

DESCRIPTION

Title of Invention

METHOD FOR PREVENTING METAL CORROSION IN WATER
SYSTEM AND CHEMICAL AGENT FOR ADDITION TO WATER
SYSTEM

Technical Field

[0001] The present invention relates to a method for preventing metal corrosion in a water system and a chemical agent for addition to a water system. More particularly, the present invention relates to a method for preventing metal corrosion in a water system by using a nitrite-based anticorrosive, wherein reduction of nitrite ions in the water system caused by nitrite-oxidizing bacteria is suppressed, and a chemical agent for addition to a water system used for the method.

Background Art

[0002] A nitrite-based anticorrosive is an anode type inhibitor that is utilized as an anticorrosive for various metals in a water system, such as iron, copper, aluminum and zinc. The nitrite-based anticorrosive exhibits a strong corrosion suppressing effect on a metal by oxidizing the metal to form an anticorrosive coating film and thereby passivating the metal surface, so that it is widely used. For example, it is widely used for preventing or suppressing corrosion of metal parts in a water system in industrial fields such as fields of building air-conditioning facilities, air-conditioned facilities, factories, and transport piping.

[0003] In a water system, however, various autotrophic bacteria called nitrite-oxidizing bacteria, which grow using energy given when nitrite ions are oxidized to nitrate ions, may be present. Furthermore, nitrite-oxidizing bacteria may also contaminate the water system from the atmosphere.

It is known that nitrite-oxidizing bacteria grow in a water system where oxygen is present under the temperature conditions of about 5 to 50°C.

If nitrite-oxidizing bacteria grow in a water system where anticorrosion treatment with a nitrite-based anticorrosive such as a nitrite is carried out, nitrite ions in the water system are oxidized to nitrate ions and are consumed, therefore, they are reduced, and an anticorrosion effect is impaired.

[0004] On this account, as a method for suppressing growth of nitrite-oxidizing bacteria in a water system and thereby suppressing consumption and reduction of nitrite ions, a method in which various antibacterial agents are added to the system has been proposed.

In Patent Literature 1, a method in which alkyl dimethylbenzylammonium chloride is added to a water system together with a nitrite-based anticorrosive is disclosed.

In Patent Literature 2, a method in which nitrosohydroxylamine or its salt is allowed to be present in a water system as an antibacterial agent against nitrite-oxidizing bacteria is disclosed.

Moreover, a method in which an antibacterial agent such as sodium hypochlorite or 5-chloro-2-methyl-4-isothiazolin-3-one (Cl-MIT) is added to a water system is also thought.

[0005] On the other hand, there has been also proposed a method for suppressing growth of nitrite-oxidizing bacteria in a water system and thereby suppressing consumption and reduction of nitrite ions, wherein an antibacterial agent is not used.

In Patent Literature 3, a method in which not only is air in a system replaced with nitrogen but also nitrogen is dissolved in a water system to reject dissolved oxygen in nitrite-oxidizing bacterial growth environment at a water temperature of 5 to 50°C is disclosed.

In Patent Literature 4, a method in which a germicidal lamp is provided in a system is disclosed.

Furthermore, a method in which in order to limit dissolution of oxygen into water in a system and to reduce a dissolved oxygen concentration, a gas-liquid contact surface is covered with an oxygen dissolution shield is thought, as shown in Patent Literature 5.

[0006] From the viewpoints of prevention of corrosion of various metals, safety, human health, environmental response, diversion to daily use water at the time of disaster or the like, etc., the method of adding an antibacterial agent against nitrite-oxidizing bacteria cannot be adopted when use of an antibacterial agent is not preferred. Moreover, even when this method is adopted, the antibacterial agent is decomposed with time to decrease the effect, therefore, the nitrite-oxidizing bacteria grow unexpectedly, and nitrite ions are consumed, so that the anticorrosion effect is not exhibited sometimes. In order to prevent this, addition of the antibacterial agent needs to be repeated periodically, and in this case, labor and cost therefor are required.

Thus, it is difficult to suppress reduction of nitrite ions in a water system caused by nitrite-oxidizing bacteria, by the addition of an antibacterial agent.

[0007] In the method in which contact between oxygen and nitrite-oxidizing bacteria in a water system is prevented, it is difficult to completely carry out rejection of oxygen in a system or shielding of a system, and inclusion of a slight amount of oxygen into the system cannot be prevented, so that reduction of nitrite ions due to consumption in the water system cannot be suppressed though the reduction is slow. In addition, in a water system in which rejection of oxygen or shielding is difficult, such as one having a water tank with a large gas-liquid contact area, or in a water system in which there are many opportunities for contact with the outside air, such as one having an open type cooling tower, this method is hard to apply.

[0008] Under the above circumstances, in a water system where presence of nitrite-oxidizing bacteria is confirmed or contamination of nitrite-oxidizing bacteria is predicted, use of the nitrite-based anticorrosive has been frequently avoided conventionally.

