

METHOD AND APPARATUS FOR RECOVERING COOLING WATER EFFLUENT

Field of the Invention

[0001] The present invention relates to a method and an apparatus for recovering cooling water effluent from a cooling system for building air conditioning and industrial processes such as those in chemical, papermaking, ironmaking, and electric power industries.

Background of the Invention

[0002] In water systems such as cooling water systems and boiler water systems, scale forms on heat transfer surfaces and pipes in contact with water. In high-concentration operation, in which the amount of cooling water discharged outside the system (blowdown) is reduced for resource and energy conservation, salts dissolved in the water are concentrated and readily corrode heat transfer surfaces, and insoluble salts precipitate as scale. Scale deposited on wall surfaces of units, for example, would cause serious problems with the operation of boilers and heat exchangers, including decreased thermal efficiency and pipe clogging.

[0003] Recently, efforts have been made to utilize water as effectively as possible for water and energy conservation. For high-concentration operation, the inhibition of scale precipitation is limited.

[0004] Attempts have been made to recover blowdown water discharged from a cooling tower through a recovery system

and then return the treated water to the cooling tower. This recovery system typically removes salts (ions) through a reverse osmosis (RO) membrane and then returns the treated water to the cooling tower. For example, the following systems have been discussed (Patent Literatures 1 to 3).

[0005] System 1: flocculation → sand filtration → safety filter → RO membrane

System 2: flocculation → sand filtration → pretreatment membrane → RO membrane

System 3: flocculation → dissolved-air pressure flotation → sand filtration → safety filter → RO membrane

System 4: decarbonation tower → pretreatment membrane → RO membrane

System 5: RO membrane

[0006] Although System 5 is a simple system composed only of an RO membrane unit, it is not suitable for stable treatment since the RO membrane is clogged by suspended solids contained in blowdown water.

[0007] In Systems 1 to 4, suspended solids are removed from blowdown water by flocculation or through a pretreatment membrane upstream of the RO membrane. Removing suspended solids from the blowdown water allows for stable RO membrane treatment. However, a dispersant added to the circulating cooling water system and contained in the blowdown water impedes flocculation. Thus, Systems 1 to 3

require a considerable amount of flocculant to be added for flocculation.

[0008] The RO membrane unit requires a dispersant for dispersing scale components to perform stable treatment at high water recovery rates. However, the dispersant present in the blowdown water is removed during flocculation. It is therefore necessary to add additional dispersant to the RO membrane feed water to disperse scale components for stable treatment through the RO membrane.

[0009] In System 4, which removes suspended solids from blowdown water through a pretreatment membrane without performing flocculation, the dispersant present in the blowdown water is removed by the pretreatment membrane. It is therefore necessary to add additional dispersant to the RO membrane feed water to perform stable treatment in the RO membrane unit.

[0010] Patent Literature 1: Japanese Patent Publication 2003-1256 A

Patent Literature 2: Japanese Patent Publication 2002-18437 A

Patent Literature 3: Japanese Patent Publication 2009-297600 A

Summary of Invention

[0011] Conventional water recovery systems require dispersants to be added to RO membrane feed water so that RO

membrane units can operate stably. This adds more cost and workload and thus results in increased treatment cost.

[0012] An object of the present invention is to provide a method and an apparatus for recovering a cooling water effluent such as blowdown water discharged from a circulating cooling water system through stable RO membrane treatment with reduced water treatment cost and improved water recovery rate.

[0013] After conducting extensive research to achieve the foregoing object, the inventor has obtained the following findings: the addition of a dispersant to a water recovery system for recovering a cooling water effluent such as blowdown water discharged from a circulating cooling water system during RO membrane treatment can be eliminated or reduced by providing a pretreatment membrane that allows a dispersant added to the circulating cooling water system to pass through the pretreatment membrane so that the dispersant added to the circulating cooling water system and present in the cooling water effluent passes through the pretreatment membrane and can be effectively utilized as a dispersant in the RO membrane. This allows for stable water treatment with reduced water treatment cost and improved water recovery rate.

[0014] The present invention is based on the foregoing findings, and the gist thereof is as follows.

[0015] [1] A method for recovering a cooling water effluent discharged from a circulating cooling water system, the circulating cooling water system being added with a dispersant for dispersing a scale component,

the method comprising:

a step of treating the effluent through a water recovery system including a pretreatment membrane and a reverse osmosis membrane to obtain treated water; and

a step of returning the treated water to the circulating cooling water system,

wherein the dispersant added to the circulating cooling water system passes through the pretreatment membrane.

[0016] [2] The method for recovering a cooling water effluent according to [1], wherein a permeability of the pretreatment membrane for the dispersant is 80% or more as determined by the following equation:

$$\text{Permeability} = (\text{dispersant concentration of pretreatment membrane permeate water} / \text{dispersant concentration of pretreatment membrane feed water}) \times 100$$

[0017] [3] The method for recovering a cooling water effluent according to [1] or [2], wherein the pretreatment membrane is a microfiltration membrane or an ultrafiltration membrane.

[0018] [4] The method for recovering a cooling water effluent according to any one of [1] to [3], wherein the

effluent supplied to the pretreatment membrane has a pH of 5 or more.

[0019] [5] The method for recovering a cooling water effluent according to any one of [1] to [4], wherein the pretreatment membrane has a molecular weight cutoff of 30,000 or more.

[0020] [6] The method for recovering a cooling water effluent according to any one of [1] to [5], wherein the dispersant is a polymer having a sulfo group and a carboxyl group.

[0021] [7] The method for recovering a cooling water effluent according to [6], wherein the dispersant is a copolymer of methacrylic acid and/or acrylic acid with 3-allyloxy-2-hydroxy-1-propanesulfonic acid and/or 2-acrylamido-2-methylpropanesulfonic acid.

[0022] [8] The method for recovering a cooling water effluent according to any one of [1] to [7], further comprising adjusting the pH of feed water supplied to the reverse osmosis membrane to 4.0 to 7.5.

[0023] [9] The method for recovering a cooling water effluent according to any one of [1] to [8], further comprising measuring the dispersant concentration of feed water supplied to the reverse osmosis membrane and adjusting the dispersant concentration to a predetermined level by adding the dispersant to the reverse osmosis membrane feed

water.

