

DESCRIPTION

TITLE OF INVENTION

5 METHOD FOR CONTROLLING SLIME ON SEPARATION MEMBRANE

TECHNICAL FIELD

[0001]

The present invention relates to a method for controlling slime on a separation
10 membrane such as a reverse osmosis membrane (RO membrane).

BACKGROUND ART

[0002]

Known methods for controlling slime on separation membranes such as reverse
15 osmosis membranes (RO membranes) include methods using various slime inhibitors.
Chlorine-based oxidizing agents such as hypochlorous acid are typically representative
slime inhibitors, and these inhibitors are usually added to a stage prior to the separation
membrane for the purpose of controlling slime within the system. Because chlorine-based
oxidizing agents have a high probability of degrading the separation membrane, these
20 chlorine-based oxidizing agents are generally either reductively decomposed immediately
prior to reaching the separation membrane, or are used in a manner that allows the
chlorine-based oxidizing agent to intermittently flow onto the separation membrane (see
Patent Document 1).

25 CITATION LIST

PATENT LITERATURE

[0003]

Patent Document 1: JP H09-057076 A

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0004]

It is known that if trihalomethane precursors such as humins exist in the water, then chlorine-based oxidizing agents react with these precursors and generate trihalomethanes such as chloroform. Investigations by the inventors of the present invention showed quite clearly that these trihalomethanes generated by chlorine-based oxidizing agents are difficult to remove with separation membranes, and tend to leak readily into the permeate from the separation membrane.

[0005]

An object of the present invention is to provide a method for controlling slime on a separation membrane in a membrane separation apparatus that uses a feed water or a wash water containing trihalomethane precursors, wherein the method is capable of reducing the trihalomethane content in the permeate while exhibiting a satisfactory slime-controlling effect.

SOLUTION TO PROBLEM

[0006]

The present invention provides a method for controlling slime on a separation membrane, the method including incorporating a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent (reaction components composed of a bromine compound and a chlorine-based oxidizing agent), in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.

[0007]

The present invention also provides a method for controlling slime on a separation membrane, the method including incorporating a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a

sulfamic acid compound, in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.

[0008]

The present invention also provides a method for controlling slime on a separation membrane, the method including incorporating a reaction product of a sulfamic acid compound with a bromine-based oxidizing agent, or with a reaction product of a bromine compound and a chlorine-based oxidizing agent, in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.

[0009]

The present invention also provides a method for controlling slime on a separation membrane, the method including incorporating a mixture of bromine and a sulfamic acid compound, or a reaction product of bromine and a sulfamic acid compound, in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.

[0010]

In the above method for controlling slime on a separation membrane, the reaction product of bromine and a sulfamic acid compound is preferably obtained by a method including a step of adding and reacting bromine, under an inert gas atmosphere, with a mixed liquid containing water, an alkali and a sulfamic acid compound.

[0011]

In the above method for controlling slime on a separation membrane, the concentration of trihalomethane precursor in the feed water or wash water, as a trihalomethane formation potential, is preferably at least 0.001 mg/L.

[0012]

In the above method for controlling slime on a separation membrane, the separation membrane is preferably a polyamide-based polymer membrane.

[0013]

In the above method for controlling slime on a separation membrane, the trihalomethane precursor preferably contains humins.

[0014]

In the above method for controlling slime on a separation membrane, the feed water
5 or wash water preferably also contains bromide ions.

[0015]

In the above method for controlling slime on a separation membrane, the bromide ion concentration in the feed water or wash water is preferably at least 5 mg/L.

[0016]

10 In the above method for controlling slime on a separation membrane, the membrane separation apparatus with a separation membrane is a membrane separation apparatus that undergoes both operating periods and operating downtimes, and during an operating downtime:

the bromine-based oxidizing agent, or the reaction product of a bromine compound
15 and a chlorine-based oxidizing agent is added,

the bromine-based oxidizing agent, or the reaction product of a bromine compound and a chlorine-based oxidizing agent, and the sulfamic acid compound are added,

the reaction product of a sulfamic acid compound with a bromine-based oxidizing agent, or with a reaction product of a bromine compound and a chlorine-based oxidizing
20 agent is added, or

the reaction product of bromine and a sulfamic acid compound is added.

[0017]

In the above method for controlling slime on a separation membrane, the pH of the water introduced into the membrane separation apparatus is preferably 5.5 or higher.

25 [0018]

In the above method for controlling slime on a separation membrane, the water introduced into the membrane separation apparatus is preferably at least one of seawater and salt water.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0019]

In the present invention, by incorporating, in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation
5 membrane: a bromine-based oxidizing agent or a reaction product of a bromine compound and a chlorine-based oxidizing agent; a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a sulfamic acid compound; a reaction product of a sulfamic acid compound with a bromine-based
10 oxidizing agent, or with a reaction product of a bromine compound and a chlorine-based oxidizing agent; a mixture of bromine and a sulfamic acid compound; or a reaction product of bromine and a sulfamic acid compound, the trihalomethane content in the permeate can be reduced while a satisfactory slime-controlling effect is achieved.

BRIEF DESCRIPTION OF DRAWINGS

15 [0020]

FIG. 1 is a schematic structural diagram illustrating one example of a membrane separation system according to an embodiment of the present invention.

FIG. 2 is a diagram illustrating the total trihalomethane concentration (mg/L) in the treated water relative to the bromide ion concentration (mg/L) in the water undergoing
20 treatment in Examples 4 and 5 and Comparative Example 2.

DESCRIPTION OF EMBODIMENTS

[0021]

Embodiments of the present invention are described below. These embodiments
25 are merely examples of implementing the present invention, and the present invention is in no way limited by these embodiments.

[0022]

<Method for Controlling Slime on Separation Membrane>

The method for controlling slime on a separation membrane according to an embodiment of the present invention is a method of incorporating a "bromine-based oxidizing agent" as a slime inhibitor, or a method of incorporating a "reaction product of a bromine compound and a chlorine-based oxidizing agent" such as hypobromous acid as a
5 slime inhibitor, in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.

[0023]

The method for controlling slime on a separation membrane according to another embodiment of the present invention is a method of incorporating a "bromine-based
10 oxidizing agent" and a "sulfamic acid compound" as a slime inhibitor, or a method of incorporating a "reaction product of a bromine compound and a chlorine-based oxidizing agent" and a "sulfamic acid compound" as a slime inhibitor, in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane. It is thought that this method results in the production of a
15 stabilized hypobromous acid composition in the feed water or wash water.

[0024]

Further, the method for controlling slime on a separation membrane according to another embodiment of the present invention is a method of incorporating a stabilized hypobromous acid composition that is a "reaction product of a bromine-based oxidizing
20 agent and a sulfamic acid compound" as a slime inhibitor, or a method of incorporating a stabilized hypobromous acid composition that is a "reaction product of a sulfamic acid compound with a reaction product of a bromine compound and a chlorine-based oxidizing agent" as a slime inhibitor, in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.

25 [0025]

Specifically, the method for controlling slime on a separation membrane according to an embodiment of the present invention is a method of incorporating, for example, "bromine", "bromine chloride", "hypobromous acid" or a "reaction product of sodium

bromide and hypochlorous acid" in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.

[0026]

The method for controlling slime on a separation membrane according to another embodiment of the present invention is a method of incorporating, for example, "bromine", "bromine chloride", "hypobromous acid" or a "reaction product of sodium bromide and hypochlorous acid", and a "sulfamic acid compound" in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.

[0027]

Furthermore, the method for controlling slime on a separation membrane according to another embodiment of the present invention is a method of incorporating, for example, a "reaction product of bromine and a sulfamic acid compound", a "reaction product of bromine chloride and a sulfamic acid compound", or a stabilized hypobromous acid composition that is a "reaction product of a sulfamic acid compound with a reaction product of sodium bromide and hypochlorous acid" in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane. It is not entirely clear what type of compound is formed as the "reaction product of bromine and a sulfamic acid compound", but it is thought that the stabilized hypobromous acid compound "bromosulfamic acid" is produced.

[0028]

By using these methods, the trihalomethane content in the permeate can be reduced while controlling slime generation on the separation membrane in the membrane separation apparatus that uses the trihalomethane precursor-containing feed water or wash water. Further, membrane contamination by microbes can be reliably suppressed, with almost no deterioration in the performance of the separation membrane. By using the method for controlling slime on a separation membrane according to an embodiment of the present invention, a slime control treatment having a superior slime-controlling effect can

be achieved while suppressing any effects on the membrane performance and the water quality in subsequent stages to a minimum.

[0029]

Bromine-based oxidizing agents and stabilized hypobromous acid compositions
5 react with trihalomethane precursors and generate trihalomethanes in a similar manner to
chlorine-based oxidizing agents, but it is thought that the trihalomethanes generated by
bromine-based oxidizing agents and stabilized hypobromous acid compositions contain
mainly bromine-based trihalomethanes such as bromoform, which are more readily
rejected by the separation membrane than chlorine-based trihalomethanes such as
10 chloroform that are generated by chlorine-based oxidizing agents, enabling the
trihalomethane concentration in the permeate from the separation membrane to be
dramatically reduced. Although details regarding the reasons that the rejection rate for
bromine-based trihalomethanes by the separation membrane is high remain unclear, it is
surmised that the fact that bromine-based trihalomethanes have a relatively large molecular
15 weight compared with chlorine-based trihalomethanes is a significant factor.

