

the two-stage RO.

- 3) Author: S.Lee, Y.Aurette, H.Roques
Title: Concentration polarization, membrane fouling and cleaning ultrafiltration of soluble oil, *J.Membr. Sci.*, 19(1), p23-38, 1984.
Abstract: When soluble oil is treated by UF, the gel polarization of about 40% oil content is made. Membrane fouling is mainly the adsorption of oil on membrane surfaces. Cleaning by 1.9% NaDS and 3.7% n-pentanol is effective.
- 4) Author: H.Paul
Title: Two phase ultrafiltration as an economical unit operation for recycling of detergents, *Desalination*, Vol.47, p293-304, 1983.
Abstract: The combination of MF and UF is effective. MF could not decrease the concentration of oil in permeate down to 20 ppm(That in feed water was 7000 to 8000ppm).
- 5) Author: S.I.Graham, R.L.Reitz, C.Hickman
Title: Improving reverse osmosis performance through periodic cleaning, *Desalination*, Vol.74, p113-124, 1989.
Abstract: Substantial maintenance work for the fouling in RO plants is periodic cleaning. In general, high pH values are effective in removing colloidal silica. In case of hollow fiber type equipment the timing of cleaning is generally determined by the pressure drop in the module. FLOCREAN is an effective cleaning chemical.
- 6) Author: S.Takadono, H.Iwahori, Yabushita, Y.Imamura
Title: Treatment of highly fouling waste waters with tubular membrane systems, *Desalination*, Vol.49, p347-355, 1984.
Abstract: The tubular-type RO and UF can maintain membrane performance even for highly fouled feed water by installing automatic sponge ball cleaning equipment.

(c) DIALOG

Key word: Reverse osmosis, Oil, Fouling, Seawater, Cleaning

Number of retrieval operations = 108

Number of acquired original reports = 4

The author, title of paper and abstracts of acquired original 10 reports was shown as following:

- 1) Author: R.Brandt, M.Hoodlebrink
 Title: Apparatus for processing coolant, *US4895649*, 23, Jan., 1990
 Abstract: Removal of oil and particles by installing RO or UF on the cooling equipment attached to a metal processing machine.

- 2) Author: W.Ligh, J.Perlman, A.Riedinger, D.Needham
 Title: Desalination of non-chlorinated surface seawater using TFC[®], *Desalination*, Vol.70, p47-64, 1988
 Abstract: TFC membranes of the Fluid Systems can prevent bacteria on the membranes from propagating by adding copper sulfate to surface seawater. This method is more economical than the chlorine-dechlorine method. Though the membrane that had been used for one year was cultured, the propagation of bacteria could not be seen.

- 3) Author: L.Applegate, C.Erkenbrecher
 Title: Monitoring and control of biological activity in Permasep seawater RO plant *Desalination*, Vol.65, p331-359, 1987.
 Abstract: Minor: Analysis at the time of starting the plant operation and then every 3 months by AODC and INT methods. Cleaning of the pretreatment system is made by the treatment with chlorine of 100 to 1000ppm for 12 to 24 hours with pH values of 6 to 7. For RO, the treatment with 1% HCOH for 24 hours and with 0.5% detergent which is approved by DUPONT with pH values of 10 to 11 is effective. Water without chlorine and with TDS 5000ppm or less is used to clean membranes. Piping should be shielded from sunlight.

- 4) Author: S.Ebrahim, A.Malik
 Title: Pretreatment of surface seawater feed at DROP, *Desalination*, Vol.63, p95-107, 1987.
 Abstract: Three kinds of membranes have been tested and pretreatment corresponding to each membrane has been done(SDI<4). Appropriate pretreatment can reduce the frequency of cleaning. The DUPONT membrane does not need SHMP(recommendation by manufacture), if its recovery ratio is 40% or less. For other membranes, SHMP is charged.

3.1.2 Summary of Results of Literature Survey

Though we investigated information submitted by membrane manufacturers and literatures acquired by using the online retrieval system, we could hardly find information on the

effect of oil and the removal of oil from the RO membrane. As a result, the effect of oil and the removal of oil from the RO membrane are the subject that we must investigate future experiments.

Though we also planned to sort and arrange the effects on the membrane performance by type, we could not accomplish this plan due to the lack of information.

This matter is also a subject that we have to investigate in future experiments.

We also sorted and arranged the results of literature retrieval on general fouling. However, in this case also, the number of membrane types employed was small and there is not enough examples to sort and arrange the fouling of membranes by type.

Though we used three kinds of retrieval systems, many papers were duplicated, and the number of papers found were few.

3.2 Elucidation of the Cause of Membrane Performance Degradation

The causes of membrane performance degradation and their phenomena are classified in Table 3.2.1. To elucidate the causes of membrane performance degradation, these phenomena must be analyzed; and real causes must be concluded judging systematically from feed water quality to operating and maintenance conditions. Furthermore, these phenomena must be diligently analyzed because membrane deterioration may result from membrane fouling.

3.3 RO Membrane Fouling and Performance Maintaining Method

RO membrane fouling can be sorted as follows:

- (1) Accumulation of colloidal substances existing in feed water on the membrane surface.
- (2) Precipitation of a minute amount of dissolved organic or inorganic substances on the membrane surface.
- (3) Propagation of bacteria or adhesion to the membrane in the system.
- (4) Physical or chemical action of components in feed water on the membrane surface.
- (5) On the membrane surface, organic or inorganic components flocculate and accumulate as insoluble molecules.

The mechanism of membrane fouling is suggested as follows: ⁶

(1) Concentration Polarization ⁷

Concentration polarization is an irreversible phenomena in all separation processes. It occurs due to the selective rejection of solute and its removal from the solution. The concentration gradient between feed flow to membrane surface results from the convection transporta

Table 3.2.1 Classification of membrane performance degradation and their causes ¹

	Classification	Phenomena			
		Flux	Salt Rejection	Pressure Drop	
Type	Physical	Compaction	decrease	decrease	no effect
		Embossing	increase	decrease	no effect
		Dehydration	decrease	decrease	no effect
of	Chemical	Hydrolysis	increase	decrease	no effect
		Oxidation	increase	decrease	no effect
Damage	Biological	Bacteria affect	increase	decrease	no effect
		Fouling	Inorganic	decrease	decrease
		Organic	decrease	decrease	increase
	Scaling	Inorganic	decrease	decrease	increase

tion of solute and solvent. The concentration is normally higher on the membrane surface. The high-concentration interface of this membrane induces partially high reverse osmotic pressure against the driving pressure and reduces membrane flux, degrading its performance.

(2) Gel Formation

Compressible Gel Foulants:

The formation of compressible gel depends on the content of membrane feed. Compressible gel is formed when molecules with extremely low diffusion coefficients are supplied in the feed. The most general foulants of this type are humic matter, biological slime, phenol, insecticides, macro molecules (protein, cheese whey, grease, oil, and tannin).

Noncompressible Gel Foulants:

The formation of noncompressible gel closely relates with precipitation on the membrane surface of gel foulants such as calcium sulfate, calcium carbonate, magnesium hydroxide, strontium sulfate, iron hydroxide, and barium sulfate. Many other metal hydroxides tend to form gels. Amorphous silica is one of the worst foulants that are hardly removed from feed water or membranes once gel is formed.

The highest concentration of silica at which no fouling occurs in the RO module is 10 ppm in crystal form and 120 ppm in amorphous form.

(3) Precipitation

Precipitation is similar to the formation of incompressible gel. In this case, however, fouling degrades the membrane permeability through the formation of scale. It is generally recognized that the degradation is a mechanism resulting from the solubility of foulants in water. There are cases where calcium carbonate of 100 ppm deposited CO_3^{2-} ions on the hollow fiber type RO module with 8 inch dia. at the rate of 100 g/hr, and coated the inside of the module up to 1cm thick in 48 hours.

The precipitation of iron on the membrane generally forms Fe_2O_3 or $\text{Fe}(\text{OH})_3$ by the flocculation reaction with hydrolyzing ability of Fe^{3+} ions in feed solution.

The precipitation of this type does not generally become an issue when the concentration is approximately 4 ppm and the recovery is below 80%.

(4) Plugging

Plugging of the membrane surface is generally caused by dispersed or suspended fine particles. Major foulants which plug the membrane module are iron, organic or inorganic colloid, and humic matter. Humic acid is cumbersome because it reacts with chlorine to form haloform such as CHCl_3 . Several colloidal substances containing silica are more cumbersome than humic acid because they are hardly removed from feed water.

A fraction sizes of the colloidal substances are generally 40 angstroms in size. Larger colloidal substances are 0.45 to 2 microns in size.

The most general compositions of inorganic colloid in the membrane process are aluminum nitrate, silica, clay, iron and alumina. In case aluminum is used in the pretreatment of feed water to the membrane, pores are plugged with $\text{Al}(\text{OH})_3$.

Protein (hydrophobic fouling) adheres to the membrane. In some research results, a two-layer effect is proposed for the flocculation and stability of colloid. The stability of colloid can be determined by the electric charge existing in the outer layer of a particle and the particle distance from the membrane surface. These parameters can be predicted from the zeta potential of

feed water. The electric charge in the diffusion layer is measured by zeta potential.

The colloid with the largest negative value of the zeta potential parameters is the most stable. The zeta potential of colloid decreases at high pH values. Thus membrane colloidal fouling is dependent on the pH, ionic strength and values of the treated feed.

Humic matter and highly oxidized polynucleic acid exist in nature, and when present in the feed could cause the blocking of membranes. The molecular weight of these amorphous substances is typically between 100 to 10,000. They are very active same as Fe^{3+} and Al^{3+} and are strongly adsorbed to clay colloid.

(5) Biological Fouling

Biological fouling usually occurs by one of the following two mechanisms. Biological fouling is caused mainly by attachment of cells to the membrane surface cells, the remains of cells, virus, and the derivatives of humic acid. These matters deposit on the membrane surface also plug the fine pores, and reduce the flux. A biological fouling layer is 10 to 20 microns thick.

The second mechanism is membrane decomposition by the direct attack of membranes by bacteria. This type of biological fouling is encountered with cellulose acetate membrane receiving improperly disinfected feed. The aromatic polyamide membrane, however, is not biodegradable and hence are immune to bacteria attack but are liable to other form of biological fouling.

Biofilms formed on membranes differ in property which depend on membrane chlorine tolerance. Biofilms formed on high chlorine tolerant membranes generally have properties such that they are inactive against chlorine and autolyze cells and are likely to be more compressed than those on low chlorine tolerant membranes. In case of higher chlorine concentration tolerance, it is unnecessary to prevent chlorine adsorption on the membrane surface. This fact is necessary for determining the optimal chlorination. In aromatic polyamide membrane, chlorine can not be used because of their high reactivity with inorganic chlorine.

To predict and control these kinds of membrane fouling, several measure are normally taken.

- (1) Pretreatment of feed water and/or membranes
- (2) Periodic cleaning of membranes
- (3) Evaluation of system performance in pilot plants
- (4) Use of predictive models

Among them, the pretreatment of feed water is the most general and effective. Methods of

reducing membrane fouling by coating or treating the membrane surface are also studied, but they are not general.

It is widely recognized that the performance of a membrane can be maintained for a long time by cleaning it periodically. In actual cleaning, the optimal cleaning method for the system is employed according to the type and form of membrane as well as its susceptibility to foulants. The timing of cleaning is also determined by checking the change in system performance.

In some commercial plants, pilot plants are also built to evaluate the system performance by conducting tests for several thousand hours. But it is not generally used, since such a test is costly and requires lengthily testing time. Though various predictive models have also been studied, at the present no one has been established yet for practical use.

Judging from the above, the optimal pretreatment of feed water and a suitable periodic cleaning of membranes foulant are the two essential techniques for maintaining membrane system performance and prevention of serious membrane fouling.

3.4 Elucidation of the Cause of Membrane Fouling

3.4.1 Foulant Analysis

If degradation in membrane performance is presumed to result from membrane fouling, the elucidation of the cause of fouling is needed to recover the membrane performance and to prevent recurrence. For that purpose, foulants must be analyzed. This work is important in order to understand the fouling and scaling formation process and to determine methods of their removing.

For the analysis of foulants on membrane surfaces, the following items are suggested.

- * Visual observation and odor analysis (sensory analysis) of attached substances
- * Determination of amount of attached substances
- * SEM observation of membrane surface
- * XMA analysis of membrane surface — Analysis of elements attached to membrane surface
- * X-ray diffraction and emission spectral analysis of attached substances — Analysis of inorganic substances
- * IR analysis of attached substances — Analysis of organic substances
- * FT-IR analysis of membrane surface and analysis of organic substances deposited on the membrane
- * Incubation and identification of microorganisms — Analysis of microorganisms.

The analysis of feed water as well as the analysis of substances attached to the membrane surfaces are needed for elucidating the cause of fouling. While the membrane system is in serv-

ice, it is necessary to perform this analysis on feed water periodically and accumulate and analyze data. To analyze feed water, the following methods are employed:

- * Measurement of SDI (FI)
- * Incubation and identification of microorganisms
- * Oil analysis
- * Analysis of soluble inorganic components
- * Analysis of soluble organic components
- * pH measurement
- * Analysis of surface active agents

3.4.2 Experiments for Elucidating the Cause of Membrane Fouling

By means of the analysis of foulants on the membrane surface and the analysis of feed water, the cause of fouling can be determined. Sometimes, however, it is necessary to set a hypothesis and verify it by conducting tests to elucidate the real causes. To avoid fouling, the RO facilities should be able to perform the following functions.