Citation List

Patent Literature

[0009] PTL1: JPS 49-27019 B

PTL2: JPS 55-89202 A

PTL3: JPS 60-187683 A

PTL4: JPS 58-92999 A

PTL5: JP 2000-319953 A

Summary of Invention

[0010] It is an object of the present invention to provide a method for preventing metal corrosion in a water system by using a nitrite-based anticorrosive, wherein reduction of nitrite ions in the water system caused by nitrite-oxidizing bacteria is suppressed.

It is another object of the present invention to provide a chemical agent for addition to a water system, which is capable of suppressing reduction of nitrite ions in a water system when metal corrosion in the water system is prevented by using a nitrite-based anticorrosive.

Solution to Problem

[0011] The present inventor has found that the above objects are achieved by using a nitrite-based anticorrosive and a water-soluble tungstic acid compound in combination, and he has completed the present invention.

A water-soluble tungstic acid compound is used as an anticorrosive in a water system. However, it has not yet been known that the water-soluble tungstic acid compound is useful as a chemical agent for suppressing oxidation of nitrite ions to nitrate ions in a water system, particularly in a water system where nitrite-oxidizing bacteria are present or contamination of nitrite-oxidizing bacteria is predicted.

[0012] The gist of the present invention is as follows.

[0013] [1] A method for preventing metal corrosion in a water system, comprising adding a nitrite-based anticorrosive and a water-soluble tungstic acid compound to a water system where nitrite-oxidizing bacteria are present or contamination of nitrite-oxidizing bacteria is predicted.

[0014] [2] The method for preventing metal corrosion in a water system according to [1], wherein a concentration of 16S rDNA derived from nitrite-oxidizing bacteria in the water system is 1.0×10^2 copies/mL or more.

[0015] [3] The method for preventing metal corrosion in a water system according to [1] or [2], wherein a nitrite ion concentration in the water system is 10 mg-N/L or more.

[0016] [4] The method for preventing metal corrosion in a water system according to any one of [1] to [3], wherein the water-soluble tungstic acid compound is added in such a manner that a tungstic acid ion concentration in the water system becomes 0.1 mg-W/L or more.

[0017] [5] The method for preventing metal corrosion in a water system according to any one of [1] to [4], wherein the water system is a cooling water system.

[0018] [6] The method for preventing metal corrosion in a water system according to any one of [1] to [4], wherein the water system is a closed cooling water system.

[0019] [7] The method for preventing metal corrosion in a water system according to any one of [1] to [4], wherein the water system is an open cooling water system.

[0020] [8] The method for preventing metal corrosion in a water system according to any one of [1] to [4], wherein the water system is a cooling water system during storage after stopping of cooling water facility operation.

[0021] [9] The method for preventing metal corrosion in a water system according to any one of [1] to [8], wherein the water-soluble tungstic acid compound is added in an amount corresponding to a tungsten

concentration 300 times or more higher than a molybdenum concentration in the water system in terms of a weight ratio.

[0022] [10] A chemical agent for addition to a water system, suppressing oxidation of nitrite ions to nitrate ions in a water system and comprising a water-soluble tungstic acid compound.

Advantageous Effects of Invention

[0023] According to the present invention, in a method for preventing metal corrosion in a water system by using a nitrite-based anticorrosive, reduction of nitrite ions in the water system caused by nitrite-oxidizing bacteria can be suppressed, and an anticorrosion effect due to the nitrite-based anticorrosive can be stably maintained over a long period of time.

Brief Description of Drawings

[0024] [Fig. 1] Fig. 1 is a system diagram showing a circulating water flow test device used in the examples.

[Fig. 2] Fig. 2 shows photographs of test pieces on the 70th day after the start of the test in Example 5.

Description of Embodiments

[0025] Hereinafter, embodiments of the present invention will be described in detail.

[0026] [Method for preventing metal corrosion in water system]

A water system to which the method for preventing metal corrosion in a water system of the present invention is applied (sometimes referred to as a "target water system of the present invention" hereinafter) is a

water system where nitrite-oxidizing bacteria are present or contamination of nitrite-oxidizing bacteria is predicted.

Examples of the nitrite-oxidizing bacteria include, but are not limited to, one or more of various bacterial species, such as *Nitrobacter*, *Nitrospira* and *Nitrococcus*.

[0027] The target water system of the present invention is a water system where nitrite-oxidizing bacteria have been already contained or nitrite-oxidizing bacteria may be contained in the future.

For example, the following water systems (1) to (3) can be mentioned.

(1) Water system in which nitrite-oxidizing bacteria are contained, and reduction of nitrite ions and increase in nitrate ions are observed.

(2) Water system in which nitrite-oxidizing bacteria are contained, and reduction of nitrite ions and increase in nitrate ions are predicted in the future.

