

DESCRIPTION

Title of Invention

METHOD FOR OPERATING DESALTING DEVICE

Technical Field

[0001]

The present invention relates to a method for operating a desalting apparatus, and particularly to a method for operating a desalting apparatus having a first desalting apparatus and a second desalting apparatus.

Background Art

[0002]

In a desalting apparatus such as a reverse osmosis membrane, precipitation of scale of calcium carbonate, silica, calcium fluoride, etc. and membrane clogging caused by organic substances occur due to long-term operation, resulting in performance degradation such as decrease in salt rejection rate and decrease in permeated water volume. In the case of scale clogging, in order to prevent the performance degradation of the desalting apparatus, an operation method including measuring the ion concentration of the raw water not to exceed the saturation index of the concentrated water in the desalting apparatus is employed. Here, the saturation index generally refers to a logarithmic value of a value obtained by dividing the product of the concentration and ionic strength of each ion species involved in scale generation by the solubility product. Operation of the desalting apparatus is performed such that the

saturation index does not exceed zero. Further, in the case where the saturation index exceeds zero, the desalting apparatus is operated with suppression of the generation of scale, for example, by adding a scale preventing agent.

[0003]

In the case where the water quality greatly exceeds the saturation index, which is uncontrollable even by adding a scale preventing agent, chemical cleaning such as acid cleaning and alkaline cleaning has been conventionally performed to remove the scale. However, since the general cleaning includes steps of stopping the apparatus, cleaning after preparing a cleaning liquid, collecting the cleaning liquid, and then starting passing water, there is a problem that the cleaning cost increases. Therefore, it has been desired to operate a desalting apparatus which causes no performance degradation even after long-term operation and requires no chemical cleaning.

[0004]

One of the methods for operating a desalting apparatus is a flushing method. Here, flushing refers to an operation of discharging the feed water from a concentrated water discharge pipe to the outside of the system by opening an on-off valve of the concentrated water discharge pipe while continuously operating a feed water pump. By passing water at a higher flow velocity than during normal operation, fouling substances with which the membrane surface is clogged can be effectively washed away. Flushing is generally performed at a frequency of 1 to 10 times/day for 30 to 120 seconds/time. However, the flushing for several minutes/time is not sufficient to recover a desalting apparatus with deteriorated performance, and the problem is that cleaning is required

after all. Further, since the on-off valve of the concentrated water pipe is opened for flushing, the permeated water cannot be produced during flushing, resulting in lowered recovery ratio of the desalting apparatus. [0005]

Another method includes reversing the flow direction of the water to be treated of a module. According to the method, suspended substances accumulated in a raw water spacer can be easily peeled off, so that the stability of the desalting apparatus can be improved. However, the problem is that the number of valves required to reverse the flow is greatly increased, resulting in great increase in the initial cost. Further, in case of breakdown of a valve, the valve cannot be switched, so that the stability of the apparatus is greatly impaired. Furthermore, the peeling effect on scale substances caused by flow reversal has not been described.

Citation List

Patent Literature

[0006]

PTL1: JP 2004-141846 A

PTL2: JP 2004-261724 A

Summary of Invention

Technical Problem

[0007]

In view of the problem described above, an object of the present invention is to provide a method for operating a desalting apparatus capable of recovering the deteriorated desalting performance of the

desalting apparatus without stopping operation of the desalting apparatus.

Solution to Problem

[0008]

The method for operating a desalting apparatus of the present invention is a method for operating a desalting apparatus having a first desalting apparatus and a second desalting apparatus, the method comprising: a normal operation step of supplying water to be treated to the first desalting apparatus to separate a first concentrated water and a first desalted water, and supplying the first concentrated water to the second desalting apparatus to separate a second concentrated water and a second desalted water; and a recovery operation step of supplying water to be treated to the first desalting apparatus to separate a first concentrated water and a first permeated water, and passing a dilute water having a lower concentration than the first concentrated water through the second desalting apparatus to recover the desalting performance of the second desalting apparatus.

[0009]

In one aspect of the present invention, a plurality of the second desalting apparatuses are installed in parallel, and while the normal operation step is performed in some of the second desalting apparatuses, the recovery operation step is performed in other second desalting apparatuses.

[0010]

In one aspect of the present invention, in the recovery operation step, dilute water is passed through the second desalting apparatus for 5 to 60 minutes.

[0011]

In one aspect of the present invention, the water to be treated is used as the dilute water.

[0012]

In one aspect of the present invention, the desalted water of the first desalting apparatus is used as the dilute water.

[0013]

In an aspect of the present invention, a scale preventing agent is added to the dilute water.

[0014]

In an aspect of the present invention, the desalting apparatus is a reverse osmosis membrane apparatus.

[0015]

In one aspect of the present invention, a rate of water passing of the dilute water is 0.001 to 0.1 m/s.

[0016]

In one aspect of the present invention, the water quality of the first concentrated water is any of the following a to c:

a. a calcium ion concentration of 0.1 to 10 mg/L, and a fluoride ion concentration of 3000 to 8000 mg-F/L;

b. a calcium ion concentration of 500 to 1500 mg/L, and a fluoride ion concentration of 50 to 150 mg-F/L;

c. a calcium ion concentration of 400 to 1500 mg/L, and an M alkalinity of 800 to 2000 mg/L.

