

METHOD FOR CONTROLLING CONCENTRATION OF COOLING-WATER
TREATMENT CHEMICAL IN CIRCULATING COOLING-WATER SYSTEM,
METHOD FOR RECOVERING COOLING EFFLUENT, AND APPARATUS FOR
TREATING COOLING EFFLUENT

Field of Invention

[0001] The present invention relates to a method for controlling the concentration of a cooling-water treatment chemical which is applied to cooling facilities used in air conditioning systems for buildings and industrial processes such as chemical industry, paper industry, steelmaking industry, and electric power industry. The present invention also relates to a method for recovering cooling effluent and an apparatus for treating cooling effluent.

Background of Invention

[0002] Scaling may occur on a heating surface and inside a pipe included in a cooling-water system, a boiler-water system, or the like which are brought into contact with water. In the case where such a system is operated at high cycles of concentration by reducing the amount of cooling water (blowdown) discharged to the outside of the system in order to save resources and energy, the salts dissolved in the water become concentrated, which increases the likelihood of the heating surface being corroded, change into poorly soluble salts, and precipitate as scale. The scale deposited on the walls and the like of the apparatus

may cause significant malfunctions in the operation of a boiler, a heat exchanger, or the like, such as a reduction in thermal efficiency and clogging of pipes.

[0003] Water is effectively used to the extent possible in order to save water and energy. However, in the case where such a system is operated at higher cycles of concentration, it becomes not possible to prevent the precipitation of scale.

[0004] Malfunctions that may occur in a circulating cooling-water system are not only scaling but also the formation of slime by microorganisms. When a circulating cooling-water system is operated at high cycles of concentration, the qualities of cooling water are likely to be degraded, which increases the likelihood of slime being formed by microorganisms such as bacteria, mold, and algae being mixed with sand particles, dust particles, and the like. This reduces the thermal efficiency of a heat exchanger and inhibits passing of water. Furthermore, local corrosion of the equipment or pipes may be induced at portions of the equipment or pipes to which the slime particles are adhered.

[0005] In order to prevent the above malfunctions from being caused by the scale and the slime, commonly, a scale dispersant and a slime-controlling agent that is a chlorine chemical or a chlorine-free microorganism repellent are

added to circulating cooling water and the concentrations of these chemicals are controlled to be optimal concentrations. For controlling the concentrations of the chemicals, a tracer is used in Japanese Patent Publication 2009-291693A, and a microorganism contamination monitor is used in Japanese Patent Publication 2012-101194A.

[0006] There has been an effort to recover cooling-water blowdown water with a water recovery system and return the treated water to a cooling tower in order to effectively use water resources. Common water recovery systems remove salts contained in cooling-water blowdown water through a reverse osmosis membrane (RO membrane) and return the treated water to a cooling tower. Since the slime and the scale may be formed also in an RO-membrane device included in the above water recovery system, commonly, it is necessary to use a slime-controlling agent and a scale dispersant at a position upstream of the RO membrane and control the concentrations of the chemicals in order to operate the RO-membrane device with consistency. In Japanese Patent Publication 2001-099595A, a silica dispersant is used on the basis of the silica concentration in water that is to be treated through an RO membrane. In Japanese Patent Publication 2003-275761A, water condensed with an RO membrane is subjected to electrolysis in order to generate free chlorine, which contributes to the control of slime, from concentrated

chloride ions contained in the condensed water; and the electrolyzed water is added at a position upstream of the RO membrane and used as a slime-controlling agent, while a scale inhibitor is added at a position upstream of the RO membrane.

[0007]

Patent Literature 1: Japanese Patent Publication 2009-291693A

Patent Literature 2: Japanese Patent Publication 2012-101194A

Patent Literature 3: Japanese Patent Publication 2001-099595A

Patent Literature 4: Japanese Patent Publication 2003-275761A

[0008] The water recovery systems of the related art require the addition of a slime-controlling agent and a scale dispersant to RO-membrane feedwater in order to operate an RO-membrane device with consistency. The cost and effort required by the addition of the slime-controlling agent and the scale dispersant increase the treatment cost.

Summary of Invention

[0009] The present invention provides a technique in which cooling effluent discharged from a circulating cooling-water system, such as blowdown water, is recovered with a water recovery system including a separation membrane. This

technique may reduce the water-treatment cost, increase the water recovery ratio, and improve the consistency of the water recovery.

[0010] The inventors of the present invention found that the quality of the water treatment performed in the circulating cooling-water system affects a system for recovering cooling effluent which includes an RO membrane. Specifically, insufficient control of slime in the circulating cooling-water system may increase the amount of microorganisms contained in the system and the concentrations of metabolites emitted by the microorganisms. This causes clogging of an RO membrane included in a water recovery system that treats cooling-water blowdown water, which is discharged from such a circulating cooling-water system. Moreover, insufficient concentration of a scale dispersant in the circulating cooling-water system may result in the occurrence of scaling on the RO membrane of the water recovery system. This limits the water recovery ratio and degrades the advantages of water recovery.

[0011] On the basis of the above findings, the inventors of the present invention found that it is possible to operate not only a circulating cooling-water system but also a water recovery system with consistency and exploit water recovery by controlling the concentrations of chemicals used for treating cooling-water in the circulating cooling-water

system by feedback control based on a change in the performance of a separation membrane included in the water recovery system, such as pressure, the amount of the treated water, or the quality of the treated water. A separation-membrane device included in the water recovery system can be used as a device that monitors the effective concentrations of chemicals contained in the circulating cooling-water system.

[0012] The summary of the present invention is as described below.

Advantageous Effects of Invention

[0013] [1] A method for controlling concentration of a cooling-water treatment chemical in a circulating cooling-water system including the cooling-water treatment chemical, the circulating cooling-water system being provided with a water recovery system that treats water discharged from the circulating cooling-water system through a separation membrane and returns the treated water to the circulating cooling-water system, the method comprising controlling the concentration of the cooling-water treatment chemical in the circulating cooling-water system on the basis of a change in the performance of the separation membrane.