[0024] [10] The method for recovering a cooling water effluent according to any one of [1] to [9], further comprising measuring the conductivity of at least one of the effluent, reverse osmosis membrane feed water, and reverse osmosis membrane concentrated water and adjusting the water recovery rate of the reverse osmosis membrane depending on the measured conductivity.

[0025] [11] The method for recovering a cooling water effluent according to any one of [1] to [10], further comprising measuring the dispersant concentration of the effluent and/or reverse osmosis membrane feed water and adjusting the water recovery rate of the reverse osmosis membrane depending on the measured dispersant concentration.

[0026] [12] The method for recovering a cooling water effluent according to any one of [1] to [11], further comprising adding a polymeric compound having a phenolic hydroxyl group to the effluent.

[0027] [13] The method for recovering a cooling water effluent according to any one of [1] to [12], wherein on an occasion when the water recovery system is stopped, before stopping the water recovery system, a step of circulating the reverse osmosis membrane permeate water is conducted, or a step of supplying pure water or deionized water to the reverse osmosis membrane and discharging the reverse osmosis

membrane concentrated water outside the system is conducted.

[0028] [14] An apparatus for recovering a cooling water effluent, comprising:

a pretreatment membrane unit to which an effluent discharged from a circulating cooling water system is supplied,

a reverse osmosis membrane unit to which permeate water flowing from the pretreatment membrane unit is supplied, and

returning means for returning permeate water flowing from the reverse osmosis membrane unit to the circulating cooling water system,

wherein the circulating cooling water system includes dispersant-adding means for adding a dispersant for dispersing a scale component to the water system and wherein the dispersant passes through the pretreatment membrane.

[0029] [15] The apparatus for recovering a cooling water effluent according to [14], wherein the permeability of the pretreatment membrane for the dispersant is 80% or more as determined by the following equation:

$$\text{Permeability} = (\text{dispersant concentration of pretreatment membrane permeate water} / \text{dispersant concentration of pretreatment membrane feed water}) \times 100$$

[0030] [16] The apparatus for recovering a cooling water effluent according to [14] or [15], wherein the pretreatment membrane is a microfiltration or ultrafiltration membrane.

[0031] [17] The apparatus for recovering a cooling water effluent according to any one of [14] to [16], wherein feed water supplied to the pretreatment membrane has a pH of 5 or more.

[0032] [18] The apparatus for recovering a cooling water effluent according to any one of [14] to [17], wherein the pretreatment membrane has a molecular weight cutoff of 30,000 or more.

[0033] [19] The apparatus for recovering a cooling water effluent according to any one of [14] to [18], wherein the dispersant is a polymer having a sulfo group and a carboxyl group.

[0034] [20] The apparatus for recovering a cooling water effluent according to [19], wherein the dispersant is a copolymer of methacrylic acid and/or acrylic acid with 3-allyloxy-2-hydroxy-1-propanesulfonic acid and/or 2-acrylamido-2-methylpropanesulfonic acid.

[0035] [21] The apparatus for recovering a cooling water effluent according to any one of [14] to [20], further comprising pH-adjusting means for adjusting the pH of feed water supplied to the reverse osmosis membrane to 4.0 to 7.5.

[0036] [22] The apparatus for recovering a cooling water effluent according to any one of [14] to [21], further comprising:

dispersant-concentration measuring means for measuring

the dispersant concentration of feed water supplied to the reverse osmosis membrane; and

dispersant-adjusting means for adjusting the dispersant concentration measured by the dispersant-concentration measuring means to a predetermined level by adding the dispersant to the reverse osmosis membrane feed water.

[0037] [23] The apparatus for recovering a cooling water effluent according to any one of [14] to [22], further comprising:

conductivity-measuring means for measuring the conductivity of at least one of the effluent, reverse osmosis membrane feed water, and reverse osmosis membrane concentrated water, and

water-recovery-rate adjusting means for adjusting the water recovery rate of the reverse osmosis membrane depending on the conductivity measured by the conductivity-measuring means.

[0038] [24] The apparatus for recovering a cooling water effluent according to any one of [14] to [23], further comprising:

dispersant-concentration measuring means for measuring the dispersant concentration of the effluent and/or reverse osmosis membrane feed water, and

water-recovery-rate adjusting means for adjusting the water recovery rate of the reverse osmosis membrane

depending on the dispersant concentration measured by the dispersant-concentration measuring means.

[0039] [25] The apparatus for recovering a cooling water effluent according to any one of [14] to [24], further comprising flocculant-adding means for adding a polymeric compound having a phenolic hydroxyl group to the effluent.

[0040] [26] The apparatus for recovering a cooling water effluent according to any one of [14] to [25], wherein the reverse osmosis membrane unit includes:

permeate-water circulating means for circulating the reverse osmosis membrane permeate water upstream of the reverse osmosis membrane unit or means for supplying pure water or deionized water to the reverse osmosis membrane unit;

concentrated-water discharging means for discharging the reverse osmosis membrane concentrated water outside the system; and

control means for stopping the apparatus for recovering a cooling water effluent,

wherein the control means stops the apparatus after a step of circulating the reverse osmosis membrane permeate water upstream is conducted, or a step of supplying pure water or deionized water and discharging the reverse osmosis membrane concentrated water outside the system is conducted.

Advantageous Effects of Invention

[0041] According to the present invention, the cooling water effluent can be treated through the pretreatment membrane upstream of the RO membrane to remove suspended solids, thereby stabilizing the subsequent RO membrane treatment.

[0042] According to the present invention, the dispersant added to the circulating cooling water system and present in the cooling water effluent passes through the pretreatment membrane and can be effectively utilized as a dispersant in the RO membrane. This eliminates the need to supplement the loss of the dispersant upstream of the RO membrane as in conventional systems and thus provides a greater efficiency in terms of cost and process, which results in a significant reduction in treatment cost. The dispersant that has passed through the pretreatment membrane can be used to perform stable RO membrane treatment with improved water recovery rate.