[0017]

In one aspect of the present invention, the first concentrated water is a concentrated water obtained by concentrating the feed water of the first desalting apparatus at a concentration ratio of 3 or more.

Advantageous Effects of Invention

[0018]

In the normal operation step of the operation method of a desalting apparatus of the present invention, water to be treated is passed through a first desalting apparatus to separate a first desalted water and a first concentrated water, and the first concentrated water is passed through a second desalting apparatus to separate a second desalted water and a second concentrated water. When the desalting performance of the second desalting apparatus deteriorates resulting from the normal operation, dilute water is passed through the second desalting apparatus while continuing the operation of the first desalting apparatus, so that the desalting performance of the second desalting apparatus can be recovered.

[0019]

In an aspect where the desalted water of the first desalting apparatus is used as the dilute water in the flux recovery operation of the second desalting apparatus, ancillary facilities such as a tank are not required, so that the apparatus structure can be simplified. Further, by using the permeated water of the first desalting apparatus having a low salt concentration as the dilute water, the recovery effect of the second desalting apparatus with deteriorated performance can be greatly

improved as compared with the case where the water to be treated is used as the dilute water.

Brief Description of Drawings

[0020]

[Fig. 1 (a) and Fig. 1 (b)] Fig. 1 (a) and Fig. 1 (b) are flow charts illustrating a method for operating a desalting apparatus in an embodiment.

[Fig. 2] Fig. 2 is a cross sectional view of a test cell.

[Fig. 3 (a) and Fig. 3 (b)] Fig. 3 (a) and Fig. 3 (b) are graphs showing results in an Example and a Comparative Example, respectively.

[Fig. 4] Fig. 4 is a flow chart illustrating a method for operating a desalting apparatus in an embodiment.

[Fig. 5] Fig. 5 is a flow chart illustrating a method for operating a desalting apparatus in an embodiment.

[Fig. 6] Fig. 6 is a flow chart illustrating a method for operating a desalting apparatus in an embodiment.

Description of Embodiments

[0021]

Hereinafter, a first embodiment will be described with reference to Fig. 1. In the embodiment, a reverse osmosis membrane apparatus (RO apparatus) is described as an example of desalting apparatus, though the present invention is not limited thereto. A polyamide reverse osmosis membrane is suitable as reverse osmosis membrane, though not limited thereto. Examples of the desalting apparatus other than the reverse osmosis membrane apparatus include a nanofiltration membrane

apparatus, a forward osmosis membrane apparatus, a membrane distillation apparatus, an electrodialysis apparatus, and an electrodeionization apparatus.

[0022]

In Fig 1, the structure of a desalting apparatus used in the method for operating the desalting apparatus according to the embodiment is shown. Note that in Fig. 1 (a), the water flow during the normal operation is shown by a thick solid line, and in Fig. 1 (b), the water flow during the flux recovery operation is shown by a thick solid line.

[0023]

[During normal operation]

During normal operation, as shown in Fig. 1 (a), the raw water in a raw water tank 1 is supplied to a first RO apparatus 4 through a pump 2 and a pipe 3, and a permeated water is taken out as a first permeated water through a pipe 6 having a valve 5.

[0024]

A concentrated water of the first RO apparatus 4 (first concentrated water) is introduced into a relay tank 10 through pipes 7 and 8, and a valve 9. The first concentrated water in the relay tank 10 is supplied to a second RO apparatus 15 from a pipe 13 having a pump 11 and a valve 12 through a pipe 14.

[0025]

A permeated water in the second RO apparatus 15 is taken out as a second permeated water through a pipe 17 having a valve 16. A concentrated water of the second RO apparatus 15 is taken out as a second concentrated water through a pipe 18, a valve 19, and pipes 20 and 21.

[0026]

During the normal operation of passing water, the pumps 2 and 11 are operated. Further, the valves 5, 9, 12, 16 and 19 are opened and valves 24 and 28 to be described below are closed.

[0027]

In the desalting apparatus in Fig. 1, the pipes 7 and 21 are bypass-connected through a pipe 23, the valve 24 and a pipe 25. Further, the pipes 3 and 14 are bypass-connected through a pipe 27, the valve 28 and a pipe 29.

[0028]

In the drawing, PI indicates a pressure sensor and FI indicates a flow rate sensor.

[0029]

[During flux recovery operation]

During flux recovery operation to recover the flux of the second RO apparatus 15, as shown in Fig. 1 (b), the pump 2 is operated and the pump 11 is stopped. Further, the valves 9 and 12 are closed and other valves are opened.

[0030]

The raw water in the raw water tank 1 is supplied to the first RO apparatus 4 through the pump 2 and the pipe 3, and the first permeated water is taken out from the pipe 6 through the valve 5. The first concentrated water is taken out through the pipes 7 and 23, the valve 24 and the pipes 25 and 21.

[0031]

Further, during the flux recovery operation of the second RO apparatus 15, a part of the raw water sent from the pump 2 as the dilute

water is supplied to the second RO apparatus 15 through the pipe 27 branched from the pipe 3, the valve 28, and the pipes 29 and 14. The permeated water of the second RO apparatus 15 is taken out through the valve 16 and the pipe 17. The concentrated water of the second RO apparatus 15 flows out to the pipe 21 through the pipe 18, the valve 19, and the pipe 20 and merges with the first concentrated water from the pipe 25 to be taken out as the concentrated water.

