive strengths of the hardened products (hardened cement bodies) obtained therefrom. The compressive strengths of the hardened products at material ages of Day 1, Day 5, and Day 28 were measured after curing underwater at 20°C.

[0104]

The conditions for measuring the fresh properties of the cement compositions shown in Table 3 and the compressive strengths of the hardened products obtained therefrom are as follows.

[0105]

The slump values were measured in accordance with JIS A 1101 (Method of test for slump of concrete).

[0106]

The air contents were measured in accordance with JIS A 1128 (Method of test for air content of fresh concrete by pressure method).

[0107]

The concrete temperatures (temperatures of fresh concretes) were measured in accordance with JIS A 1156 (Method of measurement for temperature of fresh concrete).

[0108]

The compressive strengths of the hardened cement bodies obtained were measured in accordance with JIS A 1108 (Method of test for compressive strength of concrete). The average value of the compressive strength of three specimens at each material age was adopted.

[0109]

The shape of the hardened cement bodies used for the compressive strength test, the method for producing the hardened cement bodies, and the curing conditions were in accordance with JIS A 1132 (Method of making and curing concrete specimens). Specifically, the hardened cement bodies were columnar specimens having a diameter of 100 mm and a height of 200 mm in accordance with Section 4.1 (Size of specimens); the production method was in accordance with Section 4.3 (Method of packing concrete); and curing was performed underwater at 20°C in accordance with Section 7 (Removal of mold and curing).

[0110]

[Table 3]

Case		Fresh properties			Compression strength		
Symbol	Identification	Slump (cm)	Air amount (%)	Concrete temperature (°C)	σ1 (N/mm^2)	σ5 (N/mm^2)	σ28 (N/mm^2)
Reference Example 2	Base	10.5	4.3	20.2	6.37	24.5	37.1
Comparative Example 3	CHA-PLA	13.5	4.6	20.5	4.32	25.4	37.8
Example 1	CHA-PLA, Antimicrobial Agent t S	13.0	4.0	20.2	4.57	25.8	40.3
Example 2	CHA-PLA, Antimicrobial Agent C	13.5	4.5	20.2	3.12	25.7	40.1
Comparative Example 4	*Bacillus subtilis var. natto*	11.0	4.7	19.6	6.31	27.0	41.9
Example 3	*Bacillus subtilis var. natto*, Antimicrobial Agent S	12.0	4.4	19.5	5.35	24.5	39.8
Example 4	*Bacillus subtilis var. natto*, Antimicrobial Agent C	14.0	4.6	19.6	3.87	24.5	40.1

[0111]

ii) Preparation of Cracked Samples of Hardened Cement Bodies for Water-Leak Test

Figure 6 is a flow chart illustrating the procedure for preparing cracked samples of hardened cement bodies for the water-leak test in Test 2 of the Examples. First, each of the cement compositions of Examples 1 to 4, Reference Example 2, and Comparative Examples 3 and 4 was poured into a cylindrical mold F having an inner diameter of 100 mm and a height of 200 mm, to form a specimen with a height of 100 mm, followed by wet-air

curing at 20°C and 90% RH (step i). After demolding, the specimen was further subjected to curing in standard water for 26 days (step ii). The specimen was then air-cured in a high-humidity thermostatic chamber at 20°C and 60% RH for 7 days (step iii). At the final stage of the air curing, the outer periphery of the hardened cement body was reinforced with a tape T (step iv). Finally, a load was applied from both sides in the width direction to forcibly generate a crack in the reinforced hardened cement body (step v).

[0112]

The cracked sample thus obtained was placed back into the mold F, and the peripheral surface of its bottom portion was sealed to the lower edge of the mold F with a sealing material, thereby preparing a specimen S to be subjected to the water-leak test (step vi).

[0113]

iii) Water leak test (evaluation of self-repairing performance)

Fig. 7 is a schematic view illustrating the water leak test related to Test 2 of Examples. As shown in the figure, the specimen S prepared in step vi was fixed in position, for example, with an unillustrated clamp, and a water-receiving container V was placed beneath it. Then, 700 mL of water was poured onto the top of the cracked hardened cement body from above the mold F. After 10 minutes, the amount of water that had leaked into the

water-receiving container V was measured using an electronic balance M.

