

## DESCRIPTION

### TREATMENT APPARATUS AND TREATMENT METHOD FOR HARDNESS COMPONENT-CONTAINING WATER

5

#### TECHNICAL FIELD

[0001]

The present invention relates to a treatment apparatus and a treatment method for a hardness component-containing water.

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#### BACKGROUND

[0002]

One method that is used for reducing the volume of wastewater involves concentrating the wastewater using a reverse osmosis membrane and recovering the permeate. In recent years, the need for reducing wastewater volumes has grown stronger, meaning the concentration ratio for wastewater is being increased as much as possible, and there is a growing number of factories and the like that are now operating under ZLD (Zero Liquid Discharge).

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[0003]

As a result, methods are being employed in which the concentrate from the reverse osmosis membrane is subjected to further treatment with a reverse osmosis membrane, or is further concentrated using a method such as evaporative concentration. When the wastewater concentration ratio is increased in this manner, there is a concomitant increase in the risk of scaling due to hardness components and the like in the wastewater. When scale develops, the reverse osmosis membrane may become blocked, leading to a reduction in the permeate volume and/or the heat transfer surface used in the evaporative concentration may become coated with scale, leading to a deterioration in the heat transfer efficiency.

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[0004]

Accordingly, it is desirable to reduce the hardness components in the wastewater as much as possible by performing a softening treatment or the like prior to the reverse osmosis membrane treatment. As disclosed in Patent Document 1, one known example of a method for subjecting a wastewater containing hardness components to a softening treatment involves precipitating the hardness components in the wastewater such as calcium carbonate and magnesium hydroxide, and then performing a solid-liquid separation. In those cases where the wastewater contains calcium as a hardness component, the softened water that has undergone the solid-liquid separation contains a saturated concentration of calcium carbonate, and therefore a method is employed in which an acid is added to increase the solubility of the calcium carbonate, and a decarbonation is also performed, thereby suppressing precipitation of calcium carbonate in the latter stages.

[0005]

The softened water obtained from this softening treatment typically retains from several mg/L to several tens of mg/L of dissolved hardness components. The calcium hardness component is removed as calcium carbonate, and therefore the calcium concentration in the softened water is determined by the concentration of residual carbonate ions in the softened water, so that provided the carbonate ion concentration is high, the calcium hardness is reduced, although this requires an associated increase in the injection amount of carbonic acid, resulting in increased costs. The magnesium hardness component is removed as magnesium hydroxide, and therefore the magnesium concentration in the softened water changes with the pH. If the pH is 11.0 or higher, then the magnesium hardness component can be removed down to 1 mg/L or less, but if the pH reaches 10.5, then about several mg/L to several tens of mg/L of magnesium hardness component is retained.

[0006]

In this manner, even when the hardness components in a wastewater are reduced by a softening treatment prior to the reverse osmosis membrane treatment, some hardness

components still remain in the softened water, and therefore if the concentration ratio during the concentration conducted in a latter-stage reverse osmosis membrane is further increased, the risk of scaling in the latter stages also increases.

[0007]

5           A method that employs treatment with an ion exchange resin to further remove residual hardness components from a softened water also exists, but results in increased treatment costs.

## CITATION LIST

10           PATENT LITERATURE

[0008]

Patent Document 1: JP 5906892 B

## SUMMARY

15           TECHNICAL PROBLEM

[0009]

An object of the present invention is to provide a treatment apparatus and a treatment method for performing a reverse osmosis membrane treatment after a softening treatment on a hard component-containing water, wherein the apparatus and method are capable of  
20       reducing the amount of hardness components in the concentrate that flows out in the latter stage.

## SOLUTION TO PROBLEM

[0010]

25           The present invention provides a treatment apparatus for a hardness component-containing water that includes: a reaction tank for adding at least one of an alkaline agent and a carbonate compound to a water to be treated containing a hardness component, thereby insolubilizing the hardness component, a solid-liquid separation unit for

performing a solid-liquid separation of the obtained insoluble material, a reverse osmosis membrane treatment unit for treating the obtained solid-liquid separation liquid with a reverse osmosis membrane to obtain a concentrate and a permeate, and a return unit for returning at least a portion of the obtained concentrate to a stage prior to the solid-liquid separation unit.

[0011]

In the above treatment apparatus for a hardness component-containing water, the return destination for the concentrate returned by the return unit is preferably the reaction tank.