[0032]

In the operation method of the desalting apparatus, when the flux of the second RO apparatus 15 decreases resulting from the normal operation, the operation of passing dilute water through the second RO apparatus 15 is performed while continuing the operation of producing permeated water in the first RO apparatus 4. As a result, the flux of the second RO apparatus 15 is recovered, so that great decrease in recovery ratio can be prevented without stopping the desalting apparatus. In particular, by passing the dilute water (in the case shown in Fig. 1, raw water) for 5 minutes or more (preferably 10 minutes or more and 60 minutes or less, particularly 30 minutes or less), the scale adhered to a membrane surface is dissolved, so that the membrane separation performance can be greatly recovered.

[0033]

The dilute water is usually passed from the feed water side of the desalting apparatus, though the dilute water may be passed from the concentrated water side of the desalting apparatus.

[0034]

Hereinafter, the second embodiment will be described with reference to Figs. 4, 5 and 6. In the description of Figs. 4 to 6, the

permeated water of the reverse osmosis membrane apparatus is referred to as desalted water. In Figs. 4 to 6, the pipes through which water is flowing are shown by thick solid lines, and the pipes through which water is not flowing are shown by fine solid lines.

[0035]

In the embodiment shown in Figs. 4 and 5, two second RO apparatuses 51 and 52 are installed in parallel. In Fig. 4, the one second RO apparatus 51 is in normal operation and the other second RO apparatus 52 is in flux recovery operation, and in Fig. 5, the one second RO apparatus 51 is in flux recovery operation and the other second RO apparatus 52 is in normal operation.

[0036]

[During operation shown in Fig. 4]

As shown in Fig. 4, the raw water in a raw water tank 1 is supplied to a first RO apparatus 4 through a pump 2 and a pipe 3, and the desalted water (permeated water) is taken out as desalted water through a pipe 31, a valve 32, and a pipe 33.

[0037]

The concentrated water (first concentrated water) of the first RO apparatus 4 is supplied to the one second RO apparatus 51 through pipes 34 and 35, a valve 36, and a pipe 37.

[0038]

The desalted water (permeated water) of the second RO apparatus 51 is merged with the pipe 33 through pipes 61 and 62 to be taken out as desalted water. The concentrated water of the second RO apparatus 51 is taken out as concentrated water through a pipe 63, a valve 64, a pipe 65, a valve 66 and a pipe 67.

[0039]

A pipe 38 branched from the pipe 34 is connected to a feed water inlet of the other second desalting apparatus 52 through a valve 39 and a pipe 40. In Fig. 4, the valve 39 is closed.

[0040]

In the desalting apparatus in Fig. 4, the pipes 31 and 37 are connected through a pipe 41 and a valve 42. Further, the pipes 31 and 40 are connected through a pipe 43 and a valve 44. In Fig. 4, the valve 42 is closed and the valve 44 is opened. Accordingly, a part of the first desalted water in the pipe 31 is supplied to a feed water inlet of the second desalting apparatus 52 through the pipes 43 and 40 to perform the flux recovery operation of the second desalting apparatus 52.

[0041]

During flux recovery operation of the other second desalting apparatus 52, the desalted water of the other second desalting apparatus 52 is merged with the pipe 33 through a pipe 73 and the pipe 62 to be taken out as desalted water. The concentrated water of the second RO apparatus 52 is returned to the raw water tank 1 through pipes 74 and 77, a valve 78 and pipes 79 and 71.

[0042]

[During operation shown in Fig. 5]

Contrary to the situation shown in Fig. 4, one second desalting apparatus 51 is in flux recovery operation and another second desalting apparatus 52 is in normal operation in Fig. 5. In this case also, the raw water in a raw water tank 1 is supplied to a first RO apparatus 4 through a pump 2 and a pipe 3, and the desalted water (permeated water) is taken out as desalted water through a pipe 31, a valve 32 and a pipe 33.

[0043]

In Fig. 5, a valve 36 is closed and a valve 39 is opened. Accordingly, the concentrated water of the first RO apparatus 4 (first concentrated water) is supplied to the other second RO apparatus 52 through pipes 34 and 38, the valve 39 and a pipe 40.

[0044]

The desalted water (permeated water) of the second RO apparatus 52 is merged with the pipe 33 through pipes 73 and 62 to be taken out as desalted water. The concentrated water of the second RO apparatus 52 flows into a pipe 65 through a pipe 74 and a valve 76 to be taken out as concentrated water.

[0045]

Further, in Fig. 5, a valve 42 is opened and a valve 44 is closed. Accordingly, a part of the first desalted water in the pipe 31 is supplied to the feed water inlet of the one second desalting apparatus 51 through the pipes 42 and a pipe 37, and the second desalting apparatus 51 is in flux recovery operation. The desalted water of the one second RO apparatus 51 is merged with the pipe 33 through a pipes 61 and the pipe 62 to be taken out as desalted water. The concentrated water of the one second RO apparatus 51 is returned to the raw water tank 1 through pipes 63 and 68, a valve 69, and pipes 70 and 71.

[0046]

As described above, in the method for operating the desalting apparatus in Figs. 4 and 5, while performing normal operation of one of the two second desalting apparatuses 51 and 52 installed in parallel, flux recovery operation of the other one is performed by passing the first

desalted water, so that great decrease in recovery ratio can be prevented without stopping the desalting apparatus.