[0030]

In this manner, the method for controlling slime on a separation membrane
according to an embodiment of the present invention is able to exhibit a slime-controlling
effect similar or superior to a chlorine-based oxidizing agent such as hypochlorous acid,
20 and yet exhibits a much higher rejection rate for the generated bromine-based
trihalomethanes at the separation membrane compared with chlorine-based oxidizing
agents, and therefore the amount of trihalomethanes in the permeate from the separation
membrane can be dramatically reduced. As a result, the slime inhibitor used in this
method for controlling slime on a separation membrane according to the present invention
25 is preferable as a slime inhibitor for separation membranes.

[0031]

Among the methods for controlling slime on a separation membrane according to
these embodiments, the method of incorporating a "bromine-based oxidizing agent" and a
"sulfamic acid compound", the method of incorporating a "reaction product of a bromine

compound and a chlorine-based oxidizing agent" and a "sulfamic acid compound", the method of incorporating a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound", or the method of incorporating a "reaction product of a sulfamic acid compound with a reaction product of a bromine compound and a chlorine-based oxidizing agent" exhibit extremely low degradation effects on the separation membrane, meaning slime control can be achieved by introducing the slime inhibitor directly onto the separation membrane. As a result, the slime inhibitors used in these methods for controlling slime are particularly suitable as slime inhibitors for separation membranes. [0032]

Among the methods for controlling slime on a separation membrane according to these embodiments, when the "bromine-based oxidizing agent" or the "reaction product of a bromine compound and a chlorine-based oxidizing agent" is bromine, then because a chlorine-based oxidizing agent does not exist, the amount of chlorine-based trihalomethanes produced, which suffer from a low rejection rate by the separation membrane, is also reduced, which is particularly desirable as a slime inhibitor for separation membranes. When a chlorine-based oxidizing agent is included, the production of chloric acid may be a concern. [0033]

Trihalomethanes are compounds in which three hydrogen atoms of methane have been substituted with halogens, and examples include chloroform, bromodichloromethane, dibromochloromethane and bromoform. There are no particular limitations on the trihalomethane precursor, which may be any substance that functions as a precursor to a trihalomethane, and examples include compounds having a 1,3-diketone structure and compounds having a 1,3-dihydroxybenzene structure. Specific examples of trihalomethane precursors include humins containing humic acid and fulvic acid. Here, humins (humic substances) are organic components generated by the humification of portions of plants such as leaves and stems, and the fraction within humins that is precipitated by acid is called humic acid, whereas the fraction that does not precipitate is called fulvic acid.

[0034]

Trihalomethane precursors can be measured in terms of the trihalomethane formation potential (THMFP) (mg/L) using a measurement method based on the "Law concerning special measures for water quality conservation at water resource areas in order to prevent specified difficulties in water utilization". Specifically, the method involves adding sodium hypochlorite to the sample so that following reaction under conditions including a pH of 7.0, a temperature of 20°C and a reaction time of 24 hours, the free residual chlorine concentration after 24 hours is 1 to 2 mg/L, and then measuring and determining the amount of trihalomethane produced by simultaneous analysis by purge-trap gas chromatography mass spectrometry. Further, the trihalomethane precursors can also be measured using a TOC meter or the like.

[0035]

If the trihalomethane precursors exist in an amount that yields a trihalomethane formation potential (THMFP) (mg/L) of 0.001 mg/L or greater, then trihalomethanes tend to be produced readily, and therefore if the trihalomethane formation potential of the feed water or wash water supplied to the membrane separation apparatus is at least 0.001 mg/L, preferably at least 0.01 mg/L, and more preferably 0.02 mg/L or greater, then the method for controlling slime on a separation membrane according to an embodiment of the present invention is more effective. Although there are no particular limitations on the upper limit for the trihalomethane formation potential of the feed water or wash water supplied to the membrane separation apparatus, the formation potential is, for example, typically not more than 1 mg/L.

[0036]

Further, if the trihalomethane precursors exist in an amount that yields a TOC value of 0.5 mg/L or greater, then trihalomethanes tend to be produced readily, and therefore if the TOC of the feed water or wash water supplied to the membrane separation apparatus is at least 0.5 mg/L, preferably at least 5.0 mg/L, and more preferably 10.0 mg/L or greater, then the method for controlling slime on a separation membrane according to an embodiment of the present invention is more effective. Although there are no particular

limitations on the upper limit for the TOC of the feed water or wash water supplied to the membrane separation apparatus, the TOC is, for example, typically not more than 500 mg/L. When measured in the examples described below, a trihalomethane formation potential of 0.01 mg/L was equivalent to a TOC of 5.0 mg/L.

5 [0037]

Particularly in those cases where the trihalomethane precursors include humic acid, if 0.89 mg/L or more of humic acid exists, then trihalomethanes tend to be produced readily, and therefore if the humic acid concentration of the feed water or wash water supplied to the membrane separation apparatus is at least 0.89 mg/L, preferably at least 8.9
10 mg/L, and more preferably 890 mg/L or greater, then the method for controlling slime on a separation membrane according to an embodiment of the present invention is more effective. Although there are no particular limitations on the upper limit for the humic acid in the feed water or wash water supplied to the membrane separation apparatus, the humic acid concentration is, for example, typically not more than 180 mg/L. When measured in
15 the examples described below, a trihalomethane formation potential of 0.01 mg/L was equivalent to a humic acid concentration of 8.9 mg/L.

[0038]

The method for controlling slime of a separation membrane according to an embodiment of the present invention is even more effective in those cases where the feed
20 water or wash water supplied to the membrane separation apparatus also contains bromide ions. By using the method for controlling slime on a separation membrane according to an embodiment of the present invention in a membrane separation apparatus that uses a feed water or a wash water containing trihalomethane precursors and bromide ions, the trihalomethane content in the permeate can be reduced, while providing a satisfactory
25 slime-controlling effect.

[0039]

As described above, when a chlorine-based oxidizing agent such as hypochlorous acid is added to water containing trihalomethane precursors, trihalomethanes such as chloroform are produced, but in the case of seawater or the like, where the water contains

bromide ions (for example, at least 5 mg/L) and trihalomethane precursors such as humins, if hypochlorous acid is added as a slime inhibitor, then bromine-based trihalomethanes are mainly produced. Because bromine-based trihalomethanes have a larger molecular weight than chlorine-based trihalomethanes, the total trihalomethane concentration increases.

5 [0040]

The slime inhibitors such as the "hypobromous acid" or the "stabilized hypobromous acid composition containing both a bromine-based oxidizing agent and sulfamic acid" exhibit a slime-controlling effect (sterilization effect) equivalent or superior to hypochlorous acid. Further, in those cases where trihalomethane precursors and bromide ions exist in the system, bromine-based trihalomethanes are mainly produced. However, unlike typical hypochlorous acid, these slime inhibitors such as "hypobromous acid" or the "stabilized hypobromous acid composition" exhibit almost no increase in the amount of trihalomethanes produced as the bromide ion concentration increases. As a result, it is thought that by using the method for controlling slime on a separation membrane according to the present embodiment, which uses a slime inhibitor such as "hypobromous acid" or a "stabilized hypobromous acid composition containing both a bromine-based oxidizing agent and sulfamic acid", the concentration of produced trihalomethanes can be lowered compared with a method using hypochlorous acid for water containing bromide ions.

15 20 [0041]

On the other hand, a "stabilized hypochlorous acid" such as chlorosulfamic acid is stabilized, and therefore the trihalomethane formation potential is suppressed, but the sterilizing power is lower than that of "hypobromous acid" or a "stabilized hypobromous acid composition", meaning a satisfactory slime-controlling effect cannot be achieved.

25 [0042]

Despite exhibiting a slime-controlling effect similar or superior to hypochlorous acid, in those cases where the water to be treated contains bromide ions, the slime inhibitor used in the method for controlling slime on a separation membrane according to an embodiment of the present invention produces a smaller amount of trihalomethanes than

hypochlorous acid. As a result, the method for controlling slime on a separation membrane according to an embodiment of the present invention is preferable as a method for controlling slime in a membrane separation apparatus that uses a feed water or wash water containing trihalomethane precursors and bromide ions.

5 [0043]

In this manner, the method for controlling slime on a separation membrane according to an embodiment of the present invention enables a slime control treatment to be performed that suppresses the trihalomethane concentration in the permeate from the separation membrane to a minimum, while also exhibiting a superior slime-controlling
10 effect.

[0044]

Particularly in those cases where the feed water or wash water supplied to the membrane separation apparatus contains at least 5 mg/L of bromide ions, if hypochlorous acid is used then trihalomethanes tend to be produced readily, and therefore the method for
15 controlling slime on a separation membrane according to an embodiment of the present invention is particularly effective in those cases where the concentration of bromide ions in the feed water or wash water supplied to the membrane separation apparatus is at least 5 mg/L, and preferably 18 mg/L or higher. Although there are no particular limitations on the upper limit for the bromide ion concentration of the feed water or wash water supplied
20 to the membrane separation apparatus, the bromide ion concentration is, for example, typically not more than 1,000 mg/L.