[0012]

In the above treatment apparatus for a hardness component-containing water, return of the concentrate is preferably performed so as to achieve a  $\text{CaCO}_3$  concentration in the reaction tank of at least 100 mg/L.

[0013]

The above treatment apparatus for a hardness component-containing water preferably also includes an ion concentration measurement unit that measures the ion concentration of the concentrate, wherein the amount of the concentrate returned by the return unit is adjusted in accordance with the measured value from the ion concentration measurement unit.

[0014]

Further, the present invention also provides a treatment method for a hardness component-containing water that includes: an insolubilization step of adding at least one of an alkaline agent and a carbonate compound to a water to be treated containing a hardness component, thereby insolubilizing the hardness component, a solid-liquid separation step of performing a solid-liquid separation of the obtained insoluble material, a reverse osmosis membrane treatment step of treating the obtained solid-liquid separation liquid with a reverse osmosis membrane to obtain a concentrate and a permeate, and a return step

of returning at least a portion of the obtained concentrate to a stage prior to the solid-liquid separation step.

[0015]

5 In the above treatment method for a hardness component-containing water, the return destination for the concentrate in the return step is preferably a reaction tank to which at least one of the alkaline agent and the carbonate compound is added.

[0016]

10 In the above treatment method for a hardness component-containing water, return of the concentrate is preferably performed so as to achieve a  $\text{CaCO}_3$  concentration in the reaction tank of at least 100 mg/L.

[0017]

15 In the above treatment method for a hardness component-containing water, it is preferable that the ion concentration of the concentrate is measured, and the amount of the concentrate returned in the return step is adjusted in accordance with the measured value for the ion concentration.

## ADVANTAGEOUS EFFECTS OF INVENTION

[0018]

20 In the present invention, in a treatment apparatus and a treatment method for performing a reverse osmosis membrane treatment after a softening treatment on a hard component-containing water, the apparatus and method are capable of reducing the amount of hardness components in the concentrate that flows out in the latter stage.

## BRIEF DESCRIPTION OF DRAWINGS

25 [0019]

FIG. 1 is a schematic structural diagram illustrating one example of treatment apparatus for a hard component-containing water according to an embodiment of the present invention.

FIG. 2 is a schematic structural diagram illustrating a treatment apparatus used in Example 1.

FIG. 3 is a schematic structural diagram illustrating a treatment apparatus used in Comparative Example 1.

5        FIG. 4 is a graph illustrating the Ca concentration (mg-CaCO<sub>3</sub>/L) relative to the reaction time (min) in Example 2.

FIG. 5 is a graph illustrating the solubility (mg/L) of calcium carbonate relative to the pH of water of 25°C.

10       FIG. 6 is a graph illustrating the solubility (mg-SiO<sub>2</sub>/L) of silica relative to the pH of water of 25°C.

## DESCRIPTION OF EMBODIMENTS

[0020]

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

[0021]

A schematic illustration of one example of the treatment apparatus for a hard  
component-containing water according to an embodiment of the present invention is  
20       shown in FIG. 1, and the structure of that apparatus is described below.

[0022]

The treatment apparatus 1 for a hardness component-containing water includes a  
reaction tank 12 for adding at least one of an alkaline agent and a carbonate compound to  
the water to be treated containing a hardness component, thereby insolubilizing the  
25       hardness component, a settling tank 16 that functions as a solid-liquid separation unit for  
performing a solid-liquid separation of the obtained insoluble material, and a reverse  
osmosis membrane treatment device 20 that functions as a reverse osmosis membrane  
treatment unit for treating the obtained solid-liquid separation liquid with a reverse osmosis

membrane to obtain a concentrate and a permeate. The hardness component-containing water treatment apparatus 1 may also include a treatment water tank 10 for storing the water to be treated, a polymer reaction tank 14 for adding a polymer flocculant to the reaction liquid obtained in the reaction tank 12 to conduct a flocculation reaction, and a solid-liquid separation liquid tank 18 for storing the solid-liquid separation liquid obtained in the settling tank 16.