(3) Water system in which nitrite-oxidizing bacteria are not contained, but in the future, nitrite-oxidizing bacteria may contaminate the water system from the outside air or the like that is in contact therewith.

[0028] The presence or absence of the nitrite-oxidizing bacteria in a water system can be confirmed qualitatively and quantitatively by, for example, MPN method, antibody method or quantitative PCR method.

The amount of the nitrite-oxidizing bacteria present in a water system may be, for example, 1.0×10^2 copies/mL or more, 1.0×10^3 copies/mL or more, or 1.0×10^4 to 1.0×10^5 copies/mL, in terms of a 16S rDNA concentration in the quantitative PCR method.

[0029] The reduction of nitrite ions and increase in nitrate ions in a water system can be confirmed by known chemical analysis methods, etc.

[0030] The target water system of the present invention may be any of a closed circulation cooling water system, a semi-closed circulation water system, and an open circulation cooling water system. These water systems are, for example, thermal storage cold and hot water systems or cooling water systems, which are closed or semi-closed circulation water systems in air-conditioned facilities, air-conditioning facilities, plants, engines, etc., or open circulation water systems equipped with cooling towers. The target water system of the present invention is preferably a cooling water system, and more preferably a closed cooling water system.

[0031] The pH of the target water system of the present invention is not particularly limited, but it is, for example, pH 5.5 to 9.5 (weakly acidic to weakly alkaline), and preferably pH 6.5 to 8.5 (nearly neutral to weakly alkaline).

The temperature of the target water system of the present invention is 55°C or lower, preferably 0 to 50°C, particularly preferably 10 to 40°C, and still more preferably 20 to 30°C. The nitrite-oxidizing bacteria thermally die out at temperatures exceeding 55°C, and particularly 60°C or higher.

[0032] The target water system of the present invention may be any of a highly concentrated water system, a lowly concentrated water system, and an unconcentrated water system. Examples of such water systems include, but are not limited to, a lowly concentrated water system having a concentration ratio of less than two times, preferably a concentration ratio of 1.9 times or less, and an unconcentrated water system, which are not highly concentrated water systems having a concentration ratio of two times or more.

[0033] In order that the nitrite-based anticorrosive may exhibit an anticorrosion effect, the nitrite ion concentration in water needs to be always maintained to be an effective concentration. Therefore, the target water system of the present invention is economically preferably a system in which water in the system does not need to be discharged (blown) or a system in which the amount of water discharged is small. However, the target water system of the present invention is not limited to such a water system.

[0034] The target water system of the present invention may be a cooling water system during circulation operation, or may be a cooling water system at rest or in storage. For example, the target water system may be a cooling water system during storage after stopping of cooling water facility operation.

[0035] The target water system of the present invention may be a water system containing a dispersant, or may be a water system containing no dispersant.

[0036] The metal that becomes an anticorrosion target is, for example, one or more metals selected from the group consisting of iron (carbon steel), stainless steel, copper, a copper alloy, zinc, aluminum, and an aluminum alloy. Preferable is one or more metals selected from the group consisting of carbon steel, copper, a copper alloy, and zinc. These metals are used as materials of pipes in a water system, a heat exchanger, a refrigerating machine, an air conditioner, a tank, etc.

[0037] The nitrite-based anticorrosive is not particularly limited as long as it contains a water-soluble nitrite compound. The nitrite-based anticorrosive is, for example, one or more selected from the group consisting of water-soluble nitrites and nitrous acid, such as a nitrous

acid alkali metal salt and ammonium nitrite. Preferable is one or more nitrites selected from the group consisting of sodium nitrite, potassium nitrite and ammonium nitrite.

[0038] The nitrite-based anticorrosive is added in such an amount that the nitrite ion concentration in the target water system of the present invention usually becomes 10 mg-N/L or more, preferably 20 to 500 mg-N/L, more preferably 50 to 200 mg-N/L, and still more preferably 100 to 200 mg-N/L.

[0039] In order to adjust the nitrite ion concentration in the water system to a required concentration, the nitrite-based anticorrosive can be added at an arbitrary point in time. The timing for addition of the nitrite-based anticorrosive is, for example, one or more of the following (1) to (6).

(1) at the time of construction of water system (at the time of start-up)

(2) at the time of start of steady operation

(3) at the time of inspection

(4) at the time determined based on measurement results of nitrite ion concentrations

(5) at the time after a lapse of a certain period of time since the last introduction

(6) at the time of storage after stopping of operation of water system

[0040] The water-soluble tungstic acid compound is not particularly limited as long as it includes a tungstic acid compound capable of generating tungstate ions when added to a water system. The water-soluble tungstic acid compound is, for example, one or more selected from the group consisting of an alkali metal tungstate, ammonium tungstate, and hydrates thereof. Preferable is one or more selected from the group

consisting of lithium tungstate, sodium tungstate, potassium tungstate, ammonium tungstate, and hydrates thereof.