- * Pretreatment facilities — Shall be capable of supplying feed water with a low SDI value and is capable of removing microorganisms, oil, and surface active agents in the raw water. It shall also be capable of controlling pH value and temperature.
- * RO facilities — Shall be capable of performing experiments using various forms of membranes, and is capable of controlling its operating conditions arbitrarily, as well as capable of recording operating conditions and performance continuously.
- * Chemicals supply facilities — Shall be capable of supplying exact chemicals dosing.
- * Post-treatment facilities — Shall be capable of removing injected chemicals and making them harmless, if they adversely affect the environment.

The following flow chart can be considered for establishing such experimental facilities (Fig.3.4.1).

3.5 Removal of Membrane Foulants

3.5.1 Method of Removing Membrane Foulants

Methods of removing membrane foulants are classified in Table 3.5.1.

Almost all RO plants that are used in the desalination of sea water use the spiral-wound type or hollow fiber type, and all employ a flushing system. In some plants, the flushing is automatically performed at the time of start and stop of plants, without use of chemical. In addi-

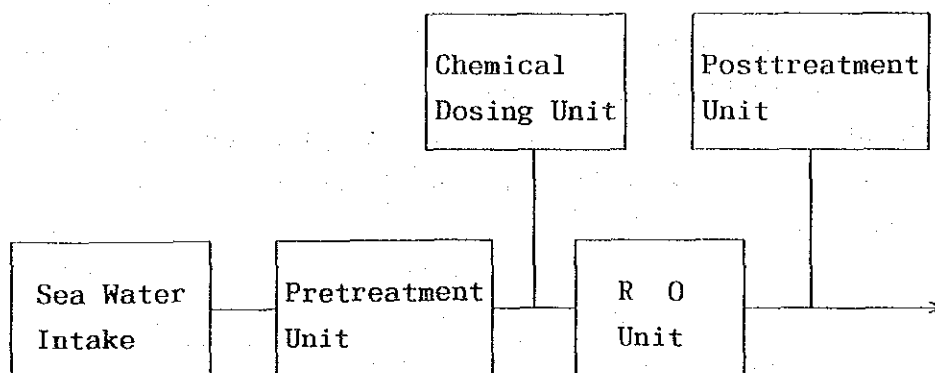


Fig.3.4.1 Schematic Flow Chart for Experimental RO Facility

Table 3.5.1 Cleaning of foulants on RO Membrane ²

Classification	Method	
Physical Cleaning	Flushing	Discharge the foulant under low pressure and high speed flow condition
	Sponge Ball Cleaning	Remove the foulant with sponge ball
	Ultrasonic Cleaning	Remove the foulant with ultrasonic wave
Chemical Cleaning	Acid Cleaning	Dissolve inorganic salts with citric acid or oxalic acid
	Chelating Agent Cleaning	Dissolve slightly soluble salts inorganic with chelating agent
	Oxidizing Agent Cleaning	Decompose foulant with oxidizing agent such as sodium hypochlorite
	Biocide Cleaning	Sterilize the membrane surface
	Surfactant Cleaning	Suspend organic foulant

Though ultrasonic cleaning is described in literature, no example is found in practical plants. The reasons seem to be that it is difficult to apply it to large-size plants and ultrasonic waves damage membranes physically. Sponge ball cleaning is the cleaning method that can be applied to the tubular type module alone. It can not be applied to the spiral-wound type and hollow fiber type.

3.5.2 Mechanism of Chemical Cleaning

Cleaning is a reactions between the clean solution and the fouled layer. The clean process occurs in six stages.

(1) Bulk reaction of detergents

The detergent requirement rises with the increase in degree of fouling. To avoid high consumption of detergent, it is best to wash the system with clean water before adding detergents.

(2) Transport of detergents to the fouled surface.

In this stage, detergents are transported to the fouled layer

(3) Transport into the fouled layer

Detergents are transported to the fouled layer by means of the capillary phenomenon or the molecular diffusion, and they permeate the fouled layer through pores and cracks by the action of lowering the surface tension of surface active agent by their adsorption characteristics. By that, the bonding between the membrane and foulants and their adherence to the membrane surface is weakened.

(4) Cleaning reactions

Cleaning reactions can be subdivided into physico-chemical deterioration and chemical reactions when detergents come into contact with the fouled layer. The physical and physico-chemical deterioration include fusion, mechanical and chemical stresses, wetting, dipping, swelling, dissolution, shrinking, and emulsification. The chemical reactions are hydrolysis, deflocculation, colloid, saponification, solubilization, dispersion, and blocking. These reactions always produce some soluble substances and finally produce dispersible substances. These reactions are helpful to overcome the adhesion power and bonding power between the membrane surface and foulant particulates.

(5) Transport of cleaning reaction products back to the interface.

(6) Transport of products to the bulk solution.

Products by cleaning reaction are carried through the boundary layer by concentration gradient or turbulence. Mechanical/thermal stress and physical/physico-chemical actions weaken the bonding between the membrane surface and foulants, and that between foulants. The flow of cleaning solution in the state of turbulence erodes the fouled layer. This mechanical cleaning mechanism is strengthened when the bonding between foulants has been weakened by physical changes or the reactions indicated in (4).

3.5.3 Detergent

The following are example of detergents used for specific foulants(Table 3.5.2). In addition to these detergents, other detergents are reported in literature.

* For inorganic substances(Metallic oxide, calcium carbonate, etc.). Oxalic acid, Phosphoric acid, Sodium citrate, Nitric acid, Sodium hydrogen-sulfite are used.

* For organic substances use:

Sodium hypochlorite, Caustic soda, Surface active agent:

Anionic agent: Alkyl sodium sulfate, alkyl sodium sulfonate, etc.

Cationic agent: Quarternar ammonium salt.

Nonionic agent: Enzyme detergent, Oxidizing agent, Sodium hypochlorite is also and oxidizing agent, and besides it, there are hydrogen peroxide, ozone, iodine, etc.

Examples of mixed detergent: Dodecyl sodium sulfate + n-pentanol+ Water Borax + EDTA + Trisodium phosphate

* Detergents on the market

3.5.4 Selection of Detergent

Though various detergents are suggested as mentioned above, it must be studied carefully what kind of detergent is to be used. The greatest caution should be given to membrane material resistance to pH and chemicals as well as to the affinity of membrane material to detergent. In general, in case of calcium carbonate, metallic oxide, and inorganic colloid, the lower the pH value is, the higher the solubility and the better is the cleaning effect. By contrast, in case of silica, organic substances and oil, the higher is the pH value, the higher is the cleaning effect. Judging from the above facts, it is important in practical cleaning to observe the pH value range

Table 3.5.2 Foulant and Corresponding detergent³

Detergent	Foulant							
	CaCO ₃	CaSO ₄ BaSO ₄	Metal oxide	Inorganic colloid	SiO ₂	Microorganism	Organics	
HCl (pH 4.0)	X			X				
2% Citric Acid + NH ₄ OH (pH 4.0)	X		X	X				
2% Citric Acid + NH ₄ OH (pH 8)		X						
1.5% Na ₂ EDTA ¹ + NaOH (pH 7 - 8)		X						
1.5% Na ₄ EDTA + HCl (pH 7 - 8)		X						
NaOH (pH 11)				X	X		X	
1% Na ₂ S ₂ O ₄		X	X					
2% Citric Acid + + 2% Na ₂ EDTA + NH ₄ OH (pH 4.0)	X		X					
0.5% Biz ² (with phosphate) + NaOH (pH 11)				X	X		X	
1% NaHMP			X	X			X	
1% Drowsperse 738				X				
1/4-2% Formalin 0.25% "Biz" (with phosphate)						X		

1. EDTA : ethylene diamine tetraacetic acid
2. "Biz" : Product of Procter and Gamble, U. S. A.

Use also the following table
given by DuPont

recommended by each membrane manufacturer and to select the most effective detergent. In case of cleaning microorganisms and bacteria, sodium hypochlorite is effective. However, attention must be given to RO membranes chlorine resistance.

Some of surface active agents and organic chemicals degrade the membrane performance due to their adsorption to the membrane. As mentioned above, the suitability of detergent varies depending on the membrane material.

It is therefore necessary to ask the opinion of membrane manufacturers or to investigate in advance the effects of cleaning agent on the membranes. Cleaning specifications of RO modules used in practical plants are shown in Table 3.5.3.

3.5.5 Membrane Cleaning Methods

It is natural that cleaning methods are different depending on detergents. In general, higher cleaning temperature is more effective. However, attention should be given to the working temperature because it is limited for each membrane material. The cleaning methods that are described in literature are shown in Table 3.5.4.

3.6 *Experimental Plan for Removing Membrane Foulants*

3.6.1 Fundamental Consideration

The causes of membrane performance degradation and the phenomena at that time have been described in Paragraph 2. These phenomena can also be used for the evaluation of the results of cleaning experiments.

The most necessary evaluation measure is the membrane performance before and after cleaning. For this reason, the performance test of the RO membrane before and after cleaning should be conducted under certain conditions as close as possible to standard operating conditions. Measurement items in the RO operation are pressures, flow rates, concentration values, temperatures and pH values of feed water, concentrate, and permeate. From these data, changes in pure water permeability, salt permeability, and the pressure loss of the module gained and performance recovery by cleaning can be obtained. Besides, in the cleaning experiments, the cleaning effects can be evaluated even by the analysis and comparison of cleaning solution at the beginning and the end of cleaning. To investigate the optimum cleaning conditions, it is also important to investigate the change of cleaning solution during cleaning. Attention should be given to the pH value of cleaning solution, in particular, because the rate of change varies with the amount of foulants.

Further, if the destructive investigation of the membrane is allowed, more detailed evaluation becomes possible by the analysis of the amount of attached foulants and the quantitative analysis of attached substances. The analysis of foulants is important even for optimizing the

Table 3.5.3 Properties of Some Seawater Commercial Membranes⁴

	TORAY	TOYOBO	DUPONT	DOW (Filmtec)	Allied Signal/ (Fluid System)
Model	UTC-80	HM10255FI	B-10	FT-30	PA 1501
Membrane Material / Figure	Polyamide/SW	CTA/HF	Polyamide/HF	Polyamide/SW	Polyamide Urea/SW
Allowable pH	2-10	3-8	4-11	2-11	4-11
Residual Chlorine	0	0.2 - 1.0	0	<0.1	0
Feed Temperature	<40	<40	<35	<40	<45
SDI ₁₅	<4	<4	<3	<4	<4

Table 3.5.4 Cleaning method for each membrane⁵

Membrane	Detergent	Conc. (%)	Temp. (°C)	P H (-)	Time (Hrs.)
PA1501	Solution Y (Citric acid)	2.0	25	2.5	0.75
TFC-PA	Solution Z (Borax + EDTA-Na + Na ₃ PO ₄)				
B-10	Ultrasiel 10	0.5	35	12	25
HF-PA	Citric acid	2.0	35	4	25
GKSS G4	Citric acid	1.5	35	3	1
PF-CA/CTA	Ultrasiel 50	1.5			1
	Bevaloid	150(g)		9	1
CA	P3-Ultrasiel 53 (Enzyme)	1.0			1-1.5
	P3-Ultrasiel 75 (Acid)	0.3			0.3
PA	P3-Ultrasiel 30 (Alkaline)	1.0			0.5
	P3-Ultrasiel 75 (Acid)	0.5			0.3
CA	Citric acid	2.0		3	
	Triton X-100	0.1			
	CMC	0.001			
CA	Sodium Tripolyphosphate	2.0		6	
	Na-EDTA	0.8			
	CMC	0.0015			
	Triton X-100	0.1			
Amicon S400	Na-Dodecylsulfate n-pentanol				
	Oxalic acid	0.2		3-4	1
	TC-100 (Surfactant)	5		8-9	1

pretreatment conditions. By means of the observation of the state of attached foulants, it can also be evaluated whether or not the operating conditions are appropriate. Whether or not detergents and cleaning conditions were appropriate can be evaluated by investigating the occurrence of chemical deterioration by means of the measurement of membrane properties. Through the observation of the membrane surface, the degree of cleaning can be judged and physical changes of the membrane surface also can be seen.

Synthetic evaluation must be carried out through these evaluation method combined. However, to examine the relationship between the frequency of cleaning and the recovery of performance and the change in membrane property are necessary when a marginal cleaning method for membranes has been selected.

The evaluation of the results of cleaning can be summarized in Fig. 3.6.1.