[0023]

In the hardness component-containing water treatment apparatus 1 of FIG. 1, the outlet of the treatment water tank 10 and the treatment water inlet of the reaction tank 12 are connected by a line 26 via a pump 22. The outlet of the reaction tank 12 and the inlet of the polymer reaction tank 14 are connected by a line 28. The outlet of the polymer reaction tank 14 and the inlet of the settling tank 16 are connected by a line 30. The solid-liquid separation liquid outlet from the settling tank 16 and the inlet of the solid-liquid separation liquid tank 18 are connected by a line 32. A sludge line 58 is connected to the sludge outlet of the settling tank 16. The outlet of the solid-liquid separation liquid tank 18 and the inlet of the reverse osmosis membrane treatment device 20 are connected by a line 34 via a pump 24. A permeate line 36 is connected to the permeate outlet from the reverse osmosis membrane treatment device 20. The concentrate outlet from the reverse osmosis membrane treatment device 20 and a return water inlet for the reaction tank 12 are connected, via a valve 54, by a return line 38 that functions as a return unit for returning at least a portion of the obtained concentrate to a stage prior to the settling tank 16. A concentrate line 40 is connected, via a valve 56, to a location in the return line 38 between the concentrate outlet and the valve 54. A carbonate compound addition line 42 that functions as a carbonate compound addition unit and an alkaline agent addition line 44 that functions as an alkaline agent addition unit are connected to the reaction tank 12, and a stirring device 50 fitted with a stirring blade is provided as a stirring unit. A polymer flocculant addition line 46 that functions as a polymer flocculant addition unit is connected to the polymer reaction tank 14, and a stirring device 52 fitted with a stirring blade is

provided as a stirring unit. A pH adjuster addition line 48 that functions as a pH adjuster addition unit is connected to the line 32.

[0024]

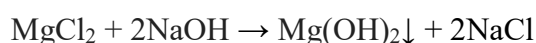
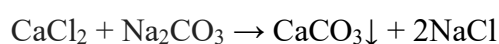
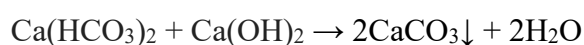
5 The treatment method for a hardness component-containing water, and the operation of the hardness component-containing water treatment apparatus 1 according to the present embodiment are described below.

[0025]

10 The hardness component-containing water that represents the water to be treated is stored in the treatment water tank 10 as required, and is then fed through the line 26 into the reaction tank 12 using the pump 22. In the reaction tank 12, at least one of an alkaline agent and a carbonate compound is added to the hardness component-containing water, thereby insolubilizing the hardness component (insolubilization step). The alkaline agent is added to the reaction tank 12 through the alkaline agent addition line 44, whereas the carbonate compound is added to the reaction tank 12 through the carbonate compound addition line 42. The reaction liquid in the reaction tank 12 may be stirred using the stirring device 50.

[0026]

20 The insolubilization reaction may be represented, for example, by the formulas shown below. The calcium hardness component that represents a temporary hardness component is insolubilized as calcium carbonate using, for example, calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) as an alkaline agent. Further, the calcium hardness component that represents a permanent hardness component is insolubilized as calcium carbonate using, for example, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) as a carbonate compound. The magnesium hardness component is insolubilized as magnesium hydroxide using, for example, sodium hydroxide (NaOH) as an alkaline agent.



[0027]

The reaction liquid obtained in the insolubilization step is fed from the reaction tank 12 through the line 28 and into the polymer reaction tank 14. In the polymer reaction tank 14, if required, a polymer flocculant may be added to the reaction liquid through the polymer flocculant addition line 46 to perform a flocculation reaction (flocculation step). In the polymer reaction tank 14, the flocculated liquid may be stirred with the stirring device 52.

[0028]

The flocculated liquid obtained in the flocculation step is fed from the polymer reaction tank 14 through the line 30 and into the settling tank 16. In the settling tank 16, a solid-liquid separation is performed by allowing the obtained insolubilized material to settle naturally (solid-liquid separation step).

[0029]

The solid-liquid separation liquid obtained in the solid-liquid separation step is fed, as required, from the settling tank 16 through the line 32 and into the solid-liquid separation liquid tank 18 for storage. In the line 32, if required, a pH adjuster may be added to the solid-liquid separation liquid through the pH adjuster addition line 48 to adjust the pH of the solid-liquid separation liquid (pH adjustment step). The pH adjustment may also be performed in the solid-liquid separation liquid tank 18. On the other hand, the sludge obtained in the solid-liquid separation step is discharged through the sludge line 58.