[0014] [2] The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to [1], wherein the concentration of

the cooling-water treatment chemical is controlled on the basis of a change in at least one selected from pressure applied onto the separation membrane, quality of the treated water, and an amount of the treated water.

[0015] [3] The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to [1] or [2], wherein the concentration of the cooling-water treatment chemical in the circulating cooling-water system is controlled to be equal to or higher than a predetermined concentration of the cooling-water treatment chemical at which the performance of the separation membrane is consistent.

[0016] [4] The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to any one of [1] to [3], wherein the cooling-water treatment chemical includes a slime-controlling agent and/or a scale dispersant.

[0017] [5] The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to [4], wherein the slime-controlling agent includes a combined-chlorine agent.

[0018] [6] The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to [4] or [5], wherein the cooling-water treatment chemical includes the slime-controlling

agent and the scale dispersant, and wherein the concentration of one chemical selected from the slime-controlling agent and the scale dispersant is controlled first and the concentration of the other chemical is subsequently controlled.

[0019] [7] The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to any one of [1] to [6], wherein the separation membrane is a reverse osmosis membrane.

[0020] [8] The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to [7], wherein the water recovery system includes a microfiltration membrane or an ultrafiltration membrane that serves as a pretreatment membrane disposed upstream of the reverse osmosis membrane.

[0021] [9] A method for recovering cooling effluent, the method comprising treating water discharged from a circulating cooling-water system including a cooling-water treatment chemical with a water recovery system including a separation membrane and returning the treated water to the circulating cooling-water system, wherein the concentration of the cooling-water treatment chemical in the circulating cooling-water system is controlled by the method for controlling the concentration of a cooling-water treatment chemical according to any one of [1] to [8].

[0022] [10] An apparatus for treating cooling effluent, the apparatus treating water discharged from a circulating cooling-water system including a cooling-water treatment chemical with a separation-membrane device and returning the treated water to the circulating cooling-water system, the apparatus comprising a chemical-concentration control unit that controls concentration of the cooling-water treatment chemical in the circulating cooling-water system on the basis of a change in the performance of the separation membrane.

[0023] [11] The apparatus for treating cooling effluent according to [10], wherein the chemical-concentration control unit controls the concentration of the cooling-water treatment chemical on the basis of a change in at least one selected from pressure applied onto the separation membrane, quality of the treated water, and an amount of the treated water.

[0024] [12] The apparatus for treating cooling effluent according to [10] or [11], wherein the chemical-concentration control unit controls the concentration of the cooling-water treatment chemical in the circulating cooling-water system to be equal to or higher than a predetermined concentration of the cooling-water treatment chemical at which the performance of the separation membrane is consistent.

[0025] [13] The apparatus for treating cooling effluent according to any one of [10] to [12], wherein the cooling-water treatment chemical includes a slime-controlling agent and/or a scale dispersant.

[0026] [14] The apparatus for treating cooling effluent according to [13], wherein the slime-controlling agent includes a combined-chlorine agent.

[0027] [15] The apparatus for treating cooling effluent according to [13] or [14], wherein the cooling-water treatment chemical includes the slime-controlling agent and the scale dispersant, and wherein the chemical-concentration control unit controls the concentration of one chemical selected from the slime-controlling agent and the scale dispersant first and subsequently controls the concentration of the other chemical.

[0028] [16] The apparatus for treating cooling effluent according to any one of [10] to [15], wherein the separation-membrane device is a reverse-osmosis-membrane device.

[0029] [17] The apparatus for treating cooling effluent according to [16], the apparatus further comprising a microfiltration-membrane device or an ultrafiltration-membrane device that serves as a pretreatment-membrane device disposed upstream of the reverse-osmosis-membrane device.

[0030] According to the present invention, the concentrations of cooling-water treatment chemicals in the circulating cooling-water system are controlled by feedback control based on a change in the performance of a separation membrane included in a water recovery system that treats cooling effluent. This method improves the consistency of the operations of not only the circulating cooling-water system but also the water recovery system and increases the water recovery ratio. Specific examples of the method include the following:

(1) The concentrations of cooling-water treatment chemicals, at which the circulating cooling-water system can be operated with consistency, are controlled such that the separation membrane can be operated with consistency at the concentrations.

(2) The concentrations of cooling-water treatment chemicals in the circulating cooling-water system are each controlled to be equal to or higher than predetermined concentration of the treatment chemical at which the separation membrane can be operated with consistency.

[0031] In the present invention, a separation-membrane device included in a water recovery system that treats cooling effluent can be used as a device that monitors the concentrations of the cooling-water treatment chemicals in the circulating cooling-water system. This eliminates the

need to dispose another monitoring device in the circulating cooling-water system.

According to the present invention, the control of the concentrations of the water-treatment chemicals, which has been conducted in the circulating cooling-water system and the water recovery system separately in the related art, is integrally conducted by concentration control based on a change in the performance of the separation membrane of the water recovery system. This achieves consistent operations of both the circulating cooling-water system and the water recovery system.

According to the present invention, cooling-water treatment chemicals added to the circulating cooling-water system can be effectively used also as water-treatment chemical in the water recovery system. This reduces the water-treatment cost.

Brief Description of Drawings

[0032] Fig. 1 is a graph illustrating changes in the operating pressures of RO membranes with time which were measured in Example 1 and Comparative Example 1.

Fig. 2 is a graph illustrating a change in the ratios relative to the initial amounts of recovered water which were measured in Example 1 and Comparative Example 1.

Description of Embodiments

[0033] Embodiments of the present invention are described

below in detail.

[0034] Cooling Effluent

A typical example of cooling effluent that is treated through a separation membrane included in a water recovery system and returned to a circulating cooling-water system is blowdown water discharged from a cooling tower. However, the present invention is not directed to only blowdown water but also directed to various type of effluent discharged from a circulating cooling-water system. Specifically, part or the entirety of the circulating cooling water extracted from a circulation pipe of a circulating cooling-water system may be treated through a separation membrane, and returned to the circulating cooling-water system. In another case, effluent diverted from a pipe through which cooling water is fed to a cooling tower or to a device that filters circulating cooling water may be treated and recovered.

