Rejuvenation Chemical Agent for Degraded RO Membrane

RYO KAMITO[*1] **YOSHIAKI ITO**[*2]

KOKI OKUBO[*3] **SHO YOKOGAWA**[*4]

TAKAYOSHI HORI[*5]

Seawater desalination plants, one of the solutions to the global shortage of fresh water, are now mainly using a reverse osmosis (RO) membrane method, which has energy saving potential, instead of the conventional evaporation method. The desalination performance of RO membranes degrades over time, and eventually they no longer satisfy the required desalination performance. In such cases, the degraded RO membranes are replaced with virgin ones and disposed of in landfills. Therefore, reduction of the membrane replacement costs and the environmental impact have become issues. To address these issues, Mitsubishi Heavy Industries, Ltd. (MHI) has developed a chemical agent (desalination performance rejuvenation agent) that selectively repairs degraded areas of cellulose acetate RO membranes and rejuvenates the desalination performance, thereby reducing the frequency of membrane replacement (prolonging the membrane life). This report introduces the characteristics and effects of the chemical agent for rejuvenating desalination performance of cellulose acetate RO membranes.

1. Introduction

Today, a pressing global concern is the shortage of freshwater. Desalination technology, especially desalination from seawater as a virtually unlimited resource, is attracting attention as a solution to this problem. In recent years, desalination technology has been shifting from the conventional evaporation method, which was the mainstream method, to the membrane method, which consumes less energy. Of the current total desalination capacity of 115 Mm^3/d, 88 Mm^3/d uses reverse osmosis (RO) membranes[(1)]. We also have delivered a large seawater desalination plant that employs the membrane method.

RO seawater desalination plants require appropriate design of the RO membrane feed water treatment (sand filtration, membrane filtration, etc.) and the operation method because the operating rate and operating costs are affected if the water permeability decreases and the differential pressure increases due to fouling and scaling of the RO membrane, or if the desalination performance decreases due to membrane degradation. If fouling or scaling occurs, cleaning the membrane with acid or alkali is effective. However, membrane degradation (membrane structure defects) is irreversible, so there is no alternative but to replace the membrane, which increases the replacement cost and environmental impact due to disposal. Therefore, a new maintenance method that can address this issue is strongly needed.

One of the most promising methods is to rejuvenate desalination performance by using a chemical agent. This method rejuvenates desalination performance by selectively coating the degraded areas of the membrane with a desalination performance rejuvenation agent to inhibit salt

*1 Chemical Research Department, Research & Innovation Center, Mitsubishi Heavy Industries, Ltd.
*2 Research Manager, Chemical Research Department, Research & Innovation Center, Mitsubishi Heavy Industries, Ltd.
*3 Service Engineering Department, Research & Innovation Center, Mitsubishi Heavy Industries, Ltd.
*4 Nagasaki Solution Business Department, Steam Power Maintenance Innovation Business Division, Energy Transition & Power Headquarters, Energy Systems, Mitsubishi Heavy Industries, Ltd.
*5 Engineering Manager, Nagasaki Plant Engineering Department, Steam Power Maintenance Innovation Business Division, Energy Transition & Power Headquarters, Energy Systems, Mitsubishi Heavy Industries, Ltd.

permeation through the membrane, thereby reducing the frequency of membrane replacement (extending the membrane life), which is expected to reduce membrane replacement costs and environmental impact. There are two types of commercially available RO membranes: polyamide and cellulose acetate, and for the former, which has a large market share, the use of desalination performance rejuvenation agents has already been reported[(2)-(5)]. On the other hand, there has been no commercial application of desalination performance rejuvenation agents for cellulose acetate RO membranes, which are widely used in plants we have delivered. Therefore, we have independently developed and commercialized a chemical agent to rejuvenate desalination performance for RO membranes made of cellulose acetate. This report describes the features and effects of this chemical agent.

2. Development policy of desalination performance rejuvenation agent

There are two degradation mechanisms of cellulose acetate RO membranes: hydrolysis and oxidative degradation, as shown in **Figure 1**[(6)]. Hydrolysis degradation is a phenomenon in which an acetyl group (-$COCH_3$) in cellulose acetate is replaced by a hydroxy group (-OH), and oxidative degradation is a phenomenon in which the cellulose acetate main chains are broken by an oxidant such as chlorine injected as a preventive measure against biofouling. Site defects resulting from these phenomena become salt permeation pathways, causing a reduction in desalination performance.

