QUANTITATIVE ANALYSIS OF REVERSE OSMOSIS MEMBRANES FOR EFFICIENT DESALINATION

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I. INTRODUCTION

Reverse osmosis (RO) membrane has been used in water treatment plants worldwide as a countermeasure to recent water resource depletion. With the proliferation of RO technology, the applications and processes of RO technology have become more diverse and complex, resulting in an increase in cases where a stable plant operation is more difficult than before.

Stable operations of water treatment plants can be achieved by maintaining not only equipment including pumps, valves, and pipes, but also RO membranes by maintaining pretreatment facilities, optimizing operating conditions, and performing regular cleaning.

However, the performance of RO membrane may degrade due to many different factors such as fluctuations in operating conditions and inadequate management of pretreatment facilities. To keep the excellent performance of RO membrane, it is crucial to take appropriate measures according to the major cause of degradation. The main cause of degradation is sometimes identified by inspection and evaluation of the RO membrane taken from a plant. Although many narrowing-down methods are used for inspection of the returned RO membrane, it is difficult to identify the main cause due to the multiple suspicious factors involved in performance deterioration.

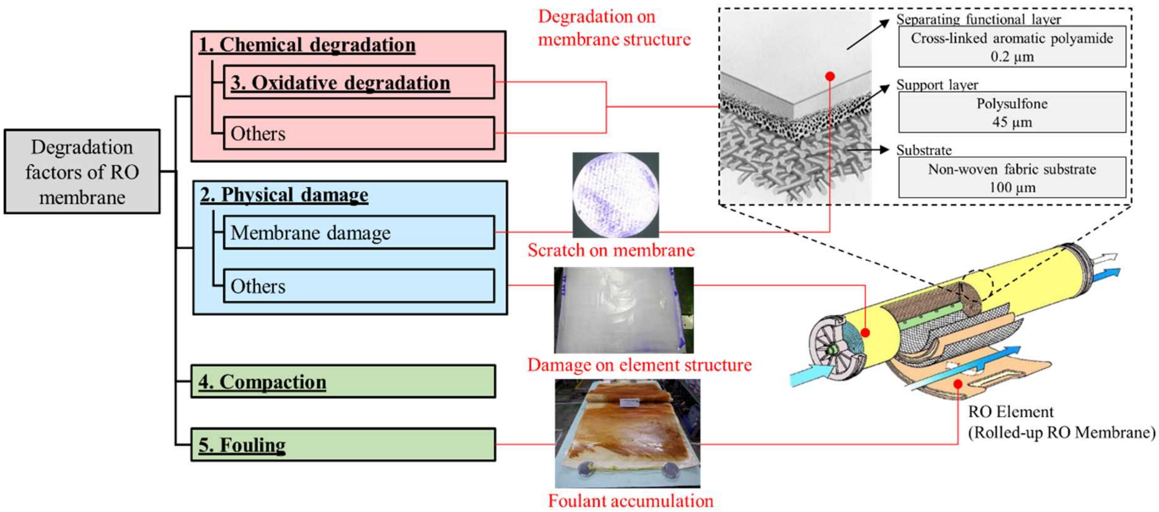

Figure 1: Five Major Degradation Factors of RO Membrane

II. QUANTITATIVE ANALYSIS METHODS

In this study, we classified the degradation factors that occur in RO membranes into five major categories shown in Figure 1 and quantified the effect of each on performance deterioration to identify the main cause. The following are the five categories and how their contribution is calculated:

1. “Chemical degradation”, which occurs when the chemical structure of a membrane surface is degraded by chemicals, is quantified by analyzing the removal performance ratio of monovalent ions and divalent ions, since each degradation factor, Chemical degradation and Physical damage, has a different contribution ratio to the removal performance of monovalent ions and divalent ions [1]. (Figure 2)
2. “Physical damage”, which occurs when a membrane surface is scratched with solid or the structure of a rolled RO membrane is broken, is also quantified by the method explained in the Category 1.