In the present invention, the above types of cooling effluent are used as water-to-be-treated and treated through a separation membrane included in a water recovery system. The treated water is returned to the circulating cooling-water system.

[0035] Water Recovery System

A water recovery system that treats cooling effluent through a separation membrane and returns the treated water

to the circulating cooling-water system, which corresponds to the apparatus for treating cooling effluent according to the present invention, may be any water recovery system that includes a separation membrane, that is, a separation-membrane device. The separation membrane through which cooling effluent is treated is preferably a reverse osmosis membrane (RO membrane). A microfiltration-membrane (MF membrane) device or an ultrafiltration-membrane (UF membrane) device that serves as a pretreatment-membrane device is preferably disposed upstream of the RO-membrane device. A strainer is preferably further disposed upstream of the pretreatment-membrane device.

A water recovery system that includes the strainer, the pretreatment-membrane device, and the RO-membrane device that are arranged in this order is described below.

[0036] Strainer

While the above-described cooling effluent may be directly treated with the pretreatment-membrane device, the cooling effluent may contain coarse particles of suspended matter or foreign matter. The coarse particles are preferably removed through a strainer disposed upstream of the pretreatment-membrane device before the cooling effluent is subjected to a clarification treatment in the pretreatment-membrane device. It is even possible to operate the system without using the strainer. However, in

such a case, the coarse particles of suspended matter or foreign matter contained in the cooling effluent may break the pretreatment membrane.

[0037] The strainer is preferably a self-cleaning, automatic strainer.

[0038] The shape of the strainer is not limited; various shapes of strainers, such as a Y-shaped strainer and a bucket-shaped strainer, may be used.

The diameter of openings formed in the strainer is preferably 100 to 500 μm . If the diameter of the openings of the strainer is smaller than 100 μm , clogging of the strainer may significantly occur. If the diameter of the openings of the strainer is larger than 500 μm , the likelihood of the coarse particles of suspended matter or foreign matter which have permeated through the strainer breaking the pretreatment membrane may be increased.

[0039] The strainer may be replaced with a string-wound filter, a pleated filter, or the like. However, a strainer is suitable in consideration of exchange frequency and cleaning efficiency.

[0040] Pretreatment-Membrane Device

The cooling effluent that has been subjected to the clarification treatment in the strainer is preferably treated in a pretreatment-membrane device.

[0041] The pretreatment-membrane device removes suspended

matter and a colloidal component contained in cooling effluent, which contaminate the membrane of the RO-membrane device. The pretreatment-membrane device may include an MF membrane or a UF membrane. The form of each membrane is not limited; a hollow-fiber-membrane filtering device, a spiral-membrane filtering device, and the like can be employed. The filtering method is not limited; internal-pressure filtration, external-pressure filtration, cross-flow filtration, and dead-end filtration can be employed.

[0042] The cut-off molecular weight of the UF membrane used as a pretreatment membrane is preferably 30,000 or more. A UF membrane having a cut-off molecular weight of 30,000 or more allows the cooling-water treatment chemical that has been added to the circulating cooling-water system and transported into the water recovery system by being contained in the cooling effluent to permeate therethrough. This cooling-water treatment chemical can be effectively used for, for example, preventing the occurrence of scaling and controlling slime in the RO-membrane device disposed downstream of the pretreatment-membrane device. This eliminates the need to add the above chemicals again at a position upstream of the RO-membrane device. While the upper limit of the cut-off molecular weight of the UF membrane is not specified, a UF membrane having a cut-off molecular weight of 1,000,000 or less is capable of removing

high-molecular-weight polysaccharides contained in the cooling effluent, which may cause clogging of the RO membrane. The diameter of pores formed in the MF membrane used as a pretreatment membrane is preferably about 0.1 to 0.01 μm for the same reason as in the limitation of the cut-off molecular weight of the UF membrane.

[0043] In order to allow the cooling-water treatment chemicals that have been added to the circulating cooling-water system and transported into the water recovery system by being contained in the cooling effluent to permeate through the above pretreatment membrane with high permeability, it is preferable to control the pH of water fed to the pretreatment membrane to be 5 or more as well as using the suitable cooling-water treatment chemicals described below as a cooling-water treatment chemical. If the pH of water fed to the pretreatment membrane is less than 5, the permeability of the pretreatment membrane may be reduced even when the cooling-water treatment chemicals and, in particular, the polymer including a sulfo group and a carboxyl group described below, which serves as a scale dispersant, are used. In such a case, it becomes difficult to effectively use the chemicals for preventing the occurrence of scaling in the RO-membrane device. The pH of water fed to the pretreatment membrane is set to 5 or more, and the upper limit thereof is not specified. Since the

cooling effluent such as blowdown water discharged from a cooling tower commonly has a pH of 8 to 10 and, in most cases, about 8 to 9, it can be directly treated in the pretreatment-membrane device.

[0044] RO-Membrane Device

The water produced by treating the cooling effluent preferably with the above-described pretreatment-membrane device (pretreatment-membrane permeated water) is subsequently desalinated with an RO-membrane device.

[0045] The type of an RO membrane included in the RO-membrane device is not limited and selected appropriately depending on the qualities of the cooling effluent that is to be treated (qualities of raw water fed to the circulating cooling-water system and the cycles of concentration of the circulating cooling-water system). The salt rejection of the RO membrane is preferably 80% or more and is particularly preferably 85% or more. An RO membrane having a salt rejection lower than the above limit reduces the efficiency of desalination and makes it impossible to produce treated water (permeated water) having good qualities. The material of the RO membrane is not limited, and RO membranes made of various materials, such as a polyamide composite membrane and a cellulose acetate membrane, can be used. The shape of the RO membrane is not limited; various shapes of RO membranes, such as a hollow-

fiber RO membrane and a spiral RO membrane, can be used.