In Figs. 4 and 5, one first RO apparatus 4 and two second RO apparatuses 51 and 52 are installed in total, though more first and second RO apparatuses may be installed, respectively.

In Fig. 6 where one of the examples thereof is shown, four first RO apparatuses 4A to 4D are installed in parallel, and four second RO apparatuses 51 to 54 are installed in parallel.

To each of the first RO apparatuses 4A to 4D, the water to be treated is distributed and supplied through a pipe 3 and a pipe 81 branched from the pipe 3, and the desalted water of each of the first RO apparatuses 4A to 4D is taken out as desalted water through pipes 82, 31 and 33.

The concentrated water of the first RO apparatuses 4A to 4D is switchably supplied to the second RO apparatuses 51 and 52 or the second RO apparatuses 53 and 54 from a pipe 83 through branch pipes 88 to 91 having valves 84 to 87, respectively. Further, each of the branch pipes 88 to 91 is connected to the desalted water pipe 31 through the pipe 91 and pipes 93, 95 and 97 having valves 92, 94, 96 and 98, respectively.

In Fig. 6, the normal operation is performed in the second RO apparatuses 51 and 52, and the flux recovery operation is performed in the second RO apparatuses 53 and 54. In other words, the valves 84 and 85 are opened and the valves 86 and 87 are closed. Further, the valves 92 and 94 are closed and the valves 96 and 98 are opened.

The desalted water of each of the second RO apparatuses 51 to 54 is merged with the pipe 33 from pipes 101, 103, 105 and 107 to be taken out as desalted water.

The concentrated water of the second RO apparatuses 51 to 54 is taken out as concentrated water through pipes 102, 104, 106 and 108 and a pipe 109.

By reversing the opening/closing of the valves 84 to 87 and the valves 92, 94, 96 and 98 to the above, the flux recovery operation is performed in the second RO apparatuses 51 and 52, and the normal operation is performed in the second RO apparatuses 53 and 54.

Although the four first RO apparatuses and the four second RO apparatuses are shown in Fig. 6, the number of the RO apparatuses may be 2, 3, or 5 or more.

Although the number of the second RO apparatuses in normal operation and the number of the second RO apparatuses in flux recovery operation are the same in Figs. 4 to 6, the numbers may be different. Further, in Fig. 6 also, the concentrated water of the second RO apparatus in flux recovery operation may be returned to a raw water tank 1.

[0047]

[Rate of water passing of dilute water]

The rate of water passing of the dilute water may be appropriately determined corresponding to the clogging state of the desalting apparatus, and, for example, in the case of reverse osmosis member, the rate is 0.001 to 1 m/s, particularly preferably 0.02 to 0.2 m/s. Specifically, 300 to 2000 L/Hr per 4-inch module is preferred, and 1.8 to 10 m³/Hr per 8-inch module is preferred. Further, it is preferable that the pressure on the discharge side of the concentrated water of the desalting apparatus be 0.1 to 2 MPa.

[0048]

[Timing for switching from normal operation to recovery operation]

In the present invention, although it is possible to switch to the recovery operation when the normal operation is performed for a predetermined time, it is preferable to switch to the recovery operation at the timing when the scale is generated in the second desalting apparatus. For example, in the case shown in drawing where a reverse osmosis membrane is used as the desalting apparatus, switching is performed when the permeation flux of the second RO apparatus decreases by a set ratio from the initial stage of operation, for example, by 5%. It should be noted that 5% is an example, and the set ratio may be a value selected from 1 to 20%, particularly 1 to 10%. In particular, it is preferable to measure the change in the permeation flux of a terminal RO, which is most concentrated in the second RO apparatus.

[0049]

Since the actual permeation flux is affected by the operating pressure, water temperature, and salt concentration in the feed water, it is preferred to specify a corrected permeation flux as data indicating the performance of the RO apparatus.

[0050]

Here, the corrected permeation flux is generally calculated by a method described in the method for standardizing permeated water volume performance data of reverse osmosis membrane element and module as shown in JIS K 3805: 1990.

[0051]

That is, the permeated water volume performance data is calculated as corrected permeation flux F_{ps} through correction by the following formula (1).

[0052]

$$F_{ps} = (Q_{pa}) \times \frac{\left[P_{fa} - \frac{\Delta P_{fba}}{2} - P_{pa} - \pi_{fba} + \pi_{pa} \right]}{\left[P_{fs} - \frac{\Delta P_{fbs}}{2} - P_{ps} - \pi_{fbs} + \pi_{ps} \right]} \times \frac{(TCF_a)}{(TCF_s)} \quad (1)$$

[0053]

wherein

Q_{pa} : Permeated water volume under actual operating conditions
(m³/d)

P_{fa} : Operating pressure under actual operating conditions (kPa)

ΔP_{fba} : Differential pressure of module under actual operating
conditions (kPa)

P_{pa} : Pressure on the permeated water side under actual operating
conditions (kPa)

Π_{fba} : Osmotic pressure of the average solute concentration on the
supply side and concentration side under actual operating conditions
(kPa)

TCF_a : Temperature conversion coefficient under actual operating
conditions

P_{fs} : Operating pressure under standard operating conditions (kPa)

ΔP_{fbs} : Differential pressure of module under standard operating
conditions (kPa)

P_{ps} : Pressure on the permeated water side under standard
operating conditions (kPa)

Π_{fbs} : Osmotic pressure of average solute concentration on the
supply side and concentration side under standard operating conditions
(kPa)

TCF_s: Temperature conversion coefficient under standard operating conditions.