[0041] In the present invention, the water-soluble tungstic acid compound is added to a water system using a nitrite-based anticorrosive in order to suppress oxidation of nitrite ions to nitrate ions caused by nitrite-oxidizing bacteria.

[0042] The water-soluble tungstic acid compound can be added to the water system singly or together with other components at an arbitrary time. The timing for addition of the water-soluble tungstic acid compound is, for example, one or more of the following (1) to (9).

- (1) at the time of construction of water system (at the time of start-up)
- (2) at the time of start of steady operation of water system
- (3) at the time of inspection of water system
- (4) at the time calculated as the timing for addition based on measurement results of nitrite ion concentrations in water system
- (5) at the time after a lapse of a certain period of time since the last introduction
- (6) at the time of storage after stopping of operation of water system
- (7) at the time determined as the timing for addition based on measurement results of nitrite ion concentrations in water system
- (8) at the time of addition of nitrite-based anticorrosive to adjust nitrite ion concentration in water system
- (9) at the time when 16S rDNA concentration of nitrite-oxidizing bacteria in water system based on arbitrary fixed amount method becomes a predetermined value

[0043] The water-soluble tungstic acid compound is added in such an amount that the tungstic acid ion concentration in the target water

system of the present invention usually becomes 0.1 mg-W/L or more, preferably 0.1 to 500 mg-W/L, more preferably 0.1 to 200 mg-W/L, still more preferably 0.5 to 100 mg-W/L, particularly preferably 1.0 to 50 mg-W/L, and most preferably 5 to 20 mg-W/L.

[0044] The addition amount of the water-soluble tungstic acid compound can be adjusted according to the types and amounts of various ions present in the water system other than the tungstic acid ions. In one example, when a slight amount of molybdenum or molybdic acid is contained in the water system, the water-soluble tungstic acid compound is added in such an amount that the tungstic acid ion concentration becomes 0.1 mg-W/L or more, and in such an amount that the tungsten concentration becomes 300 times or more, preferably 500 times or more, more preferably 500 to 20000 times, and still more preferably 700 to 15000 times, higher than the molybdenum concentration in the water system, in terms of a weight ratio.

[0045] Control of the addition amount of the water-soluble tungstic acid compound based on the molybdenum concentration is carried out for the following reasons.

Since a nitrite oxidase system held by the nitrite-oxidizing bacteria contains an enzyme having molybdenum as an active center, molybdenum is a micronutrient necessary for growth of the nitrite-oxidizing bacteria. It is thought that tungsten inhibits the enzyme system as an analogue of molybdenum, so that the ratio between tungsten and molybdenum needs to be taken into consideration.

[0046] The ratio of the tungstic acid ion concentration to the nitrite ion concentration in the water system is, for example, 1/5000 to 500/100, preferably 1/2000 to 400/100, more preferably 1/400 to 200/100, still more

preferably 1/200 to 100/100, and particularly preferably 1/40 to 40/100, in terms of tungstic acid ion concentration (mg-W/L)/nitrite ion concentration (mg-N/L).

[0047] In the present invention, the nitrite-based anticorrosive and the water-soluble tungstic acid compound may be added to the water system simultaneously, or may be added separately. When the nitrite-based anticorrosive is added, all of it may be added at a time, or part of it may be added stepwise. Also when the water-soluble tungstic acid compound is added, it can be added in the same manner as above. Moreover, the order of the addition of the nitrite-based anticorrosive and the water-soluble tungstic acid compound is not particularly limited. Appropriate amounts of both the components may be added alternately.

[0048] To the target water system of the present invention, known additives can be added as needed, in addition to the nitrite-based anticorrosive (nitrite ions) and the water-soluble tungstic acid compound (tungstate ions). Examples of such additives include a dispersant, an antibacterial agent, a scale inhibitor, and a pH adjuster. Such additives may be added simultaneously with the addition of the nitrite-based anticorrosive (nitrite ions) and the water-soluble tungstic acid compound (tungstate ions), or after the treatment, or they may be added before the treatment with the nitrite-based anticorrosive (nitrite ions) and the water-soluble tungstic acid compound (tungstate ions) is started.

[0049] [Chemical agent for addition to water system]

The chemical agent for addition to a water system of the present invention is used in the method for preventing metal corrosion in a water system of the present invention.

Here, the water-soluble tungstic acid compound and the water system are the same as the water-soluble tungstic acid compound and the water system described in the above [Method for preventing metal corrosion in water system], respectively.

[0050] In the chemical agent for addition to a water system of the present invention, the components described in the above [Method for preventing metal corrosion in water system], such as a nitrite-based anticorrosive, a dispersant, an antibacterial agent, a scale inhibitor, and a pH adjuster, may be contained. The blending amounts of these components can be appropriately adjusted according to the nitrite ion concentration, the molybdenum concentration, etc. in the target water system of the present invention.