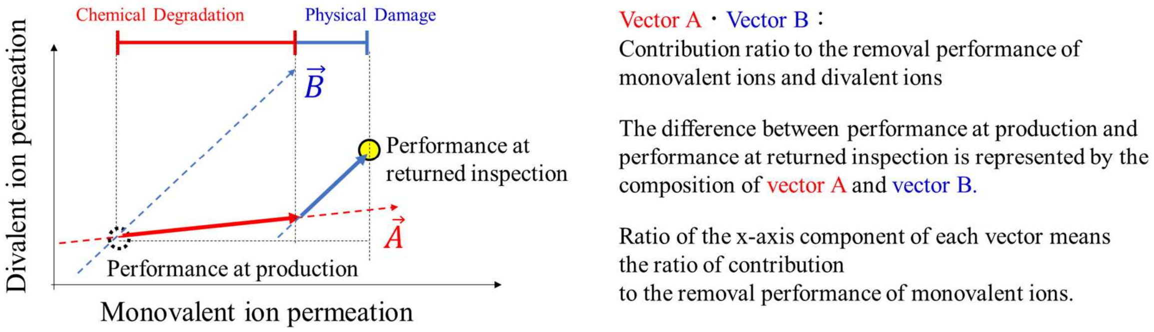

Figure 2: Quantifying Method of Chemical Degradation Dividing

3. “Compaction”, which is caused by the high temperature and high pressure conditions during plant operation, is quantified by the empirical formula based on the accumulation of plant operation data. The degradation curve of compaction is determined by operation conditions, and the effect of compaction on the flow rate is quantified by substituting the operation period into the curve equation.

4. “Fouling”, which occurs when foulant accumulates on a membrane surface, is quantified by comparing the performance difference between before and after cleaning a returned RO membrane with several chemicals. The result of the cleaning condition that the performance of water production is most restored by the cleaning is considered as the effect level of fouling.

5. “Oxidative degradation”, which is included in “Chemical degradation” and occurs when an oxidant reacts with a membrane, is quantified by analyzing the chemical structure of a returned RO membrane surface. By especially focusing on the halogenation of RO membrane chemical structure, it is revealed that there is a correlation between structural parameters and membrane performance. After cleaning the surface of the membrane, X-ray photoelectron spectroscopy (ESCA) and fourier transform infrared spectroscopy (FT-IR) are available to analyze the elemental ratio in the separated functional layer.
From the ESCA analysis results, the ratio between the presence ratio of carbon to the presence ratio of halogens which is the sum of chlorine, bromine, and iodine is calculated as the halogenation ratio. By substituting this value into the empirical formula that represents the relationship between the

halogenation ratio and the performance of the oxidatively degraded membrane, the performance impact due to oxidative degradation is quantified.

III. INSPECTION RESULTS OF RETURNED RO MEMBRANE

The superiority of quantitative analysis over conventional methods were demonstrated by application in some actual cases. The comparison summary of the inspection results based on conventional methods and quantitative methods for the representative eight cases is shown in Table 1.
By using the quantitative methods, it has become possible to compare different degradation factors on the same scale and to identify the main factors. In addition, it is enabled to exclude the unrelated factors and detect the factors that the conventional methods cannot detect.
For example, in Plant B, fouling was identified as the main degradation factor by comparing to other factors using the quantitative method.
Physical damage from scratches on the membrane surface was mentioned as one of the factors by the conventional method, but the quantitative method indicated that it was not a degradation factor.
Also, oxidative degradation was mentioned as a factor by the conventional method, but in reality, the contribution of oxidative degradation was small, and the impact of other chemical degradation was detected.

Table 1: Comparison Summary of the Inspection Results

Plant operation information			Result					
Plant name	Feed water type	Operation period [year]		Physical damage	Chemical degradation	Compaction	Fouling	Oxidative degradation
A	Seawater	2.5	Conventional method				✓	✓
			Quantitative method		✓✓	✓	✓	
B	Industrial wastewater	0.33	Conventional method	✓			✓	✓
			Quantitative method		✓		✓✓	
C	Industrial wastewater	0.5	Conventional method				✓	✓
			Quantitative method	✓	✓		✓✓	
D	Brackish water	1.1	Conventional method				✓	
			Quantitative method				✓✓	✓
E	Seawater	3	Conventional method	✓				✓
			Quantitative method	✓	✓✓			
F	Brackish water	0.17	Conventional method	✓			✓	✓
			Quantitative method	✓	✓✓		✓✓	
G	Brackish water	0.17	Conventional method	✓	✓		✓	
			Quantitative method	✓	✓✓		✓✓	
H	Seawater	2.5	Conventional method				✓	✓
			Quantitative method		✓✓	✓	✓	

✓✓: Main Degradation factor

✓: Degradation factor

The following figure shows the details of the results for Plant E and Plant H.
RO membrane inspection was conducted on Plant E, where a deterioration in water quality occurred. According to conventional methods, physical damage was suspected because scratches were observed on the membrane surface, and oxidative degradation was suspected because the halogenation of the membrane was detected by ESCA analysis. (Figure 3)
On the other hand, the results of the quantitative analysis revealed that the chemical degradation other than oxidative degradation was the main cause of deterioration in water quality, and that the effects of oxidative degradation and physical damage were relatively minor. (Figure 3)