[0043] Thus, the method and apparatus for recovering a cooling water effluent according to the present invention can prevent scale formation in the RO membrane unit using a simpler system to enable stable water recovery over a long period of time.

Description of Embodiments

[0044] Embodiments of the present invention will now be described in detail.

[0045] <Cooling Water Effluent>

A typical cooling water effluent to be subjected to a water recovery process in the present invention is blowdown water discharged from a cooling tower. The present invention, however, is not limited to the recovery of blowdown water, but may be applied to the recovery of all types of effluents discharged from circulating cooling water systems. For example, part or all of circulating cooling water may be extracted from a circulating pipe of a circulating cooling water system and treated according to the present invention before the treated water is returned to the circulating cooling water system. An effluent discharged from a branch of a pipe of a side filter or light filter may also be treated and recovered.

[0046] In the present invention, the cooling water effluent selected for treatment is sequentially treated through a pretreatment membrane unit and an RO unit before the treated water is returned to the circulating cooling water system.

[0047] <Strainer>

Although the cooling water effluent may be directly treated through the pretreatment membrane unit, it is preferred to allow the cooling water effluent to pass through a strainer disposed upstream of the pretreatment membrane unit to remove coarse suspended solids and foreign

particles from the cooling water effluent before clarification in the pretreatment membrane unit. Although the system can be operated without a strainer, the pretreatment membrane might be damaged by coarse suspended solids and foreign particles present in the cooling water effluent.

[0048] The strainer is preferably an automatic self-cleaning strainer.

[0049] The strainer may be any type of strainer, such as a Y-strainer or bucket strainer.

[0050] The strainer preferably has a pore size of 100 to 500 μm . If the strainer has a pore size of less than 100 μm , it will clog quickly. If the strainer has a pore size of more than 500 μm , coarse suspended solids and foreign particles are likely to pass through the strainer and damage the pretreatment membrane.

[0051] The strainer may be replaced with other filters such as string-wound filters and pleat filters. Strainers are preferred for reasons of replacement frequency and cleaning efficiency.

[0052] <Pretreatment Membrane Unit>

The cooling water effluent, either as-discharged or after clarification through the strainer, is then treated through a pretreatment membrane unit.

[0053] The pretreatment membrane unit removes suspended

solids and colloidal components, which are responsible for membrane fouling of RO membrane units, from the cooling water effluent. The pretreatment membrane unit may include a microfiltration (MF) or ultrafiltration (UF) membrane. The pretreatment membrane unit may include any type of membrane, such as a hollow-fiber membrane or spiral-wound membrane. The pretreatment membrane unit may employ any type of filtration, such as inside-out filtration, outside-in filtration, cross-flow filtration, or dead-end filtration.

[0054] The UF membrane used as the pretreatment membrane preferably has a molecular weight cutoff of 30,000 or more. If the UF membrane has a molecular weight cutoff of less than 30,000, the dispersant present in the cooling water effluent may be unable to pass through the membrane, and additional dispersant may therefore need to be added upstream of the RO membrane unit. Although there is no particular upper limit to the molecular weight cutoff of the UF membrane, a UF membrane having a molecular weight cutoff of 1,000,000 or less can remove, for example, polymer polysaccharides, which are responsible for clogging of RO membranes, from the cooling water effluent. The pore size of the MF membrane used as the pretreatment membrane is preferably about 0.1 to 0.01 μm for the same reason as the molecular weight cutoff of the UF membrane.

[0055] The permeability of the pretreatment membrane for

the dispersant, described later, is preferably 80% or more, particularly 85% or more, as determined by the following equation:

Permeability = (dispersant concentration of pretreatment membrane permeate water / dispersant concentration of pretreatment membrane feed water) $\times$ 100

If the permeability of the pretreatment membrane for the dispersant falls below the above lower limit, the advantageous effects of the present invention cannot be effectively achieved. The upper limit of the permeability of the pretreatment membrane for the dispersant is typically 100%.

[0056] To achieve such dispersant permeability, it is preferred to use a suitable dispersant, described later, and to supply pretreatment membrane feed water having a pH of 5 or more to the pretreatment membrane unit. If the pretreatment membrane feed water has a pH of less than 5, the advantageous effects of the present invention may not be achieved because of low permeability of the pretreatment membrane for the dispersant, even if the dispersant is a polymer having sulfo groups and carboxyl groups, described later. The pretreatment membrane feed water may have any pH not lower than 5, and there is no particular upper limit to the pH of the pretreatment membrane feed water. It is preferred to directly treat a cooling water effluent such as

cooling tower blowdown water, which generally has a pH of about 8 to 10, typically about 8 to 9.

[0057] <Dispersant>

The dispersant added to the circulating cooling water system in the present invention passes through the pretreatment membrane.

[0058] The dispersant is preferably a polymer having sulfo groups and carboxyl groups.

The dispersant dissociates and functions more effectively as a dispersant at a higher pH. In the RO membrane unit downstream of the pretreatment membrane unit, however, concentrated components such as calcium readily precipitate as scale at a high pH; therefore, RO membrane feed water is treated at a low pH, as described later. If the dispersant has only carboxyl groups and no sulfo groups, the dispersant is insolubilized and does not function as a dispersant at a low pH in the RO membrane unit. Thus, the dispersant is preferably a polymer having sulfo groups and carboxyl groups.

[0059] Examples of polymers having sulfo groups and carboxyl groups, that are suitable as dispersants include copolymers of monomers having a sulfo group and monomers having a carboxyl group and terpolymers of these monomers with other monomers that can be copolymerized therewith.

[0060] Examples of monomers having a sulfo group include

conjugated diene sulfonic acids such as 2-methyl-1,3-butadiene-1-sulfonic acid, unsaturated (meth)allyl ether monomers having a sulfo group such as 3-(meth)allyloxy-2-hydroxypropanesulfonic acid, 2-(meth)acrylamido-2-methylpropanesulfonic acid, 2-hydroxy-3-acrylamidopropanesulfonic acid, styrenesulfonic acid, methallylsulfonic acid, vinylsulfonic acid, allylsulfonic acid, isoamylenesulfonic acid, and salts thereof, preferably 3-allyloxy-2-hydroxy-1-propanesulfonic acid (HAPS) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS). These monomers having a sulfo group may be used alone or in a mixture.