[0054]

Other than based on the volume decreased from the initial corrected permeation flux, switching from the normal operation to the recovery operation may be performed based on the excess of differential pressure of the second desalting apparatus, the decrease in volume of the treated water of the second desalting apparatus, the decrease in volume of permeated water of a small RO set further on the concentrated water side of the second desalting apparatus, presence or absence of supersaturated precipitates in the pipe detected by a sensor using ultrasonic waves, etc.

[0055]

In the embodiment, raw water is used as dilute water, though permeated water of the first RO apparatus or the second RO apparatus may be used as dilute water. Alternatively, a mixture of the permeated water of the first RO apparatus or the second RO apparatus and the raw water may be used as the dilute water. Further, a mixture of the permeated water of the first RO apparatus or the second RO apparatus and the first concentrated water may be used as dilute water.

[0056]

[Water quality of first concentrated water]

The present invention can be suitably used in the case where calcium fluoride scale or calcium carbonate scale is generated in the second RO apparatus. Specifically, the present invention can be suitably used in the case where the first concentrated water supplied to the second RO apparatus applies to any of the following a to c. It is to be noted that

a and b are the cases where calcium fluoride scale is generated, and c is the case where calcium carbonate scale is generated.

a. A calcium ion concentration of 0.1 to 10 mg/L, and a fluoride ion concentration of 3000 to 8000 mg-F/L.

b. A calcium ion concentration of 500 to 1500 mg/L, and a fluoride ion concentration of 50 to 150 mg-F/L.

c. A calcium ion concentration of 400 to 1500 mg/L, and an M alkalinity of 800 to 2000 mg/L.

[0057]

[Scale preventing agent added to dilute water]

It is preferable that a scale preventing agent is added to the dilute water. By adding a scale preventing agent, effects of improving scale dissolving power and preventing readherence of the dissolved scale can be obtained.

[0058]

The scale preventing agent may be appropriately selected depending on the type of desalting apparatus used and the raw water. In the case where a reverse osmosis membrane apparatus is used as desalting apparatus for the water to be treated that generates calcium carbonate scale, a phosphonic acid such as 2-phosphonobutane-1,2,4-tricarboxylic acid, a copolymer of acrylic acid and 2-acrylamide-2-methylpropanesulfonic acid, and polyacrylic acid and the like may be used. In the case where the water to be treated generates calcium fluoride scale, phosphonic acid such as 2-phosphonobutane-1,2,4-tricarboxylic acid, and polyacrylic acid and the like may be used. The addition amount of the scale preventing agent is about 10 to 1000 mg/L.

[0059]

A pH adjuster may be added to the dilute water to obtain an effect of improving of scale dissolving power and preventing readherence of the dissolved scale.

[0060]

[Direction of passing dilute water]

In the case where raw water is passed as dilute water as shown in Fig. 1, it is preferable that water passing is performed from the feed water side of the second RO apparatus. In the case where a dilute water having good water quality such as the permeated water of the first RO apparatus is used as shown in Figs. 4 to 6, water passing may be performed from the outlet side of the concentrated water of the second RO apparatus. Further, during passing dilute water, the water passing may be performed while producing treated water, with the recovery ratio of the concentrated water of the desalting apparatus being maintained within less than the saturation solubility.

[0061]

Although the RO apparatus is installed in two stages in the embodiment described above, it may be installed in three or more stages. In the case of installation in 3 stages or more, it is preferable that the desalting apparatus for passing dilute water be in the latest stage.

Example

[0062]

[Scale dissolution test]

<Purpose of test>

A calcium carbonate fine particle dispersion and a calcium fluoride fine particle dispersion are prepared. To each of the dispersions, dilute

water is added to measure the dissolution characteristics of the fine particles.

[0063]

<Preparation of calcium carbonate fine particle dispersion>

Into a 500 mL conical beaker, 500 mL of ultrapure water was poured. An aqueous solution containing 340 mg/L of calcium chloride, 10 mg/L of a scale preventing agent, and 1300 mg/L of sodium hydrogen carbonate was prepared. Further, the pH was adjusted to 8.5 with an aqueous solution of sodium hydroxide or an aqueous solution of hydrochloric acid to prepare a starting solution. The starting solution was stirred with a stirrer at conditions of room temperature of 25°C until occurrence of scale, and left standing for a predetermined time. Scale solutions with different particle sizes were prepared by varying the time of standing.

[0064]

<Preparation of calcium fluoride fine particle dispersion>

Into a 500 mL conical beaker, 500 mL of ultrapure water was poured. An aqueous solution containing 100 mg/L of sodium fluoride, 5 mg/L of a scale preventing agent, and 400 mg/L of calcium chloride was adjusted. Further, the pH was adjusted to 5.5 with an aqueous solution of sodium hydroxide or an aqueous solution of hydrochloric acid to prepare a starting solution. The starting solution was stirred with a stirrer at conditions of room temperature of 25°C until occurrence of scale, and left standing for a predetermined time. Scale solutions with different particle sizes were prepared by varying the time of standing.

[0065]

The particle size of the scale generated in each dispersion was measured using a particle size analyzer (SALD-7500 nano, manufactured by Shimadzu).