3.6.2 Research Plan

When assuming the period of research to be 2 years, the former half is allocated to fundamental research and the latter half is to pilot research. The fundamental research includes a beaker test and a bench plant test. The fundamental research must start with the procurement and adjustment of analyzing instruments, and the installation of RO experimental facilities. The establishment of the analytic method of foulants is the research item that should be performed first. For membrane properties also, basic data should be collected and properties should be confirmed by the analytic experiments in advance. The next research item is to foul the membrane. Though experiments often become accelerated tests, it is necessary that the degree of adhesion(adsorption) of foulants to the membrane is close to the fouling conditions in actual plants. Though the degree of fouling seems to vary depending on the type of membrane, such an experimental method that quantitative data can be obtained should be studied. Detergents have to be selected based on the mechanisms of fouling and cleaning. It is necessary to examine in advance whether or not there detergents affect the membrane physically or chemically.

In pilot research, major experiments are carried out using the actual RO module, on the basis of data obtained in the fundamental research. Since it is anticipated that, depending on the module structure, the degree of fouling varies and the degree of influence on the module performance also varies, this also requires quantitative experiments. The optimum cleaning method should be established by conducting quantitative comparison experiments for detergents, cleaning conditions, and cleaning effects, and by confirming influence on membrane properties.

Further, in this research, the treatment method of detergents should also be picked up as a subject of study. It is important to select a cleaning method which can be applied to practical plants, taking account of ease of handling, economical efficiency, safety(for human bodies and the environment).

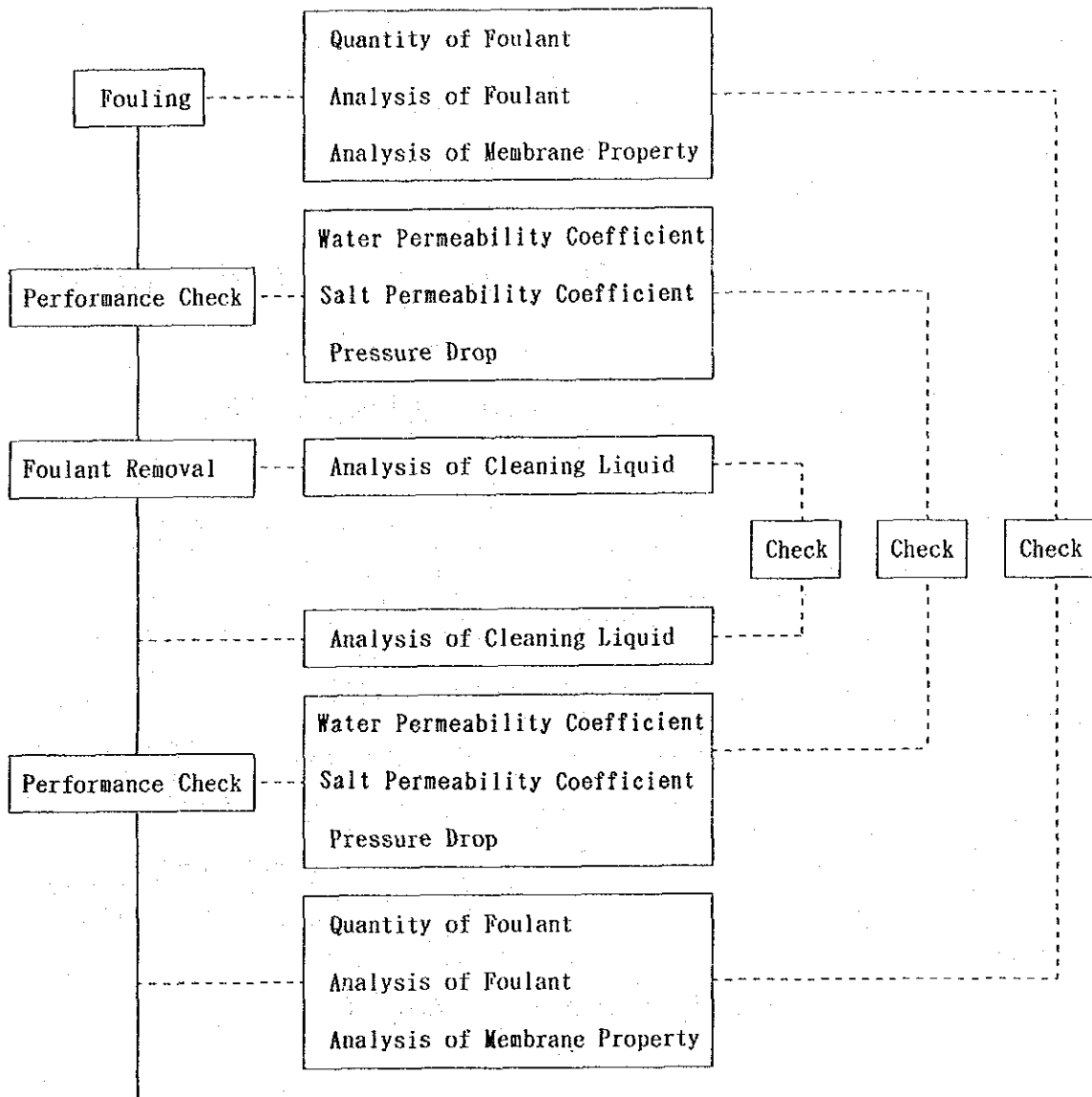


Fig.3.6.1 Evaluation of the Results of Cleaning

	I t e m s
Fundamental Test	Establishment of Quantitative Analysis of Foulant
	Confirmation of Membrane Property
	Selection of Suitable Detergent on Membrane
	Fouling Test
	Confirmation of Influence of Detergent on Membrane
Pilot Scale Test	Fouling Test with Module
	Examination of Cleaning
	Confirmation of Cleaning effect
	Confirmation of Influence of Cleaning on Membrane
	Investigation of Waste Water Treatment Method
	Selection of Suitable Waste Water Treatment Method

Fig. 3.6.2 Time Schedule of Research

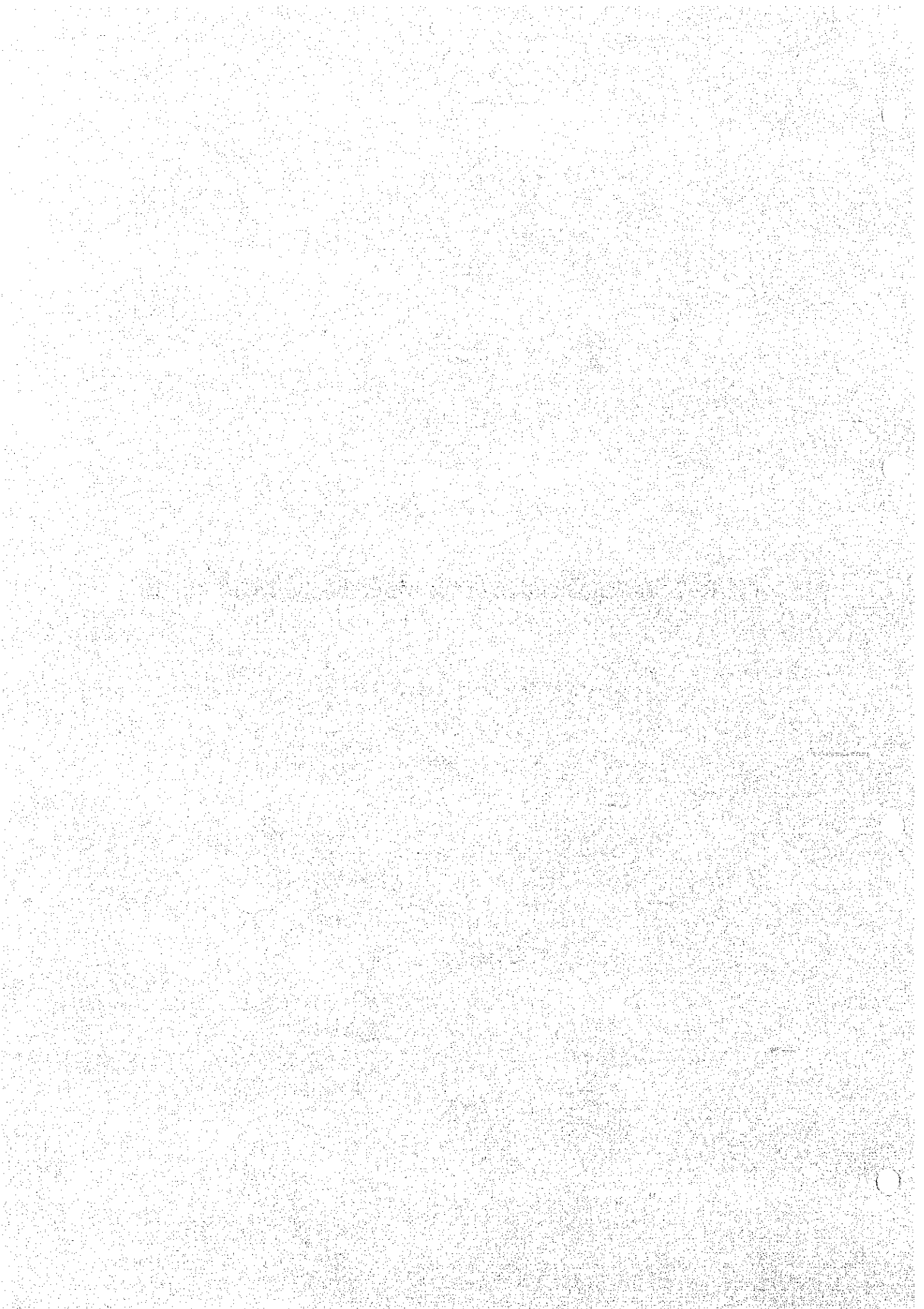
The pilot experiments are conducted in various RO modules, and for experimental facilities, the equipment and functions indicated in Paragraph 4 are required.

The time schedule is shown in Fig 3.6.2.

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4.7 R-7 Standardization of the Main Analytical Methods



**RO DESALINATION
LITERATURE SURVEY NO. 7, R-7**

STANDARDIZATION OF THE MAIN ANALYTICAL METHODS

JULY 1992

By

Tanaka Yoshihiro

JAPAN INTERNATIONAL COOPERATION AGENCY

And

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SALINE WATER CONVERSION CORPORATION

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1. Introduction

The analytical methods used in RO process can be divided into five main categories.

- (1) Qualitative analysis of water from each RO process
- (2) Qualitative analysis of the factors which may cause fouling of the membrane
- (3) Analysis of seawater pollution
- (4) Analysis for the quality of drinking water produced by RO desalination
- (5) Analysis of wastewater from the RO process

The importance of individual category is further explained below:

- (1) Qualitative analysis of water from each RO process

It is necessary to analyze each of the following steps to control the quality of water produced by RO desalination plant .

- (a) raw feed seawater
- (b) seawater after the pretreatment process (pH adjustment, flocculation, filtration and sterilization etc.)
- (c) the concentration of wastewater from the membrane separation process
- (d) the permeate(processed water) from the membrane separation process

- (2) Qualitative analysis of the factors which may cause fouling of the membrane

The applied pressure and recovery rate of the membrane modules is effected by the salt concentration of the raw seawater, temperature, flocculant, suspended solids and micro-organisms.

There is also the occurrence of fouling due to the formation of layers, e.g., cake layer, adhesive layer, scale layer, gel layer and the plugging layer, that accumulate on the surfaces of the membrane.

In the experiments for countermeasures for the prevention of fouling, it will be necessary to use various analytical instruments to verify the phenomena and structure of these fouled layers.

- (3) Analysis of seawater pollution

The water quality of seawater is known to change quite considerably within the space of a year. The salt concentration of seawater in the Middle and Near East sea region is very high (4.2–6%), at temperatures in the range of between 30–40°C, the effect of salt is undesirable for

the RO desalination process. In recent years, sea pollution and oil pollution due to daily wastewater (sewage) and industrial wastewater are beginning to cause concern. The pollution of seawater in the Arabian Gulf in the eastern province of Saudi Arabia is high due to industrial effluents, oil tankers movements and a few incidents of oil spill.

Consequently, the analysis of the contaminants found in minute quantities in raw seawater, will be considered to be of great importance in the future.

(4) Analysis for the quality of the drinking water produced by RO desalination process

It is necessary to analyze drinking water to ascertain presence of deleterious materials associated with oil pollution, even if in only minuscule amounts.

(5) Analysis of wastewater from RO plants

In small scale RO plants, the treatment of wastewater is not really considered a problem but in large scale RO plants wastewater treatment facilities should be set up to deal with the preservation liquors of the membrane modules and washing wastewater of RO plants. Therefore it is necessary to define an analytical method that conforms with the water quality regulations as well as suitable for analysis relating to operation and management.

It is our aim to introduce analytical methods for each field mentioned above and to examine the necessary documentation for selection of required standardized analytical methods for the RO seawater desalination plants in Saudi Arabia.

2. Methods

A. Standardization of Analytical Methods

The guidelines for the standardization of analytical methods are given as reference by several agencies, as in principles, it is desired that they should only be used strictly as guideline. Some methods those do not promote standardization are also included as reference.