[0061] Examples of monomers having a carboxyl group include acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, vinylacetic acid, atropic acid, maleic acid, fumaric acid, itaconic acid, hydroxyethylacrylic acid, and salts thereof, preferably acrylic acid and methacrylic acid. These monomers having a carboxyl group may be used alone or in a mixture.

[0062] Examples of monomers that can be copolymerized with these monomers include amides such as N-tert-butylacrylamide (N-tBAA) and N-vinylformamide.

[0063] Examples of dispersants suitable for the present invention include, but not limited to, a copolymer of acrylic acid (AA) and 2-acrylamido-2-methylpropanesulfonic

acid (AMPS) in an AA/AMPS ratio (molar ratio) of 70 to 90 : 10 to 30, a copolymer of AA, AMPS, and an amide such as N-tert-butylacrylamide (N-tBAA) in an AA/AMPS/amide ratio (molar ratio) of 40 to 90 : 5 to 30 : 5 to 30, and a copolymer of AA and 3-allyloxy-2-hydroxypropanesulfonic acid (HAPS) in an AA/HAPS ratio (molar ratio) of 70 to 90 : 10 to 30.

[0064] The polymer having sulfo groups and carboxyl groups preferably has a weight average molecular weight of 1,000 to 30,000. A polymer having a weight average molecular weight of less than 1,000 has an insufficient dispersion effect. A polymer having a weight average molecular weight of more than 30,000 does not easily pass through the pretreatment membrane and may itself adsorb onto and clog the pretreatment membrane or the RO membrane.

[0065] The dispersant is preferably added to the circulating cooling water system in an amount of 3 to 30 mg/L, particularly 5 to 20 mg/L, as the active ingredient (i.e., the polymer) for reasons of dispersion effect and economy in the cooling tower and dispersion effect in the RO membrane feed water. The dispersant may be added at any location in any manner.

[0066] Instead of the polymers having sulfo groups and carboxyl groups, other dispersants having a sufficient dispersion effect may be used, including other polymers and

phosphoric acid compounds such as phosphonic acid. The scale components that can form may be determined from the quality of the raw water supplied to the circulating cooling water system, and any dispersant that can prevent the formation of these scale components may be added in an effective concentration.

[0067] <RO Membrane Unit>

The cooling water effluent treated through the pretreatment membrane unit described above (pretreatment membrane permeate water) is then desalinated through the RO membrane unit.

[0068] The RO membrane unit may include any suitable RO membrane selected depending on the quality of the cooling water effluent to be treated (the quality of the raw water supplied to the circulating cooling water system and the concentration ratio in the circulating cooling water system). The RO membrane preferably has a salt rejection of 80% or more, particularly 85% or more. An RO membrane having a salt rejection of less than 80% has low desalination efficiency and thus cannot produce high-quality treated water (permeate water). The RO membrane may be made of any material, such as a polyamide composite membrane or cellulose acetate membrane. The RO membrane may be any type of membrane, such as a hollow-fiber membrane or spiral-wound membrane.

[0069] As described below, there is a suitable pH for the RO membrane feed water (i.e., the feed water that is supplied and treated through the RO membrane unit). To adjust the pH of the RO membrane feed water, it is preferred to provide pH-adjusting means for adjusting the pH by adding an acid between the pretreatment membrane unit and the RO membrane unit. The pH-adjusting means may be, for example, means for adding an acid directly to an RO membrane feed water inlet line or to a line mixer disposed in that line, or to a separate pH adjustment tank, by a chemical feed pump or other device. Examples of acids suitable for use herein include, but not limited to, inorganic acids such as hydrochloric acid, sulfuric acid, and nitric acid.

[0070] The pH of the cooling water circulating through the circulating cooling water system normally increases to about 8 to 9 during high-concentration circulation operation. Such high pH levels are suitable for the dispersant to pass through the pretreatment membrane unit. The cooling water effluent is further concentrated in the RO membrane unit, which increases the risk of scale formation. To inhibit scale formation, it is preferred to operate the RO membrane unit at a lower pH. The RO membrane feed water preferably has a pH of 4.0 to 7.5. If the RO membrane feed water has a pH of more than 7.5, scale components such as calcium carbonate, calcium phosphate, calcium sulfate, and barium

sulfate may precipitate, depending on the water quality.

[0071] When the cooling water effluent contains silica in a concentration of more than 30 mg/L, it is preferred to reduce the pH of the RO membrane feed water to 4.0 to 5.5 to inhibit silica precipitation. RO membrane feed water having a lower pH is preferred to inhibit scale precipitation. RO membrane feed water having a pH of less than 4.0 is economically undesirable since it requires a large amount of acid.

[0072] When the cooling water effluent contains large amounts of humic and fulvic acids, they may clog the RO membrane. In this case, it is preferred to adjust the pH of the cooling water effluent to 5.5 to 7.0, particularly 5.5 to 6.5. At such pH levels, humic and fulvic acids dissociate and are thus less likely to clog the RO membrane, and the calcium present in the cooling water is more effectively dispersed by the dispersant and is thus less likely to form a complex with fulvic acids.

[0073] In the present invention, a dispersant that passes through the pretreatment membrane is added to the circulating cooling water system so that the dispersant present in the cooling water effluent and entering the water recover system passes through the pretreatment membrane into the treated water (permeate water). The dispersant that has passed through the pretreatment membrane is used for scale

dispersion in the RO membrane unit. The dispersant therefore needs to be present in the RO membrane feed water in a concentration effective for scale dispersion.

[0074] The dispersant concentration of the RO membrane feed water required for scale dispersion in the RO membrane unit varies depending on factors such as the quality of the cooling water effluent and the treatment conditions (e.g., water recovery rate) of the pretreatment membrane and the RO membrane and cannot be exactly determined. Generally, the dispersant concentration of the RO membrane feed water is preferably about 3 mg/L or more, particularly about 5 to 30 mg/L.