[0066]

<Mixing with dilute water>

The fine particle dispersion prepared as described above and the dilute water (RO-permeated water, i.e. RO membrane-permeated water of drainage water recovered at Kurita Industrial Development Center (Nogi-cho, Shimotsuga-gun, Tochigi Prefecture)) were mixed at the ratio shown in Table 1 in a 500 mL conical beaker. After a lapse of 5 minutes, the mixed solution was subjected to visual observation and particle size distribution measurement, and the presence or absence of dissolution of fine particles was measured. The results are shown in Table 1.

[0067]

[Table 1]

No	Scale species	Scale particle size (Average size)	Mixing ratio (Scale solution/Dilute water)	Visual observation	Particle size analysis result
1	CaCO ₃	5 μm	10/90	Absence of particles	Absent
2	CaCO ₃	5 μm	20/80	Absence of particles	Absent
3	CaF ₂	0.1 μm	10/90	Absence of particles	Absent
4	CaCO ₃	5 μm	50/50	Presence of particles	Present
5	CaCO ₃	5 μm	60/40	Presence of particles	Present
6	CaCO ₃	20 μm	10/90	Presence of particles	Present
7	CaCO ₃	20 μm	20/80	Presence of particles	Present
8	CaCO ₃	20 μm	50/50	Presence of particles	Present
9	CaCO ₃	20 μm	60/40	Presence of particles	Present
10	CaF ₂	0.1 μm	20/80	Presence of particles	Present
11	CaF ₂	0.1 μm	50/50	Presence of particles	Present
12	CaF ₂	0.1 μm	60/40	Presence of particles	Present

[0068]

<Discussion>

In Nos. 1 and 2 (CaCO₃ scale particle size: 5 μm), scale fine particles were dissolved by adding dilute water. In Nos. 4 and 5 (mixing ratio: 50/50 or 60/40) and Nos. 6 to 9 (CaCO₃ scale particle size: 20 μm), the scale fine particles remained undissolved.

[0069]

In No. 3 (CaF₂ scale particle size: 0.1 μm, mixing ratio: 10/90), the fine particles were dissolved by adding dilute water. In Nos. 10 to 12 (mixing ratio: 20/80 to 60/40), the scale fine particles remained undissolved.

[0070]

[Examples 1 to 6]

Through a flat membrane type RO apparatus 200 in Fig. 2 provided with a rectangular RO membrane having a membrane surface size of 95 mm × 146 mm, the simulated raw water and simulated dilute water (in Example 4, simulated dilute water with addition of scale preventing agent) prepared as described below were passed in the following three steps in order. The RO apparatus 200 has a lower cell 201, an upper cell 202, a mesh spacer 203 between the cells, an RO membrane 204, and a spacer 205 on the permeated water side.

[0071]

<Sequence of water passing>

Step of passing first simulated raw water: The simulated raw water was passed so as to have an initial permeation flux of 0.45 m/D and a water passing flow rate of 0.1 m/s, and an operation was performed at a constant volume of permeated water. (Accordingly, the corrected permeation flux gradually decreased over time.)

Step of passing dilute water: After the corrected permeation flux after water passing for a specified time decreased by 20 to 25% in comparison with the initial corrected permeation flux, dilute water was passed at a water passing flow rate of 0.1 m/s for a time period shown in Table 2.

Step of passing second simulated raw water: Simulated raw water was passed at the same pressure and the same permeated water volume as in the step of passing first simulated raw water.

[0072]

<Simulated raw water>

Calcium chloride dihydrate and sodium hydrogen carbonate were dissolved in pure water to prepare so as to have a Ca concentration of 600 mg/L and an Na concentration of 600 mg/L.

[0073]

M alkalinity: 850 mg/L as CaCO_3

pH: 8.4 to 8.5

Water temperature: 30°C

[0074]

<Simulated dilute water>

The water having Ca and Na concentrations at 1/10 of those in the simulated raw water was used. pH: 7.2 to 7.3, Water temperature is 30°C.

[0075]

<Simulated dilute water with addition of scale preventing agent>

To the simulated dilute water, 2-phosphonobutane-1,2,4-tricarboxylic acid was added at a concentration of 10 mg/L as a scale preventing agent for use.

[0076]

[Comparative Example 1]

The simulated raw water was passed in the same manner as in Example 1, except that the dilute water was not passed.

[0077]

[Results and discussion]

The ratio between the flux F immediately before the end of the step of passing the first simulated raw water and the initial flux F_0 , i.e. F/F_0 , is shown as "Flux ratio before passing dilute water" in Table 2.

[0078]

The ratio between the flux F' immediately after the start of the step of passing the second simulated raw water and the initial flux F_0 , i.e. F'/F_0 , is shown as "Flux ratio after passing dilute water" in Table 2.

[0079]

The value $[\text{Flux ratio after passing dilute water}]/[\text{Flux ratio before passing dilute water}]$ is shown as "Recovery ratio" in Table 2.