[0114]

The water-leak test was performed on the day following the 7-day air curing in step iii (measurement day = 1 day). The specimen was then air-cured in a high-humidity thermostatic chamber at 20°C and 60% RH for 3 days from the day after the measurement day (air curing = 3 days), followed by curing in standard water for an additional 3 days (curing in standard water = 3 days). This total period of one week was defined as one test cycle, and 12 test cycles were repeated. The total amount of water leaked in all water-leak tests was calculated and defined as the cumulative water permeation volume (mL) of the specimen. Figure 8 shows the results. In Figure 8, the ordinate axis represents the cumulative water permeation volumes of the specimens (mL), and the abscissa axis represents the crack widths of the specimens (mm).

[0115]

As shown in the figure, Comparative Examples 3 and 4, which contain only the microorganisms that generate carbon dioxide through metabolism, exhibit a high crack self-repairing effect as compared with Reference Example 2, which contains neither the antimicrobial agent nor the microorganisms that generate carbon dioxide through metabolism. Accordingly, the cumulative water permeation volumes of Comparative Examples 3 and 4 are low.

[0116]

Similarly, because the cumulative water permeation volumes of Examples 1 to 4—which contain both the antimicrobial agent and the microorganisms that generate carbon dioxide through metabolism—are low, it has been confirmed that when water is used as the dispersant instead of the finely powdered dispersant (blast-furnace slag fine powder), the antimicrobial agent does not affect the growth of the microorganisms that generate carbon dioxide through metabolism.

[0117]

When Examples 1 and 2, which use CHA-PLA as the microorganisms that generate carbon dioxide through metabolism, are compared with Examples 3 and 4, which use Bacillus subtilis var. natto as the microorganisms, the cumulative water permeation volumes of Examples 3 and 4 are lower. This demonstrates that Bacillus subtilis var. natto exhibits a higher self-repairing effect than CHA-PLA.

Claims

[Claim 1]

A liquid admixture for cement, comprising:

a first component comprising microorganisms that generate carbon dioxide through metabolism; and

a second component comprising a proliferation inhibitor of bacteria having a capability to oxidize sulfur.

[Claim 2]

The liquid admixture for cement according to claim 1, wherein

the second component is different from the first component, both the first component and the second component are liquid, and

the admixture is a two-component admixture in which the first component and the second component are separately mixed into a cement directly before use.

[Claim 3]

The liquid admixture for cement according to claim 1, wherein the microorganisms are selected from *Bacillus* bacteria having alkali resistance.

[Claim 4]

The liquid admixture for cement according to claim 3, wherein the *Bacillus* bacteria having alkali resistance are *Bacillus subtilis var. natto*, and biotin is further comprised as a coenzyme.

[Claim 5]

The liquid admixture for cement according to claim 3, wherein the *Bacillus* bacteria having alkali resistance are *Bacillus pumilus*.

[Claim 6]

The liquid admixture for cement according to claim 1, wherein the proliferation inhibitor of the bacteria having the capability to oxidize sulfur is selected from the group consisting of nickel, nickel compounds, tungsten, tungsten compounds, dicarboxylate compounds, and mixtures thereof.

[Claim 7]

A cement composition comprising the liquid admixture for cement according to any one of claims 1 to 6 and a cement.

[Claim 8]

A hardened cement body obtained by curing the cement composition according to claim 7.

[Claim 9]

A method for producing a hardened cement body, comprising:

a mixing step of adding a liquid admixture for cement comprising a first component containing microorganisms that generate carbon dioxide through metabolism and a second component containing a proliferation inhibitor of bacteria having sulfur-oxidizing capability to a cement or a ready-mix concrete comprising a cement, and mixing them to yield a cement composition; or, when the liquid

admixture for cement is a two-component admixture, separately adding a liquid first component containing microorganisms that generate carbon dioxide through metabolism and a liquid second component containing a proliferation inhibitor of bacteria having sulfur-oxidizing capability to a cement or a ready-mix concrete comprising a cement, and mixing them to yield a cement composition; and

a curing step of curing the cement composition to obtain a hardened cement body.