[0046] In the present invention, there is the preferable range of the pH of the RO-membrane feedwater (water passed into the RO-membrane device as water-to-be-treated) as described below. Accordingly, it is preferable to dispose a pH-control unit that controls the pH of the RO-membrane feedwater by adding an acid to the feedwater between the pretreatment-membrane device and the RO-membrane device in order to control the pH of the RO-membrane feedwater. An example of the pH-control unit is a unit capable of adding an acid directly to a line through which the water fed to the RO membrane is introduced or an inline mixer disposed on the line or to an optionally disposed pH-control tank by using a chemical feed pump or the like. The acid used in this unit is not limited; inorganic acids such as hydrochloric acid, sulfuric acid, and nitric acid can be suitably used.

[0047] In the circulating cooling-water system operated at high cycles of concentration, commonly, the pH of the circulating cooling water is increased to about 8 to 9. While cooling effluent having such a high pH is suitable for allowing the scale dispersant to permeate through the pretreatment-membrane device, scaling may occur in the RO-membrane device, in which the cooling effluent is further condensed. Thus, it is suitable to operate the RO-membrane

device at a reduced pH in order to reduce the occurrence of scaling. The pH of the RO-membrane feedwater is preferably 4.0 to 7.5. If the pH of the RO-membrane feedwater exceeds 7.5, calcium carbonate, calcium phosphate, calcium sulfate, and barium sulfate may precipitate as scale depending on the qualities of the RO-membrane feedwater.

[0048] When the concentration of silica in the cooling effluent exceeds 30 mg/L, it is preferable to reduce the pH of the RO-membrane feedwater to 4.0 to 5.5 in order to reduce the precipitation of silica. The lower the pH of the RO-membrane feedwater, the better the reduction in the precipitation of scale. However, reducing the pH of the feedwater to be less than 4.0 significantly increases the amount of acid required, which is not advantageous from an economic viewpoint.

[0049] A large content of humic acid or fulvic acid in the cooling effluent may cause clogging of the RO membrane. In such a case, the pH of the cooling effluent is preferably set to 5.5 to 7.0 and is particularly preferably set to 5.5 to 6.5. When the pH of the cooling effluent falls within the above range, humic acid or fulvic acid undergoes acid dissociation and reduces the occurrence of clogging of the RO membrane. In addition, Ca contained in the cooling water is effectively dispersed with a dispersant. This reduces the likelihood of Ca forming a complex with fulvic acid.

[0050] Other Treatment

A high-molecular-weight compound including a phenolic hydroxyl group (hereinafter, may be referred to as "phenolic high-molecular-weight compound") which serves as a coagulant aid may be added to the cooling effluent that is to be treated in the water recovery system in order to improve the consistency of the pretreatment-membrane device and the RO-membrane device.

[0051] Examples of the phenolic high-molecular-weight compound include polyvinylphenol polymers such as a homopolymer of vinylphenol, a homopolymer of a modified vinylphenol, a copolymer of vinylphenol with a modified vinylphenol, and a copolymer of vinylphenol and/or a modified vinylphenol with a hydrophobic vinyl monomer; and phenolic resins such as a polycondensate of phenol with formaldehyde, a polycondensate of cresol with formaldehyde, and a polycondensate of xylenol with formaldehyde. In the present invention, it is particularly preferable to use a compound produced by the resole-type second reaction of the novolac-type phenolic resin described in Japanese Patent Publication . 2010-131469, Japanese Patent Publication . 2013-255922, Japanese Patent Publication . 2013-255923, or the like.

[0052] The melting point of the phenolic high-molecular-weight compound produced by the resole-type second reaction

of the novolac-type phenolic resin is preferably 130°C to 220°C and is particularly preferably 150°C to 200°C. The weight-average molecular weight of the phenolic high-molecular-weight compound is preferably 5,000 to 50,000 and is more preferably 10,000 to 30,000.

While the amount of phenolic high-molecular-weight compound used changes depending on the qualities of the cooling effluent and is not limited, the amount of phenolic high-molecular-weight compound used is preferably set such that the concentration of the active constituent is about 0.01 to 10 mg/L.

[0053] In the case where the cooling effluent contains heavy-metal ions such as copper ions and iron ions originating from a heat exchanger, the accelerated degradation of the RO membrane may occur in the presence of a chemical having oxidizing or reducing power, such as sodium hypochlorite or hydrazine and the heavy-metal ions. In such a case, using a substance (e.g., EDTA) capable of chelating the heavy metal ions prevents the heavy metal ions from coming into contact with the membrane and prevents the occurrence of the accelerated degradation.

[0054] Cleaning of Membrane Device

Treating the cooling effluent for a long period of time may cause clogging of the pretreatment-membrane devices such as an MF-membrane device and the RO-membrane device and

reduce the amount of treated water (permeated water) produced (i.e., water recovery ratio) even when the concentrations of the chemicals are controlled as described below. In such a case, cleaning the membrane devices enables the clogging objects to be removed and restores the amount of treated water. The chemical used for cleaning the membrane devices may be selected appropriately depending on the clogging objects and the materials of the membranes from hydrochloric acid, sulfuric acid, nitric acid, sodium hypochlorite, sodium hydroxide, citric acid, oxalic acid, and the like.

[0055] Cooling-Water Treatment Chemicals

Preferable examples of the cooling-water treatment chemicals added to the circulating cooling-water system include, but are not limited to, a scale dispersant and a slime-controlling agent. Only one of the scale dispersant and the slime-controlling agent may be used alone. Alternatively, both scale dispersant and slime-controlling agent may be used in combination. It is preferable to use both scale dispersant and slime-controlling agent.

[0056] Scale Dispersant

Examples of the scale dispersant include inorganic polyphosphates such as sodium hexametaphosphate and sodium tripolyphosphate; and phosphonic acids such as hydroxyethylidenediphosphonic acid and

phosphonobutanetricarboxylic acid. The scale dispersant is preferably a polymer including a sulfo group and a carboxyl group.

[0057] A dispersant including phosphorus may cause Ca phosphate to precipitate in the form of scale when the degree of Ca hardness is high.