[0045]

In the method for controlling slime on a separation membrane according to an embodiment of the present invention, the "bromine-based oxidizing agent" or the "reaction
25 product of a bromine compound and a chlorine-based oxidizing agent" may be injected, using a chemical feed pump or the like, into the feed water or wash water supplied to the membrane separation apparatus that uses the feed water or wash water containing trihalomethane precursors. The "bromine compound" and the "chlorine-based oxidizing

agent" may be added to the water system separately, or the neat liquids may be mixed together and then added to the water system.

[0046]

For example, the "bromine-based oxidizing agent" or the "reaction product of a
5 bromine compound and a chlorine-based oxidizing agent", and the "sulfamic acid
compound", may be injected, using a chemical feed pump or the like, into the feed water or
wash water supplied to the membrane separation apparatus that uses the feed water or wash
water containing trihalomethane precursors. The "bromine-based oxidizing agent" or the
"reaction product of a bromine compound and a chlorine-based oxidizing agent", and the
10 "sulfamic acid compound", may be added to the water system separately, or the neat
liquids may be mixed together and then added to the water system.

[0047]

Further, the "reaction product of a bromine-based oxidizing agent and a sulfamic
acid compound" or the "reaction product of a sulfamic acid compound with a reaction
15 product of a bromine compound and a chlorine-based oxidizing agent" may be injected,
using a chemical feed pump or the like, into the feed water or wash water supplied to the
membrane separation apparatus that uses the feed water or wash water containing
trihalomethane precursors.

[0048]

20 The aforementioned slime inhibitor added to the feed water or wash water supplied
to the membrane separation apparatus may be decomposed with a reducing agent or the
like immediately prior to reaching the separation membrane.

[0049]

By using the method for controlling slime on a separation membrane according to
25 an embodiment of the present invention, even in membrane separation systems that
undergo both operating periods and operating downtimes, degradation of the separation
membrane can be suppressed, and the separation membrane can be effectively sterilized
during an operating downtime.

[0050]

<Membrane Separation System>

The outline of one example of a membrane separation system according to this embodiment of the present invention is illustrated in FIG. 1, and the structure of that system is described below. The membrane separation system 1 includes a raw water tank 10 and a membrane separation apparatus 12.

[0051]

In the membrane separation system 1 of FIG. 1, a raw water line 16 is connected to the inlet of the raw water tank 10. The outlet of the raw water tank 10 and the inlet of the membrane separation apparatus 12 are connected by a raw water supply line 18 via a pump 14. A permeate line 20 is connected to the permeate outlet of the membrane separation apparatus 12, and a concentrate line 22 is connected to the concentrate outlet. A fungicide supply line 24 is connected to the raw water supply line 18 at a location between the pump 14 and the membrane separation apparatus 12.

[0052]

The operation of the membrane separation system 1 according to this embodiment and the method of sterilizing the separation membrane are described below.

[0053]

The raw water that represents the treatment target may be stored in the raw water tank 10 as required, and is then supplied through the raw water supply line 18 to the membrane separation apparatus 12 using the pump 14. In the membrane separation apparatus 12, a membrane separation treatment is performed using a separation membrane (membrane separation treatment step). The permeate (treated water) obtained from the membrane separation treatment is discharged through the permeate line 20, and the concentrate is discharged through the concentrate line 22. The concentrate may be recirculated back into the raw water tank 10 or the raw water supply line 18.

[0054]

For example, a fungicide supply mechanism may be installed in the raw water supply line 18 between the pump 14 and the inlet of the membrane separation apparatus 12, and a fungicide of a prescribed concentration introduced through the fungicide supply

line 24 from the fungicide supply mechanism and added to the raw water as the raw water is fed from the raw water tank 10 to the membrane separation apparatus 12. Alternatively, in those cases where operation of the membrane separation system 1 is paused, the pump 14 is stopped, and the fungicide may be left inside the membrane separation apparatus 12 during the operating downtime for the membrane separation system 1. The fungicide supply mechanism may also be installed in the raw water supply line 18 or the raw water tank 10.

[0055]

Further, a prescribed concentration of a fungicide may be introduced through the fungicide supply line 24 from the fungicide supply mechanism and added to the raw water as the raw water is fed from the raw water tank 10 to the membrane separation apparatus 12, and then when operation of the membrane separation system 1 is to be paused, a prescribed concentration of the fungicide may be introduced through the fungicide supply line 24 from the fungicide supply mechanism and added to the raw water, the pump 14 subsequently halted, and the fungicide left inside the membrane separation apparatus 12 during the operating downtime of the membrane separation system 1.

[0056]

Here, an "operating downtime" describes a state where no treated water (permeate) is being obtained in the membrane separation system 1.

[0057]

In those cases where the membrane separation apparatus 12 is subjected to backwashing, either using a backwash water or using the permeate as a backwash water, a fungicide may be added to the backwash water and the fungicide introduced into the membrane separation apparatus 12 during an operating downtime for the membrane separation system 1.

[0058]

In the membrane separation system 1, a level switch may be installed in the raw water tank 10, and then control performed such that when the water level inside the raw water tank 10 detected by the level switch during system operation falls below a prescribed

height, operation is paused, and when the water level inside the raw water tank 10 detected by the level switch exceeds a prescribed height during an operating downtime, operation is restarted.

[0059]

5 The method for controlling slime on a separation membrane according to an embodiment of the present invention is a method of introducing a "bromine-based oxidizing agent" and a "sulfamic acid compound" as a fungicide (slime inhibitor) into the membrane separation apparatus 12, or a method of introducing a "reaction product of a bromine compound and a chlorine-based oxidizing agent" and a "sulfamic acid compound"

10 as a fungicide into the membrane separation apparatus 12, during an operating downtime of the membrane separation system 1 that undergoes both operating periods and operating downtimes. By using such a method, it is thought that a stabilized hypobromous acid composition is generated in the fungicide-containing backwash water or fungicide-containing water.

15 [0060]

Further, the method for controlling slime on a separation membrane according to an embodiment of the present invention is a method of introducing a stabilized hypobromous acid composition that is a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound" as a fungicide (slime inhibitor) into the membrane separation

20 apparatus 12, or a method of introducing a stabilized hypobromous acid composition that is a "reaction product of a sulfamic acid compound with a reaction product of a bromine compound and a chlorine-based oxidizing agent" as a fungicide into the membrane separation apparatus 12, during an operating downtime of the membrane separation system 1 that undergoes both operating periods and operating downtimes.

25 [0061]

Specifically, the method for controlling slime on a separation membrane according to an embodiment of the present invention is a method of introducing, for example, "bromine", "bromine chloride", "hypobromous acid" or a "reaction product of sodium bromide and hypochlorous acid", and a "sulfamic acid compound" into the membrane

separation apparatus 12 during an operating downtime of the membrane separation system 1 that undergoes both operating periods and operating downtimes.

[0062]

Further, the method for controlling slime on a separation membrane according to another embodiment of the present invention is a method of introducing a stabilized hypobromous acid composition which is, for example, a "reaction product of bromine and a sulfamic acid compound", a "reaction product of bromine chloride and a sulfamic acid compound" or a "reaction product of a sulfamic acid compound with a reaction product of sodium bromide and hypochlorous acid" into the membrane separation apparatus 12, during an operating downtime of the membrane separation system 1 that undergoes both operating periods and operating downtimes.

[0063]

By using these methods, degradation of the separation membrane of the membrane separation apparatus 12 can be suppressed, and the separation membrane can be effectively sterilized during an operating downtime of the membrane separation system 1 that undergoes both operating periods and operating downtimes. Further, cumbersome additional equipment to supply the fungicide periodically need not be provided, meaning the system can be simplified.

[0064]

In the method for controlling slime on a separation membrane according to an embodiment of the present invention, a "bromine-based oxidizing agent" or a "reaction product of a bromine compound and a chlorine-based oxidizing agent", and a "sulfamic acid compound" may be injected into the water system by a chemical feed pump or the like during an operating downtime of the membrane separation system 1 that undergoes both operating periods and operating downtimes. The "bromine-based oxidizing agent" or the "reaction product of a bromine compound and a chlorine-based oxidizing agent", and the "sulfamic acid compound" may be added separately to the water system, or the neat liquids may be mixed together and then added to the water system.

[0065]

Further, in another example, a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound" or a "reaction product of a sulfamic acid compound with a reaction product of a bromine compound and a chlorine-based oxidizing agent" may be injected into the water system by a chemical feed pump or the like during an operating
5 downtime of the membrane separation system 1 that undergoes both operating periods and operating downtimes.

[0066]

In the method for controlling slime on a separation membrane according to an embodiment of the present invention, the ratio of the equivalent weight of the "sulfamic
10 acid compound" relative to the equivalent weight of the "bromine-based oxidizing agent" or the "reaction product of a bromine compound and a chlorine-based oxidizing agent" is preferably 1 or greater, and is more preferably within a range from at least 1 to not more than 2. If the ratio of the equivalent weight of the "sulfamic acid compound" relative to the equivalent weight of the "bromine-based oxidizing agent" or the "reaction product of a
15 bromine compound and a chlorine-based oxidizing agent" is less than 1, then there is a possibility that degradation of the membrane may occur, whereas if the ratio exceeds 2, then the production costs may sometimes increase.