[0075] When the dispersant concentration of the RO membrane feed water is insufficient to achieve a sufficient scale dispersion effect in the RO membrane unit, it is preferred to add additional dispersant to the inlet side of the RO membrane unit (between the pretreatment membrane unit and the RO membrane unit). The dispersant added herein may be a dispersant suitable for use in the circulating cooling water system as described above. The dispersant, however, does not necessarily have to be the same as the dispersant added to the circulating cooling water system, but may be different.

[0076] The dispersant concentration of the RO membrane feed water may be measured and adjusted to a predetermined

level by controlling the amount of dispersant added. The dispersant concentration may be measured by nephelometry (e.g., the method disclosed in Japanese Unexamined Patent Application Publication No. 2006-64498). Additional dispersant may be added to the RO membrane feed water, for example, by dispersant-adding means that cooperates with means for measuring the dispersant concentration of the RO membrane feed water.

[0077] To utilize the dispersant added to the circulating cooling water system as a dispersant in the RO membrane unit according to the present invention, the dispersant added to the circulating cooling water system and present in the cooling water effluent needs to be supplied to the RO membrane unit while having sufficient activity to function as a dispersant. The activity of the dispersant depends on the residence time of the cooling water in the cooling tower of the circulating cooling water system. It may be preferred to adjust the residence time of the cooling water in the cooling tower of the circulating cooling water system so that the dispersant has sufficient activity in the RO membrane unit.

[0078] The water recovery rate of the RO membrane unit is preferably determined by taking into account the tendency for scale to precipitate in the RO membrane unit. The water recovery rate of the RO membrane may be adjusted depending

on factors such as the conductivity and calcium and magnesium concentrations of the RO concentrated water since the conductivity of the cooling water effluent to be treated according to the present invention and the concentrations of scale-forming constituents such as calcium and magnesium in the cooling water effluent can vary. The water recovery rate may also be set by determining whether scale is likely to form from factors such as pH, dispersant concentration, and water quality.

[0079] Specifically, the conductivity of at least one of the cooling water effluent, the RO membrane feed water, and the RO membrane concentrated water may be measured using a conductivity meter, and the water recovery rate of the RO membrane unit may be controlled by evaluating the tendency for scale to precipitate in the RO membrane unit based on the measured conductivity. In this case, when the conductivity measured using the conductivity meter is high, the tendency for scale to precipitate is determined to be high, and the water recovery rate is decreased by decreasing the degree of valve opening on the permeate side of the RO membrane. In the contrary case where the conductivity measured using the conductivity meter is low, the tendency for scale to precipitate is determined to be low, and the water recovery rate is increased by increasing the degree of valve opening on the permeate side of the RO membrane unit.

[0080] Alternatively, the dispersant concentration of the cooling water effluent and/or the RO membrane feed water is measured. If the measured dispersant concentration is high, the tendency for scale to precipitate is determined to be low, and the water recovery rate is increased by increasing the degree of valve opening on the permeate side of the RO membrane unit. Conversely, if the measured dispersant concentration is low, the tendency for scale to precipitate is determined to be high, and the water recovery rate is decreased by decreasing the degree of valve opening on the permeate side of the RO membrane.

[0081] The RO membrane unit is preferably flushed with the unconcentrated cooling water effluent, the RO membrane permeate water, pure water, or deionized water before the RO membrane unit is stopped, particularly if there is a risk of silica scale formation. If the RO membrane unit is stopped while concentrated water remains in the RO membrane unit, silica or other scale may form depending on the standby time, and the RO membrane unit may become unstable when restarted. In this case, for example, the RO membrane unit may be stopped after the RO membrane is purged with the RO membrane permeate water both on the primary (feed) side and on the secondary (concentrate) side by circulating the RO membrane permeate water to the inlet side of the RO membrane unit and discharging the RO membrane concentrated water outside the

system.

[0082] <Other Treatments>

A slime control agent may be added to the circulating cooling water system according to the present invention. Examples of slime control agents include hypochlorites such as sodium hypochlorite (NaClO); chlorine agents such as chlorine gas, chloramine, and chlorinated isocyanurates; combined-chlorine agents such as monochlorosulfamic acid, which are obtained by the reaction of chlorine with amidosulfuric acid or a compound having an amidosulfuric acid group; hypobromites such as sodium hypobromite; bromine agents such as dibromohydantoin; combined-bromine agents, which are obtained by the reaction of bromine with an amine, ammonia, or a compound having an amidosulfuric acid group; organic agents such as dibromonitrilopropionamide (DBNPA) and methylisothiazolone (MIT); and other compounds such as hydrazine and hydantoin (5,5-dimethylhydantoin). These may be used alone or in combination.

[0083] The slime control agent added to the circulating cooling water system may be used for slime control in the RO membrane unit. Additional slime control agent may be added for slime control upstream of the RO membrane unit. If the RO membrane is susceptible to oxidative deterioration with, for example, a chlorine agent, the chlorine agent may be reductively removed from the cooling water effluent before a

slime control agent is added thereto.

[0084] One or more of the above slime control agents may be added simultaneously or alternately and may be added continuously or intermittently.

[0085] If the cooling water effluent contains heavy metal ions, such as copper and iron ions, derived from heat exchangers, the RO membrane may undergo accelerated deterioration in the presence of an oxidizing or reducing chemical such as sodium hypochlorite or hydrazine and the heavy metal ions. In this case, a substance (e.g., EDTA) capable of chelating with the heavy metals may be added to prevent the contact between the membrane and the heavy metals and thereby to prevent accelerated deterioration.

[0086] Polyamide-based RO membranes deteriorate in contact with hypochlorites irrespective of whether heavy metals are present or absent. The use of hypochlorites should be avoided since they are likely to cause membrane deterioration. When hypochlorites are used, it is preferred to remove residual chlorine before supplying the cooling water effluent to the RO membrane unit.

[0087] To stabilize the pretreatment membrane unit and the RO membrane unit, a polymeric compound having phenolic hydroxyl groups (hereinafter also referred to as "phenolic polymer") may be added as a flocculant to the cooling water effluent to be treated.