Regarding the timing for addition of the chemical agent for addition to a water system of the present invention to the water system, etc., the timing for addition of the nitrite-based anticorrosive and the water-soluble tungstic acid compound described in the above [Method for preventing metal corrosion in water system] can be adopted.

Examples

[0051] The present invention will be described in more detail with reference to examples, but the present invention is in no way limited to these examples.

[0052] [Example 1]

Water was sampled from an air-conditioning thermal storage cooling water system in Tokyo, the cooling water system being a closed cooling water system in which water treatment with a nitrite-based anticorrosive was being carried out. The concentration of 16S rDNA

derived from Nitrobacter in the present water was examined by a quantitative PCR method, and as a result, it was 1.2×10^4 copies/mL, and oxidation of nitrite ions to nitrate ions utilizing oxygen dissolved from the gas-liquid contact part was always observed.

[0053] In each of test tubes, 5 mL of the sampled water was introduced, then sodium tungstate dihydrate was added in such a manner that the final concentration became 0 to 100 mg-W/L, then shaking was carried out under the aerobic conditions at 25°C and 200 rpm, and nitrite ion concentrations were examined for 14 days. The nitrite ion concentrations were colorimetrically determined using "Digital Pack Test High-Concentration Nitrite Reagent" manufactured by KYORITSU CHEMICAL-CHECK Lab., Corp. In the experiment, the sodium tungstate concentration was examined in two systems, and an average value of the two systems was calculated and taken as a result.

[0054] The results are set forth in Table 1.

In the sodium tungstate dihydrate-free system, marked consumption of nitrite ions due to conduction of active supply of oxygen under the aerobic conditions was observed. On the other hand, it was found that in the system in which sodium tungstate dihydrate had been added in such an amount that the final concentration became 1 mg-W/L or more, consumption of nitrite ions was suppressed. In the system in which the final concentration was 5 mg-W/L or more, it was possible to almost completely suppress consumption of nitrite ions.

[0055] [Table 1]

		Addition amount of sodium tungstate dihydrate (final concentration (mg-W/L))					
		0	1	5	20	50	100
Nitrite ion concentration (mg-N/L)	0 day after	61.8	61.8	61.8	61.8	61.8	61.8
	3 days after	26.7	60.3	61.8	59.4	61.0	61.4
	5 days after	1.3	53.0	59.3	59.6	60.2	59.7
	7 days after	1.3	51.4	63.3	61.4	60.7	63.3
	14 days after	0.9	28.6	57.7	66.6	65.6	65.0

[0056] [Example 2]

In each of three beakers, 1 L of water sampled from an air-conditioning thermal storage cooling water system in Tokyo was introduced, the cooling water system being a closed cooling water system in which water treatment with a nitrite-based anticorrosive was being carried out, and to each of the beakers, common salt was added in such a manner that the final concentration became 100 mg-Cl/L. The nitrite ion concentration in the water was 71.2 mg-N/L.

Among the three beakers, to a beaker of a "tungsten-loaded system", sodium tungstate dihydrate was added in such a manner that the final concentration became 5 mg-W/L. To a "molybdenum-loaded system", sodium molybdate dihydrate was added in such a manner that the final concentration became 5 mg-Mo/L. The remaining one beaker was taken as an "additive-free system", and the above substances were not added thereto.

[0057] A carbon steel test piece was immersed in the water in each of the beakers, thereafter, stirring was carried out at 300 rpm using a

magnetic stirrer to promote the reaction at 20°C, and the nitrite ion concentrations for 32 days were colorimetrically determined using "Digital Pack Test High-Concentration Nitrite Reagent" manufactured by KYORITSU CHEMICAL-CHECK Lab., Corp.

The nitrite ion concentrations of the "additive-free system" and the "molybdenum-loaded system" each became a detection limit (less than 1.0 mg-N/L) after 11 days, but in the "tungsten-loaded system", 58.9 mg-N/L was maintained even after 32 days.

The test pieces after 32 days from the start of the reaction were observed, and as a result, in the "tungsten-loaded system", rust was not observed at all, but in the "additive-free system" and the "molybdenum-loaded system", rust was locally observed.

[0058] [Table 2]

		Additive-free system	Tungsten-loaded system	Molybdenum-loaded system
Nitrite ion concentration (mg-N/L)	0 day after	71.2	71.2	71.2
	4 days after	26.8	65.3	28.2
	11 days after	Less than 1.0	64.1	Less than 1.0
	17 days after	Less than 1.0	61.2	Less than 1.0
	21 days after	Less than 1.0	63.0	Less than 1.0
	28 days after	Less than 1.0	54.5	Less than 1.0
	32 days after	Less than 1.0	58.9	Less than 1.0

[0059] The iron ion concentrations in water after 32 days from the start of the reaction were simply determined using "Pack Test Iron" manufactured by KYORITSU CHEMICAL-CHECK Lab., Corp.