[0067]

The effective halogen concentration contacting the separation membrane,
20 calculated as an effective equivalent chlorine concentration, is preferably from 0.01 to 100 mg/L. If this concentration is less than 0.01 mg/L, then a satisfactory slime-controlling effect may not be obtainable, whereas if the concentration is greater than 100 mg/L, then there is a possibility that degradation of the separation membrane or corrosion of the supply lines or the like may occur.

25 [0068]

Examples of the bromine-based oxidizing agent include bromine (liquid bromine), bromine chloride, bromic acid, bromate salts, and hypobromous acid and the like.

[0069]

Among these, compared with the formulation of "hypochlorous acid, a bromine compound and sulfamic acid" and the formulation of "bromine chloride and sulfamic acid" and the like, formulations that use bromine such as "bromine and a sulfamic acid compound (a mixture of bromine and a sulfamic acid compound)" or a "reaction product of bromine and a sulfamic acid compound" tend to exhibit lower production amounts of trihalomethanes, exhibit less degradation of reverse osmosis membranes (RO membranes) and the like, and suffer from less leakage of effective halogen into the membrane permeate such as the reverse osmosis membrane (RO membrane) permeate, and are consequently preferred as slime inhibitors for separation membranes such as reverse osmosis membranes (RO membranes).

[0070]

In other words, the method for controlling slime on a separation membrane according to an embodiment of the present invention is preferably a method of incorporating bromine and a sulfamic acid compound (a mixture of bromine and a sulfamic acid compound) in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation device containing the separation membrane. Further, incorporating a reaction product of bromine and a sulfamic acid compound in the trihalomethane precursor-containing feed water or wash water supplied to a membrane separation device containing the separation membrane is also preferred.

[0071]

Examples of the bromine compound include sodium bromide, potassium bromide, lithium bromide, ammonium bromide and hydrobromic acid. Among these, in terms of production costs and the like, sodium bromide is preferred.

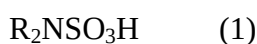
[0072]

Examples of the chlorine-based oxidizing agent include chlorine gas, chlorine dioxide, hypochlorous acid or salts thereof, chlorous acid or salts thereof, chloric acid or salts thereof, perchloric acid or salts thereof, and chlorinated isocyanuric acid or salts thereof. Among these, examples of the salts include alkali metal salts of hypochlorous acid such as sodium hypochlorite and potassium hypochlorite, alkaline earth metal salts of

hypochlorous acid such as calcium hypochlorite and barium hypochlorite, alkali metal salts of chlorous acid such as sodium chlorite and potassium chlorite, alkaline earth metal salts of chlorous acid such as barium chlorite, other metal salts of chlorous acid such as nickel chlorite, alkali metal salts of chloric acid such as ammonium chlorate, sodium chlorate and potassium chlorate, and alkaline earth metal salts of chloric acid such as calcium chlorate and barium chlorate. Any one of these chlorine-based oxidizing agents may be used alone, or a combination of two or more oxidizing agents may be used. In terms of ease of handling and the like, the use of sodium hypochlorite as the chlorine-based oxidizing agent is preferred.

10 [0073]

The sulfamic acid compound is a compound represented by general formula (1) shown below.



(In the formula, each R independently represents a hydrogen atom or an alkyl group having a carbon number of 1 to 8.)

15 [0074]

Examples of the sulfamic acid compound, in addition to sulfamic acid (amidosulfuric acid) in which the two R groups are both hydrogen atoms, include sulfamic acid compounds in which one of the two R groups is a hydrogen atom and the other is an alkyl group having a carbon number of 1 to 8, such as N-methylsulfamic acid, N-ethylsulfamic acid, N-propylsulfamic acid, N-isopropylsulfamic acid and N-butylsulfamic acid, sulfamic acid compounds in which the two R groups are both alkyl groups having a carbon number of 1 to 8, such as N,N-dimethylsulfamic acid, N,N-diethylsulfamic acid, N,N-dipropylsulfamic acid, N,N-dibutylsulfamic acid, N-methyl-N-ethylsulfamic acid and N-methyl-N-propylsulfamic acid, and sulfamic acid compounds in which one of the two R groups is a hydrogen atom and the other is an aryl group having a carbon number of 6 to 10, such as N-phenylsulfamic acid, as well as salts of the above acids. Examples of the sulfamic acid salts include alkali metal salts such as sodium salts and potassium salts, alkaline earth metal salts such as calcium salts, strontium salts and barium salts, other

20

25

metal salts such as manganese salts, copper salts, zinc salts, iron salts, cobalt salts and nickel salts, as well as ammonium salts and guanidine salts. One of these sulfamic acid compounds or salts may be used alone, or a combination of two or more compounds or salts may be used. In terms of the environmental burden and the like, the use of sulfamic acid (amidosulfuric acid) as the sulfamic acid compound is preferred.

[0075]

In the method for controlling slime on a separation membrane according to an embodiment of the present invention, an alkali is preferably also introduced. Examples of the alkali include alkali hydroxides such as sodium hydroxide and potassium hydroxide. In terms of achieving good product stability and the like at low temperatures, a combination of sodium hydroxide and potassium hydroxide may also be used. The alkali is typically used not as a solid, but in the form of an aqueous solution.

[0076]

Examples of the separation membrane include a reverse osmosis membrane (RO membrane), nanofiltration membrane (NF membrane), microfiltration membrane (MF membrane), and ultrafiltration membrane (UF membrane). Among these, the method for controlling slime on a separation membrane according to an embodiment of the present invention can be applied particularly favorably to reverse osmosis membranes (RO membranes). Further, the method for controlling slime on a separation membrane according to an embodiment of the present invention can be used favorably with polyamide-based polymer membranes, which are currently the most widely used reverse osmosis membranes. Polyamide-based polymer membranes have comparatively low resistance to oxidizing agents, and if free chlorine or the like is kept in continuous contact with a polyamide-based polymer membrane, then a marked deterioration may occur in the performance of the membrane. However, in the method for controlling slime on a separation membrane according to an embodiment of the present invention, this type of marked deterioration in the membrane performance is almost non-existent, even for polyamide polymer membranes.

[0077]

In the method for controlling slime on a separation membrane according to an embodiment of the present invention, in the case where the membrane separation apparatus is an RO apparatus having a reverse osmosis membrane (RO membrane) as the separation
5 membrane, the pH of the feed water supplied to the RO apparatus is preferably 5.5 or higher, more preferably 6.0 or higher, and still more preferably 6.5 or higher. If the pH of the feed water supplied to the RO apparatus is less than 5.5, then the volume of permeate may sometimes decrease. Further, there are no particular limitations on the upper limit for the pH of the feed water supplied to the RO apparatus, provided that the pH is no higher
10 than the typical upper limit pH for reverse osmosis membranes (RO membranes) (for example, pH 10), but if scale deposition of hard components such as calcium is also considered, then operating the RO apparatus at a pH of, for example, 9.0 or lower is preferred. When the method for controlling slime on a separation membrane according to an embodiment of the present invention is used, by operating the RO apparatus with the pH
15 of the feed water supplied to the apparatus set to 5.5 or higher, degradation of the reverse osmosis membrane (RO membrane) and deterioration in the quality of the treated water (permeate) can be suppressed, a satisfactory slime-controlling effect can be achieved, and a satisfactory permeate volume can also be ensured.

[0078]

20 In those cases where scale develops in the RO apparatus when the pH of the feed water supplied to the RO apparatus is 5.5 or higher, a dispersant may be used for the purpose of scale inhibition in combination with the bromine-based oxidizing agent or stabilized hypobromous acid composition. Examples of the dispersant include polyacrylic acid, polymaleic acid and phosphonic acid. The amount of the dispersant added to the feed
25 water, for example in terms of the concentration within the RO concentrate, is typically within a range from 0.1 to 1,000 mg/L.

[0079]

Further, one method for inhibiting the occurrence of scale without using a dispersant involves adjusting the operating conditions for the RO apparatus such as the recovery rate so that the silica concentration in the RO concentrate is no higher than the degree of solubility, and the Langelier index, which is an indicator for calcium scale, is not more than 0.

[0080]

Examples of applications for the RO apparatus include seawater desalination and wastewater recovery.

[0081]

10 <Slime Inhibitor Composition for Separation Membrane>

A slime inhibitor composition for a separation membrane according to this embodiment is a composition containing a "bromine-based oxidizing agent", or a "reaction product of a bromine compound and a chlorine-based oxidizing agent", and a "sulfamic acid compound", and may also include an alkali.

15 [0082]

Furthermore, the slime inhibitor composition for a separation membrane according to this embodiment may also be a composition containing a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound" or a "reaction product of a sulfamic acid compound with a reaction product of a bromine compound and a chlorine-based oxidizing agent", and may also include an alkali.

20

[0083]

The bromine-based oxidizing agent, the bromine compound, the chlorine-based oxidizing agent, and the sulfamic acid compound are as described above.