As shown in **Figure 2**, the concept of the desalination performance rejuvenation method we have invented is that the desalination performance rejuvenation agent selectively coats defects caused by hydrolysis or oxidative degradation and inhibits salt permeation through the membrane. The desalination performance rejuvenation agent is required to have a high affinity for the defective (degraded) part of the cellulose acetate RO membrane. We selected a promising agent from a large number of candidate agents, and verified its effectiveness in rejuvenating desalination performance through laboratory-scale and pilot-scale tests.

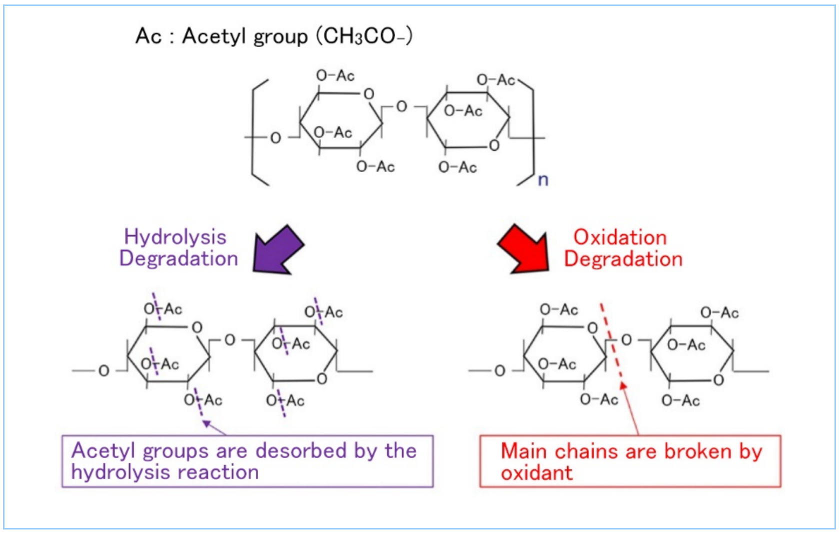

Figure 1 Degradation mechanism of cellulose acetate RO membrane

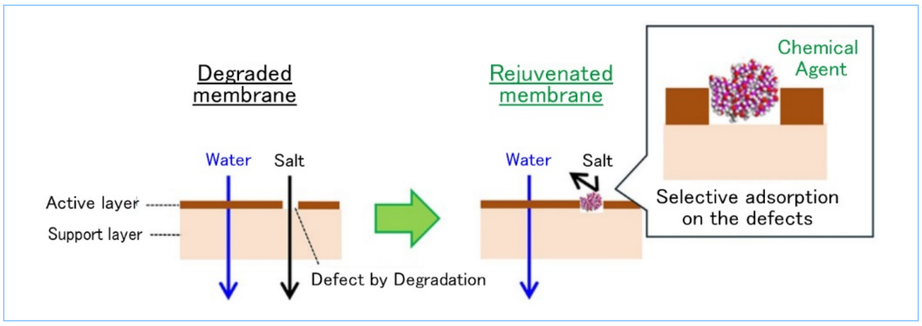

Figure 2 Rejuvenation mechanism of desalination performance rejuvenation agent

3. Effects of desalination performance rejuvenation agent

3.1 Laboratory-scale test

Laboratory-scale tests were conducted using the procedure shown in **Figure 3**. Degraded RO membranes were prepared by forcing virgin cellulose acetate RO membranes (flat membrane, effective membrane area 140 cm^2) to undergo hydrolysis or oxidative degradation using chemicals. The degraded RO membranes were rejuvenated using the selected agent, and by comparing the separation performance before and after the degradation and rejuvenation (NaCl: 35,000 mg/L, feed flow rate: 3 L/min, feed pressure: 3 MPa, water temperature: 30°C, evaluation time: 2 hours), the effect of the chemical agent as a desalination performance rejuvenation agent was verified. As a result, as shown in **Figure 4**, it was confirmed that the degraded desalination performance (salt rejection) of both hydrolysis and oxidative degraded membranes was increased (rejuvenated) by the rejuvenation. This indicates that the chemical agent is effective in rejuvenating desalination performance regardless of the degradation mechanism and is a promising desalination performance rejuvenation agent.