The results are set forth in Table 3.

In the "tungsten-loaded system", the concentration was 0.2 mg/L and was not different from the concentration at the time of the start of the reaction, but in the "additive-free system" and the "molybdenum-loaded system", the concentration was 5.0 mg-Fe/L.

[0060] [Table 3]

	Rust of test piece	Iron ion concentration in water (mg-Fe/L)
Additive-free system	Yes	5.0
Tungsten-loaded system	No	0.2
Molybdenum-loaded system	Yes	5.0

[0061] From the above results, it was found that in the "additive-free system" and the "molybdenum-loaded system", nitrite ions were consumed, and the anticorrosion effect was decreased, and as a result, corrosion of carbon steel occurred and elution of iron ions was observed, but in the "tungsten-loaded system", an anticorrosion effect due to nitrite ions was maintained, and elution of iron ions was suppressed. From this, it can be seen that although tungsten and molybdenum were homologous elements, anticorrosion due to the nitrite-based anticorrosive was able to be maintained in the case of sodium tungstate dihydrate, but in the case of sodium molybdate dihydrate, an anticorrosion effect due to the nitrite-based anticorrosive was impaired, and corrosion and elution of iron ions accompanying it were not able to be suppressed.

[0062] [Example 3]

In each of test tubes, 5 ml of water sampled from an air-conditioning thermal storage cooling water system in Tokyo was introduced, the cooling water system being a closed cooling water system

in which water treatment with a nitrite-based anticorrosive was being carried out, and to each of the test tubes, sodium tungstate dihydrate was added in such a manner that the final concentration became 10 mg-W/L. Further, sodium molybdate dihydrate was added in such a manner that the final concentration became 0 to 300 $\mu\text{g-Mo/L}$, then shaking was carried out under the conditions of 25°C and 200 rpm, and nitrite ion concentrations were examined until 19 days after. The nitrite ion concentrations were colorimetrically determined using "Digital Pack Test High-Concentration Nitrite Reagent" manufactured by KYORITSU CHEMICAL-CHECK Lab., Corp. Furthermore, also in the case where neither sodium tungstate dihydrate nor sodium molybdate dihydrate was added, the nitrite ion concentrations were examined until 19 days after. [0063] The results are set forth in Table 4.

When sodium molybdate dihydrate of 30 $\mu\text{g-Mo/L}$ or more was added, there was observed a phenomenon that the nitrite ion consumption suppressing effect due to sodium tungstate dihydrate decreased.

In Example 3, it was found that setting the addition amount of sodium molybdate dihydrate to such an amount that the final concentration became at least 10 $\mu\text{g/L}$ or less in order to maintain the nitrite ion consumption suppressing effect due to sodium tungstate dihydrate was particularly effective. It is thought that a tungstic acid concentration 1000 times or more higher than the molybdic acid concentration in water in terms of a metal weight ratio is particularly preferable.

[0064] [Table 4]

Addition amount of sodium tungstate dihydrate (final concentration (mg-W/L))		0	10	10	10	10	10	10	10
Addition amount of sodium molybdate dihydrate (final concentration (μg-Mo/L))		0	0	1	3	10	30	100	300
Nitrite ion concentration (mg-N/L)	0 day after	81.3	81.3	81.3	81.3	81.3	81.3	81.3	81.3
	4 days after	45.8	75.4	73.1	74.6	74.0	72.2	62.0	45.8
	12 days after	8.6	83.6	80.3	79.5	79.1	65.7	40.6	16.3
	19 days after	0.8	77.1	78.1	75.6	73.9	48.8	13.5	4.6

[0065] [Reference Example 1]

In each of three beakers, 1 L of dechlorinated city water of Nogi-machi in Tochigi Prefecture was introduced, and to each of the beakers, common salt was added in such a manner that the concentration became 100 mg-Cl/L.

Among the three beakers, to a beaker of a "nitrite-loaded system", sodium nitrite was added in such a manner that the final concentration became 80 mg-N/L. To a "tungsten-loaded system", sodium tungstate dihydrate was added in such a manner that the final concentration became 5 mg-W/L. In a "nitrite- and tungsten-loaded system", not only was sodium nitrite added in such a manner that the final concentration became 80 mg-N/L but also sodium tungstate dihydrate was added in such a manner that the final concentration became 5 mg-W/L.

A carbon steel test piece having been weighed in advance was immersed in the water in each of the beakers, thereafter, while carrying out stirring at 300 rpm using a magnetic stirrer, the reaction was carried out at 20°C for 11 days, and from the weight change of the test piece after

completion of the reaction, a corrosion rate (mdd) was determined. The concentration of 16S rDNA derived from *Nitrobacter* in the Nogi-machi city water was examined by a quantitative PCR method, and as a result, it was a detection limit or less (less than 1.0×10^2 copies/mL).