- 1) ASTM
- 2) JIS: Testing Methods for Industrial Water and Industrial Wastewater.
- 3) Testing Methods for Tap Water
- 4) Testing Methods for Sewage
- 5) Testing Methods for Wastewater and Environmental Contaminants
(Notification of The Environment Agency)
- 6) Notes on Testing Methods for Hygiene(The Japan Pharmaceutical Society)
- 7) Testing Methods for Water and Wastewater
(K.Toyoda, F.Nakajima, S.Mimura-Kogaku Tosho)

- 8) Ultramicro Analysis——Geological Chemical Samples(H.Hamaguchi–Sangyo Tosho)
- 9) Experiment and Calculation for Quantitative Analysis(S.Takagi–Kyoritsu shuppan)
- 10) Standard Methods for the Examination of Water and Wastewater
- 11) Testing Methods for Membrane Performance, Fouling, Foulant, etc.
- 12) References such as JOIS, CA, etc.

B. Specific Testing Methods

<1> Water quality at each stage for RO system

(1) Raw seawater

1) Physical property

(a) Appearance

(b) Odor

(c) Temperature

(d) pH

(e) Suspended solids (turbidity)

(f) Salinity (total dissolved solids), etc.

2) Chemical constituents

(a) Cation such as Na^+ , K^+ , Li^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{3+} , Al^{3+} and others (e.g., Ba, Sr, Ni, V)

(b) Anions such as Cl^- , Br^- , I^- , F^- , NO_3^- , SO_4^{2-} , S^{2-} , SiO_3^{2-} (including colloidal SiO_2), PO_4^{3-} , etc.

(c) Dissolved gases such as oxygen, carbon dioxide or HCO_3^- , hydrocarbons(e.g., CH_4) ammonia or NH_4^+ , etc.

3) Oily matters and any other organic substances

4) Microorganisms

(2) Seawater after the pretreatment system

Seawater is supplied to RO module after pH adjustment, coagulation/filtration, sterilization, de-aeration and SBS treatment.

Important subjects related to membrane life are as follows:

1) Residual coagulant (e.g., Al^{3+} , Fe^{3+}) may cause fouling of membrane.

2) Free chlorine used for sterilization and oxidizing agents may cause deterioration of mem-

branes.

- (a) Water temperature
- (b) pH
- (c) Salinity
- (d) Turbidity
- (e) Cations
- (f) Anions
- (g) Oily matters
- (h) Organic substances
- (i) Bacteria
- (j) Residual chlorine
- (k) Dissolved oxygen
- (l) Oxidizing and reducing substances
- (m) The others

3) Concentrated brine seawater from the membrane process

Concentrated seawater may have some residual coagulant other than constituents in raw seawater. The elements for analysis are such as item(2).

4) Permeate through the membrane process

As a matter of course, permeate has very small amount of salts. Analysis will be conducted in accordance with testing methods for water and industrial water.

- (a) Observation with microscope
- (b) Surface analysis
- (c) Analysis for fouled layer
- (d) Analysis for metallic elements
- (e) Analysis for anions
- (f) Analysis for organic substances
- (g) Tests for specific microorganism
- (h) The others

<2> Qualitative analysis of the factors causing fouling of the membranes

Substances that cause fouling to the membrane modules appear to be effective in exceedingly small quantities. Further, interactions between the molecular membranes and these sub-

stances have a profound effect on the methods for elimination, by washing and this generate obstruction. For example, in the analysis of the quantities of these fouling substances, the most up-to-date, high-tech analytical instruments are used. This technology can also determine the most suitable standardization of analytical methods in the case of Saudi Arabia. Constituents, carried into the modules, that have not been eliminated in the pretreatment processes such as the flocculation, filtration, sterilization and deaeration processes, together with the constituents present in the raw seawater, concentrate in the membrane modules and plugging of the membrane occurs, due to the complicated phenomena such as salts, solubility and the extrusion of salts.

The factors that cause fouling of the membranes need to be investigated and an experimental method determined, and the results of this should be reported on.

<3> Analysis of seawater pollution

In addition to the normal substances to be analyzed in raw seawater, we will collect and investigate the seawater taken from the surrounding regions of seawater inflow. This water will be analyzed for carcinogenic substances such as trichloroethylene, tetrachloroethylene and traces of organic chlorinated compounds, as well as other harmful substances, that are thought to be present in minute quantities in industrial waste and oil pollution.

<4> Analysis for the quality of drinking water produced by RO desalination

The main purpose is to ensure the safety of drinking water, and other subjects for analysis on the above water, will be arranged and investigated for the necessary analysis techniques, when the carcinogenic and harmful substances as stated above are analyzed.

<5> Wastewater from the RO plant

From the standpoint of wastewater treatment, we need to establish analytical methods related to the regulations of wastewater, as well as controlling the analysis of wastewater treatment equipment and determine the necessary analytical methods for the planning of wastewater treatment equipment, to be used, e.g., for the concentrated water, membrane washing and preservation liquors from the membrane separation process.

3.Results

3.1 The Chemical Analysis and its Items in the RO System

The standardization of the testing methods, the chemical analysis necessary for the performance evaluation of the RO system and the operation control of the related facilities are promoted by ASTM (American Society for Testing Materials) in the U.S.A. where the RO

process is widely used as the desalination system. In Japan, the RO process is widely used in the production system of ultra pure water rather than for the desalination system, owing to its good water quality. There are only a few Japanese Industrial Standards (JIS) related to the RO process for desalination. These include the terms of the membrane¹, the method of performance tests for the RO elements and modules², the testing methods for the rejection of sodium chloride³, magnesium sulfate and isopropanol and the testing methods for the permeate flow rate, all of which are specified.

To obtain the standardized data in the RO system for sea water desalination, the rejection ratio of the salt at the average concentration, the standard rejection ratio of salt at the concentration at the inlet, the permeate flow rate, the recovery percentage, the permeability of salt (measured for the aqueous sodium chloride feed solution of 30,000 – 35,000mg/l with the gauge pressure of 50 – 60 Kg/cm²), and the obtained data of the permeate flow rate and rejection rates should be converted into the standardized condition^{2,4}.

Considering that the RO system has been widely used, the standard testing methods necessary for the RO process performance evaluation or the operation control, are to be established one by one in the near future.⁵

In the RO desalination process, salt rejection depends on the total amount of ions and the ratio of monovalent ions/ polyvalent ions in the feed water, while the permeate flow rate depends on the total amount of ions, the temperature, the pressure and the recovery of the feed water. To examine the RO desalination system, it is necessary to obtain the data of the salt rejection and the permeate flow rate. When RO system operates with the safety load to avoid the deterioration of the product water quality, the recovery depends on the salt composition in the feed water. Therefore it is essential to obtain the data of the chemical analyses of the components in the feed water to determine the maximum recovery of the product water or to control fouling action in the operation and design of RO installations to be considered, whether pretreatment of the raw water is necessary or not.

The guide to general chemical analyses to obtain such data mentioned above, is proposed by ASTM⁶. The frequency of the chemical analyses necessary for the operation control of the RO production and how to keep the records are indicated in the guide.⁷

The scale formation in the concentrate stream of RO installations may cause difficulties in design and operation control of the RO facilities, but its tendency can be predicted by calculation with TDS, the calcium ion concentration, the total alkalinity, PH, the temperature and the recovery of the feed water. Whether calcium carbonate scale is formed or not can be predicted by Langelier Saturation Index(LSI).⁸ When the TDS concentration of the concentrate stream is over 10,000 mg/l, the Stiff & Davis Stability Index (S & DSI)⁹ is used to estimate the possibility of the calcium carbonate scale formation. In addition to calcium carbonate, insoluble sulfate scale is

deposited out in the concentrate stream. The calculation of the index for estimating the deposition of these kinds of salts¹⁰ and the calculation for predicting and the controlling of silica scale formation¹¹ are already standardized. The items of the chemical analyses necessary for these calculations are shown in Table 3.1.1. Table 3.1.1 also shows the example of the chemical analyses of the raw water required for the designing of the RO desalination facilities and the example of chemical analyses carried out for the performance evaluation in the test run and the operation control. When the treatments such as the preprocessing of the feed water and the cleaning of RO membrane are provided, some residual chemicals may be hazardous and cause some troubles. The tests of the residual chemicals must be added to the items of the chemical analysis.

3.2 Research on the Standard Testing Methods of Water Related to RO System

As for the items of the test listed in the previous section, the standard methods have been established worldwide as the water quality test and analysis. In particular, the Standard Methods for the Examination of Water and Waste Water and ASTM list the many items of the standard test. The Standard Methods are generally revised every five years, but recently the interval of the revision has been accelerated. The subdivision committee of ASTM reviews the conventional methods based on the results of new research and the development of new technologies each year. The conventional methods of chemical analysis such as the colorimetry or the titration, the gravimetry are gradually being replaced by instrumental analysis. In Japan, the testing methods of industrial water and industrial wastewater are standardized as JIS K0101 and JIS K0102, respectively. JIS is reviewed and revised every four years by the committee which is composed of representatives from the users, the manufacturers and the experts or the scholars of neutral organizations (such as universities and institutes). The testing methods for industrial water (JIS K0101) were revised recently in 1991 but the revision of JIS for industrial wastewater is now under way.

Alternatively the International Standard Organization has been discussing the establishment of the ISO standards, i.e. the internationally uniform standards.

3.2.1 The Comparison of the typical Testing Methods

There are many new testing methods described in the ASTM¹², Standard Methods¹³ and JIS K0101¹⁴. The comparison of the testing methods are shown in Table 3.2.1 to 3.2.5. As shown in these tables, these testing methods have many points in common. The conventional complicated chemical analysis is gradually being replaced by instrumental analysis.

Table 3.1.1 The parameters of the test for the performance evaluation and the operation control of RO plant

parameters	unit	A S T M D4195	frequency ASTM D4472	brackish water desalination	under-ground water	seawater desalination	S & D. S. I. ^{1, 9}	estimation of sulfate scale production ¹⁰
temperature	°C	○	every day	○	○	○	○	
p H		○	every day	○	○	○	○	
S D I		○	every day	○		○		
turbidity	NTU	○	every day	○	○			
T D S	mg/ℓ	○	1/month	○	○		○	
E C	μ S/cm			○		○		
total hardness	CaCO ₃ mg/ℓ			○		○		
Ca hardness						○		
C a ²⁺	mg/ℓ	○	△	○	○	○	○	○
Mg hardness	CaCO ₃ mg/ℓ					○		
M g ²⁺		○	△	○	○		○	
N a ⁺		○	△	○	○		○	○
K ⁺		○	△	○	○		○	○
S r ²⁺		○	△	○	○			○
B a ²⁺	mg/ℓ	○	△	○	○			○
Mn ²⁺ total, dislv.		○		○				
Fe ³⁺ total, dislv.		○	△	○	○			
F e ²⁺		○						
Al ³⁺ total, dislv.		○	△	○	○			
H ₂ S		○	△	○	○			
H C O ₃ ⁻	mg/ℓ	○	△		○		○	○
C O ₃ ²⁻	CaCO ₃ mg/ℓ	○						
C O ₂		○			○		○	

1) Stiff & Davis Stability Index

Table 3.1.1 (Continued)

parameters	unit	A S T M D4195	frequency ASTM D4472	brackish water desal- ination	under- ground water	seawater desalina- tion	S & D. S. I. ⁹	estimation of sulfate scale production ¹⁰
total alkalinity	CaCO ₃ mg/l			○			○	
M-alkalinity						○		
SO ₄ ²⁻	mg/l	○	△	○	○		○	○
Cl ⁻		○	2/week	○	○	○	○	○
NO ₃ ⁻		○	△					
F ⁻		○	△		○			
PO ₄ ³⁻		○	△		○			
SiO ₂ total, dislv.		○	△		○	○		
O ₂ (DO)		○			○			
TOC		○						
residual chlorine		○	every day		○		○	
Oil					○	○		
colour		TCU			○			
total bacterial count	/100ml			○				
Langelier sat- uration index			1/week					
total analysis			at the time of starting- up and then 3 times a month					○
B					○			
I ⁻					○			
Br ⁻					○			
Cu ²⁺					○			

1) Stiff & Davis Stability Index

Table 3.2.1 The comparison of the typical testing methods ——— Physical tests

	A S T M	STANDARD METHODS -1989	J I S K0101 -1991
Temperature	(a) specified in ASTM thermometers	(a) mercury-filled capillary glass rod type Celsius thermometer	(a) mercury-filled capillary glass rod type Celsius thermometer (b) Petten Kofer's thermometer (c) thermistor thermometer (d) metal resistance thermometer
P H ⁽¹⁾	(a) pH meter associated with glass and reference electrodes	(a) pH meter associated with glass and reference electrodes	(a) pH meter associated with glass and reference electrodes
E C ⁽²⁾ (electrical conductivity)	(a) self-contained conductivity instruments	(a) self-contained conductivity instruments	(a) self-contained conductivity instruments
Salinity	(a) (specific gravity)	(a) EC (b) specific gravity	
T D S (total dissolved solids)	(a) (EC)	(a) gravimetric method with drying residue after filtration and evaporation	(a) gravimetric method with drying residue after filtration and evaporation
S D I ⁽³⁾ (silt density index)	SDI is calculated from the rate of plugging by passing water through a 0.45µm membrane filter at the constant applied gage pressure of 207 kPa.		SDI is defined as FI (fouling index) in JIS K3802-1989 and applied with nearly same test method as ASTM.
Turbidity ⁽⁴⁾ (NTU)	(a) photoelectric nephelometer (Angle of light acceptance to the detector is centered at 90° to the incident light path and not to exceed ± 30° from the 90° scatter path center line.) (b) calibrated silt turbidimeter	(a) photoelectric nephelometer	(a) photoelectric nephelometer (b) integrated sphere type photoelectric turbidimeter (The analytical curve is calibrated with the ratio of intensity of light scattered on the inner surface of a sphere to the intensity of incident light.) (c) transmitted light spectrophotometric turbidimeter (photoelectric colorimeter) (d) visual turbidimetry with standard turbidity series