[0030]

The solid-liquid separation liquid is fed through the line 34 and into the reverse osmosis membrane treatment device 20 using the pump 24. In the reverse osmosis membrane treatment device 20, the solid-liquid separation liquid is treated using the reverse osmosis membrane to obtain a concentrate and a permeate (reverse osmosis membrane treatment step). The permeate obtained in the reverse osmosis membrane treatment step is discharged through the permeate line 36, and is either collected and reused or discarded. At least a portion of the concentrate obtained in the reverse osmosis

membrane treatment step is fed through the return line 38 to the reaction tank 12 (return step), which represents a stage prior to the settling tank 16 (the solid-liquid separation step). At least a portion of the concentrate may be returned to the solid-liquid separation liquid tank 18.

5 [0031]

In this manner, in the hardness component-containing water treatment method and treatment apparatus according to the present embodiment, following softening treatments (the insolubilization step, the flocculation step and the solid-liquid separation step) for the hardness component-containing water, the solid-liquid separated water containing the  
10 hardness component is concentrated by the reverse osmosis membrane treatment, and at least a portion of the concentrate is returned to a stage prior to the solid-liquid separation step.

[0032]

In this manner, the amount of hardness component in the concentrate flowing into  
15 the latter stages can be reduced. If an additional concentration treatment such as another reverse osmosis membrane treatment or an evaporative concentration treatment is performed following the above reverse osmosis membrane treatment, then the scale of the equipment for that additional concentration treatment can be reduced. Further, precipitation of the hardness component in the additional reverse osmosis membrane  
20 treatment or evaporative concentration treatment performed following the above reverse osmosis membrane treatment can be suppressed, and the system can be operated in a more stable manner.

[0033]

In the return unit, there are no particular limitations on the return destination for the  
25 concentrate, provided the destination is a stage prior to the settling tank 16 (the solid-liquid separation step). For example, at least a portion of the concentrate may be returned to at least one of the treatment water tank 10, the reaction tank 12, the polymer reaction tank 14, and the lines 26, 28 and 30, but by returning the concentrate to the reaction tank 12, to

which at least one of an alkaline agent or a carbonate compound is added, the hardness component in the concentrate is able to promote the precipitation of calcium carbonate and/or magnesium hydroxide in the reaction tank 12, and is consequently preferable. For example, the precipitation reaction for calcium carbonate proceeds as a result of the calcium carbonate precipitating on the surface of produced crystals, and therefore it is thought that the reaction time is shorter in those cases where calcium carbonate particles already exist, or cases in which the concentration of the calcium hardness component is high.

[0034]

In these cases, the concentrate is preferably returned in such a manner to achieve a calcium carbonate ( $\text{CaCO}_3$ ) concentration in the reaction tank 12 of at least 100 mg/L. Returning the concentrate so as to achieve a concentration of at least 1,000 mg/L is more preferable. If the calcium carbonate ( $\text{CaCO}_3$ ) concentration in the reaction tank 12 falls to less than 100 mg/L, then it may sometimes become difficult to promote the precipitation of calcium carbonate in the reaction tank 12.

[0035]

The more the amount of concentrate returned to a stage prior to the settling tank 16 (the solid-liquid separation step) is increased, the more the hardness load flowing out from the reverse osmosis membrane treatment can be reduced, but in those cases where the hardness component-containing water that represents the water to be treated contains ionic components such as sodium chloride ( $\text{NaCl}$ ) that are difficult to remove by flocculation and settling, these ionic components can sometimes become concentrated within the system. If the concentration ratio becomes too high, then the osmotic pressure increases and the operating pressure in the reverse osmosis membrane increases, and therefore it is desirable that a predetermined volume of the concentrate is fed to a stage subsequent to the reverse osmosis membrane treatment. In order to enable the volume of concentrate being fed to a stage subsequent to the reverse osmosis membrane treatment to be adjusted, it is preferable that, for example, an ion concentration measuring unit that measures the ion

concentration of the concentrate is also provided, and the volume of concentrate being fed through the return unit is adjusted in accordance with the measured value from that concentration measuring unit. For example, a method may be adopted in which the conductivity of the concentrate is measured, and the volume of concentrate being fed to a stage subsequent to the reverse osmosis membrane treatment can then be adjusted so as to ensure that the conductivity is no higher than a predetermined value. Adjustment of the feed volume of the concentrate may be performed, for example, by adjusting the degree of opening of the valves 54 and 56.