The higher the pH, the higher the degree of the dissociation of the scale dispersant and the higher the performance of the scale dispersant. However, if the RO-membrane device is operated under a high-pH condition, calcium and the like concentrated in the RO-membrane device are likely to precipitate in the form of scale as described above. Accordingly, the RO-membrane device is operated under a low-pH condition. In an RO-membrane device operated under such a low-pH condition, a scale dispersant that includes only carboxyl groups but not sulfo groups may become insoluble and not capable of serving as a scale dispersant. Therefore, it is preferable to use a polymer including a sulfo group and a carboxyl group as a scale dispersant. Using such a scale dispersant enables the scale dispersant that has been added to the circulating cooling-water system, transported into the water recovery system by being contained in the cooling effluent, and passed through the pretreatment membrane to be effectively used also as a scale dispersant for the RO-membrane device.

[0058] Examples of the polymer including a sulfo group and a carboxyl group which can be suitably used as a scale dispersant include a copolymer of a monomer including a sulfo group with a monomer including a carboxyl group; and a terpolymer of the above monomers with another monomer capable of copolymerizing with the above monomers.

[0059] Examples of the monomer including a sulfo group include conjugated dienesulfonic acids such as 2-methyl-1,3-butadiene-1-sulfonic acid; unsaturated (meth)allylether monomers including a sulfo group, such as 3-(meth)allyloxy-2-hydroxypropanesulfonic acid; 2-(meth)acrylamide-2-methylpropanesulfonic acid; 2-hydroxy-3-acrylamidepropanesulfonic acid; styrenesulfonic acid; methacrylsulfonic acid; vinylsulfonic acid; allylsulfonic acid; isoamylenesulfonic acid; and the salts of the above monomers. Preferable examples of the monomer including a sulfo group include 3-allyloxy-2-hydroxy-1-propanesulfonic acid (HAPS) and 2-acrylamide-2-methylpropanesulfonic acid (AMPS). The above monomers including a sulfo group may be used alone or in a mixture of two or more.

[0060] Examples of the monomer including a carboxyl group include acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, vinyl acetate, atropic acid, maleic acid, fumaric acid, itaconic acid, hydroxyethylacrylic acid, and the salts of these monomers. Preferable examples of the

monomer including a carboxyl group include acrylic acid and methacrylic acid. The above monomers including a carboxyl group may be used alone or in a mixture of two or more.

[0061] Examples of the monomer capable of copolymerizing with the above monomers include amides such as N-tert-butylacrylamide (N-tBAA) and N-vinylformamide.

[0062] Specific examples of the scale dispersant suitable in the present invention include, but are not limited to, a copolymer produced by copolymerizing acrylic acid (AA) with 2-acrylamide-2-methylpropanesulfonic acid (AMPS) such that AA:AMPS = 70 to 95:5 to 30 (molar ratio); a copolymer produced by copolymerizing AA with AMPS and an amide such as N-tert-butylacrylamide (N-tBAA) such that AA:AMPS:amide = 40 to 90:5 to 30:5 to 30 (molar ratio); and a copolymer produced by copolymerizing AA with 3-allyloxy-2-hydroxypropanesulfonic acid (HAPS) such that AA:HAPS = 70 to 95:5 to 30 (molar ratio).

[0063] The weight-average molecular weight of the polymer including a sulfo group and a carboxyl group is preferably 1,000 to 30,000. If the weight-average molecular weight of this polymer is smaller than 1,000, the dispersion of scale may fail to be achieved at a sufficient level. If the weight-average molecular weight of this polymer is larger than 30,000, it becomes difficult for the polymer to permeate through the pretreatment membrane. Furthermore,

this polymer may adsorb onto the pretreatment membrane and the RO membrane, which results in clogging of these membranes.

[0064] The above scale dispersants may be used alone or in combination of two or more.

[0065] Slime-Controlling Agent

Examples of the slime-controlling agent include free-chlorine agents such as sodium hypochlorite (NaClO); combined-chlorine agents produced by the reaction of chlorine with amidosulfuric acid or a compound including an amidosulfuric acid group, such as chloramine and monochlorosulfamic acid; bromine agents such as dibromohydantoin; and organic agents such as DBNPA (dibromonitrilopropionamide) and MIT (methylothiazolone). The above slime-controlling agents may be used alone or in combination of two or more.

[0066] The amounts of free chlorine and combined chlorine are measured in terms of Cl_2 concentration by the DPD method described in JIS K 0400-33-10:1999 in which N,N-diethyl-1,4-phenylenediamine is used. Free chlorine is chlorine that is present in the form of hypochlorous acid, hypochlorite ions, or dissolved chlorine. Combined chlorine is chlorine that is present in the form of chloramine or organic chloramine. Total chlorine is chlorine that is present in the form of free chlorine, in the form of combined chlorine, or in the

both forms.

[0067] Examples of the free-chlorine agent that can be used in the present invention include chlorine gas; hypochlorous acid and the salts thereof; chlorous acid and the salts thereof; chloric acid and the salts thereof; perchloric acid and the salts thereof; and chlorinated isocyanuric acid and the salts thereof. Examples of the salts include salts of an alkali metal such as sodium or potassium; salts of an alkaline-earth metal such as barium; salts of another metal such as nickel; and ammonium salts. The above free-chlorine agents may be used alone or in combination of two or more. Among the above free-chlorine agents, sodium hypochlorite is preferable because of ease of handling.

[0068] Examples of the nitrogen compound to which the above free chlorine can be bonded to form the combined-chlorine agent include ammonia, ammonia compounds, melamine, urea, acetamide, sulfamide, cyclamic acid, sulfamic acid, toluenesulfonamide, succinimide, phthalic imide, isocyanuric acid, N-chlorotoluenesulfonamide, uric acid, saccharin, and the salts of the above monomers. The combined-chlorine agent used in the present invention includes one of the above nitrogen compounds and the free chlorine bonded to the nitrogen compound. The combined-chlorine agent used in the present invention is preferably produced by mixing and

reacting one of the above nitrogen compounds with the free-chlorine agent and is particularly preferably produced by mixing and reacting an aqueous solution of the nitrogen compound with an aqueous solution of the free-chlorine agent.