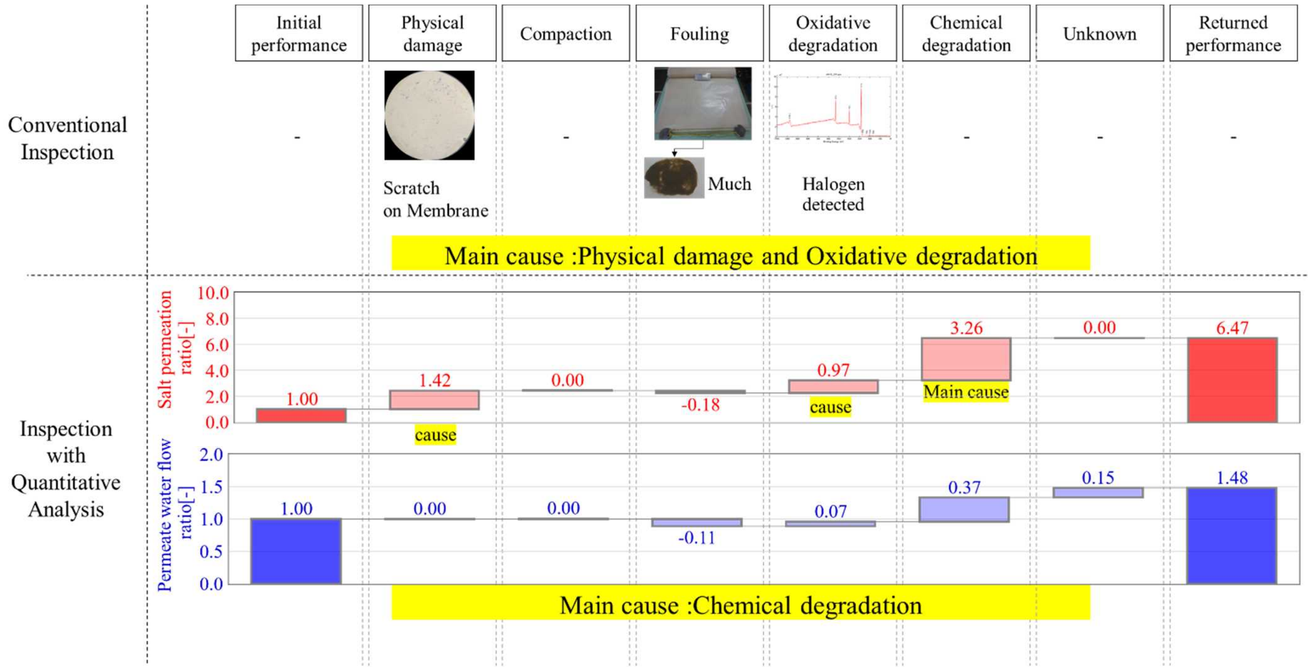

Figure 3: Comparison of Plant E RO Membrane Inspection Results Conventional Method (Upper) and Quantitative Method (Lower)

RO membrane inspection was also conducted on Plant H, where not only a decrease in water production but also deterioration in water quality occurred. According to conventional methods, fouling was suspected as the cause of the decrease in water production because foulant was observed on the membrane surface, and oxidative degradation was suspected as the cause of the deterioration in water quality because the halogenation of membrane was detected by ESCA analysis. (Figure 4)
On the other hand, the results of the quantitative analysis revealed that the compaction was more significant cause of the decrease in water production than fouling, and that chemical degradation was the main cause of deterioration in water quality. Although halogenation of the membrane surface was detected, it was a trace amount that did not cause deterioration in water quality. (Figure 4)