[0036]

In those cases where the conductivity of the concentrate is measured, and the feed volume of concentrate is adjusted accordingly, it is desirable that the conductivity has a value for which the osmotic pressure does not exceed the upper limit for the pressure during the reverse osmosis membrane treatment, and therefore the conductivity is preferably not more than 30,000  $\mu\text{S}/\text{cm}$ , and more preferably not more than 20,000  $\mu\text{S}/\text{cm}$ . If the conductivity of the concentrate exceeds 30,000  $\mu\text{S}/\text{cm}$ , then the osmotic pressure at the reverse osmosis membrane may increase, and may sometimes exceed the pressure resistance limit of the reverse osmosis membrane.

[0037]

Examples of treatments for further concentrating the concentrate at a stage subsequent to the reverse osmosis membrane treatment include a reverse osmosis membrane treatment, a thermal evaporation concentration treatment, a forward osmosis membrane treatment, and an electrodialysis treatment. From the viewpoint of keeping the treatment costs low, a reverse osmosis membrane treatment is preferable. By using the hardness component-containing water treatment method and treatment apparatus according to the present embodiment, treatment can be conducted in a stable manner even in those cases where an additional reverse osmosis membrane treatment is performed subsequent to the reverse osmosis membrane treatment.

[0038]

The hardness component-containing water that represents the treatment target may be, for example, groundwater, water used for industry, or factory wastewater or the like. The amount of calcium hardness components in the hardness component-containing water is, for example, from 50 to 5,000 mg-CaCO<sub>3</sub>/L, and the amount of magnesium hardness components is, for example, from 10 to 1,000 mg-CaCO<sub>3</sub>/L. In those cases where the hardness component-containing water contains silica, the amount of silica in the hardness component-containing water is, for example, from 10 to 400 mg/L.

[0039]

Examples of alkaline agents that may be used in the insolubilization step include calcium hydroxide (Ca(OH)<sub>2</sub>), sodium hydroxide (NaOH) and potassium hydroxide (KOH). Among these, in terms of chemical costs and the like, calcium hydroxide and sodium hydroxide are preferable. Examples of carbonate compounds that may be used in the insolubilization step include sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), sodium bicarbonate (NaHCO<sub>3</sub>) and carbon dioxide gas. Among these, in terms of chemical costs and the like, sodium carbonate is preferable.

[0040]

The amount added of the alkaline agent and the carbonate compound in the insolubilization step is preferably within a range from 1.0 mol to 1.2 mol, and more preferably within a range from 1.0 mol to 1.1 mol, per 1 mol of the amount of the calcium hardness component in the hardness component-containing water that represents the water to be treated. Further, the amount added is preferably within a range from 2.0 mol to 2.4 mol, and more preferably within a range from 2.0 mol to 2.2 mol, per 1 mol of the amount of the magnesium hardness component. If the amount added of the alkaline agent and the carbonate compound in the insolubilization step is less than an equivalent molar amount relative to the amount of the hardness component in the hardness component-containing water, then the insolubilization reaction may sometimes not proceed satisfactorily, whereas addition of an excess amount may sometimes be disadvantageous in terms of chemical costs and the like.

[0041]

The reaction temperature during the insolubilization step is not particularly limited, and is, for example, typically within a range from 15°C to 30°C.

[0042]

5        Examples of polymer flocculants that may be used in the flocculation step include acrylamide-based and acrylate ester-based polymer flocculants. Among these, in terms of chemical costs and the like, an acrylamide-based polymer flocculant is preferable.

[0043]

10       The amount added of the polymer flocculant in the flocculation step is preferably within a range from 0.5 to 5.0 mg/L, and is more preferably within a range from 1 to 2 mg/L. If the amount added of the polymer flocculant in the flocculation step is less than 0.5 mg/L, then the flocculation reaction may sometimes not proceed satisfactorily, whereas addition of an excess amount may sometimes be disadvantageous in terms of chemical costs and the like.

15       [0044]

The reaction temperature during the flocculation step is not particularly limited, and is, for example, within a range from 15°C to 30°C.

[0045]

20       There are no particular limitations on the solid-liquid separation method used in the solid-liquid separation step, and in addition to a settling tank that utilizes natural settling, other methods include sand filtration and membrane filtration. Among these, in terms of equipment costs and the like, a settling tank that utilizes natural settling is preferable.

[0046]

25       Examples of pH adjusters that may be used in the pH adjustment step include acids such as hydrochloric acid and sulfuric acid, and alkaline agents such as sodium hydroxide.