[0069] Examples of the combined-chlorine agent include chloramine; combined-chlorine agents produced from one of the above-described free-chlorine agents and a sulfamic acid compound; chloramine-T (sodium salt of N-chloro-4-methylbenzenesulfonamide); chloramine-B (sodium salt of N-chloro-benzenesulfonamide); the sodium salt of N-chloro-paranitrobenzenesulfonamide; trichloromelamine; the sodium salt or potassium salt of mono- or di-chloromelamine; trichloro-isocyanurate; the sodium salt or potassium salt of mono- or di-chloroisocyanuric acid; the sodium salt or potassium salt of mono- or di-chlorosulfamic acid; monochlorohydantoin; 1,3-dichlorohydantoin; and the derivatives of 5,5-alkyl, such as 5,5-dimethylhydantoin.

The above combined-chlorine agents may be used alone or in combination of two or more.

[0070] A polyamide RO membrane is highly likely to be degraded when being brought into contact with the salt of hypochlorous acid. Therefore, in the case where the salt of hypochlorous acid is used, it is preferable to remove residual chlorine in the water recovery system before the water is passed through a polyamide-RO-membrane device.

[0071] However, in the case where the control of the concentrations of the cooling-water treatment chemicals which is based on a change in the performance of the separation membrane as described below is exercised on the basis of a change in the performance of the RO membrane, removing the residual chlorine, which originates from the circulating cooling-water system, at a position upstream of the RO membrane makes it impossible to exercise the concentration control. Therefore, it is preferable to use a combined-chlorine agent, which does not cause the degradation of the membrane as described above, as a slime-controlling agent.

[0072] Control of Concentrations of Cooling-Water Treatment Chemicals in Circulating Cooling-Water System

In the present invention, the concentrations of the cooling-water treatment chemicals such as the scale dispersant and/or the slime-controlling agent described above in the circulating cooling-water system are controlled on the basis of a change in the performance of the separation membrane included in the water recovery system, that is, more specifically, a change in one or more items selected from the pressures applied onto the pretreatment membrane and/or the RO membrane that serve as separation membranes (operating pressures of the separation membranes (difference in the operating pressure)), the quality of the

treated water (quality of the water that permeates through the membrane), and the amount of treated water (amount of permeated water, i.e., amount of recovered water).

[0073] For example, when the pressure applied to the RO-membrane device is increased, the concentration of one of the slime-controlling agent and the scale dispersant in the circulating cooling-water system is increased by about 0.1 to 2.0 mg/L. If the pressure increase does not stop after a lapse of a predetermined amount of time, the concentration of the chemical is further increased by about 0.1 to 2.0 mg/L. In the case where the pressure increase does not stop even after the concentration control has been exercised several (about 2 to 10) times in the above manner, it is considered that increasing the concentration of the selected chemical is not effective. Thus, the control of the concentration of the chemical is stopped, and the control of the concentration of the other chemical is started in the same manner as described above. The above process is repeated certain times in order to determine the concentrations of the chemicals.

In the case where the quality of water treated in the RO-membrane device is degraded or the amount of water treated in the RO-membrane device is reduced, the concentrations of the slime-controlling agent and/or the scale dispersant are controlled by the feedback control as

described above in order to determine specific concentrations at which the performance of the RO-membrane device is consistent in terms of the above items.

[0074] The control and determination of chemical concentration described above may be exercised at any timing, that is, continuously, at regular intervals, or at irregular intervals, and is preferably exercised at regular intervals because the cycles of concentration of the cooling water vary with season, process, and the like and the rate of proliferation of slime varies with season and the like.

[0075] In the case where two or more types of chemicals are used as in the case where the slime-controlling agent and the scale dispersant are used in combination, the concentration of any one of the chemicals may be controlled first. However, in order to determine the influence of a change in the concentration of each chemical, it is preferable not to control the concentrations of plural chemicals at the same time but to change the concentration of only one chemical in one concentration control. For example, it is preferable to determine the chemical concentration of one of the slime-controlling agent and the scale dispersant by changing the concentration of the chemical first and subsequently determine the concentration of the other chemical by changing the concentration of the chemical.

[0076] After a consistent operation of the water recovery system has been achieved as a result of controlling chemical concentration as described above, in some cases, it may be possible to maintain the consistent operation by controlling only the concentration of one chemical selected from the scale dispersant and the slime-controlling agent without controlling the concentration of the other chemical.

[0077] In the case where the conditions under which the circulating cooling-water system is operated do not widely vary, specific concentrations of chemicals such as the slime-controlling agent and the scale dispersant in the circulating cooling-water system at which the water recovery system can be operated with consistency, that is, without an increase in the pressure applied to the RO-membrane device of the water recovery system, degradation of the quality of water treated in the RO-membrane device, or a reduction in the amount of water treated in the RO-membrane device, may be determined and set in advance. In such a case, the concentrations of the chemicals are controlled to be the specific concentrations by feedback control based on the results of the measurement obtained from equipment capable of measuring the concentrations of the chemicals.

[0078] The method for measuring the concentrations of the chemicals in the circulating cooling-water system is not limited, and publicly known methods can be employed.

[0079] In contrast to the methods of the related art in which the amounts of chemicals such as a scale dispersant and a slime-controlling agent added to the water recovery system are controlled, in the present invention, the amounts of chemicals added to the circulating cooling-water system but not the water recovery system are controlled on the basis of a change in the performance of the separation membrane of the water recovery system. This enables the water treatment performed in the circulating cooling-water system and the water treatment performed in the water recovery system to be integrally performed.