Table 3.2.1 (Continued)

	A S T M	STANDARD METHODS -1989	J I S K0101 -1991
Ca (5)	(a) flame atomic absorption spectro- photometric method air-C ₂ H ₂ , N ₂ O-C ₂ H ₂ flame (b) EDTA complexometric titration method	(a) flame atomic absorption spectro- photometric method air-C ₂ H ₂ flame (b) ICP (c) EDTA complexometric titration method	(a) flame atomic absorption spectro- photometric method (b) ICP (c) EDTA complexometric titration method
Mg (5)	(a) flame atomic absorption spectro- photometric method air-C ₂ H ₂ , N ₂ O-C ₂ H ₂ flame (b) EDTA complexometric titration method	(a) flame atomic absorption spectro- photometric method air-C ₂ H ₂ flame (b) ICP (c) EDTA complexometric titration method (d) gravimetric method	(a) flame atomic absorption spectro- photometric method (b) ICP (c) EDTA complexometric titration method
Total hardness (6) (CaCO ₃ mg/l or epm)	(a) EDTA complexometric titration method with Eriochrome Black T indicator H _T = H _{Mg} + H _{Ca} H _{Mg} : Mg hardness H _{Ca} : Ca hardness calculation of LSI (Langelier sat- uration index)	(a) EDTA complexometric titration method with Eriochrome Black T indicator calculation of CaCO ₃ saturation index	(a) EDTA complexometric titration method with Eriochrome Black T indicator Total hardness is calculated by following equations: total hardness: $H_T(\text{CaCO}_3 \text{ mg/l}) = \text{Ca}^{2+}(\text{mg/l}) \times 2.497$ $+ \text{Mg}^{2+}(\text{mg/l}) \times 4.118$ non-carbonate hardness(CaCO ₃ mg/l) = total hardness(CaCO ₃ mg/l) - total alkalinity(CaCO ₃ mg/l) when total alkalinity \geq total hardness, carbonate hardness = total hardness
Na (7)	(a) flame atomic absorption spectro- photometric method (b) Na ⁺ selective electrode method (continuous determination)	(a) flame atomic absorption spectro- photometric method (b) ICP (c) flame emission photometric method	(a) flame atomic absorption spectro- photometric method (b) flame emission photometric method (c) Na ⁺ selective electrode method (d) ion chromatography
K (7)	(a) flame atomic absorption spectro- photometric method	(a) flame atomic absorption spectro- photometric method (b) ICP (c) flame emission photometric method	(a) flame atomic absorption spectro- photometric method (b) flame emission photometric method (c) ion chromatography

Table 3.2.2 The comparison of the typical testing methods ——— Metallic elements

	A S T M	STANDARD METHODS -1989	J I S K0101 -1991
S r (8)	(a)flame atomic absorption spectro- photometric method	(a)flame atomic absorption spectro- photometric method (b)ICP (c)flame emission photometric method	
B a (9)	(a)flame atomic absorption spectro- photometric method N ₂ O-C ₂ H ₂ flame (b)flame less (electrothermal or graphite furnace) atomic absorp- tion spectrophotometric method (c)ICP	(a)flame atomic absorption spectro- photometric method (b)flame less (electrothermal or graphite furnace) atomic absorp- tion spectrophotometric method (c)ICP	
F e (10)	(a)flame atomic absorption spectro- photometric method, direct (b)flame atomic absorption spectro- photometric method, chelation with pyrrolidine dithiocarbamic acid - extraction with CHCl ₃ (c)flame less atomic absorption spectrophotometric method (d)bathophenanthroline photometric (colorimetric) method	(a)flame atomic absorption spectro- photometric method (b)flame less atomic absorption spectrophotometric method (c)ICP (d)bathophenanthroline photometric (colorimetric) method	(a)flame atomic absorption spectro- photometric method (b)flame less atomic absorption spectrophotometric method (c)ICP (d)bathophenanthroline photometric (colorimetric) method
M n (11)	(a)flame atomic absorption spectro- photometric method, direct (b)flame atomic absorption spectro- photometric method, chelation with pyrrolidine dithiocarbamic acid - extraction with CHCl ₃ (c)flame less atomic absorption spectrophotometric method	(a)flame atomic absorption spectro- photometric method (b)flame less atomic absorption spectrophotometric method (c)ICP (d)persulfate oxidation photometric method	(a)flame atomic absorption spectro- photometric method (b)flame less atomic absorption spectrophotometric method (c)ICP (d)periodate oxidation photometric method
A l (12)	(a)flame atomic absorption spectro- photometric method, direct N ₂ O-C ₂ H ₂ flame (b)flame atomic absorption spectro- photometric method, chelation with 8-hydroxyquinoline - extraction with CHCl ₃ N ₂ O-C ₂ H ₂ flame	(a)flame atomic absorption spectro- photometric method (b)flame less atomic absorption spectrophotometric method (c)ICP (d)Eriochrome Cyanine R photometric method (e)Pyrocatechol Violet photometric method	(a)flame atomic absorption spectro- photometric method N ₂ O-C ₂ H ₂ flame (b)flame less atomic absorption spectrophotometric method (c)ICP (d)colorimetric method, extraction 8-hydroxyquinoline complex with CHCl ₃

Table 3.2.3 The comparison of the typical testing methods — Nonmetallic elements

	A S T M	STANDARD METHODS -1989	J I S K0101 -1991
Cl ⁻ (13)	(a)mercurimetric titration method with diphenylcarbazone - Bromo-phenol Blue mixed indicator (b)argentometric titration method with K ₂ CrO ₄ indicator (Mohr Procedure) (c)Cl ⁻ selective electrode method (d)ion chromatography	(a)mercurimetric titration method with diphenylcarbazone - Xylene Cyanol FF mixed indicator (b)argentometric titration method with K ₂ CrO ₄ indicator (Mohr Procedure) (c) potentiometric titration method with AgNO ₃ and glass/Ag/AgCl electrode system (d)ferricyanide colorimetric method (e)ion chromatography	(a)mercurimetric titration method with diphenylcarbazone - Bromo-phenol Blue - Xylene Cyanol FF mixed indicator (b)argentometric titration method with uranine indicator (c)ferricyanide colorimetric method (d)Cl ⁻ selective electrode method (e)ion chromatography
NO ₃ ⁻ (14)	(a)ion chromatography (b)Cu-Cd column reduction - N-(1-naphthyl)ethylenediamine photometric method	(a)ion chromatography (b)ultra violet spectrophotometric screening method (220, 275nm) (c)NO ₃ ⁻ selective electrode method (d)Cu-Cd column reduction - N-(1-naphthyl)ethylenediamine photometric method (e)automated Cu-Cd column reduction photometric method (f)titanous chloride reduction - NO ₂ ⁻ photometric method (g)automated hydrazine reduction - NO ₂ ⁻ photometric method	(a)persulfate oxidation - NO ₃ ⁻ ultra violet spectrophotometric method (b)Cu-Cd column reduction - NO ₂ ⁻ photometric method (c)hydrazine reduction - NO ₂ ⁻ photometric method (d)NO evolution - chemi-luminescence spectroscopy
F ⁻ (15)	(a)distillation - F ⁻ selective electrode method (b)ion chromatography	(a)distillation - F ⁻ selective electrode method (b)distillation - Zr-SPADNS photometric method	(a)distillation - F ⁻ selective electrode method (b)distillation - La(NO ₃) ₃ titration method with F ⁻ selective electrode (c)distillation-La-Alizarin Complexon photometric method
SO ₄ ²⁻ (16)	(a)ion chromatography (b)BaSO ₄ nephelometric method	(a)ion chromatography (b)BaSO ₄ gravimetric method (c)BaSO ₄ turbidimetric method (d)BaCl ₂ - Methylthymol Blue photometric method	(a)ion chromatography (b)BaSO ₄ gravimetric method (c)BaSO ₄ turbidimetric method (d)BaCrO ₄ photometric method (e)BaCrO ₄ - diphenylcarbazid photometric method

Table 3.2.3 (Continued)

	A S T M	STANDARD METHODS -1989	J I S K0101 -1991
P (17)	(a)P is separated by two states of particulate and dissolved. And sum of them is called the total P. The latter is divided by three fractions, orthophosphate, condensed (hydrolyzable) and organic phosphorus. The digestion methods to orthophosphate is specified. (b)ascorbic acid reduction - Mo Blue photometric method (c)semiautomated digestion - ascorbic acid reduction - Mo Blue photometric method (d)ion chromatography	(a)P is separated by two states of particulate and dissolved. And sum of them is called the total P. The latter is divided by three fractions, orthophosphate, condensed (hydrolyzable) and organic phosphorus. The digestion methods to orthophosphate is specified. (b)Vanadomolybdophosphoric acid Yellow photometric method (c)SnCl ₂ reduction - Mo Blue photometric method (d)ascorbic acid reduction - Mo Blue photometric method	(a)P is separated by two states of particulate and dissolved. And sum of them is called the total P. The latter is divided by three fractions, orthophosphate, condensed (hydrolyzable) and organic phosphorus. The digestion methods to orthophosphate is specified. (b)SnCl ₂ reduction - Mo Blue photometric method (c)ascorbic acid reduction - Mo Blue photometric method (d)Mo Blue - MIBK extraction, photometric method
SiO ₂ (18)	(a)1-amino-4-naphthol sulfonic acid reduction - Mo Blue photometric method (b)flameless atomic absorption spectrophotometric method	(a)flame atomic absorption spectrophotometric method, Na ₂ O-CaH ₂ (b)gravimetric method (c)Mo Yellow photometric method (d)1-amino-4-naphthol sulfonic acid reduction - Mo Blue photometric method (e)ICP	(a)separation by the forms (b)gravimetric method (c)Mo Yellow photometric method (d)ascorbic acid reduction - Mo Blue photometric method (e)ascorbic acid reduction - Mo Blue - isobutanol extraction, photometric method
CO ₂ (19) (CO ₂ , HCO ₃ ⁻ , CO ₃ ²⁻) alkalinity (20) (expressed by CaCO ₃ mg/l or epm)	(a)CO ₂ gas sensing electrode (assembled gas permeable membrane) method (b)CO ₂ gas evolution - coulometric titration method (c)electrometric titration method (pH 8.1, 4.5) (with pH meter or automated electrometric titration unit)	(a)titration method with phenolphthalein indicator (pH 8.3) (b)free CO ₂ : calculation of the relations between alkalinity and pH	(a)NaOH, SrCl ₂ addition -HCl titration method (b)as inorganic carbon (TOC analyzer) (c)titration method with phenolphthalein indicator (pH 8.3) (d)titration method with Methyl Red - Bromocresol Green mixed indicator (e)electrometric titration method with pH meter(JIS K0102)
H ₂ S (21) (S ²⁻)	(a)S ²⁻ selective electrode method	(a)elimination of interferences by ZnS precipitation (b)Methylene Blue photometric method (c)iodometric titration method (d)calculation of un-ionized H ₂ S (by pH-pK relations)	(a)Methylene Blue photometric method (b)H ₂ S evolution - iodometric titration method

Table 3.2.4 The comparison of the typical testing methods — Elements related to the pretreatment

	A S T M	STANDARD METHODS -1989	J I S K0101 -1991
D O (22) (O ₂)	(a) membrane electrode method (b) iodometric titration method (Winkler's azide modification method) (c) iodometric method by potentiometric titration (d) Indigo Carmine colorimetric method	(a) membrane electrode method (b) iodometric titration method	(a) membrane electrode method (b) iodometric titration method (c) ferrous titrimetric method using Methylene Blue as indicator (Müller method)
Free-chlorine (23)	(a) amperometric titration method with phenylarsine oxide	(a) amperometric titration method with phenylarsine oxide (b) iodometric titration method (c) DPD (N,N-diethyl-p-phenylene-diamine), ferrous titrimetric method (d) DPD photometric method (e) FACTS (Syringaldazine) photometric method (f) iodometric electrode technique (Pt-I ⁻ electrode associated with pH meter)	(a) amperometric titration method with phenylarsine oxide (b) iodometric titration method (c) DPD, ferrous titrimetric method (d) DPD photometric method (e) o-toluidine photometric method
Oil and grease and petroleum hydrocarbons (24)	(a) 1,2,3-trichloro-1,2,2-trifluoro ethane extraction - IR spectrometric method (b) separation of petroleum hydrocarbons by column chromatography	(a) 1,2,3-trichloro-1,2,2-trifluoro ethane extraction - IR spectrometric method (b) 1,2,3-trichloro-1,2,2-trifluoro ethane extraction - gravimetric method	(a) CCl ₄ extraction - IR spectrometric method (b) hexane extraction - gravimetric method
Total organic carbon (25)	(a) high temperature oxidation - coulometric detection method (b) ultra violet or persulfate oxidation - nondispersive IR photometric method (c) catalytic combustion oxidation - nondispersive IR photometric method (d) catalytic CH ₄ reduction - FID detection method	(a) ultra violet or persulfate oxidation - nondispersive IR photometric method (b) catalytic combustion oxidation - nondispersive IR photometric method (c) wet oxidation by persulfate and phosphoric acid - nondispersive IR photometric method	(a) catalytic combustion oxidation - nondispersive IR photometric method
S O ₃ ²⁻ (26)		(a) iodometric titration method (b) SO ₂ evolution - Fe ²⁺ -1,10-phenanthroline photometric method	(a) iodometric titration method