[0047]

In the pH adjustment step, the pH is preferably adjusted to a value within a range from 4 to 10, and is more preferably adjusted to a value within a range from 5 to 8. If the

pH is lower than 4, then the cost of acid may sometimes become excessive, whereas if the pH exceeds 10, the inhibitory effect on calcium carbonate scale may sometimes be inadequate.

[0048]

5           The hardness component exhibits high solubility in the acidic region (see FIG. 5) and may be therefore less likely to precipitate, but in those cases where the hardness component-containing water contains a silica component, the silica component exhibits low solubility in the acidic region (see FIG. 6) and may be more likely to precipitate, and therefore the hardness component can be insolubilized and removed (by solid-liquid  
10 separation) using the method described above, and the reverse osmosis membrane treatment step can then be conducted, for example, at a pH of 9.5 or higher.

[0049]

          In those cases where the hardness component-containing water contains a silica component, a magnesium compound may be added to insolubilize the silica, either in the  
15 reaction tank 12 or in a separate reaction tank (a second reaction tank) provided at a stage either before or after the reaction tank 12, with the insolubilized silica then being removed in the solid-liquid separation step described above. In this case, the reverse osmosis membrane treatment may be performed at any desired pH.

[0050]

20           Examples of magnesium compounds that may be used for insolubilizing the silica component include inorganic salts of magnesium such as magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ), magnesium chloride ( $\text{MgCl}_2$ ) and magnesium oxide ( $\text{MgO}$ ). Among these, in terms of chemical costs and the like, magnesium hydroxide is preferable.

[0051]

25           The amount added of the magnesium compound is preferably within a range from 0.5 mol to 5.0 mol, and more preferably within a range from 1.0 mol to 2.5 mol, per 1 mol of the amount of the silica in the water to be treated. If the amount added of the magnesium compound is less than 0.5 mol per 1 mol of silica in the water to be treated,

then the insolubilization reaction may sometimes not proceed satisfactorily, whereas addition of an amount exceeding 5.0 mol may sometimes be disadvantageous in terms of chemical costs and the like.

[0052]

5        There are no particular limitations on the reverse osmosis membrane used in the reverse osmosis membrane treatment, and for example, a polyimide-based reverse osmosis membrane may be used.

## EXAMPLES

10    [0053]

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

[0054]

15    <Example 1 and Comparative Example 1>

Flow tests were performed using test equipment having the respective flows illustrated in FIG. 2 (Example 1) and FIG. 3 (Comparative Example 1). In Example 1, a portion of the concentrate was returned to the reaction tank.

[0055]

20    (Water to be Treated)

Water to be treated: a factory discharge water (containing hardness components)

Ca = 200 mg-CaCO<sub>3</sub>/L, Mg = 50 mg-CaCO<sub>3</sub>/L, HCO<sub>3</sub><sup>-</sup> = 200 mg-CaCO<sub>3</sub>/L

[0056]

25    In Example 1, the water to be treated was supplied to the reaction tank at a rate of 140 L/h. In the reaction tank, calcium hydroxide (Ca(OH)<sub>2</sub>) was added as an alkaline agent to adjust the pH to a value from 10.8 to 11.0, and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) was added as a carbonate compound in an amount of 100 mg-CaCO<sub>3</sub>/L. In the polymer reaction tank, 2 mg/L of ORFLOCK M-4020 (manufactured by Organo Corporation) was

added as a polymer flocculant. A solid-liquid separation was performed using a settling tank as the solid-liquid separation device. The solid-liquid separation liquid was fed into the solid-liquid separation liquid tank at a flow rate of 200 L/h. The solid-liquid separation liquid was fed to a 4-inch RO element (LFC-3, manufactured by Nitto Denko Corporation) used as the reverse osmosis membrane treatment device at a flow rate of 720 L/h. The reverse osmosis membrane treatment yielded a permeate at a flow rate of 120 L/h, whereas the concentrate was recirculated to the solid-liquid separation tank at a flow rate of 520 L/h, returned to the reaction tank at a flow rate of 60 L/h, and fed to a latter-stage concentration device at a flow rate of 20 L/h. In Example 1, the concentrate was returned at a rate that yielded a  $\text{CaCO}_3$  concentration in the reaction tank of 155 mg/L. The results are shown in Table 1.