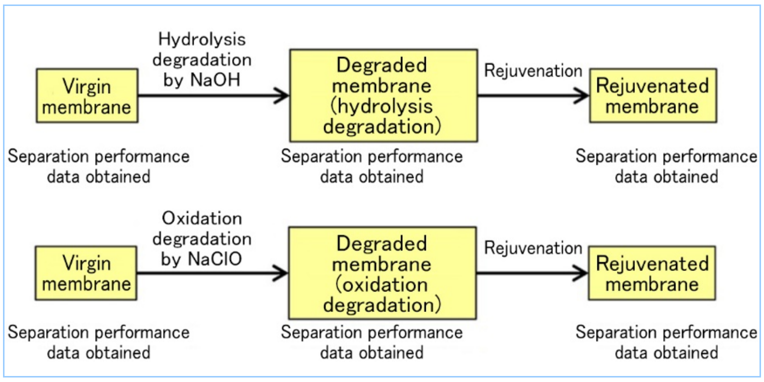

Figure 3 Laboratory-scale test procedure

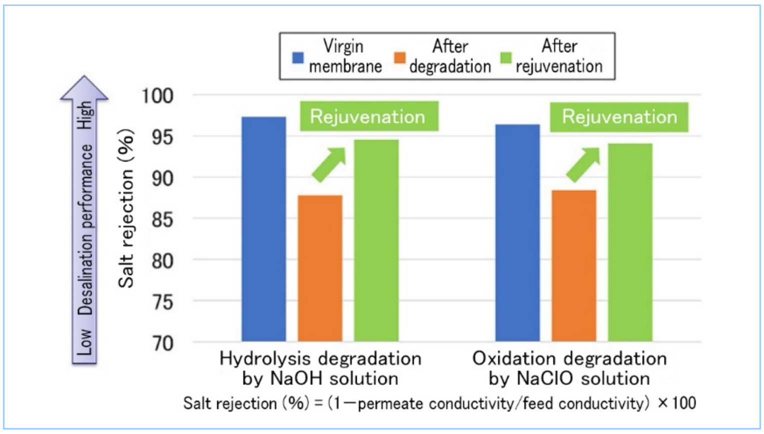

Figure 4 Laboratory-scale test result

3.2 Pilot-scale test

Pilot-scale tests were conducted using the procedure shown in **Figure 5**. In this test, membranes were used from an RO module used in a seawater desalination plant in commercial operation in Saudi Arabia. The membranes have a permeate salt concentration more than 10 times higher than that of virgin membranes. These used membranes were rejuvenated under the conditions verified in the laboratory-scale test, and the separation performance data before and after the rejuvenation (NaCl: 35,000 mg/L, recovery rate: 30%, feed pressure: 5.4 MPa, water temperature: 25°C, evaluation time: 2 hours) was obtained. Based on the changes in the A value (water permeability), B value (solute permeability), and the permeate conductivity, the effectiveness of the developed method for rejuvenating desalination performance was verified. The A and B values are defined by the following basic equations of the dissolution-diffusion theory.

$A = Jw / (\Delta P - \Delta \pi)$

where Jw is the water permeate flux (mass flux $kg/(m^2 \cdot s)$ or volumetric flux $m^3/(m^2 \cdot s)$), ΔP is the pressure difference between feed water and permeate water (kgf/cm^2), and $\Delta\pi$ is the osmotic pressure difference between feed water (membrane surface) and permeate water (kgf/cm^2).

$$B = Js / (C_M - C_P)$$

where Js is the salt permeate flux ($kg/(m^2 \cdot s)$), C_M is the salt concentration at the membrane surface (kg/m^3), and C_P is the salt concentration in the permeate (kg/m^3).

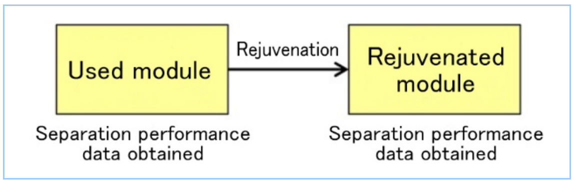

Figure 5 Pilot-scale test procedure

Figure 6 to **Figure 8** show the A value, B value, and permeate conductivity before and after the rejuvenation resulting from the test. It is indicated that the chemical agent was able to reduce the B value and salt concentration of permeate water without decreasing the A value. This result confirms that the chemical agent works effectively for actual used RO modules.

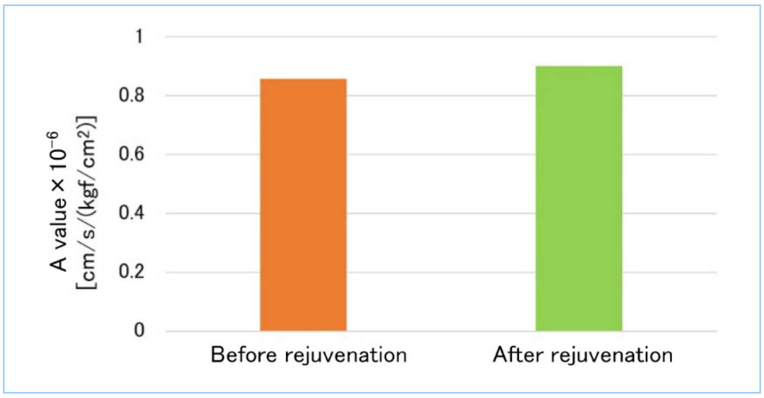

Figure 6 Pilot-scale test result (A value)