[0088] Examples of phenolic polymers include polyvinylphenols such as homopolymers of vinylphenol, homopolymers of modified vinylphenols, copolymers of vinylphenol with modified vinylphenols, and copolymers of vinylphenol and/or modified vinylphenols with hydrophobic vinyl monomers; and phenolic resins such as polycondensates of phenol with formaldehyde, polycondensates of cresol with formaldehyde, and polycondensates of xylenol with formaldehyde. Particularly preferred are phenolic polymers obtained by the resole-type secondary reaction of novolac phenolic resins such as those disclosed in Japanese Patent Publications 2010-131469A, 2013-255922A, and 2013-255923A.

[0089] Phenolic polymers obtained by the resole-type secondary reaction of novolac phenolic resins preferably have a melting point of 130°C to 220°C, particularly 150°C to 200°C. These phenolic polymers preferably have a weight average molecular weight of 5,000 to 50,000, more preferably 10,000 to 30,000.

[0090] The amount of phenolic polymer added is preferably, but not necessarily, about 0.01 to 10 mg/L as the active ingredient, depending on the quality of the cooling water effluent.

[0091] The pretreatment membrane unit, such as an MF membrane unit, and the RO membrane unit may clog after the treatment of the cooling water effluent for an extended

period of time. If the flow rate of the treated water (permeate water) decreases (i.e., the water recovery rate decreases) due to clogging, these membrane units may be cleaned to remove the clogging matter so that the flow rate of the treated water returns to its original level. A suitable cleaning chemical may be selected depending on the clogging matter and the membrane material. For example, cleaning chemicals such as hydrochloric acid, sulfuric acid, nitric acid, sodium hypochlorite, sodium hydroxide, citric acid, and oxalic acid can be selected.

Examples

[0092] The present invention is further illustrated by the following examples. However, it should be noted that the present invention is not limited to the examples.

[0093] [Dispersant]

The details of the dispersants used in the following Examples and Reference Examples are as follows:

AA/AMPS: a copolymer of acrylic acid and AMPM in an acrylic acid/AMPM ratio (molar ratio) of 70:30 with a weight average molecular weight of 10,000

AA/HAPS: a copolymer of acrylic acid and HAPS in an acrylic acid/HAPS ratio (molar ratio) of 70:30 with a weight average molecular weight of 8,000

AA/AMPS/N-tBAA: a terpolymer of acrylic acid, AMPS, and N-tert-butylacrylamide in an acrylic acid/AMPM/N-tBAA ratio

(molar ratio) of 70:20:10 with a weight average molecular weight of 12,000

AA/MA: a copolymer of acrylic acid and maleic acid in an acrylic acid/maleic acid ratio (molar ratio) of 70:30 with a weight average molecular weight of 25,000

[0094] [Cooling Water Effluent]

The cooling water effluent subjected to the water recovery processes in the following Examples and Reference Examples was blowdown water discharged from a cooling tower of a circulating cooling water system that was operating with industrial water in Chiba, Japan at a concentration ratio of 3.5 times (hereinafter simply referred to as "blowdown water").

The dispersants shown in the Examples and Reference Examples were added to the circulating cooling water system such that a predetermined dispersant concentration was maintained in the system. Sodium hypochlorite (NaClO) was added for slime control such that the residual chlorine concentration in the system was 0.5 mg/L.

The blowdown water had a pH of 8.5 to 8.9 (about 8.8).

[0095] [Example 1]

An MF membrane was used as a pretreatment membrane. The blowdown water was treated and recovered through, in sequence, a strainer, an MF membrane unit, and an RO membrane unit.

The strainer had a mesh pore size of 400 μm . The MF membrane was Puria GS (hydrophilic PVDF, pore size: 0.02 μm , outside-in) available from Kuraray Co., Ltd. The RO membrane was KROA-2032-SN (polyamide ultra-low-pressure RO membrane) available from Kurita Water Industries Ltd. The MF membrane unit was cleaned once every 30 minutes.

[0096] The blowdown water was sequentially passed through the strainer and the MF membrane unit without pH adjustment. Sulfuric acid was added to the inlet side of the RO membrane unit to adjust the pH to 5.0. Similarly, sodium bisulfite was added to the inlet side of the RO membrane unit to reduce the residual chlorine concentration to 0.05 mg/L or less. Kuriverter® IK-110 (combined-chlorine slime control agent) available from Kurita Water Industries Ltd. was added in an amount of 10 mg/L for slime control in the RO membrane unit.

[0097] The initial water recovery rates of the MF membrane unit and the RO membrane unit were 90% and 80%, respectively, and the total water recovery rate was 72%. The water recovery rates of the MF membrane unit and the RO membrane unit decreased gradually over time because of the high concentration of organic substances in the blowdown water. When the water recovery rate of the MF membrane unit or the RO membrane unit decreased below 50%, the system was stopped, cleaned, and restarted under conditions where the total

water recovery rate was 72%. The supply and recovery of the blowdown water was continued under these conditions for one month.

[0098] In the above water recovery process, the dispersant concentration of the pretreatment membrane (MF membrane) feed water was 10.5 mg/L, the dispersant concentration of the RO membrane feed water was 10.3 mg/L, and the average water recovery rate over one month was 70%.

[0099] [Example 2]

The blowdown water was recovered as in Example 1 except that AA/HAPS was used as a dispersant instead of AA/AMPS. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the average water recovery rate were as shown in Table 1.

[0100] [Example 3]

The blowdown water was recovered as in Example 1 except that AA/AMPS/N-tBAA was used as a dispersant instead of AA/AMPS. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the average water recovery rate were as shown in Table 1.

[0101] [Example 4]

The blowdown water was recovered as in Example 1 except that the pH of the MF membrane feed water was adjusted to 5.5. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the

average water recovery rate were as shown in Table 1.

[0102] [Example 5]

The blowdown water was recovered as in Example 1 except that a dispersant concentration of 3 mg/L was maintained in the circulating cooling water system, and additional dispersant was added to the RO membrane feed water in an amount of 7 mg/L. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the average water recovery rate were as shown in Table 1.

[0103] [Example 6]

The blowdown water was recovered as in Example 1 except that an alkaline solution of a phenolic polymer manufactured by the method of Example I-1 in Japanese Unexamined Patent Application Publication No. 2013-255923 and having a weight average molecular weight of 12,000 and a melting point of 170°C (active ingredient concentration: 16% by weight, pH: 12) was added to the blowdown water in an amount of 1 mg/L as the active ingredient. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the average water recovery rate were as shown in Table 1.