Table 3.2.5 The comparison of the typical testing methods — Elements related to the liquid waste of the membrane cleaning

	A S T M	STANDARD METHODS -1989	J I S K0101 -1991
Total bacterial count (27)	(a) total-count water sampler comprising a 0.45µm membrane filter and absorbent pad (cultivation at 35±2°C for 26 hours)	(a) pathogenic microbial count in water using 0.45µm membrane filter identification of each bacterial group by cultivation	(a) heterotrophic bacteria count in water with 0.45µm membrane filter water sampler assemble absorbent pad
H C H O (28)	(a) acetylacetone - n-butanol extraction, photometric method		(a) distillation - acetylacetone photometric method (JIS K0102 Testing methods for industrial wastewater)
EDTA-2Na (29)	(a) Zr-Xylenol Orange complex photometric method (unchelated EDTA: titration method with Mg ²⁺ solution.)		
Surfactants (30)	(a) anionic surfactants (expressed as Methylene Blue active substances - MBAS) MBAS-MB ion pair-CHCl ₃ extraction; photometric method (MBAS based on LAS)	(a) anionic surfactants (expressed as Methylene Blue active substances - MBAS) MBAS-MB ion pair-CHCl ₃ extraction; photometric method (MBAS based on LAS) (b) nonionic surfactants (expressed as cobalt thiocyanate active substances -CTAS) separation of surfactants by sublation with ethyl acetate - anionic and cationic surfactants separated by ion-exchange resins; CTAS-CI complex - methylene chloride extraction, photometric method	(a) anionic surfactants - Methylene Blue ion pair - CHCl ₃ extraction, photometric method (based on sodium dodecyl sulfate) (b) anionic surfactants - Ethyl Violet ion pair - toluene extraction, photometric method (c) anionic surfactants - dibenzo-18-crown-6 ion pair -MIBK extraction; Potassium ion pair is determined by flame atomic absorption spectro-photometric method. (d) nonionic surfactants: separation by ion exchange resin column chromatography; nonionic surfactants - cobalt thiocyanate complex - benzene extraction, UV (322nm) photometric method
Organic acids	Acid content of the original and the spent acid solvents used for chemically cleaning industrial equipments is determined by alkali titration method and expressed as an acid, acetic, citric, formic, or hydroxyacetic, etc.	(a) distillation - alkali titration method (expressed as acetic acid) (b) silicic acid column chromatography - alkali titration method (expressed as acetic acid)	

Some comments on the examination methods

(1) pH

pH is generally measured with the glass electrode pH meter. Its accuracy depends on the accuracy of the pH standard solutions and the type of pH meters. In Japan, four types of approved pH meters, O, I, II, and III are now commercially available. When the pH of a certain type of standard pH solution is measured with these meters, the repeatability is specified as 0.005, 0.02, 0.1 pH, respectively¹⁵. Specified standard solutions of oxalate (pH 1.68), phthalate (pH 9.18), and carbonate (pH 10.01) (each pH value shows pH at 25°C) are commercially available. These specified standard solutions are verified with secondary standard solutions qualified with primary standard solution kept with the national institution. The verification test is performed by the public organization under national supervision. The standard solution is grouped into two types; Class 1 and Class 2. The value up to the third decimal place is verified for class 1, while the value rounded off to two decimal places is verified for class 2.¹⁶

Generally type I or type II of pH meter is used except for accurate measurement. The pH meter should be corrected with the secondary standard solution before measurement. The measuring materials such as the instruments, equipment, and the reagents are generally specified by the related standards.

(2) Turbidity

The measured value of the turbidity depends on the standard solutions to be used for the calibration of the turbidimeter. Formazin polymer or styrene/divinyl benzene polymer is used for the turbidity standard in the U.S.A., while formazin and kaolin are used in Japan. Kaolin is a natural mineral which has a wide range of particle size distribution. Since kaolin is sedimentous, it is suspended in the sodium pyrophosphate solution. The middle layer of the suspension is extracted and dried after filtration with the filter of the pore size of $1\mu\text{m}$. Adding formaldehyde to the suspension made of a fixed amount of the dried substance, the standard turbidity suspension can be obtained. The suspended matter in water is mainly derived from silicate minerals, and Kaolin turbidity units have better correlation with such particulate matter in water. In addition to the scattered light turbidimeter corresponding to NTU, the transmitted light turbidimeter and the integrating sphere type turbidimeter are used as turbidimeters. For the NTU in the U.S.A., the position for fixing the optical sensor is specified as $90^\circ \pm 30^\circ$ to the incident light, while the turbidimeter for measuring the back scattering is approved in Japan. For the integrating sphere type turbidimeter, the turbidity is calculated with the ratio of intensity of the light scattered by the suspended matter on the spherical inner surface, the intensity of the transmitted light, and the analytical curve of the standard solution.

(3) Electrical Conductivity

The concentration of the dissolved electrolyte (salt) is almost proportional to its conductivity. The salt concentration (TDS) of the feed water, the concentrate, and the product water are generally expressed by the electric conductivity. To measure the electric conductivity of the sample with high ion strength like the seawater, the common electrode type conductivity meter may cause troubles resulting from the probe polarization and fouling. Hence the induced current mode electrodeless conductivity meter is adopted in the U.S.A.

(4) Instrumental Analysis

The adopted testing methods vary with the actual situations of the country and the purpose. The flame or flameless atomic absorption spectrophotometric method, the ICP for analysis of metallic elements, and the ion chromatograph or the electrode method for analysis of anions are becoming popular. In future, the unified standard testing methods of analysis will be adopted, for example, ICP for the analysis of all the metallic elements and the ion chromatograph for anions. Like the automatic analysis of amino acids with the high performance liquid chromatograph, all the data from the elements will be obtained simultaneously from one sample. ICP-MS and IC-MS integrated with the mass spectrometer have already been commercialized.

In future, the method to analyze not only the composition of elements and ions but also to clarify the state of existence of the atomic level will be standardized, and the characterization of the fouling action and the fouling matter will become easier.

3.2.2 Items Which must be Marked for the Normalization of Analysis Methods

(1) Limitation of Analysis Method

A standard analysis method must desirably be limited to one which offers highly reliable data on a sample repeatedly, whoever, whenever and wherever may make the analysis. Depending on the purpose and the objective component of an analysis, however, it is sometimes very difficult to limit to even one standard analysis method.

In a chemical analysis, when only the objective component is contained exclusively in a sample, an accurate analyses data can generally be obtained with any analytical method. When there are other co-existing substances, though, the analyses data is affected by the components each other. When the number of types and the quantity of the components are larger, analysis becomes more difficult.

To normalize an analysis method, it is necessary to make sure that unbiased data can be obtained reproducibly on any sample no matter which organization and personnel make the analysis utilizing this method at any given time and place. The method to ascertain the repeatability and the bias with the inductive statistics, is normalized,¹⁷ and the requirements of the

organizations which carry out analyses are indicated¹⁸.

(2) Improvement of Analysis Methods and Control of Interference

Sea water has a high salt concentration and a complicated matrix. Existing analytical methods are usually not applicable to such a sample directly. Normally, any analysis method indicates the effect of co-existing substances on the analyses data and controlling the interferences. For the analysis of sea water or any other enriched water, however, an existing analysis method must generally be improved to make it applicable, or a new analysis method must be established.

For example, for the determination of Cl^- in sea water or brine, titration can be carried out more easily with silver nitrate of low sensitivity than with mercury nitrate. For the nephelometry of SO_4^{2-} , sodium chloride is added to the standard solution to adjust the ionic strength. For the determination of F^- , on the contrary, a certain amount of standard solution is added to the sample, and measurement is carried out at the F^- electrode. In this way, measures to make the matrix nearer to the sample are taken.

For the application or the normalization of an analysis method, it is necessary to examine the following points in advance: the effect of the co-existing components on the data of the sample, if dilution helps carry out analysis without a hitch, and which method must be applied to eliminate interference; the standard addition method, the internal standard method, the addition of the interference control agent, or the background compensation etc.

(3) Instrumental Analysis

Compared with chemical analysis, an analyst does not need much skill for instrumental analysis. Instrument errors have been reduced remarkably due to recent technical development. Consequently, instrumental analysis is often introduced to standard analysis methods. In instrumental analysis, the concentration is measured indirectly from voltage, current and other indexes calibrated with the standard solution, and the chemical equivalent quantity is not measured as in the conventional chemical analysis. One is therefore, liable to overlook the effect of interfering components on the deviation of indexes and the measured values. For analysis with the instruments which make it possible to obtain analysis values of a component mechanically from readings, or to read analyses values directly, it is necessary to take into account internal and external error factors such as co-existing components. It is also necessary to confirm that when a certain amount of a component is added to the sample for analysis, the amount added can be read correctly. Without these processes, it is not possible to guarantee the reliability of the data obtained.

In the countries and areas where instruments are not permeated or diffused, it will probably be difficult to normalize a uniform instrumental analysis method until instruments are dif-

fused.

(4) Analysis of Materials in Their States (in situ)

In a pure solution, inorganic dissolved substances exist in water as ions. Silica, phosphorus and iron exist, however, in complicated states. Silica exists in water in an ionic, colloidal or particulate state. With normal chemical analysis, only the silica in an ionic state can be determined. As fouling by scales and others are brought about with the silica in other than ionic states, analyses data depending on the existing state are often required. The type of pretreatment, cleaning, and the solvent to be used must also be selected depending on the existing state.

In this way, the existing states of materials often become difficult factors in the normalization of analysis methods. As it is normally difficult to determine a material accurately in every state, it is necessary to classify states into the dissolved and the particulate, or to normalize the decomposing method of materials to the ionic state as metallic components and phosphorus.

When it is not possible to determine all the existing quantities of a component with an analysis method, a reaction to the chemicals used for the analysis is sometimes defined as an existing compound.

A standard analysis method which requires many complicated analyses often makes it difficult to determine surfactants, NO_3^- and some other components accurately.

The materials which exist in water, and the materials which cause the fouling of RO membranes are best analyzed in situ.

Standard methods for the analysis of scales and deposits are established to some extent.

(5) Elimination of hazardous Materials Which Cause Environmental Pollution

In the normalization of chemical analysis methods, it is desirable to establish a method excluded hazardous material, such as mercury, cadmium containing chemicals which cause potential environment pollution, or are liable to spoil human health and other things.

(6) Legal Support

In Japan, normalized analysis methods are dealt with by the Japanese Industrial Standards (JIS) and supported legally. JIS is applied to all chemical analyses of every kind of water; public water, sewage, industrial waste water, and environmental water. JIS is also applied to surveillance of the regulatory standards for the industries effluents and or the performance evaluation and the operation control of the treatment facilities for industrial wastewater.

The purpose of normalization and the way a normalized analysis method is applied, depends on whether normalized methods are legally supported or not.

3.3 Analysis of the Fouling of the RO System

3.3.1 Fouling and its Prevention

When the RO system is continuously run, the desalting rate and the water permeation decreases as time passes. This time-dependent change, which is due to the interaction between certain elements in feed water and membranes, is divided into two categories; deterioration and fouling. Table 3.3.1¹⁹ shows the factors involved in these two types of change.

Deterioration is further divided into physical deterioration caused by the creep deformation (compaction) of a membrane under pressure, chemical deterioration such as hydrolysis and oxidization, and biological deterioration caused by bacterial assimilation of membrane material. Such deterioration results from an irreversible change of the membrane and hence it is impossible to recover the performance. To prevent the deterioration, it is necessary to remove harmful substances from feed water (e.g. through pretreatment) and/or select process membranes that are resistant to deterioration and cleaning.

On the other hand, fouling is a change of membrane performance caused by external factors, and is not a change of the membrane itself. Usually, the measures shown in Table 3.3.2¹⁹ are taken to prevent fouling.

Fouling can be divided into three categories. Firstly, cake, gel, scale, adsorption, and other layers adhere to the surface of separation membranes. Secondly, solid substances or gaseous bodies intrude into the porous substrates inside of separation membranes and block them. Thirdly, the flow paths of feed/permeated water are blocked with solid substances, thereby hindering the flow of water.

Thus, fouling is caused by the quality of feed water (in the case of cake layer, scale layer, etc.) or is due to the grade or the material of membranes. The controlling measures to be taken depends on the cause.

If fouling occurs during the RO module operation, cleaning has to be done to recover the performance. To select the cleaning technique, the type of fouling layers and the type of module (including the chemical-durability of the separation membrane and other parts of the membrane module) must be taken into consideration. When cleaning solvent is employed, some ingredients may increase their viscosity or alter the oxidizability of the cleaning solvent, thereby accelerating the deterioration of the membrane. Usually, the cleaning technique shown in Table 3.3.3¹⁹ are employed.