[0084]

25 The slime inhibitor composition for a separation membrane according to this embodiment is preferably a composition containing bromine and a sulfamic acid compound (a composition containing a mixture of bromine and a sulfamic acid compound), such as a mixture of bromine, a sulfamic acid compound, an alkali and water,

or a composition containing a reaction product of bromine and a sulfamic acid compound, such as a mixture of a reaction product of bromine and a sulfamic acid compound, an alkali and water, as such compositions tend to exhibit less degradation of reverse osmosis membranes (RO membranes) and the like, and suffer from less leakage of effective halogen into the membrane permeate such as the RO permeate.

[0085]

Compared with combined chlorine-based slime inhibitors such as chlorosulfamic acid, the slime inhibitor composition for a separation membrane according to the present embodiment tends to have higher oxidizing power, and markedly higher slime inhibition and slime-detaching power, and yet causes almost none of the marked membrane degradation observed for other compositions of similar oxidizing power such as hypochlorous acid. At typical usage concentrations, the effects on membrane degradation can be substantially ignored. As a result, the composition is ideal as a slime inhibitor for separation membranes such as reverse osmosis membranes (RO membranes).

[0086]

Unlike hypochlorous acid, the slime inhibitor composition for a separation membrane according to the present embodiment tends to undergo almost no permeation through the reverse osmosis membrane (RO membrane), and therefore has almost no effect on the treated water quality. Further, because the concentration can be measured on site in a similar manner to hypochlorous acid or the like, more accurate concentration control is possible. Furthermore, the slime inhibitor composition for a separation membrane according to the present embodiment reacts with trihalomethane precursors to generate bromine-based trihalomethanes, but these are thought to be easily rejected by the separation membrane, meaning the trihalomethane concentration in the permeate from the separation membrane can be reduced significantly.

[0087]

The pH of the composition is, for example, higher than 13.0, and is preferably higher than 13.2. If the pH of the composition is 13.0 or lower, then the effective halogen in the composition may sometimes become unstable.

[0088]

5 The bromate concentration in the slime inhibitor composition for a separation membrane is preferably less than 5 mg/kg. If the bromate concentration in the slime inhibitor composition for a separation membrane is 5 mg/kg or greater, then the concentration of bromate ions in the permeate may increase.

[0089]

10 <Method for Producing Slime Inhibitor Composition for Separation Membrane>

 The slime inhibitor composition for a separation membrane according to an embodiment of the present invention is obtained by mixing a bromine-based oxidizing agent and a sulfamic acid compound, or by mixing a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a sulfamic acid compound. An alkali
15 may also be mixed into the composition.

[0090]

 The method for producing a slime inhibitor composition for a separation membrane that contains bromine and a sulfamic acid compound, or a slime inhibitor composition for a separation membrane that contains a reaction product of bromine and a sulfamic acid
20 compound preferably includes a step of adding and reacting bromine, under an inert gas atmosphere, with a mixed solution containing water, an alkali and a sulfamic acid compound, or a step of adding bromine, under an inert gas atmosphere, to a mixed solution containing water, an alkali and a sulfamic acid compound. By performing the addition and inducing the reaction under an inert gas atmosphere, or by performing the addition under
25 an inert gas atmosphere, the concentration of bromate ions in the composition can be reduced, and the bromate ion concentration in the permeate such as the RO permeate can also be reduced.

[0091]

Although there are no particular limitations on the inert gas used, at least one of nitrogen and argon is preferred from a production perspective and the like, and nitrogen is particularly preferred in terms of production costs and the like.

[0092]

5 The oxygen concentration inside the reaction vessel during the bromine addition is preferably not more than 6%, more preferably not more than 4%, still more preferably not more than 2%, and most preferably 1% or less. If the oxygen concentration inside the reaction vessel during the bromine reaction exceeds 6%, then the amount of bromic acid produced in the reaction system may sometimes increase.

10 [0093]

 The proportion of bromine added is preferably not more than 25 wt% relative to the total weight of the composition, and is more preferably at least 1 wt% but not more than 20 wt%. If the proportion of bromine added exceeds 25 wt% relative to the total weight of the composition, then the amount of bromic acid produced in the reaction system may
15 sometimes increase. If the proportion is less than 1 wt%, then the sterilization power may be poor.

[0094]

 The reaction temperature during the bromine addition is preferably controlled within a range from at least 0°C to not more than 25°C, and in terms of production costs
20 and the like, is more preferably controlled within a range from at least 0°C to not more than 15°C. If the reaction temperature during the bromine addition exceeds 25°C, then the amount of bromic acid produced in the reaction system may sometimes increase, whereas if the temperature is less than 0°C, then the reaction system may freeze.

25

EXAMPLES

[0095]

 The present invention is described below in further detail using examples and comparative examples, but the present invention is in no way limited by these examples.

[0096]

The effects of slime inhibitors on the trihalomethane concentration in the permeate and the performance of a reverse osmosis membrane (RO membrane) were compared for the case where a stabilized hypobromous acid composition that was a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound" was used as the slime inhibitor (Example 1), the case where a stabilized hypobromous acid composition that was a "reaction product of a sulfamic acid compound with a reaction product of a bromine compound and a chlorine-based oxidizing agent" was used as the slime inhibitor (Example 2), the case where a "bromine-based oxidizing agent" was used as the slime inhibitor (Example 3), and the case where hypochlorous acid was used as a typical slime inhibitor (Comparative Example 1).

[0097]

[Preparation of Composition 1]

Liquid bromine: 16.9 wt%, sulfamic acid: 10.7 wt%, sodium hydroxide: 12.9 wt%, potassium hydroxide: 3.94 wt% and water: the balance were mixed together under a nitrogen atmosphere to prepare a composition 1. The pH of the composition 1 was 14, and the effective halogen concentration (effective equivalent chlorine concentration) was 7.5 wt%. A detailed description of the method for preparing the composition 1 is presented below.

[0098]

A 2 liter four-necked flask into which nitrogen gas was injected continuously at a flow rate controlled by a mass flow controller so that the oxygen concentration inside the reaction vessel was maintained at 1% was charged with 1,436 g of water and 361 g of sodium hydroxide, and following mixing, 300 g of sulfamic acid was added and mixed, and with the flask then cooled to maintain the temperature of the reaction solution at 0 to 15°C, 473 g of liquid bromine was added, and 230 g of a 48% solution of potassium hydroxide was then added, thus obtaining the target composition 1 containing 10.7 wt% of sulfamic acid and 16.9 wt% of bromine relative to the total weight of the composition, and

having a ratio for the equivalent weight of sulfamic acid relative to the equivalent weight of bromine of 1.04. Measurement of the pH of the prepared solution using the glass electrode method yielded a value of 14. Measurement of the bromine content of the prepared solution using a method in which the bromine was substituted with iodine using potassium iodide, and a redox titration was then performed using sodium thiosulfate revealed a value of 16.9%, which was 100.0% of the theoretical content (16.9%). Further, the oxygen concentration inside the reaction vessel during the bromine reaction was measured using an "Oxygen Monitor JKO-02 LJDII" manufactured by Jikco Ltd. The bromate concentration was less than 5 mg/kg.

10 [0099]

[Preparation of Composition 2]

Sodium bromide: 11 wt%, a 12% aqueous solution of sodium hypochlorite: 50 wt%, sodium sulfamate: 14 wt%, sodium hydroxide: 8 wt%, and water: the balance were mixed together to prepare a composition 2. The pH of the composition 2 was 14, and the effective halogen concentration (effective equivalent chlorine concentration) was 6 wt%. A more detailed description of the preparation method for the composition 2 is presented below.

15 [0100]

A reaction vessel was charged with 17 g of water, 11 g of sodium bromide was added and dissolved by stirring, 50 g of a 12% aqueous solution of sodium hypochlorite was then added and mixed, 14 g of sodium sulfamate was added and dissolved by stirring, and 8 g of sodium hydroxide was then added and dissolved by stirring to obtain the target composition 2.

[0101]

25 The results of measuring the amount of chloric acid in the compositions using an ion chromatography method in accordance with the method prescribed in "JWWA K 120 (2008) Sodium hypochlorite for water supply" revealed that the amount of chloric acid was less in the composition 1 (less than 50 mg/kg) than in the composition 2 (1,100 mg/kg).

[0102]

[Composition 3]

A 9 wt% aqueous solution of sodium hypobromite (Kanto Chemical Co., Inc., Cica grade 1) was used as a composition 3.

5 [0103]

[Composition 4]

A 12 wt% aqueous solution of sodium hypochlorite was used as a composition 4.

[0104]

<Examples 1 to 3, Comparative Example 1, Reference Examples 1 and 2>

10 Under the conditions described below, each of the compositions 1 to 4 was added to the raw water for a reverse osmosis membrane apparatus, and the total trihalomethane concentration in the separation membrane feed water and the separation membrane permeate, and the rejection rate for total trihalomethane by the reverse osmosis membrane (RO membrane) were compared. In Examples 1 to 3 and Comparative Example 1, a
15 simulated water described below was used, whereas in Reference Examples 1 and 2, a pure water was used.