[0066] The results are set forth in Table 5.

It can be seen that in the "nitrite-loaded system" and the "nitrite- and tungsten-loaded system" both containing sodium nitrite, mdd (11day) was 0.2, and an excellent anticorrosion effect was exhibited, but on the other hand, in the "tungsten-loaded system", mdd (11day) was 46.7, and the anticorrosion effect was poor.

From this, it can be seen that in the water system containing no nitrite-oxidizing bacteria at 20°C, a metal corrosion preventing effect of the water-soluble tungstic acid compound (sodium tungstate dihydrate) was not able to be confirmed.

[0067] [Table 5]

Additive	mdd (11 day)
Additive-free	84.0
Nitrite-loaded system	0.2
Tungsten-loaded system	46.7
Nitrite- and tungsten-loaded system	0.2

[0068] [Example 4]

Water was sampled from an open cooling water system in Aichi Prefecture, in which cooling water system anticorrosion treatment for storage associated with the stop of winter operation of the cooling facility was being carried out using a nitrite-based anticorrosive and an isothiazoline-based antibacterial agent.

In each of two culture flasks, 100 mL of the sampled water was introduced, and to only one of the culture flasks, sodium tungstate dihydrate was added in such a manner that the final concentration became 5 mg-W/L. Both the culture flasks were shaken under the aerobic conditions at 26°C and 80 rpm, and nitrite ion concentrations were examined for 48 days. Evaporation of water was compensated by periodically adding pure water. The nitrite ion concentrations were colorimetrically determined using "Digital Pack Test High-Concentration Nitrite Reagent" manufactured by KYORITSU CHEMICAL-CHECK Lab., Corp.

[0069] The results are set forth in Table 6.

In the sodium tungstate dihydrate-free system, the nitrite ion concentration was stable until the 24th day after the start of the test, but after the 34th day, rapid consumption of nitrite ions was confirmed. On the other hand, in the system in which sodium tungstate dihydrate of a final concentration of 5 mg-W/L had been added, it was possible to almost completely suppress consumption of nitrite ions. The effective period of the isothiazoline antibacterial agent is about one month, and in the additive-free system, due to the expiration of the antibacterial activity, the nitrite-oxidizing bacteria in water recovered nitrite oxidation activity and oxidized nitrite ions, but in the tungsten-loaded system, the activity of nitrite-oxidizing bacteria seemed to be continuously suppressed even after expiration of the antibacterial activity.

[0070] [Table 6]

		Additive-free system	Tungsten-loaded system
Nitrite ion concentration (mg-N/L)	0 day after	78.1	78.1
	6 days after	77.8	79.2
	12 days after	78.4	79.9
	18 days after	78.6	78.8
	24 days after	79.8	80.7
	34 days after	2.7	81.3
	40 days after	1.9	83.1
	48 days after	Less than 1.0	79.6

[0071] [Example 5]

A water flow test was carried out using a circulating water flow test device shown in Fig. 1.

This circulating water flow test device is constructed so that water in a circulation water tank (water capacity 50 L) 1 may be circularly flown into a transparent acrylic column (diameter 20 mm) 3 loaded with an iron (SPCC) test piece (50 mm × 10 mm × 1 mm) 2 therein, by means of a pump P.

Using two circulating water flow test devices, the circulation water tanks 1 were each filled with 50 L of city water of Nogi-machi in Tochigi Prefecture subjected to dichlorination treatment with activated carbon. To one of the circulating water flow test devices, sodium tungstate dihydrate was added in such a manner that the final concentration became 5 mg-W/L (loaded system). To both the circulating water flow test devices, sodium nitrite was added in such a manner that the final concentration became 300 mg/L, further, 0.05 mL of activated sludge for

BOD measurement was added as an inoculum to prepare test water, and thereafter, the test water in the circulation water tank 1 was circularly flown into the transparent acrylic column 3 loaded with the test piece 2 therein in such a manner that the flux became 0.3 m/s.

Air flow and stirring in the circulation water tank 1 were carried out by mixing through circulating return water involving air, without carrying out aeration and mechanical stirring. The water temperature was set at 28°C, and pH shifted in the range of 7.7 to 8.1 by the course of nature. The molybdenum concentration at the time of the start of passing water was less than 10 µg-Mo/L.

[0072] The water quality analysis results after passing water for 70 days are set forth in Table 7.

The water quality analysis was carried out in accordance with JIS K0102.

In the control system in which sodium tungstate dihydrate had not been added, lowering of a nitrite ion concentration was observed on the 29th day after the start of the test, and on the 55th day, the nitrite ions were rarely detected. The nitrite ions were all oxidized to nitrate ions.