[0057]

In Comparative Example 1, the water to be treated was supplied to the reaction tank at a rate of 140 L/h. In the reaction tank, calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) was added as an alkaline agent to adjust the pH to a value from 10.8 to 11.0, and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) was added as a carbonate compound in an amount of 100 mg- $\text{CaCO}_3$ /L. In the polymer reaction tank, 2 mg/L of ORFLOCK M-4020 (manufactured by Organo Corporation) was added as a polymer flocculant. A solid-liquid separation was performed using a settling tank as the solid-liquid separation device. The solid-liquid separation liquid was fed into the solid-liquid separation liquid tank at a flow rate of 140 L/h. The solid-liquid separation liquid was fed to a 4-inch RO element (LFC-3, manufactured by Nitto Denko Corporation) used as the reverse osmosis membrane treatment device at a flow rate of 684 L/h. The reverse osmosis membrane treatment yielded a permeate at a flow rate of 84 L/h, and the concentrate was recirculated to the solid-liquid separation tank at a flow rate of 544 L/h and fed to a latter-stage concentration device at a flow rate of 56 L/h. The results are shown in Table 2.

[0058]

The amounts of Ca and Mg in the water were measured using an ion chromatograph (IC 761, manufactured by Metrohm AG), and the amount of  $\text{HCO}_3^-$  was calculated by measuring a value for inorganic carbon using a TOC meter (TOC-3000, manufactured by Shimadzu Science Co., Ltd.).

5 [0059]

[Table 1]

|                  | Units                        | Water to be treated | Settling tank outlet | RO concentrate | RO permeate |
|------------------|------------------------------|---------------------|----------------------|----------------|-------------|
| Ca               | mg- $\text{CaCO}_3/\text{L}$ | 200                 | 20                   | 50             | <1          |
| Mg               | mg- $\text{CaCO}_3/\text{L}$ | 50                  | 5.0                  | 12.5           | <1          |
| Water amount     | L/h                          | 140                 | 200                  | 20             | 120         |
| $\text{HCO}_3^-$ | mg- $\text{CaCO}_3/\text{L}$ | 200                 | 20                   | 50             | -           |
| Ca load          | g- $\text{CaCO}_3/\text{h}$  | 28                  | 4.0                  | 1.0            | -           |
| Mg load          | g- $\text{CaCO}_3/\text{h}$  | 7.0                 | 1.0                  | 0.3            | -           |

[0060]

[Table 2]

|                  | Units                        | Water to be treated | Settling tank outlet | RO concentrate | RO permeate |
|------------------|------------------------------|---------------------|----------------------|----------------|-------------|
| Ca               | mg- $\text{CaCO}_3/\text{L}$ | 200                 | 20                   | 50             | <1          |
| Mg               | mg- $\text{CaCO}_3/\text{L}$ | 50                  | 5.0                  | 12.5           | <1          |
| Water amount     | L/h                          | 140                 | 140                  | 56             | 84          |
| $\text{HCO}_3^-$ | mg- $\text{CaCO}_3/\text{L}$ | 200                 | 20                   | 50             | <1          |
| Ca load          | g- $\text{CaCO}_3/\text{h}$  | 28                  | 2.8                  | 2.8            | -           |
| Mg load          | g- $\text{CaCO}_3/\text{h}$  | 7.0                 | 0.7                  | 0.7            | -           |

10

[0061]

In Example 1, by returning a portion of the concentrate to the reaction tank at a stage prior to the settling tank (a solid-liquid separation tank), the Ca load and Mg Load of the

RO concentrate was lowered, and the amount of hardness components flowing out into the latter stage beyond the reverse osmosis membrane treatment apparatus was reduced. On the other hand, in Comparative Example 1, because no recirculation of the concentrate was performed, the amount of hardness components flowing out into the latter stage beyond the reverse osmosis membrane treatment apparatus was large.

[0062]

<Example 2>

The return destination for the concentrate was investigated. The  $\text{CaCO}_3$  precipitation reaction may proceed as a result of the  $\text{CaCO}_3$  precipitating on the surface of produced crystals, and therefore it is thought that the reaction time is shorter in those cases where  $\text{CaCO}_3$  particles already exist, or cases in which the Ca concentration is high.