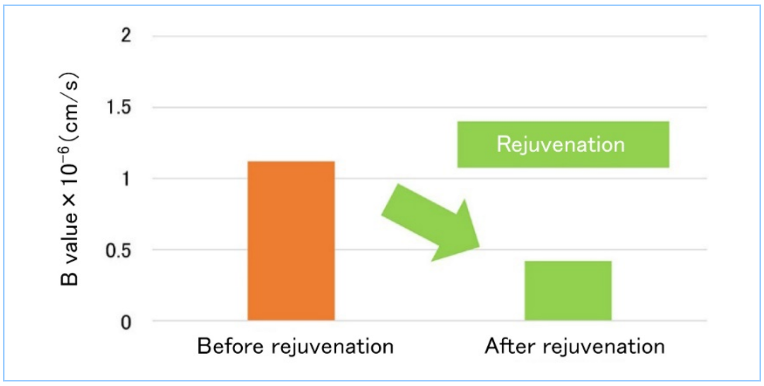

Figure 7 Pilot-scale test result (B value)

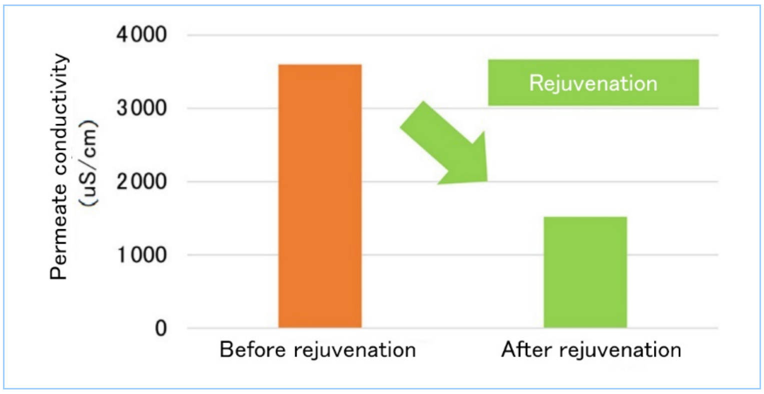

Figure 8 Pilot-scale test result (permeate conductivity)

Next, **Figure 9** shows the result of approximately 1,000 hours of operation to confirm the long-term stability of the desalination performance rejuvenation agent. As a result, it was confirmed that the rejuvenation reduced the permeate conductivity from 3,600 µS/cm to about 1,200 µS/cm, and that this condition could be maintained for 1,000 hours. This confirms that the chemical agent is effective in rejuvenating desalination performance and its long-term stability, and that it is highly applicable to actual equipment.

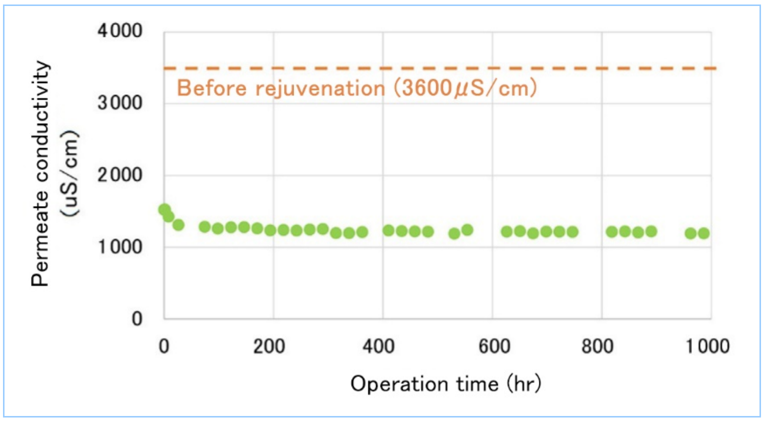

Figure 9 Long-term stability test result of desalination performance rejuvenation effect

4. Conclusion

This report reported on the discovery of an appropriate desalination performance rejuvenation agent and its application conditions for degraded RO membranes made of cellulose acetate, and the prospect of applying the chemical agent to actual equipment. This achievement was also reported at the IDA* 2022 World Congress. In September 2022, we received the first order for this chemical agent for a large seawater desalination plant in Saudi Arabia and began its commercial application. We will work to improve the desalination performance rejuvenation agent and expand its application. We have already obtained a patent for this chemical agent.

* International Desalination Association

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