On the other hand, in the loaded system, the nitrite ion concentration and the tungstic acid concentration were both stable even on the 70th day.

[0074] In the control system, rust occurred on the test piece engraved part from about the 35th day after the start of the test, and thereafter, rust spread over a wide area. Photographs of test pieces on the 70th day are shown in Fig 2. In the loaded system, rust was not observed at all. The weights of the test pieces were measured, and as a result, marked corrosion was observed in the test piece of the control system, as shown in Table 8.

[0075] [Table 8]

	Weight of test piece (g)	
	Control system	Loaded system
Time of start	5.4865	5.7303
70 day after	3.9074	5.7295
Weight loss	1.5791	0.0008

[0076] As a result of a quantitative PCR analysis using a *norB* gene (nitrite oxidoreductase gene) as an index, a significant increase in the number of *norB* genes was observed on the 55th day in the control system, but in the loaded system, the number of the genes was a detection limit or less.

[0077] From the above test results, in the control system, nitrite-oxidizing bacteria grew, and the nitrite ion concentration in the system was lowered, resulting in elimination of an anticorrosion effect and occurrence of corrosion of iron. On the other hand, in the loaded system, growth of nitrite-oxidizing bacteria was suppressed, and the nitrite ion concentration in the system was maintained, so that the anticorrosion effect proved to be stably exhibited.

[0078] [Reference Example 2]

Using a circulating water flow test device shown in Fig. 1, a circulation water tank 1 was filled with 50 L of city water of Nogi-machi in Tochigi Prefecture, which had been subjected to chlorination treatment using activated carbon, then sodium tungstate dihydrate was added in such a manner that the final concentration became 5 mg-W/L, further, 0.05 mL of activated sludge for BOD measurement was added as an inoculum, and thereafter, the water was circularly flown into a transparent acrylic column 3 loaded with a test piece 2 therein, at a flux of 0.3 m/s. Air flow and stirring in the tank were carried out by mixing through circulating return water involving air, without carrying out aeration and mechanical stirring. The water temperature was set at 28°C, and pH shifted in the range of 7.7 to 8.1 by the course of nature. The molybdenum concentration at the time of the start of water flow was less than 10 ng-Mo/L.

[0079] As a result, 7 days after the start of water flow, occurrence of rust was observed on the test piece engraved part.

From the above results, it can be seen that sodium tungstate dihydrate of a final concentration of 5 mg-W/L did not exhibit a satisfactory anticorrosion effect on iron.

[0080] The present invention has been described in detail using specific embodiments, but it is obvious to those skilled in the art that various modifications can be made without departing from the spirit and scope of the present invention.

The present application is based on Japanese patent application 2019-209685 filed on November 20, 2019, and the whole thereof is incorporated herein by reference.

Reference Signs List

- [0081] 1 Circulation water tank
 2 Test piece
 3 Transparent acrylic column

CLAIMS

[Claim 1]

A method for preventing metal corrosion in a water system, comprising adding a nitrite-based anticorrosive and a water-soluble tungstic acid compound to a water system where nitrite-oxidizing bacteria are present or contamination of nitrite-oxidizing bacteria is predicted.

[Claim 2]

The method for preventing metal corrosion in a water system according to claim 1, wherein a concentration of 16S rDNA derived from nitrite-oxidizing bacteria in the water system is 1.0×10^2 copies/mL or more.

[Claim 3]

The method for preventing metal corrosion in a water system according to claim 1 or 2, wherein a nitrite ion concentration in the water system is 10 mg-N/L or more.

[Claim 4]

The method for preventing metal corrosion in a water system according to any one of claims 1 to 3, wherein the water-soluble tungstic acid compound is added in such a manner that a tungstic ion concentration in the water system becomes 0.1 mg-W/L or more.

[Claim 5]

The method for preventing metal corrosion in a water system according to any one of claims 1 to 4, wherein the water system is a cooling water system.

[Claim 6]

The method for preventing metal corrosion in a water system according to any one of claims 1 to 4, wherein the water system is a closed cooling water system.

[Claim 7]

The method for preventing metal corrosion in a water system according to any one of claims 1 to 4, wherein the water system is an open cooling water system.

[Claim 8]

The method for preventing metal corrosion in a water system according to any one of claims 1 to 4, wherein the water system is a cooling water system during storage after stop of cooling water facility operation.

[Claim 9]

The method for preventing metal corrosion in a water system according to any one of claims 1 to 8, wherein the water-soluble tungstic acid compound is added in an amount corresponding to a tungsten concentration 300 times or more higher than a molybdenum concentration in the water system in terms of a weight ratio.

[Claim 10]

A chemical agent for addition to a water system, suppressing oxidation of nitrite ions to nitrate ions in a water system, wherein the chemical agent comprises a water-soluble tungstic acid compound.