[0105]

(Test Conditions)

- Test apparatus: flat membrane test apparatus
- 20 - Separation membrane: polyamide-based polymer reverse osmosis membrane ES15, manufactured by Nitto Denko Corporation
- Operating pressure: 0.75 MPa
- Raw water: a simulated water having a trihalomethane formation potential of 0.01 mg/L (prepared by adding 8.9 mg/L of humic acid (manufactured by Wako Pure Chemical
25 Industries, Ltd.) as a trihalomethane precursor to pure water, TOC: 5 mg/L), or pure water
- Reagent: the compositions 1 to 4 were each added in sufficient amount to produce an effective halogen concentration (effective equivalent chlorine concentration) of 3 mg/L

- Raw water pH: adjusted so that the pH of the test water following addition of the reagent was pH 8

- Test temperature: 25°C

- Method of measuring trihalomethane formation potential: sufficient sodium

5 hypochlorite was added to the sample so that following reaction under conditions including a pH of 7.0, a temperature of 20°C and a reaction time of 24 hours, the free residual chlorine concentration after 24 hours was 1 to 2 mg/L, and the amount of trihalomethane produced was then measured and determined by simultaneous analysis by purge-trap gas chromatography mass spectrometry. A "Tekmar Stratum" apparatus manufactured by
10 Teledyne Tekmar Inc. was used as the purge-trap apparatus, a "7890" apparatus manufactured by Agilent Technologies, Inc. was used as the gas chromatograph, and a "5975C" apparatus manufactured by Agilent Technologies, Inc. was used as the mass spectrometer.

- Method of measuring effective halogen concentration: measured by the DPD
15 method using a residual chlorine measuring instrument (DR-4000, manufactured by Hach Company).

[0106]

(Evaluation Methods)

[Total trihalomethane concentration in RO feed water and RO permeate, and rejection rate
20 for total trihalomethane by reverse osmosis membrane (RO membrane)]

Samples prepared by adding the compositions 1 to 4 to the simulated water or pure water in the amounts shown in Table 1 and then adjusting the pH to 8 were each adjusted to a water temperature of 25°C and circulated through an RO apparatus. After 4 hours, the total trihalomethane concentration (mg/L) in the RO feed water and the RO permeate was
25 measured. Based on these values for the total trihalomethane concentration (mg/L) in the RO feed water and the RO permeate, the rejection rate (%) for total trihalomethane by the reverse osmosis membrane (RO membrane) was determined. The results are shown in Table 1. Here, the term "total trihalomethane" indicates the combination of four

compounds, namely chloroform, bromodichloromethane, dibromochloromethane and bromoform.

[0107]

The total trihalomethane concentration was measured by simultaneous analysis by purge-trap gas chromatography mass spectrometry in accordance with the method prescribed by the Minister for Health, Labor and Welfare (Notification No. 261 from the Minister for Health, Labor and Welfare, 2003) based on the prescriptions of ministerial ordinances relating to water quality standards.

[0108]

10 [Table 1]

	Reagent	Test water	Total trihalomethane concentration (mg/L)		Rejection rate (%) for total trihalomethane by RO membrane
			RO feed water (after addition of reagent)	RO permeate (after addition of reagent)	
Example 1	Composition 1	Simulated water	0.022	<0.001	>95
Example 2	Composition 2	Simulated water	0.042	<0.001	>95
Example 3	Composition 3	Simulated water	0.036	<0.001	>95
Comparative Example 1	Composition 4	Simulated water	0.005	0.002	60
Reference Example 1	Composition 1	Pure water	<0.001	<0.001	-
Reference Example 2	Composition 4	Pure water	<0.001	<0.001	-

[0109]

In this manner, compared with Comparative Example 1, in Examples 1 to 3 the trihalomethane content in the permeate was able to be reduced, while providing a satisfactory slime-controlling effect. In the case of Reference Examples 1 and 2 in which pure water was used as the raw water, almost no trihalomethane was produced.

[0110]

[Effect on reverse osmosis membrane (RO membrane) rejection rate, effect on permeate, oxidizing power comparative test]

The case in which a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a sulfamic acid compound were used, and the case in which a typical slime inhibitor such as hypochlorous acid or hypobromous acid was used were compared in terms of the effect on the reverse osmosis membrane (RO membrane) rejection rate, the effect on the permeate, the oxidizing power, and the sterilization power.

[0111]

The compositions 1, 2, and 4 to 7 were each added to the raw water for a reverse osmosis membrane apparatus under the conditions described below, and the effect on the reverse osmosis membrane (RO membrane) rejection rate, the effect on the permeate, and the oxidizing power were compared.

[0112]

[Composition 5]

Each of the components of the composition 2 were added separately to the water.

[0113]

[Composition 6]

A composition 6 containing bromine chloride, sodium sulfamate and sodium hydroxide was used. The pH of the composition 6 was 14, and the effective halogen concentration (effective equivalent chlorine concentration) was 7 wt%.

[0114]

[Composition 7]

Sodium bromide: 15 wt% and a 12% aqueous solution of sodium hypochlorite: 42.4 wt% were added separately to the water.

[0115]

(Test Conditions)

- Test apparatus: flat membrane test apparatus

- Separation membrane: polyamide-based polymer reverse osmosis membrane ES20, manufactured by Nitto Denko Corporation

- Operating pressure: 0.75 MPa

- Raw water: Sagamihara well water (pH: 7.2, conductivity: 240 μ S/cm, bromide ion concentration: less than 1.0 mg/L)

- Reagent: each of the compositions 1, 2, and 4 to 7 was added in sufficient amount to produce an effective halogen concentration (effective equivalent chlorine concentration) of 10 mg/L.

[0116]

10 (Evaluation Methods)

- Effect on reverse osmosis membrane (RO membrane) rejection rate: the conductivity rejection rate (%) after 30 days operation

$(100 - [\text{permeate conductivity}/\text{feed water conductivity}] \times 100)$

- Effect on permeate: the effective halogen concentration (effective equivalent chlorine concentration, mg/L) within the permeate one hour after addition of the reagent was measured by the DPD method using a residual chlorine measuring instrument (DR-4000, manufactured by Hach Company)

- Oxidizing power: the oxidation-reduction potential (ORP) of the feed water after one hour was measured using an oxidation-reduction potential measuring device (RM-20P ORP meter, manufactured by DKK-TOA Corporation)

[0117]

[Comparative Test of Sterilization Power]

Under the conditions described below, each of the compositions 1, 2, and 4 to 7 was added to a simulated water, and the sterilization power was compared.

25 [0118]

(Test Conditions)

- Water: a simulated water prepared by adding normal bouillon to Sagamihara well water to adjust the number of general bacteria to 10^5 CFU/ml

- Reagent: each of the compositions 1, 2, and 4 to 7 was added in sufficient amount to produce an effective halogen concentration (effective equivalent chlorine concentration) of 1 mg/L (effective halogen concentration measurement method: measured by the DPD method using a residual chlorine measuring instrument (DR-4000, manufactured by Hach Company))

[0119]

(Evaluation Method)

The number of general bacteria 24 hours after the addition of the reagent was measured using a bacterial count measuring kit (Biochecker TTC, manufactured by San-Ai Oil Co., Ltd.).

[0120]

The test results are shown in Table 2.

[0121]

[Table 2]

	RO membrane rejection rate (after 30 days operation) (%)	Effective halogen concentration in RO permeate (mg/L)	ORP (mV)	Bacterial count after 24 hours (CFU/ml)
Composition 1	99	<0.01	650	<10 ³
Composition 2	92	0.5	620	<10 ³
Composition 5	90	1.0	660	<10 ³
Composition 6	97	0.2	630	<10 ³
Composition 4	71	5.5	790	<10 ³
Composition 7	70	2.0	800	<10 ³

[0122]

The compositions 1, 2, 5 and 6 maintained a high reverse osmosis membrane (RO membrane) rejection rate, exhibited a low effective halogen concentration (effective equivalent chlorine concentration) in the permeate, and had excellent oxidizing power and sterilization power. Among the compositions 1, 2, 5 and 6, the composition 1 maintained

the highest reverse osmosis membrane (RO membrane) rejection rate, and also exhibited the lowest effective halogen concentration (effective equivalent chlorine concentration) in the permeate.

[0123]

5 The composition 4 exhibited high oxidizing power and sterilization power, but the reverse osmosis membrane (RO membrane) rejection rate decreased, and the effective halogen concentration (effective equivalent chlorine concentration) in the permeate was also high. The composition 7 exhibited high oxidizing power and sterilization power, but the effective halogen concentration (effective equivalent chlorine concentration) in the
10 permeate was slightly high.

[0124]

[Comparative Test of Bromate Ion Concentration in Permeate]

 The bromate ion concentration in the permeate was compared for the cases where nitrogen gas purging was either performed or not performed during composition
15 preparation.

[0125]

[Preparation of Composition 1']

 In a similar manner to the composition 1, liquid bromine: 17 wt%, sulfamic acid: 10.7 wt%, sodium hydroxide: 12.9 wt%, potassium hydroxide: 3.95%, and water: the
20 balance were mixed together under a nitrogen atmosphere to prepare a composition 1'. The pH of the composition 1' was 14, the effective halogen concentration (effective equivalent chlorine concentration) was 7.5 wt%, and the bromate concentration was less than 5 mg/kg.