As a result of cleaning, the fouling layers are removed from the membrane surface. In the case of chemical cleaning, the fouling layers are mixed with the chemical solvent, and discharged to the outside as wastewater.

New membranes are preserved in formalin liquor in advance, so that the pores do not deteriorate through dehydration or the intrusion of gaseous substances and the membranes do not

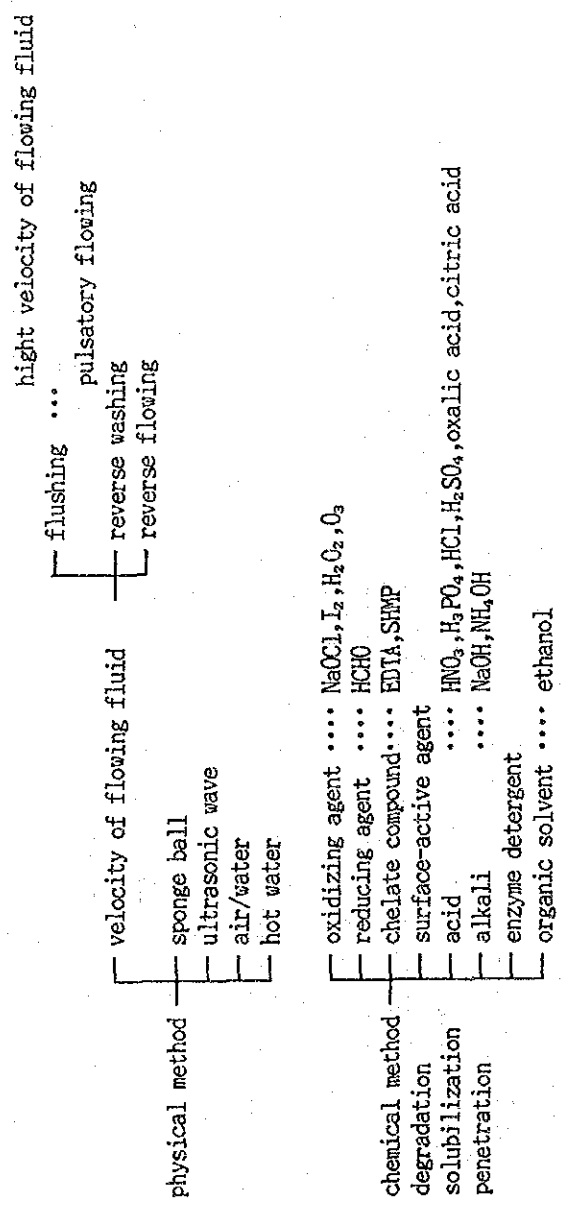
Table 3.3.1 Deterioration and fouling of membrane ¹⁹

item	definition	content	
deterioration	irreversible depression of the membrane performance due to the alteration of membrane itself	physical compaction damage drying	irreversible change of the membrane structure caused by (1)compaction due to the long-term pressure applying, (2)flaw and abrasion of membrane surface due to the attack of solids in feed solution and vibration, (3)rupture, (4)drying, and (5)contraction
		chemical hydrolysis oxidizing- degradation	decomposition of the membrane due to the influence of pH, temperature etc. change of the properties or decomposition of the membrane material by oxidizing agents
		biological	alteration of membrane due to the biological degradation by microorganisms or influence of its secretion
fouling	depression of the membrane performance arisen by the external factors, not the alteration of membrane itself	cake layer	the layer formed on the surface of membrane by the accumulation of suspended solids existing in feed solution
		gel layer	the gelatinized immobile layer formed by the concentrated soluble-macromolecules
		scale layer	the layer formed by the precipitation of refractory salts in exceeding their solubility limit
		absorption layer	the layer formed by the preferential adsorption of solute on the membrane surface
		plugging	solid: plugging due to the adsorption, deposition and trapping of solid substances in the pore of membrane gas: occupation at hydrophobic porous layer by the gaseous substance; (drying)
		flow channel blockade	blockade of channel in the module caused by solid substances

Table 3.3.2 Preventive measures of the fouling 19

	cake layer	gel layer	scale layer	adsorption layer	plugging
pretreatment of raw water	pH adjustment	△	○	○	
	soften, ion exchange		○		
	scale inhibitor		○		
	coagulating, filtration	○			○
	adding minute particles	○	○	△	
selection of membrane process	membrane material	○			
	membrane(salt rejection, fraction, pore size)	○	○	△	○
	kinds of membrane		○		
	structure of membrane	○	○		○
	pretreatment of membrane surface		○		○
condition of operation	linear velocity	○	○		
	recovery	○	○	○	△
	temperature		○	○	○

Table 3.3.3 Cleaning method for fouled membrane 19



suffer biological deterioration caused by bacteria. Also, when the RO system is out of operation, sodium hydrogensulfite is used to preserve the membranes²⁰. At the time of start/restart of the operation, such preserving liquor is discharged to the outside as wastewater.

3.3.2 Analysis of Fouling

The fouling action is caused by the interaction between the ingredients in feed water and the RO membrane. To analyze the fouling phenomena, therefore, it is necessary to obtain information about the fouling layer surface, the interface between the fouling layer and the membrane, the forms of vertical sections of the membrane surface, bonding (electronic) status, etc. To observe the forms, an optical microscope or a scanning electron microscope (SEM) is employed.

Since the RO membrane has very small pores that can remove ions of the diameter of several Å, its analysis requires the investigation into very small parts. To do this, a surface analyzer such as EPMA and SAMA (Scanning Auger Microprobe Analyzer) is used. With such a surface analyzer, the probe beam is applied to the micro parts of the sample, and the composition and status of electrons, ions, X-rays detected from probing are analyzed. In addition, through the x-y scanning and sample scanning, it is available to obtain the two dimensional information.

Moreover, to measure two dimensional distributions of surface composition and electron bound by applying X-ray micro beams as irradiation source and scanning the sample, that is, the fluorescence X-ray analysis or ESCA (Electron Spectroscopy for Chemical Analysis) can be conducted.

To obtain information on molecule structures, the infrared spectroscopic analysis is carried out.

The methods shown in Table 3.3.4¹⁹ are usually employed for analyzing the fouling.

SEM, XMA (X-ray Microanalyser), EPMA, FT-IR (Fourier Transformation Infrared Spectroscopy), and ESCA are effective for analyzing membrane surfaces or cross sections.

It is said that most of fouling constituents can be identified by observing the fouling phenomenon through the SEM, carrying out the face analysis with the XMA, and analyzing existent inorganic and organic compounds (by means of the FT-IR).¹⁹

However, the method for analyzing the RO membrane is far from being standardized. The analyzing method remains to be established to clarify many complicated reaction processes including the deposit sedimentation of the fouling particles in the vicinity of the membrane surface, adhesion and adsorption of the particles on the membrane surface, gelation caused by the compatibility of the membrane and the particles, chemical bonding of particles themselves, solvation, affinity, and permeation of the particles into the membrane. The analysis of the transition to fouling is also insufficient.

Table 3.3.4 Observation and analysis of fouled membrane 19

	cake layer	gel layer	scale layer	adsorption layer	plugging
OBSERVATION observation of adhered substances (watching, microscopic, appearance of wet surfaces)	○	○	○	○	○
determination of adhered substances	○	○	○		
incubation of microorganism	○				
SEM	○		○		○
XMA	○		○		○
X-ray diffraction			○		○
IR	○	○	○		
FT-IR	○	○	○	○	
ESCA	○	○	○	○	

Under such circumstances, it is pointed out that the results of analysis do not necessarily fit the cleaning effects.²⁰ The current surface analysis method has several problems. For example, it requires a high degree of vacuum and hence a lot of time to prepare a sample to be analyzed. Furthermore, because it is difficult to take measurements in a system containing water, the results of measurements may not reflect the actual fouling phenomena.

To overcome those difficulties, expectation is laid on the ESCA or wet SEM that can take measurements in low-level vacuum of several torrs by using differential gas exhaust, PAS (photoacoustic spectroscopy) that can take measurements in a system containing water, laser Raman spectroscopic analysis, chemiluminescence, and ultrasonic microscope.

3.3.3 Equipment to be Used for Fouling Analysis

In order to analyze the substances, structure and form of fouling membranes, it is becoming common to use surface analyzers that are capable of measuring the forms, chemical types, bonding status, and structures of fine particles of the surfaces.

The outline of such analyzers are described below. The examples of their applications are shown later.

(1) Optical Microscope

In many cases, the observation through an optical microscope is enough to identify the cause of fouling without implementing complicated, time consuming analysis of components. Moreover, while the component analysis alone cannot show the bonding status between constituents, ingredients in the fouling layer can be easily identified if they are crystalline and their optical and morphological properties are known.

There is a standardized method for microscopic examination of the deposits generated from water²¹.

(2) X-ray Diffraction Analysis

Powdered samples are irradiated with a monochromatic X-ray beam of short wavelength (from about 0.05 to 0.25nm). The X-rays interact with the atoms in the crystal lattice scattered in a unique diffraction pattern which produces a finger print of the crystal's atomic or molecular structure.

Being based on the properties of crystals, the X-ray diffraction analysis cannot be applied to non-crystalline substances.

There is a standardized method for powder X-ray diffraction analysis of crystalline compounds in the deposit generated from water³⁶. This method is not effective to identify amorphous substances such as oil and grease.

(3) Fluorescent X-Ray Analysis

When X-rays, γ -rays, or electron rays are applied to a substance, fluorescent X-rays which are unique to the substance is emitted. By using these X-rays, the types of atoms in the substance can be identified (elemental analysis). This method is often applied to identify foreign substances adhered/adsorbed on membranes.

In the case of an analyzer to be used exclusively for elemental analysis with fluorescent X-rays, the excitation source is X-rays and an energy-dispersive-type spectroscope is used for the analyzing section.

In ASTM, there is a standardized method for elemental analysis of the deposit generated from water. The method uses a wavelength-dispersive-type fluorescent X-ray analyzer, and is applied to the elements with the atomic number of 11 or more and the concentration of 0.1% or more.³⁷

(4) XMA (X-Ray Micro Analysis) or EDAX (Energy Dispersive Analysis by X-ray)

With SEM (see later (6)), electron beams are applied to the sample to retrieve secondary electrons, which are displayed on CRT. At this time, along with secondary electrons, fluorescent X-rays are emitted from the sample. By measuring the energy of these X-rays, therefore, the elemental analysis can be carried out in the same way as described in 3.3.3(3).

This method has some advantages. For instance, if combined with the SEM functions, it requires only tiny amount of sample, and produces an image that corresponds to a SEM image and shows the distribution of each element in the sample.

This type of analyzer with an energy-dispersive-type spectroscope, which is widely used for the analysis of fouling membranes, is called XMA or EDAX. EPMA (see later (7)) has many other functions added to this type of analyzer.

(5) ESCA (Electron Spectroscopy for Chemical Analysis)

When X-rays are applied to the surface of a solid sample, photoelectrons are emitted from atoms excited by the X-rays. Since the energy of radiated X-rays is constant, the measurement of the energy of the emitted photoelectrons reveals the bonding energy of electrons, that is, the energy needed to throw out inner-shell electrons bound with the atomic nucleus.

This bonding energy of photoelectrons is unique to each substance, so that the elements contained in the sample can be identified by measuring the photoelectronic spectrum. As the status of chemical bonding of atoms changes, the bonding energy changes by several electron volts. Therefore, from this chemical shift, the status of chemical bonding is estimated as well.

The method is also called XPS (X-ray Photoelectron Spectroscopy), and is used to identify elements comprising a substance, and to analyze the chemical bonding status of atoms on the

basis of chemical shift.

Measurement through ESCA is limited to only 1–3 nm depth of the sample surface. In contrast with EPMA, ESCA is applied to the most outer layer of the sample. To investigate the vertical composition of the surface layer, either a cross section is cut out by means of ion etching or the atomic layer is removed from the sample surface, thus making the linear/facial analysis possible. When photoelectrons are emitted from atoms excited by X-rays, remaining atoms becomes ionized. When the excited status becomes stable again, fluorescent X-rays and auger electrons are emitted. A method using the former is called the fluorescent X-ray analysis and a method using the latter is called the auger electron spectroscopy (AES).

These two methods are not suitable for analyzing insulating substances and have low determination. So, they are not used for fouling analysis. Nonetheless, they have some advantages such as high space resolution and hence short analyzing time. Since valence electron levels contribute to the spectrum, the auger transition of atoms is used to analyze the adsorption status, fine structure of valence electrons, type of surface adsorption, etc. Also, being particularly sensitive to certain elements, these methods are sometimes applied to identify foreign substances adhered on the surface.

(6) SEM

With SEM, electron beams with a diameter of several tens Å scan over the sample, and, by synchronizing with scanning, signals of secondary electrons which are generated as the beams pass are retrieved on CRT as an image. Besides SEM, this process provides the very basic function of XMA (see Precedent(4)) and EPMA (see next (7)).