[0080] Controlling the concentrations of chemicals on the basis of a change in the performance of the separation membrane of the water recovery system means that the cooling-water treatment chemicals that have been added to the circulating cooling-water system are transported into the water recovery system by being contained in the cooling effluent and exhibits the effect at the separation membrane of the water recovery system, that is, the effect of the cooling-water treatment chemicals still remains in the water recovery system. Needless to say that the effect of the cooling-water treatment chemicals, such as prevention of the occurrence of scaling and control of the slime, are exhibited in the circulating cooling-water system.

[0081] In the case where the performance of the separation

membrane of the water recovery system is likely to be degraded even when the concentrations of chemicals in the circulating cooling-water system are controlled by the method according to the present invention, it is considered to be impossible to restore the performance of the water recovery system by controlling the concentrations of the chemicals because of severe contamination of the separation membrane or the cooling tower. In such a case, the operation of the system is stopped, and maintenance work such as cleaning of the separation membrane of the water recovery system or cleaning of the cooling tower is conducted.

[0082] The concentration of the scale dispersant in the circulating cooling-water system is commonly about 1 to 100 mg/L, is preferably about 2 to 30 mg/L, and is more preferably about 5 to 20 mg/L in terms of the concentration of the active constituent. The concentration of the slime-controlling agent in the circulating cooling-water system is preferably about 0.1 to 200 mg/L and is more preferably about 0.1 to 100 mg/L in terms of the concentration of the active constituent. When the performance of the separation membrane of the water recovery system is not improved even after the concentrations of the above chemicals have exceeded the respective upper limits above, it is preferable to conduct maintenance work such as cleaning of the separation

membrane, the cooling tower, or the like.

[0083] An apparatus for treating cooling effluent according to the present invention includes a chemical-concentration control unit that controls the concentrations of the cooling-water treatment chemicals in the circulating cooling-water system on the basis of a change in the performance of the separation membrane by the above-described method. The chemical-concentration control unit includes, for example, a pressure gauge that detects the operating pressure of the RO membrane; a concentration meter that detects the concentrations of the chemicals in the circulating cooling-water system; and a control unit that receives the measurement data, calculates, from the received data, specific concentrations to which the concentrations of the chemicals are to be controlled, and outputs a signal that provides a chemical-addition unit disposed in the circulating cooling-water system with information about the amounts of chemicals to be added on the basis of the calculation results.

EXAMPLES

[0084] The present invention is described more specifically with reference to Examples below. However, the present invention is not limited by Examples below within the scope of the present invention.

[0085] [Example 1]

Blowdown water discharged from a cooling tower (hereinafter, referred to simply as "blowdown water") included in a circulating cooling-water system that was operated using industrial water of Chiba, Japan as raw water at cycles of concentration of 3.5 times was recovered by being treated with a strainer, an MF-membrane device, and an RO-membrane device in this order. The recovered water was returned to the circulating cooling-water system.

[0086] To the circulating cooling-water system, a scale dispersant that was a copolymer of acrylic acid with AMPM (acrylic acid:AMPM (molar ratio) = 70:30, weight-average molecular weight: 10,000; hereinafter, abbreviated as "AA/AMPS") was added such that the concentration of the scale dispersant in the system was 3 mg/L, and a slime-controlling agent that was a combined-chlorine agent prepared from sodium hydroxide, sulfamic acid, and sodium hypochlorite by the method described in Example 1 of International Publication No. W02011/125762 was added such that the concentration of the slime-controlling agent in the system (combined-chlorine concentration) was 1.0 mg/L. The above circulating cooling-water system was capable of treating cooling water at a sufficient level when the concentration of AA/AMPW was 3 mg/L and the concentration of the combined-chlorine concentration was 1.0 mg/L.

[0087] The diameter of the mesh openings formed in the

strainer was 400 μm . The MF membrane used was "Purier GS (hydrophilic PVDF; pore diameter: 0.02 μm , external pressure type)" produced by Kuraray Co., Ltd. The RO membrane used was "KROA-2032-SN (polyamide ultralow-pressure RO membrane)" produced by Kurita Water Industries Ltd. The MF-membrane device was cleaned once every 30 minutes.

[0088] The blowdown water (pH 8.5 to 8.7) was directly passed through the strainer and the MF-membrane device without the pH of the blowdown water being controlled in advance. Sulfuric acid was added at a position located on the entry side of the RO-membrane device in order to control the pH of the water to be 5.5, and the water was subsequently passed into the RO-membrane device.

[0089] The water recovery ratios of the MF-membrane device and the RO-membrane device were 90% and 75%, respectively.

[0090] After the operation had been started, the concentrations of the scale dispersant and the slime-controlling agent in the circulating cooling-water system were controlled with reference to an increase in the pressure applied to the RO-membrane device one by one. An increase in the pressure applied to the RO-membrane device was determined once every three days, and the concentration of each chemical was changed in steps of 1 mg/L. As a result, it was found that an increase in the pressure applied to the RO-membrane device was best limited when the

concentration of the scale dispersant in the circulating cooling-water system was 10 mg/L and the concentration of combined chlorine that originated from the slime-controlling agent in the circulating cooling-water system was 5 mg/L.

[0091] Under the above conditions, the water was passed through the system for 30 days while an inverter included in a device (pump) was adjusted such that the water recovery ratio of the RO-membrane device was maintained to be 75%. A change in the pressure applied onto the RO membrane with time was determined. The operating pressure of the RO membrane which was measured after a lapse of 30 days was 1.22 MPa.

[0092] Fig. 1 illustrates a change in the operating pressure of the RO membrane with time which was measured during the 30-day operation period. Fig. 2 illustrates a change, with time, in the ratio of the amount of recovered water measured in each time step to the amount of recovered water measured at the initial stage of the operation (amount of recovered water in each time step/amount of recovered water at the initial stage of operation; hereinafter, referred to as "ratio relative to the initial amount of recovered water").