[0063]

[Jar Test Procedure]

A  $\text{CaCO}_3$ -containing sludge was added to a raw water ( $\text{Ca} = 250 \text{ mg-CaCO}_3/\text{L}$ ) in amounts of 0, 100, 1,000 and 10,000 mg/L. Next, 417 mg- $\text{CaCO}_3/\text{L}$  of  $\text{Na}_2\text{CO}_3$  was added to the raw water, and sodium hydroxide ( $\text{NaOH}$ ) was used to adjust the pH to 11. Reaction was performed in a jar tester at 120 rpm. Following subsequent filtration using a  $0.45 \mu\text{m}$  filter, the Ca concentration of the treated water was measured.

[0064]

The results of the jar tests are shown in FIG. 4. The graph of FIG. 4 illustrates the Ca concentration (mg- $\text{CaCO}_3/\text{L}$ ) relative to the reaction time (min).

[0065]

In this manner, it was evident that by returning the concentrate containing  $\text{CaCO}_3$  to the reaction tank so that the amount of  $\text{CaCO}_3$  reached at least 100 mg/L, precipitation of the  $\text{CaCO}_3$  was able to be promoted.

[0066]

As illustrated in the above examples, by using an apparatus and method for performing a reverse osmosis membrane treatment following a softening treatment for the

hardness component-containing water, the amount of hardness components in the concentrate flowing out into the latter stages was able to be reduced.

#### REFERENCE SIGNS LIST

- 5 [0067]
- 1: Treatment apparatus for hardness component-containing water
- 10: Treatment water tank
- 12: Reaction tank
- 14: Polymer reaction tank
- 10 16: Solid-liquid separation tank
- 18: Solid-liquid separation liquid tank
- 20: Reverse osmosis membrane treatment device
- 22, 24: Pump
- 26, 28, 30, 32, 34: Line
- 15 36: Permeate line
- 38: Return line
- 40: Concentrate line
- 42: Carbonate compound addition line
- 44: Alkaline agent addition line
- 20 46: Polymer flocculant addition line
- 48: pH adjuster addition line
- 50, 52: Stirring device
- 54, 56: Valve
- 58: Sludge line

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## CLAIMS

1. A treatment apparatus for a hardness component-containing water comprising:
  - a reaction tank for adding at least one of an alkaline agent and a carbonate
- 5 compound to a water to be treated containing a hardness component, thereby insolubilizing the hardness component,
  - a solid-liquid separation unit for performing a solid-liquid separation of an obtained insoluble material,
  - a reverse osmosis membrane treatment unit for treating an obtained solid-liquid
- 10 separation liquid with a reverse osmosis membrane to obtain a concentrate and a permeate, and
  - a return unit for returning at least a portion of an obtained concentrate to a stage prior to the solid-liquid separation unit.
- 15 2. The treatment apparatus for a hardness component-containing water according to Claim 1, wherein
  - a return destination for the concentrate returned by the return unit is the reaction tank.
- 20 3. The treatment apparatus for a hardness component-containing water according to Claim 2, wherein
  - return of the concentrate is performed so as to achieve a  $\text{CaCO}_3$  concentration in the reaction tank of at least 100 mg/L.
- 25 4. The treatment apparatus for a hardness component-containing water according to any one of Claims 1 to 3, further comprising
  - an ion concentration measurement unit that measures an ion concentration of the concentrate, wherein

an amount of the concentrate returned by the return unit is adjusted in accordance with a measured value from the ion concentration measurement unit.

5. A treatment method for a hardness component-containing water comprising:

5 an insolubilization step of adding at least one of an alkaline agent and a carbonate compound to a water to be treated containing a hardness component, thereby insolubilizing the hardness component,

a solid-liquid separation step of performing a solid-liquid separation of an obtained insoluble material,

10 a reverse osmosis membrane treatment step of treating an obtained solid-liquid separation liquid with a reverse osmosis membrane to obtain a concentrate and a permeate, and

a return step of returning at least a portion of an obtained concentrate to a stage prior to the solid-liquid separation step.

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6. The treatment method for a hardness component-containing water according to Claim 5, wherein

a return destination for the concentrate in the return step is a reaction tank to which at least one of the alkaline agent and the carbonate compound is added.

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7. The treatment method for a hardness component-containing water according to Claim 6, wherein

return of the concentrate is performed so as to achieve a  $\text{CaCO}_3$  concentration in the reaction tank of at least 100 mg/L.

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8. The treatment method for a hardness component-containing water according to any one of Claims 5 to 7, wherein

an ion concentration of the concentrate is measured, and an amount of the concentrate returned in the return step is adjusted in accordance with a measured value for the ion concentration.