[0080]

[Table 2]

	Presence or absence of scale preventing agent in dilute water	Time period of passing dilute water	Water passing flow rate (m/s)	[1] Flux ratio before passing dilute water	[2] Flux ratio after passing dilute water	Recovery ratio ([2]/[1])
Example 1	Absent	45 minutes	0.1	78.6%	100%	1.27
Example 2	Absent	10 minutes	0.1	78.6%	83.2%	1.06
Example 3	Absent	30 minutes	0.1	78.6%	97.1%	1.24
Example 4	Present	30 minutes	0.1	74.5%	95.5%	1.28
Example 5	Absent	5 minutes	0.1	78.6%	81.2%	1.03
Example 6	Absent	3 minutes	0.1	78.6%	79.1%	1.01
Comparative Example 1	Absent	0 minute	0.1	78.6%	78.6%	1

[0081]

As shown in Table 2, the flux was recovered (increased) by performing the step of passing dilute water. In particular, as shown in Examples 1 to 4, by performing the step of passing the dilute water for 10 minutes or more, particularly for 30 minutes or more, the flux was sufficiently recovered. Further, as shown in Example 4, by adding a

scale preventing agent to the dilute water, the flux was more sufficiently recovered.

[0082]

[Example 7]

<Simulated raw water>

Calcium chloride dihydrate, magnesium chloride, aluminum chloride and sodium fluoride were dissolved in pure water for use as simulated raw water so as to have concentrations of Ca, Mg, Al and F as shown below.

[0083]

Ca: 0.5 mg/L

Mg: 4 mg/L

Al: 0.25 mg/L

F: 4000 mg/L

(Water temperature: 22 to 23°C, pH: 5.5)

[0084]

<Dilute water>

As the dilute water, the permeated water of the raw water passed through the RO apparatus in Fig. 2 was used.

[0085]

<Sequence of passing water>

The sequence of passing water was as follows. The time period of water passing in each step was set as shown in Fig. 4.

Step of passing first simulated raw water: The simulated raw water was passed at a constant volume of permeated water (0.45 m/D).

Step of passing dilute water: The dilute water was passed for 45 minutes.

Step of passing second simulated raw water: The simulated raw water was passed at the same feed water pressure as in the step of passing first simulated raw water.

[0086]

<Results and discussion>

The results are shown in Table 3 and Fig. 3 (a). As shown in Table 3 and Fig. 3 (a), the flux was sufficiently recovered according to Example 7.

[0087]

[Table 3]

	Dilute water species	[1] Flux ratio before passing dilute water	[2] Flux ratio after passing dilute water	Recovery ratio ([2]/[1])
Example 7	RO-permeated water	85.5%	97.2%	1.14
Comparative Example 2	Simulated dilute water (Ca: 0.1 mg/L, Mg: 0.8 mg·L, Al: 0.8 mg/L, F: 500 mg/L)	88%	85%	0.97

[0088]

[Comparative Example 2]

The preparation was performed in the same manner as in the preparation method of the simulated raw water in Example 7, such that the simulated raw water and the dilute water have each of the concentration of Ca, Mg, Al and F as shown below.

[0089]

The sequence of water passing was the same as in Example 7. The time period of water passing was as shown in Fig. 3 (b).

[0090]

<Simulated raw water>

Ca: 0.4 mg/L

Mg: 2 mg/L

Al: 0.25 mg/L

F: 4000 mg/L

(Water temperature: 22 to 23°C, pH: 5.5)

[0091]

<Simulated dilute water>

Ca: 0.1 mg/L

Mg: 0.8 mg/L

Al: 0.8 mg/L

F: 500 mg/L

[0092]

<Results and discussion>

The results are shown in Table 3 and Fig. 3 (b). As shown in Table 3 and Fig. 3 (b), in Comparative Example 2, the flux was not recovered even by passing the dilute water due to the high concentration of salts in the dilute water.

[0093]

[Examples 8 to 10, and Comparative Examples 3 to 6]

To the flat membrane type RO apparatus in Fig. 2, a simulated raw water and a simulated dilute water (in Examples 9 and 10 and Comparative Examples 3 to 6, simulated dilute water with addition of a scale preventing agent) prepared as described below were passed in a sequence of the following three steps.

[0094]

<Sequence of passing water>

Step of passing first simulated raw water: The first simulated raw water was passed so as to have an initial permeation flux of 0.45 m/D and a passing water flow rate of 0.1 m/s, and an operation was performed at a constant volume of permeated water. (Accordingly, the corrected permeation flux gradually decreased over time.)

Step of passing dilute water: After the corrected permeation flux after water passing for a specified time decreased by 20 to 25% in comparison with the initial corrected permeation flux, the dilute water was passed at a water passing flow rate of 0.1 m/s for a time period shown in Table 2.

Step of passing second simulated raw water: The simulated raw water was passed at the same pressure and the volume of the permeated water as in the step of passing the first simulated raw water.

[0095]

<Simulated feed water>

Calcium chloride dihydrate and sodium fluoride were dissolved in pure water to prepare so as to have a Ca concentration of 650 mg/L and an F concentration of 70 mg/L.

pH: 5.5

Water temperature: 22 to 23°C

[0096]

<Simulated dilute water>

In Example 8, as the simulated dilute water, an RO-treated water of the RO facility in drainage water treatment facility of Kurita Industrial Development Center was used. (pH: 5.5)

[0097]

<Simulated dilute water with addition of scale preventing agent>

In Example 9, the simulated dilute water in Example 8 with addition of 2-phosphonobutane-1,2,4-tricarboxylic acid at a concentration of 10 mg/L was used.

In Example 10, the simulated dilute water in Example 9 with further addition of calcium chloride dihydrate and sodium fluoride so as to have the concentrations shown in Table 3 was used.