[0104] [Reference Example 1]

The blowdown water was recovered as in Example 1 except that the pH of the MF membrane feed water was adjusted to

4.5. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the average water recovery rate were as shown in Table 1.

[0105] [Reference Example 2]

The blowdown water was recovered as in Example 1 except that the pretreatment membrane was a UF membrane (PW2540C30 available from General Electric Company) having a molecular weight cutoff of 10,000. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the average water recovery rate were as shown in Table 1.

[0106] [Reference Example 3]

The blowdown water was recovered as in Example 1 except that the pH of the RO membrane feed water was adjusted to 7.0. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the average water recovery rate were as shown in Table 1.

[0107] [Reference Example 4]

The blowdown water was recovered as in Example 1 except that AA/MA was used as a dispersant instead of AA/AMPS. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the average water recovery rate were as shown in Table 1.

[0108] [Reference Example 5]

The blowdown water was recovered as in Example 1 except

that a dispersant concentration of 1 mg/L was maintained in the circulating cooling water system. The dispersant concentrations of the pretreatment membrane feed water and the RO membrane feed water and the average water recovery rate were as shown in Table 1.

[0109]

[Table 1]

	Type of dispersant		pH of pretreatment membrane feed water	pH of RO membrane feed water	Dispersant concentration of pretreatment membrane feed water (mg/L)	Dispersant concentration of RO membrane feed water (mg/L)	Permeability of pretreatment membrane for dispersant (%)	Average water recovery rate (%)
	Type	Concentration maintained (mg/L)						
Example 1	AA/AMPS	10	8.8	5.0	10.5	10.3	98.1	70
Example 2	AA/HAPS	10	8.8	5.0	10.5	10.0	95.2	70
Example 3	AA/AMPS/ N-t-BAA	10	8.8	5.0	10.5	9.0	85.7	70
Example 4	AA/AMPS	10	5.5	5.0	10.5	9.7	92.4	69
Example 5	AA/AMPS	3	8.8	5.0	3.0	10.0 (※1)	100	70
Example 6	AA/AMPS	10	8.8	5.0	10.5 (※2)	10.3	98.1	72
Reference Example 1	AA/AMPS	10	4.5	4.5	10.5	3.2	30.5	63
Reference Example 2	AA/AMPS	10	8.8	5.0	10.5 (※3)	0.8	7.6	57
Reference Example 3	AA/AMPS	10	8.8	7.0	10.5	10.3	98.1	61
Reference Example 4	AA/MA	10	8.8	5.0	10.5	8.2	78.1	62
Reference Example 5	AA/AMPS	1	8.8	5.0	1.0	0.9	90.0	60

※1: Additional dispersant was added to inlet side of RO membrane

※2: Phenolic polymer flocculant was added to blowdown water

※3: UF membrane with molecular weight cutoff of 10,000 was used

[0110] According to Table 1, the following is recognized:

The treatment according to the present invention allows an effective amount of dispersant to remain in RO membrane feed water so that stable treatment can be continued at a high water recovery rate.

[0111] In Reference Example 1, where the pH of the membrane feed water was low, the average water recovery rate decreased since the RO membrane feed water had a low dispersant concentration because of the low permeability of the pretreatment membrane for the dispersant.

In Reference Example 2, where the pretreatment membrane was a UF membrane having a low molecular weight cutoff, the average water recovery rate decreased since the RO membrane feed water had a low dispersant concentration because of the low permeability of the pretreatment membrane for the dispersant.

In Reference Example 3, where the pH of the RO membrane feed water was high, the average water recovery rate decreased because of the problem of precipitation of calcium scale and clogging of the RO membrane.

In Reference Example 4, where the dispersant was a polymer having only carboxyl groups and no sulfo groups, the average water recovery rate decreased because of unstable RO membrane treatment since the dispersant was insolubilized and did not function as a dispersant at a low pH in the RO

membrane feed water.

In Reference Example 5, where a low dispersant concentration was maintained in the circulating cooling water system, the average water recovery rate decreased because of unstable RO membrane treatment since the RO membrane feed water had a low dispersant concentration even though the dispersant passed through the pretreatment membrane.

[0112] Whereas particular embodiments of the present invention have been described in detail, it will be obvious to those skilled in the art that various modifications are possible without departing from the spirit or scope of the present invention.

The present application is based on Japanese Patent Application No. 2014-052048 filed on March 14, 2014, the entire contents of which are incorporated herein by reference.

CLAIMS

[Claim 1]

A method for recovering a cooling water effluent discharged from a circulating cooling water system, the circulating cooling water system being added with a dispersant for dispersing a scale component,

the method comprising:

a step of treating the effluent through a water recovery system including a pretreatment membrane and a reverse osmosis membrane to obtain treated water; and

a step of returning the treated water to the circulating cooling water system,

wherein the dispersant added to the circulating cooling water system passes through the pretreatment membrane.

[Claim 2]

The method for recovering a cooling water effluent according to Claim 1, wherein a permeability of the pretreatment membrane for the dispersant is 80% or more as determined by the following equation:

Permeability = (dispersant concentration of pretreatment membrane permeate water / dispersant concentration of pretreatment membrane feed water) × 100

[Claim 3]

The method for recovering a cooling water effluent according to Claim 1 or 2, wherein the pretreatment membrane

is a microfiltration membrane or an ultrafiltration membrane.

[Claim 4]

The method for recovering a cooling water effluent according to any one of Claims 1 to 3, wherein the effluent supplied to the pretreatment membrane has a pH of 5 or more.

[Claim 5]

The method for recovering a cooling water effluent according to any one of Claims 1 to 4, wherein the pretreatment membrane has a molecular weight cutoff of 30,000 or more.

[Claim 6]

The method for recovering a cooling water effluent according to any one of Claims 1 to 5, wherein the dispersant is a polymer having a sulfo group and a carboxyl group.