[0126]

25 [Preparation of Composition 8]

 Without performing nitrogen purging, liquid bromine: 17 wt%, sulfamic acid: 10.7 wt%, sodium hydroxide: 12.9 wt%, potassium hydroxide: 3.95%, and water: the balance were mixed together under normal atmospheric conditions to prepare a composition 8. The

pH of the composition 8 was 14, the effective halogen concentration (effective equivalent chlorine concentration) was 7.4 wt%, and the bromate concentration was 63 mg/kg.

[0127]

(Test Conditions)

- 5 - Test device: flat membrane test apparatus
 - Separation membrane: polyamide-based polymer reverse osmosis membrane

ES20, manufactured by Nitto Denko Corporation

- Operating pressure: 0.75 MPa
 - Raw water: Sagamihara well water (pH: 7.2, conductivity: 240 μ S/cm)
 10 - Reagent: the compositions 1' and 8 were each added in sufficient amount to produce an effective halogen concentration (effective equivalent chlorine concentration) of 50 mg/L

[0128]

(Evaluation Method)

- 15 The bromate ion concentration in the permeate was measured using an ion chromatography post-column absorbance method.

[0129]

The test results are shown in Table 3.

[0130]

- 20 [Table 3]

	In feed water (μ g/L)	In permeate (μ g/L)
Composition 1'	<1	<1
Composition 8	42	1

[0131]

In the composition 1', the bromate ion concentration in both the feed water and the permeate was less than 1 μ g/L. In the composition 8, the bromate ion concentration in

both the feed water and the permeate was higher than the corresponding value for the composition 1'.

[0132]

5 Next, the case where a stabilized hypobromous acid composition that is a "reaction product of a bromine-based oxidizing agent and a sulfamic acid compound" was used as a slime inhibitor (Example 4), the case where a "bromine-based oxidizing agent" was used as a slime inhibitor (Example 5), the case where hypochlorous acid was used as a typical slime inhibitor (Comparative Example 2), and the case where a stabilized hypochlorous acid composition that is a "reaction product of hypochlorous acid and a sulfamic acid
10 compound" was used as a slime inhibitor (Comparative Example 3) were compared in terms of the trihalomethane concentration in the treated water and the effect on the sterilization performance.

[0133]

[Composition 9]

15 A 12% aqueous solution of sodium hypochlorite: 50 wt%, sulfamic acid: 10 wt%, sodium hydroxide: 8 wt%, and water: the balance were mixed together to prepare a composition 9. The pH of the composition 9 was 14, and the effective halogen concentration (effective equivalent chlorine concentration) was 6 wt%.

[0134]

20 <Examples 4 and 5, Comparative Examples 2 and 3>

Under the conditions described below, each of the compositions 1, 3 and 4 was added to a raw water, and the total trihalomethane concentration in the treated water was compared. The simulated water described below was used as the raw water.

[0135]

25 (Test Conditions)

- Raw water: a simulated water (prepared by adding, to pure water, 8.9 mg/L of humic acid (manufactured by Wako Pure Chemical Industries, Ltd.) as a trihalomethane precursor, and sodium bromide (manufactured by Kanto Chemical Co., Inc., special grade)

as a bromide ion source in sufficient amount to produce a concentration of 0.1 to 300 mg/L)

- Reagent: the compositions 1, 3 and 4 were each added in sufficient amount to produce an effective halogen concentration (effective equivalent chlorine concentration) of

5 3 mg/L

- Raw water pH: adjusted so that the pH of the test water following addition of the reagent was pH 8

- Test temperature: 25°C

- Method of measuring effective halogen concentration: measured by the DPD

10 method using a residual chlorine measuring instrument (DR-4000, manufactured by Hach Company).

[0136]

(Evaluation Methods)

[Total trihalomethane concentration in treated water]

15 Samples prepared by adding the compositions 1, 3 and 4 to the simulated water and then adjusting the pH to 8 were each adjusted to a water temperature of 25°C and then stirred for 4 hours. After stirring for 4 hours, the total trihalomethane concentration (mg/L) in the treated water was measured. The results are shown in FIG. 2. Here, the term "total trihalomethane" indicates the combination of four compounds, namely chloroform,

20 bromodichloromethane, dibromochloromethane and bromoform.

[0137]

The total trihalomethane concentration was measured by simultaneous analysis by purge-trap gas chromatography mass spectrometry in accordance with the method prescribed by the Minister for Health, Labor and Welfare (Notification No. 261 from the
25 Minister for Health, Labor and Welfare, 2003) based on the prescriptions of ministerial ordinances relating to water quality standards.

[0138]

[Comparative Test of Sterilization Power]

Under the conditions described below, each of the compositions 1 and 9 was added to a simulated water, and the sterilization power was compared.

[0139]

(Test Conditions)

5 - Water: a simulated water prepared by adding normal bouillon to Sagami-hara well water to adjust the number of general bacteria to 10^5 CFU/ml

 - Reagent: each of the compositions 1 and 9 was added in sufficient amount to produce an effective halogen concentration (effective equivalent chlorine concentration) of 1 mg/L (effective halogen concentration measurement method: measured by the DPD
10 method using a residual chlorine measuring instrument (DR-4000, manufactured by Hach Company))

[0140]

(Evaluation Method)

 The number of general bacteria 24 hours after the addition of the reagent was
15 measured using a bacterial count measuring kit (Biochecker TTC, manufactured by San-Ai Oil Co., Ltd.).

[0141]

The test results are shown in Table 4.

[0142]

20 [Table 4]

	Initial bacterial count (CFU/ml)	Bacterial count after 24 hours (CFU/ml)
Example 4 (Composition 1)	10^5	$<10^3$
Comparative Example 3 (Composition 9)	10^5	10^4

[0143]

In this manner, compared with Comparative Examples 2 and 3, in Examples 4 and 5, slime production in the water containing trihalomethane precursors and bromide ions

was able to be better suppressed, and the production of trihalomethanes was able to be easily controlled.

[0144]

[Change over time in effective halogen concentration in trihalomethane precursor-

5 containing water]

[Preparation of Composition 2']

Based on content disclosed in JP H11-506139 A, a composition was prepared using the following procedure. The pH of the composition 2' was 14, the effective halogen concentration (effective equivalent chlorine concentration) was 5 wt%, and the bromate
10 concentration was 15 mg/kg.

(1) First, 41.7 g of a 12% aqueous solution of sodium hypochlorite was added to 27.0 g of a 40 wt% pure water solution of sodium bromide.

(2) A stabilized solution was prepared from 56.0 g of pure water, 26.0 g of sulfamic acid and 18.0 g of sodium hydroxide.

15 (3) Finally, 31.3 g of the stabilized solution of (2) was added under stirring to the solution of (1) to obtain the target composition 2'.

[0145]

<Example 6, Comparative Example 4>

Under the conditions shown in Table 5, the composition 1, the composition 2' or
20 the composition 4 was added to a simulated seawater A having a trihalomethane formation potential of 0.11 mg/L (prepared by adding 8.9 mg/L of humic acid (manufactured by Wako Pure Chemical Industries, Ltd.) as a trihalomethane precursor to an artificial seawater, TOC: 5 mg/L), or a simulated seawater B having a trihalomethane formation potential of 0.04 mg/L (prepared by adding 8.9 mg/L of humic acid (manufactured by
25 Wako Pure Chemical Industries, Ltd.) as a trihalomethane precursor to an artificial seawater, TOC: 5 mg/L), or a simulated water C having a trihalomethane formation potential of 0.01 mg/L (prepared by adding 8.9 mg/L of humic acid (manufactured by Wako Pure Chemical Industries, Ltd.) as a trihalomethane precursor to pure water, TOC: 5

mg/L), in an amount sufficient to produce an effective halogen concentration of 10 mg/L as Cl_2 or 5 mg/L as Cl_2 . Using an aqueous solution of sodium hydroxide or an aqueous solution of sulfuric acid, the pH of the test solution was adjusted to 8.4, and the solution was then left to stand in dark conditions at room temperature (25°C), while the change in the total halogen concentration was measured over time. The results are shown in Table 5. The simulated seawaters A and B were prepared using an artificial seawater (Aquamarine (a registered trademark), manufactured by Yashima Pure Chemicals Co., Ltd.), by dissolving the various components in pure water to achieve the compositions shown in Table 6. The trihalomethane formation potential was measured using the same method to that described in Example 1.

[0146]

The total halogen concentration (effective equivalent chlorine concentration) was measured in accordance with the procedure described below.

[0147]

The effective halogen concentration refers to the value (mg/L as Cl_2) obtained by diluting the sample, and then performing measurement by the effective chlorine measurement method (namely, the DPD (diethyl-p-phenylenediamine) method), using a multipurpose water quality analyzer DR/4000 manufactured by Hach Company (in the case of total halogen concentration, the measured item is "total chlorine"). The total halogen concentration mentioned here is deemed to be the value obtained by measurement using the effective chlorine measurement method (DPD method). Further, the effective bromine concentration (mg/L as Cl_2), reported as a chlorine-equivalent effective halogen concentration, can be calculated from the effective chlorine concentration, and is calculated as the measured value from the effective chlorine measurement method (DPD method) multiplied by 2.25 (159.8 (g/mol) / 70.9 (g/mol)) (wherein the molecular weight of chlorine is deemed 70.9 (g/mol), and the molecular weight of bromine is deemed 159.8 (g/mol)).