In Comparative Example 3, the simulated dilute water in Example 9 with further addition of calcium chloride dihydrate and sodium fluoride so as to have the concentrations shown in Table 3 was used.

In Comparative Example 4, the simulated dilute water in Comparative Example 3 with pH adjustment to 3.5 by hydrochloric acid was used.

In Comparative Examples 5 and 6, the simulated dilute water in Comparative Example 9 with further addition of calcium chloride dihydrate and sodium fluoride so as to have the concentrations shown in Table 3 and with pH adjustment to 3 by hydrochloric acid was used.

[0098]

[Results and discussion]

The ratio between the flux F immediately before the end of the step of passing the first simulated raw water and the initial flux F_0 , i.e. F/F_0 , is shown as "Flux ratio before passing dilute water" in Table 4.

[0099]

The ratio between the flux F' immediately after the start of the step of passing the second simulated raw water and the initial flux F_0 , i.e. F'/F_0 , is shown as "Flux ratio after passing dilute water" in Table 4.

[0100]

The value [Flux ratio after passing dilute water]/[Flux ratio before passing dilute water] is shown in Table 4 as "Recovery ratio".

[0101]

[Table 4]

	Water quality of dilute water				[1] Flux ratio before passing dilute water	[2] Flux ratio after passing dilute water	Recovery ratio ([2]/[1])
	Ca	F	pH	Scale preventing agent			
	mg/L	mg/L	-	mg/L			
Example 8	<0.1	<0.1	5.5	0	94.8%	99.8%	1.05
Example 9	<0.1	<0.1	5.5	10	95.2%	99.8%	1.05
Example 10	3.2	0.8	5.5	10	95.6%	98.8%	1.03
Comparative Example 3	32	8	5.5	10	94.3%	94.5%	1.00
Comparative Example 4	32	8	3.5	10	96.0%	95.3%	0.99
Comparative Example 5	64	40	3	10	95.8%	95.5%	1.00
Comparative Example 6	32	20	3	10	93.4%	93.8%	1.00

[0102]

As shown in Table 4, the flux is recovered (increased) by performing the step of passing dilute water. In particular, as shown in Examples 8 and 9, by lowering the concentration of salts in the dilute water, the flux is sufficiently recovered.

[0103]

Although the present invention has been described in detail with reference to specific embodiments, it will be apparent to those skilled in the art that various modifications can be made without departing from the intent and scope of the present invention.

The present application is based on JP 2020-151433 filed on September 9, 2020, and JP 2021-005064 filed on January 15, 2021, which are incorporated by reference in their entirety.

Reference Signs List

[0104]

1: Raw water tank

4 and 4A to 4D: First RO apparatus

10: Relay tank

15 and 51 to 54: Second RO apparatus

CLAIMS

[Claim 1]

A method for operating a desalting apparatus having a first desalting apparatus and a second desalting apparatus, the method comprising:

a normal operation step of supplying water to be treated to the first desalting apparatus to separate a first concentrated water and a first desalted water, and supplying the first concentrated water to the second desalting apparatus to separate a second concentrated water and a second desalted water; and

a recovery operation step of supplying water to be treated to the first desalting apparatus to separate a first concentrated water and a first permeated water, and passing a dilute water having a lower concentration than the first concentrated water through the second desalting apparatus to recover the desalting performance of the second desalting apparatus.

[Claim 2]

The method for operating a desalting apparatus according to claim 1, wherein a plurality of the second desalting apparatuses are installed in parallel, and while the normal operation step is performed in some of the second desalting apparatuses, the recovery operation step is performed in other second desalting apparatuses.

[Claim 3]

The method for operating a desalting apparatus according to claim 1 or 2, wherein, in the recovery operation step, dilute water is passed through the second desalting apparatus for 5 to 60 minutes.

[Claim 4]

The method for operating a desalting apparatus according to any one of claims 1 to 3, wherein the water to be treated is used as the dilute water.

[Claim 5]

The method for operating a desalting apparatus according to any one of claims 1 to 3, wherein the desalted water of the first desalting apparatus is used as the dilute water.

[Claim 6]

The method for operating a desalting apparatus according to any one of claims 1 to 5, wherein a scale preventing agent is added to the dilute water.

[Claim 7]

The method for operating a desalting apparatus according to any one of claims 1 to 6, wherein the desalting apparatus is a reverse osmosis membrane apparatus.

[Claim 8]

The method for operating a desalting apparatus according to claim 7, wherein a rate of water passing of the dilute water is 0.001 to 0.1 m/s.

[Claim 9]

The method for operating a desalting apparatus according to any one of claims 1 to 8, wherein the water quality of the first concentrated water is any of the following a to e:

a. a calcium ion concentration of 0.1 to 10 mg/L, and a fluoride ion concentration of 3000 to 8000 mg-F/L;

b. a calcium ion concentration of 500 to 1500 mg/L, and a fluoride ion concentration of 50 to 150 mg-F/L;

c. a calcium ion concentration of 400 to 1500 mg/L, and an M alkalinity of 800 to 2000 mg/L.

[Claim 10]

The method for operating a desalting apparatus according to any one of claims 1 to 9, wherein the first concentrated water is a concentrated water obtained by concentrating the feed water of the first desalting apparatus at a concentration ratio of 3 or more.