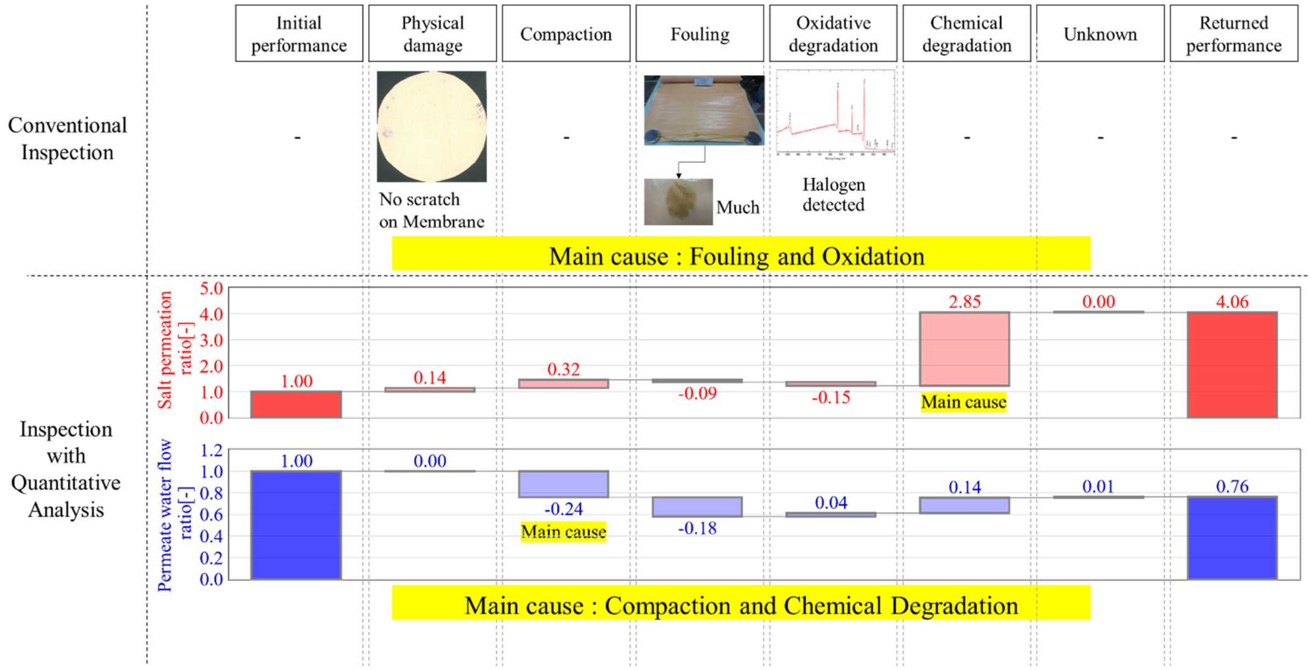

Figure 4: Comparison of Plant H RO Membrane Inspection Results Conventional Method (Upper) and Quantitative Method (Lower)

The determination process of the degradation main factor in Plant H, which led to the analysis mentioned above, is explained below.

Table 2 shows the performance of the returned element for autopsy. The removal of NaCl and the flow rate decreased, while the removal of $MgSO_4$ did not change significantly.

Table 2: Element Performance

Element performance

	At Production	At Returned	Evaluation condition
NaCl Rej. [%]	99.85	99.40	*1
$MgSO_4$ Rej. [%]	99.95	99.85	*2
Flow rate [m^3/d]	36.03	27.50	*1

*1：NaCl 32000 mg/L
Feed Pressure: 5.5 MPa
Recovery rate: 8%
Feed pH: 7
Feed Temp.: 25 deg.C.

*2：NaCl 32000 mg/L MgSO4 2000 mg/L
Feed Pressure: 5.5 MPa
Brine Flow rate: 80 L/min
Feed pH: 7
Feed Temp.: 25 deg.C.

Chemical degradation and physical damage are quantified based on the element performance shown in Table 2. In this case, the removal performances of NaCl and $MgSO_4$ were utilized to quantify the removal performances of monovalent and divalent ions. Contribution ratio of chemical degradation was 95%, which meant that chemical degradation was estimated to be the main factor of degradation (Figure 5).

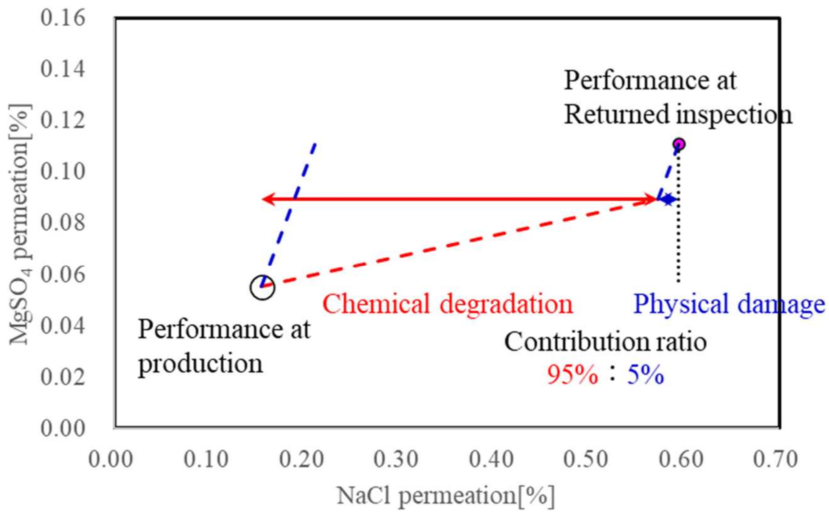

Figure 5: Quantification Example of Chemical Degradation Dividing

Compaction was quantified based on the plant operation data shown in Table 3. In this case, the effect on Flowrate was 0.76.