[0148]

[Table 5]

	Example 6-1	Example 6-2	Example 6-3	Example 6-4	Comparative Example 4-1	Comparative Example 4-2	Comparative Example 4-3
Reagent added	Composition 1	Composition 1	Composition 1	Composition 2'	Composition 4	Composition 4	Composition 4
Water	Simulated seawater A	Simulated seawater B	Simulated water C	Simulated seawater A	Simulated seawater A	Simulated seawater B	Simulated water C
	Total halogen [mg/L]	Total halogen [mg/L]	Total halogen [mg/L]	Total halogen [mg/L]	Total halogen [mg/L]	Total halogen [mg/L]	Total halogen [mg/L]
Start	10.0	5.0	10.0	10.0	10.0	5.0	10.0
after 1 day	8.6	3.8	8.5	8.1	6.5	3.2	8.3
after 3 days	8.2	3.4	8.3	7.3	3.2	2.0	7.2
after 7 days	7.5	3.1	7.7	6.7	0.8	0.4	6.6

[0149]

[Table 6]

	Component	Simulated seawater A	Simulated seawater B
Amount of each component contained in 20 L of simulated seawater [g]	Magnesium chloride hexahydrate	222.23	16.988
	Calcium chloride dihydrate	30.70	2.347
	Strontium chloride hexahydrate	0.85	0.065
	Potassium chloride	13.89	1.062
	Sodium hydrogen carbonate	4.02	0.307
	Potassium bromide	2.01	0.154
	Boric acid	0.54	0.041
	Sodium fluoride	0.06	0.005
	Sodium chloride	490.68	37.509
	Sodium sulfate (anhydrous)	81.88	6.259
	Humic acid	0.18	0.18
Pure water		balance	balance
Bromide ion concentration [mg/L]		67.5	5.2

5

[0150]

Based on a comparison of the Examples and Comparative Examples in Table 5, it is evident that, compared with the composition 4, the composition 1 and the composition 2'

were able to maintain a high residual halogen concentration over a long period, meaning the separation membrane can be effectively sterilized even when the membrane separation apparatus is stopped for a long period. Based on a comparison of Comparative Examples 4-1, 4-2 and 4-3, it is thought that the reason that the rate of decrease in the total halogen concentration in the simulated seawaters A and B was greater than in the simulated water C was because the hypochlorous acid reacted with the bromide ions in the simulated seawaters, causing a change to a more unstable hypobromous acid. On the other hand, comparing Examples 6-1, 6-2 and 6-4 reveals that, compared with the composition 4, the decrease in the total halogen concentration was also suppressed in the simulated seawaters for the stabilized hypobromous acid compositions of the compositions 1 and 2'. It is thought that the reason for this observation is not only because the stabilized hypobromous acid composition exhibits superior stability to hypochlorous acid or hypobromous acid, but also because a portion of the stabilized hypobromous acid composition reacts with the chloride ions in the artificial seawater, producing extremely stable combined chlorine.

[0151]

[Effects on reverse osmosis membrane (RO membrane) rejection rate and permeate volume following storage immersed in fungicide solution]

<Example 7>

Separation membranes were stored for 30 days immersed in various fungicide solutions, and the results of subsequently measuring the conductivity rejection rate of the membrane and the permeate volume retention rate are shown in Table 7.

[0152]

(Test Conditions)

- Separation membrane: polyamide-based polymer reverse osmosis membrane

ES15, manufactured by Nitto Denko Corporation

- Test water: Simulated seawater A or simulated seawater B or simulated water C

- Reagent: added in sufficient amount to achieve a total halogen concentration of 10 mg/L as Cl₂

- Test water pH: adjusted to prescribed pH using aqueous solution of sodium hydroxide or aqueous solution of sulfuric acid

- Separation membrane immersed storage period: 30 days

- Immersed storage conditions: dark conditions, room temperature (25°C)

5 [0153]

(Method of Measuring Rejection Rate)

- Test apparatus: flat membrane test apparatus

- Operating pressure: 0.75 MPa

- Raw water: Sagamihara well water (pH: 7.2, conductivity: 24 mS/m)

10 - Conductivity rejection rate [%] = $100 - [\text{permeate conductivity} / \text{feed water conductivity}] \times 100$

- Permeate volume retention rate [%] = $[\text{permeate volume of separation membrane after storage immersed in test water} / \text{permeate volume of new separation membrane}] \times 100$

[0154]

[Table 7]

	Example 7-1	Example 7-2	Example 7-3	Example 7-4	Example 7-5	Example 7-6	Example 7-7	Comparative Example 5-1	Comparative Example 5-2
Reagent added	Composition 1	Composition 1	Composition 1	Composition 1	Composition 1	Composition 1	Composition 2'	Composition 4	Composition 4
Test water	Simulated seawater A	Simulated water C	Simulated seawater B	Simulated seawater B	Simulated seawater B	Simulated seawater B	Simulated water C	Simulated seawater A	Simulated water C
Test water pH	8.4	8.4	8.4	6.0	5.5	5.0	8.4	8.4	8.4
RO membrane conductivity rejection rate [%]	98	98	98	98	98	98	98	<70	<70
RO membrane permeate volume retention rate [%]	>90	>90	>90	>90	79	60	>90	>90	>90

[0155]

When the separation membrane was stored immersed in the composition 4 for a long period, the separation membrane deteriorated and the rejection rate decreased considerably, but even when the separation membrane was stored immersed in the

5 composition 1 or 2' for a long period, the rejection rate was maintained at a high value, and membrane deterioration was suppressed.

[0156]

In this manner, it was evident that in those examples where a stabilized hypobromous acid composition was used, even in a membrane separation apparatus that
10 undergoes both operating periods and operating downtimes, degradation of the separation membrane can be suppressed, and the separation membrane can be effectively sterilized during the operating downtimes.

REFERENCE SIGNS LIST

15 [0157]

1: Membrane separation system

10: Raw water tank

12: Membrane separation apparatus

14: Pump

20 16: Raw water line

18: Raw water supply line

20: Permeate line

22: Concentrate line

24: Fungicide supply line

25

CLAIMS

1. A method for controlling slime on a separation membrane, the method comprising incorporating a bromine-based oxidizing agent, or a reaction product of a bromine
5 compound and a chlorine-based oxidizing agent, in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.
2. A method for controlling slime on a separation membrane, the method comprising
10 incorporating a bromine-based oxidizing agent, or a reaction product of a bromine compound and a chlorine-based oxidizing agent, and a sulfamic acid compound, in a trihalomethane precursor-containing feed water or wash water supplied to a membrane separation apparatus with a separation membrane.
- 15 3. A method for controlling slime on a separation membrane, the method comprising incorporating a reaction product of a sulfamic acid compound with a bromine-based oxidizing agent, or with a reaction product of a bromine compound and a chlorine-based oxidizing agent, in a trihalomethane precursor-containing feed water or wash water
20 supplied to a membrane separation apparatus with a separation membrane.
4. A method for controlling slime on a separation membrane, the method comprising incorporating a mixture of bromine and a sulfamic acid compound, or a reaction product of bromine and a sulfamic acid compound, in a trihalomethane precursor-containing feed
25 water or wash water supplied to a membrane separation apparatus with a separation membrane.
5. The method for controlling slime on a separation membrane according to Claim 4, wherein the reaction product of bromine and a sulfamic acid compound is obtained by a

method including a step of adding and reacting bromine, under an inert gas atmosphere, with a mixed liquid comprising water, an alkali and a sulfamic acid compound.

6. The method for controlling slime on a separation membrane according to any one of Claims 1 to 5, wherein a concentration of trihalomethane precursor in the feed water or wash water, as a trihalomethane formation potential, is at least 0.001 mg/L.

7. The method for controlling slime on a separation membrane according to any one of Claims 1 to 6, wherein the separation membrane is a polyamide-based polymer membrane.

8. The method for controlling slime on a separation membrane according to any one of Claims 1 to 7, wherein the trihalomethane precursor comprises humins.

9. The method for controlling slime on a separation membrane according to any one of Claims 1 to 8, wherein the feed water or wash water also comprises bromide ions.

10. The method for controlling slime on a separation membrane according to Claim 9, wherein the bromide ion concentration in the feed water or wash water is at least 5 mg/L.

11. The method for controlling slime on a separation membrane according to any one of Claims 1 to 10, wherein the membrane separation apparatus with a separation membrane is a membrane separation apparatus that undergoes both operating periods and operating downtimes, and during an operating downtime:

the bromine-based oxidizing agent, or the reaction product of a bromine compound and a chlorine-based oxidizing agent is added,

the bromine-based oxidizing agent, or the reaction product of a bromine compound and a chlorine-based oxidizing agent, and the sulfamic acid compound are added,

the reaction product of a sulfamic acid compound with a bromine-based oxidizing agent, or with a reaction product of a bromine compound and a chlorine-based oxidizing agent is added, or

the reaction product of bromine and a sulfamic acid compound is added.

5

12. The method for controlling slime on a separation membrane according to Claim 11, wherein a pH of the water introduced into the membrane separation apparatus is 5.5 or higher.

10 13. The method for controlling slime on a separation membrane according to Claim 10 or 11, wherein the water introduced into the membrane separation apparatus is at least one of seawater and salt water.