[0093] [Comparative Example 1]

A treatment of cooling water and water recovery were performed as in Example 1, except that the concentration of

the scale dispersant in the circulating cooling-water system was fixed at 3 mg/L, the concentration of the slime-controlling agent was fixed at 2 mg/L in terms of the concentration of combined chlorine, and the water recovery ratio of the RO membrane was set to 65%. The water was passed through the system for 30 days as described above. A change in the pressure applied onto the RO membrane was determined. After a lapse of 21 days from the start of operation, the operating pressure of the RO membrane exceeded 1.4 MPa, and it became impossible to achieve a pump head high enough to produce a sufficient amount of water. After a lapse of 30 days since the water was started being passed through the system, it became necessary to clean the RO membrane.

[0094] In Comparative Example 1, it was impossible to operate the water recovery system with consistency, although the concentration of the scale dispersant was 3 mg/L, which was at a level sufficient for the treatment of cooling water in the circulating cooling-water system, the concentration of the combined-chlorine agent was 2 mg/L, which was higher than the required concentration, and the water recovery ratio of the RO-membrane device of the water recovery system was set to be lower than that set in Example 1.

[0095] Fig. 1 illustrates a change in the operating pressure of the RO membrane with time which was measured

during the 30-day operation period. Fig. 2 illustrates a change in ratio relative to the initial amount of recovered water with time.

[0096] The results obtained in Example 1 and Comparative Example 1 confirm that, according to the present invention, it is possible to improve the consistency of the operation of a water recovery system with efficiency without adding water-treatment chemicals to the water recovery system by controlling the concentrations of cooling-water treatment chemicals in a circulating cooling-water system on the basis of a change in the performance of a separation membrane included in the water recovery system.

[0097] Although the present invention has been described in detail with reference to a particular embodiment, it is apparent to a person skilled in the art that various modifications can be made therein without departing from the spirit and scope of the present invention.

The present application is based on Japanese Patent Application No. 2014-103434 filed on May 19, 2014, which is incorporated herein by reference in its entirety.

CLAIMS

[Claim 1]

A method for controlling concentration of a cooling-water treatment chemical in a circulating cooling-water system including the cooling-water treatment chemical, the circulating cooling-water system being provided with a water recovery system that treats water discharged from the circulating cooling-water system through a separation membrane and returns the treated water to the circulating cooling-water system, the method comprising controlling the concentration of the cooling-water treatment chemical in the circulating cooling-water system on the basis of a change in the performance of the separation membrane.

[Claim 2]

The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to Claim 1, wherein the concentration of the cooling-water treatment chemical is controlled on the basis of a change in at least one selected from pressure applied onto the separation membrane, quality of the treated water, and an amount of the treated water.

[Claim 3]

The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to Claim 1 or 2, wherein the

concentration of the cooling-water treatment chemical in the circulating cooling-water system is controlled to be equal to or higher than a predetermined concentration of the cooling-water treatment chemical at which the performance of the separation membrane is consistent.

[Claim 4]

The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to any one of Claims 1 to 3, wherein the cooling-water treatment chemical includes a slime-controlling agent and/or a scale dispersant.

[Claim 5]

The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to Claim 4, wherein the slime-controlling agent includes a combined-chlorine agent.

[Claim 6]

The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to Claim 4 or 5, wherein the cooling-water treatment chemical includes the slime-controlling agent and the scale dispersant, and wherein the concentration of one chemical selected from the slime-controlling agent and the scale dispersant is controlled first and the concentration of the other chemical is

subsequently controlled.

[Claim 7]

The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to any one of Claims 1 to 6, wherein the separation membrane is a reverse osmosis membrane.

[Claim 8]

The method for controlling the concentration of a cooling-water treatment chemical in a circulating cooling-water system according to Claim 7, wherein the water recovery system includes a microfiltration membrane or an ultrafiltration membrane that serves as a pretreatment membrane disposed upstream of the reverse osmosis membrane.

[Claim 9]

A method for recovering cooling effluent, the method comprising treating water discharged from a circulating cooling-water system including a cooling-water treatment chemical with a water recovery system including a separation membrane and returning the treated water to the circulating cooling-water system, wherein the concentration of the cooling-water treatment chemical in the circulating cooling-water system is controlled by the method for controlling the concentration of a cooling-water treatment chemical according to any one of Claims 1 to 8.

[Claim 10]

An apparatus for treating cooling effluent, the apparatus treating water discharged from a circulating cooling-water system including a cooling-water treatment chemical with a separation-membrane device and returning the treated water to the circulating cooling-water system, the apparatus comprising a chemical-concentration control unit that controls concentration of the cooling-water treatment chemical in the circulating cooling-water system on the basis of a change in the performance of the separation membrane.

[Claim 11]

The apparatus for treating cooling effluent according to Claim 10, wherein the chemical-concentration control unit controls the concentration of the cooling-water treatment chemical on the basis of a change in at least one selected from pressure applied onto the separation membrane, quality of the treated water, and an amount of the treated water.

[Claim 12]

The apparatus for treating cooling effluent according to Claim 10 or 11, wherein the chemical-concentration control unit controls the concentration of the cooling-water treatment chemical in the circulating cooling-water system to be equal to or higher than a predetermined concentration of the cooling-water treatment chemical at which the performance of the separation membrane is consistent.

[Claim 13]

The apparatus for treating cooling effluent according to any one of Claims 10 to 12, wherein the cooling-water treatment chemical includes a slime-controlling agent and/or a scale dispersant.

[Claim 14]

The apparatus for treating cooling effluent according to Claim 13, wherein the slime-controlling agent includes a combined-chlorine agent.

[Claim 15]

The apparatus for treating cooling effluent according to Claim 13 or 14, wherein the cooling-water treatment chemical includes the slime-controlling agent and the scale dispersant, and wherein the chemical-concentration control unit controls the concentration of one chemical selected from the slime-controlling agent and the scale dispersant first and subsequently controls the concentration of the other chemical.

[Claim 16]

The apparatus for treating cooling effluent according to any one of Claims 10 to 15, wherein the separation-membrane device is a reverse-osmosis-membrane device.

[Claim 17]

The apparatus for treating cooling effluent according to Claim 16, the apparatus further comprising a

microfiltration-membrane device or an ultrafiltration-membrane device that serves as a pretreatment-membrane device disposed upstream of the reverse-osmosis-membrane device.