[Claim 7]

The method for recovering a cooling water effluent according to Claim 6, wherein the dispersant is a copolymer of methacrylic acid and/or acrylic acid with 3-allyloxy-2-hydroxy-1-propanesulfonic acid and/or 2-acrylamido-2-methylpropanesulfonic acid.

[Claim 8]

The method for recovering a cooling water effluent according to any one of Claims 1 to 7, further comprising adjusting the pH of feed water supplied to the reverse

osmosis membrane to 4.0 to 7.5.

[Claim 9]

The method for recovering a cooling water effluent according to any one of Claims 1 to 8, further comprising measuring the dispersant concentration of feed water supplied to the reverse osmosis membrane and adjusting the dispersant concentration to a predetermined level by adding the dispersant to the reverse osmosis membrane feed water.

[Claim 10]

The method for recovering a cooling water effluent according to any one of Claims 1 to 9, further comprising measuring the conductivity of at least one of the effluent, reverse osmosis membrane feed water, and reverse osmosis membrane concentrated water and adjusting the water recovery rate of the reverse osmosis membrane depending on the measured conductivity.

[Claim 11]

The method for recovering a cooling water effluent according to any one of Claims 1 to 10, further comprising measuring the dispersant concentration of the effluent and/or reverse osmosis membrane feed water and adjusting the water recovery rate of the reverse osmosis membrane depending on the measured dispersant concentration.

[Claim 12]

The method for recovering a cooling water effluent

according to any one of Claims 1 to 11, further comprising adding a polymeric compound having a phenolic hydroxyl group to the effluent.

[Claim 13]

The method for recovering a cooling water effluent according to any one of Claims 1 to 12, wherein on an occasion when the water recovery system is stopped, before stopping the water recovery system, a step of circulating the reverse osmosis membrane permeate water is conducted, or a step of supplying pure water or deionized water to the reverse osmosis membrane and discharging the reverse osmosis membrane concentrated water outside the system is conducted.

[Claim 14]

An apparatus for recovering a cooling water effluent, comprising:

a pretreatment membrane unit to which an effluent discharged from a circulating cooling water system is supplied,

a reverse osmosis membrane unit to which permeate water flowing from the pretreatment membrane unit is supplied, and

returning means for returning permeate water flowing from the reverse osmosis membrane unit to the circulating cooling water system,

wherein the circulating cooling water system includes dispersant-adding means for adding a dispersant for

dispersing a scale component to the water system and wherein the dispersant passes through the pretreatment membrane.

[Claim 15]

The apparatus for recovering a cooling water effluent according to Claim 14, wherein the permeability of the pretreatment membrane for the dispersant is 80% or more as determined by the following equation:

$$\text{Permeability} = (\text{dispersant concentration of pretreatment membrane permeate water} / \text{dispersant concentration of pretreatment membrane feed water}) \times 100$$

[Claim 16]

The apparatus for recovering a cooling water effluent according to Claim 14 or 15, wherein the pretreatment membrane is a microfiltration or ultrafiltration membrane.

[Claim 17]

The apparatus for recovering a cooling water effluent according to any one of Claims 14 to 16, wherein feed water supplied to the pretreatment membrane has a pH of 5 or more.

[Claim 18]

The apparatus for recovering a cooling water effluent according to any one of Claims 14 to 17, wherein the pretreatment membrane has a molecular weight cutoff of 30,000 or more.

[Claim 19]

The apparatus for recovering a cooling water effluent

according to any one of Claims 14 to 18, wherein the dispersant is a polymer having a sulfo group and a carboxyl group.

[Claim 20]

The apparatus for recovering a cooling water effluent according to Claim 19, wherein the dispersant is a copolymer of methacrylic acid and/or acrylic acid with 3-allyloxy-2-hydroxy-1-propanesulfonic acid and/or 2-acrylamido-2-methylpropanesulfonic acid.

[Claim 21]

The apparatus for recovering a cooling water effluent according to any one of Claims 14 to 20, further comprising pH-adjusting means for adjusting the pH of feed water supplied to the reverse osmosis membrane to 4.0 to 7.5.

[Claim 22]

The apparatus for recovering a cooling water effluent according to any one of Claims 14 to 21, further comprising:

dispersant-concentration measuring means for measuring the dispersant concentration of feed water supplied to the reverse osmosis membrane; and

dispersant-adjusting means for adjusting the dispersant concentration measured by the dispersant-concentration measuring means to a predetermined level by adding the dispersant to the reverse osmosis membrane feed water.

[Claim 23]

The apparatus for recovering a cooling water effluent according to any one of Claims 14 to 22, further comprising:

conductivity-measuring means for measuring the conductivity of at least one of the effluent, reverse osmosis membrane feed water, and reverse osmosis membrane concentrated water, and

water-recovery-rate adjusting means for adjusting the water recovery rate of the reverse osmosis membrane depending on the conductivity measured by the conductivity-measuring means.

[Claim 24]

The apparatus for recovering a cooling water effluent according to any one of Claims 14 to 23, further comprising:

dispersant-concentration measuring means for measuring the dispersant concentration of the effluent and/or reverse osmosis membrane feed water, and

water-recovery-rate adjusting means for adjusting the water recovery rate of the reverse osmosis membrane depending on the dispersant concentration measured by the dispersant-concentration measuring means.

[Claim 25]

The apparatus for recovering a cooling water effluent according to any one of Claims 14 to 24, further comprising flocculant-adding means for adding a polymeric compound having a phenolic hydroxyl group to the effluent.

[Claim 26]

The apparatus for recovering a cooling water effluent according to any one of Claims 14 to 25, wherein the reverse osmosis membrane unit includes:

permeate-water circulating means for circulating the reverse osmosis membrane permeate water upstream of the reverse osmosis membrane unit or means for supplying pure water or deionized water to the reverse osmosis membrane unit;

concentrated-water discharging means for discharging the reverse osmosis membrane concentrated water outside the system; and

control means for stopping the apparatus for recovering a cooling water effluent,

wherein the control means stops the apparatus after a step of circulating the reverse osmosis membrane permeate water upstream is conducted, or a step of supplying pure water or deionized water and discharging the reverse osmosis membrane concentrated water outside the system is conducted.