Table 3: Quantification Example of Compaction

Operation Period	[year]	2.5
Maximum Feed Pressure	[bar]	70.0
Maximum Temperature	[deg.C.]	37.4
Minimum Temperature	[deg.C.]	18.4
Compaction effect on Flowrate	[-]	0.76

The effect level of fouling was quantified based on the results of membrane evaluation. In this case, the returned membranes were divided into two groups.
The membranes of Group 1 were evaluated without any cleaning, while each of the membrane of Group 2 were evaluated after chemically cleaning under six different conditions shown in Figure 6. The performances of the membranes of Group 1 and Group 2 were compared. In this case, the effect of fouling on the flux was 0.88, considered on the results of the cleaning with oxalic acid.

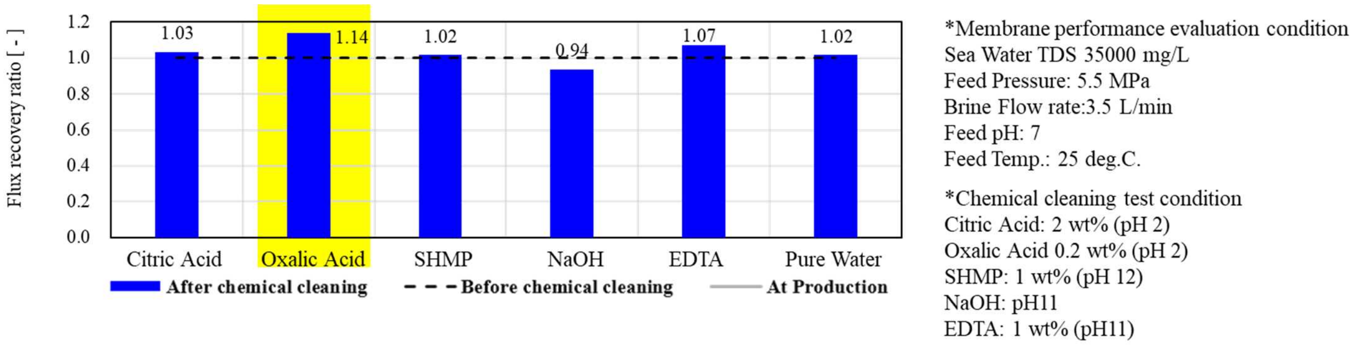

Figure 6: Quantification Example of Fouling

The effect level of oxidative degradation was quantified based on the halogenation ratio of the returned membrane determined by ESCA analysis after cleaning the surface of the membrane. In this case, the effect on the salt permeation was 0.88, which meant that oxidative degradation was not occurred.

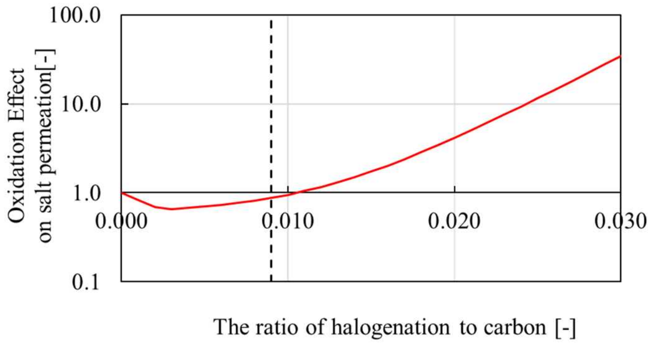

Figure 7: Quantification Example of Oxidation

IV. CONCLUSIONS

As shown in the above results, the proper inspection and analysis of the RO membrane taken from the plant enables not only to estimate the cause of performance deterioration, but also to identify the main cause of degradation by evaluating and comparing the degree of deterioration depending on each degradation factor.
This technology has been in operation for returned RO membrane inspections undertaken by Toray and is contributing to stable plant operations worldwide. There is also a plan to expand inspection bases in the future.

V. REFERENCES

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