The sample for SEM need not be very thin. Cut out a sample as thick as 3 mm, clean the surface to be observed, and put it on the sample stand. The section to be observed must be fixed on the stand with conductive adhesive. For insulating substances, carry out vapor deposition with gold of 10–100 nm thickness.

Secondary electron image is made by collecting low-energy electrons of 50 eV or less and partly contains reflected electrons.

This image is sensitive to the form of the sample surface, face direction (in case the sample is crystalline), electric potential and magnetic field of the sample. When the electronic beams irradiates the sample surface, secondary electrons reach the detector in the proportion to the angle made by the sample surface and the incident ray. Because of this, the change of the angle due to the local irregularities on the sample surface produces the contrast in the image.

Also, since the rate of the generation of reflected electrons depends on the atomic numbers, the image has an atomic number contrast, too. Normally, the resolution is 20–100Å.

(7) EPMA (Electron Probe Micro Analyzer)

With EPMA, thin electron beams of 50–60Å is irradiated over the sample, and the characteristic X-rays emitted from the irradiated part are detected to identify the existent elements (${}_{4}\text{Be} - {}_{92}\text{U}$), their places (μm order) and the amounts (0.001 W % – 100 %). Besides the qualitative/quantitative analysis of the elements of small particles, this analyzer is used to analyze the geometric forms, electric characteristics, crystalline status of the particles from the electronic and optical signals.

Normally, EPMA has four analyzing functions; (1) Surface observation (2) elemental analysis (3) bonding status analysis, and (4) inner characteristic and crystal analysis.

When electron beams are irradiated to the sample, most of the incident electrons will be transformed into heat, but, as shown in Fig.3.3.1²², a lot of signals will be generated as well.

- (i) A part of the incident electrons are reflected in the vicinity of the sample surface, and scatter out of the sample as back scattering electrons (i.e. as reflected electrons). The intensity of the back scattering electrons changes according to irregularities on the sample surface. Moreover, the intensity increases as the atomic number increases. Thus it can be used for estimating the status of the sample surface and the average atomic number.
- (ii) The incident electrons that scattered into the sample repeat the collision with atoms in the sample, emit secondary electrons, electromagnetic waves, X-rays, soft X-rays, ultraviolet rays, visible rays, near ultraviolet rays, and infrared rays of various energies, thereby losing their kinetic energy and flowing into the earth as electric current. Such electric current is called the "sample current" or the "absorption electrons" and serves for monitoring the amount of the incident electrons. In addition, in contrast with back scattering electrons, this current decreases as the atomic number increases, which is useful for estimating the rough composition of the part under analysis.
- (iii) Among the electrons emitted from the sample, those secondary ones which have the energy of 50 eV or less have some unique characteristics that cannot be found in back scattering electrons, and hence provides the most important signals for SEM.
- (iv) Among the electromagnetic waves excited by the collision with incident electrons, characteristic X-rays are used for the qualitative analysis of the elements at the point of incident electron irradiation, because there is a certain relationship between the wavelength of such X-rays and the atomic number of the sample. The quantitative analysis is also made possible by measuring the intensity of the X-rays. In addition, the wavelength, waveform and peak intensity of the X-rays slightly change according to the chemical bonding, so that it is possible to measure the bonding status of elements on the micro area.

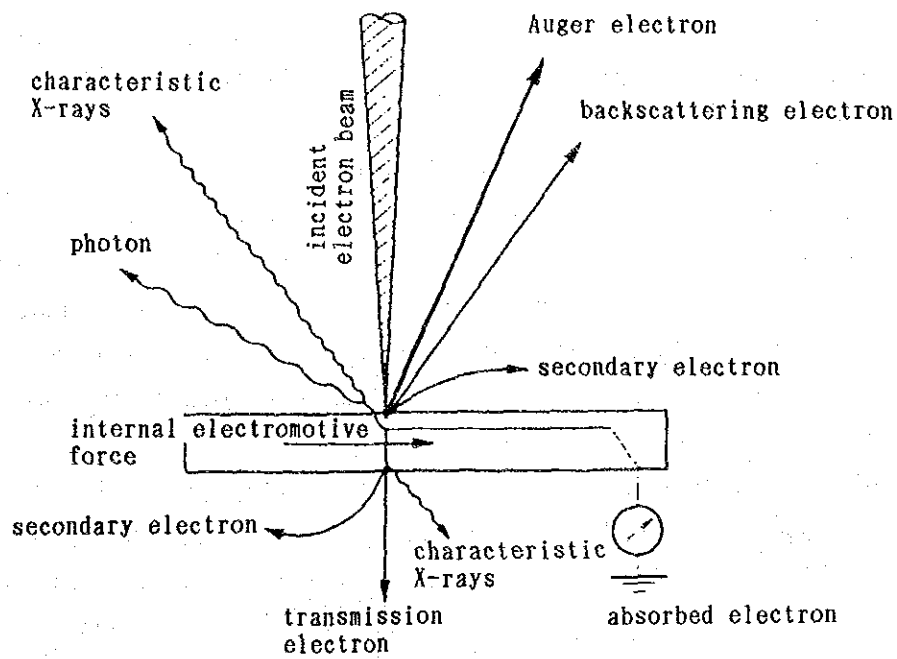


Fig. 3.3.1 Signals generated by the irradiation of electron beam ²²

- (v) Light whose waves are longer than those of X-rays (i.e. cathode luminescence) has a spectrum unique to each substance, and hence is useful for estimating the status change or the crystalline structure.
- (vi) Internally generated current is used for investigating flaws and characteristics of semiconductors and other products.
- (vii) When the sample is thin enough, a part of the incident electrons pass through the sample.

Such signals are used with STEM (Scanning Transmitted Electron Microscope).

The analyzer consists of an electron gun (to radiate electron beams), an electronic lens (to narrow down electron beams), a scan coil (to scan electron beams over the sample), a sample fine-adjustment system (to move the sample in the x-y horizontal direction and the z vertical direction, and to rotate or tilt the sample), a detector (for electrons or X-rays), a vacuum pump and other parts.

Thermo-electrons emitted from filament are controlled by Wehnelt, and then, after being accelerated by the electric potential between cathode and anode, are narrowed down to 50\AA – $500\mu\text{m}$ with a convergent/objective lenses to be irradiated over the sample.

Electrons are guided by an astigmatism compensation coil (to make electrons describe an exact circle over the sample) and an electron beam deflecting coil (to control the movement of incident electrons over the sample within the range of $1\mu\text{m}^2$ – 10mm^2). By scanning CRT synchronously with the electron beam deflecting coil, every signal can be displayed on CRT. Because the scanning width of CRT is constant, the magnification of the displayed image can be freely determined on the basis of the ratio between the scanning range on the sample and the area of CRT.

Together with the sample fine-adjustment system, the optical observation system must be used to detect and confirm the analyzing location. The optical observation system is indispensable for adjusting the analyzing location to the focus of the X-ray spectroscope. Furthermore, the signals of the cathode luminescence is retrieved and guided to the optical spectroscope through the optical observation system.

As for the X-ray detector, two types are available, that is, the wavelength-dispersive-type and the energy-dispersive-type. In the case of the wavelength-dispersive-type spectroscope, usually more than one units are used to simultaneously analyze one or more elements

${}^4\text{Be}$ – ${}^{92}\text{U}$.

Diffraction spectrum is gained from retrieved X-rays by using a concentration-type spectrum crystal before entering into the detector. By driving the spectrum crystal and changing the diffraction angle, any element can be selected for measurement.

The detector is installed in the vicinity of the objective lens and the sample. It consists of a scintillator and a multiplier phototube with around 10 kV of applied voltage, and detects

secondary or reflected electrons through off and on of this voltage. For the detection of reflected electrons, the semiconductor detector is also used.

With a rotary pump and a diffusion pump, the whole system is kept in a vacuum of 10^{-5} – 10^{-6} torrs.

The electric system consists of a power control system and a signal processing system. The power control system includes control circuits for high-pressure generation, exciting power, scanning, vacuum, etc. The signal processing system includes AC/DC signal processing circuits, a scaler (to display/record the results of measurement), a CRT, a recorder, etc.

When incident electrons scan over the sample two-dimensionally, the beams on the CRT are scanned synchronously and the signals generated from the sample enter the grids of the electron gun on the CRT. Brightness on the CRT being modulated according to the amount of signals, the structural forms on the sample are projected on the CRT. Thus, the intensity of signals is translated into the brightness on the CRT.

EPMA is mainly used for the component analysis of micro parts. The parts to be analyzed are determined on the basis of the results of surface observation.

For analyzing, the "point", "line", and "face" modes are available.

- 1) Point analysis: The point analysis includes the qualitative/status analysis by means of wavelength scanning and the quantitative analysis using the spectroscope fixed on a specific wavelength.
- 2) Line analysis: By moving either incident electron beams or the sample one-dimensionally, the change of element distribution on the line is analyzed.
- 3) Face analysis: By moving electron beams two-dimensionally, various signals are displayed on the CRT.

Examples of the application for fouling analysis are shown later.

(8) Infrared Absorption Spectrum Analysis

When infrared rays (IR) are applied on a molecule, only those IR which has the same frequency as the molecule are absorbed. Therefore, if light coming through the sample is divided into spectrum and then the frequency and absorption intensity of IR are measured, molecular structure will be estimated.

There are two types of infrared spectroscopy. One is the dispersive type IR spectroscopy that produces spectrum with a diffraction grid or a prism and detects rays with a thermo couple.

The other is the Fourier transformation type IR spectroscopy (FT-IR).

With the FT-IR spectroscopy, IR rays that have passed through an interferometer are applied to the sample. The interferometer consists of a beam splitter, a fixed mirror and a mobile mirror. Incident light is splitted into two parts with the splitter. Each of the splitted light is reflected on the fixed/mobile mirrors, and again merged into one with the splitter. When light passes through the interferometer, it is detected as interference waves in the detector. This phenomena occurs because its phase is displaced due to the difference of routes of reflected light, and light becomes interference waves. Since the interference waves have undergone Fourier transformation from normal spectrum, to obtain the original spectrum, measure the interference pattern by scanning with the mobile mirror, and carry out the reverse Fourier transformation.

Normally, scanning with the mobile mirror is done in seconds, and the whole wave number range is scanned by one operation. Fourier transformation is carried out by a computer.

Compared with the conventional dispersive type spectroscopy, the FT-IR spectroscopy has the following advantages.

- 1) No dispersion by diffraction grid or prism takes place. Neither is light slitted. So, use of light is very efficient and highly sensitive analysis becomes possible.
- 2) Since the whole wave number range is measured at the same time, time need for measurement can be greatly reduced.
- 3) Since the wave number compensation is done with laser beams, the wave number precision is high.

The FT-IR spectroscopy can be applied for the analysis of organic substances adhered on the RO membranes or the surface analysis of micro parts. It can also used for the analysis of dark or blackish samples or water solution.

In addition to the normal permeation method, the IR analysis include, according to the form of the sample, the reflection (ATR) method and the powder reflection method, both of which are applied for the analysis of fouling membranes.

Since a specific functional group of an organic substance has, even if molecules are different, an absorption approximately in the same wave area, the functional group and molecular structure can be estimated from the absorption wave number.

3.3.4 Examples of the Analysis of Fouling

(1) Analysis of Substances Deposited on the Membrane Surface Using EPMA

Deposit of particles or refractory salt in feed water lead to the formation of a cake/scale layer, or blocking of flow routes.

As the index for the substances contributing to the formation of a cake/scale layer, turbidity (NTU) and SDI are used. Using sample water (under the pressure of 206 kPa) and a membrane filter ($0.45\mu\text{m}$), SDI is calculated from the time needed to filter out first 500 ml of sample water, and the time need to another 500 ml after continuous filtering for 15 minutes. In Japan, SDI is defined as FI(fouling index).

Usually, SDI is correlated with turbidity. However, at the breeding season of seaweed, for example, SDI often rises while NTU is low, thereby a target value not being reached.

The analysis using EPMA shows that, as seen in Fig.3.3.2²³, the characteristics X-ray image of Si, Al roughly corresponds to the SC particle image, and hence the substances contributing to NTU seems to be diatom and clay particles of aluminosilicate family. No SEM image is obtained for the substances cause the rise of SDI but do not contribute to NTU.

As a result of the fluorescent X-ray analysis, elements P and S are detected. In the surface pattern, no characteristics of particles are recognized except some differences in spot density. This implies that the substances adhere over the membrane surface evenly. These substances seem to be macro molecular products of seaweed metabolism that are either colloidal or soluble.

This relates to the effectiveness of SDI as an index, and has nothing to do with the question if macro molecular substances captured on the membrane filter really contribute to the formation of fouling of RO membrane.

Fig.3.3.3²² shows the SEM image of diatom captured on the membrane filter. As can be seen, EPMA is also used for the observation of microorganism. With regard to the pretreatment, it is reported that aluminum sulfate and anionic high molecular coagulant are effective for removing turbidity of sea water in the Mediterranean that contains seaweed particles (less than 10^3 /ml).²⁴

However, in some cases where ground water was desalted with the RO membrane, PAC (polyaluminium chloride) used for the pretreatment leaked and produced a cake layer on the membrane surface. Fig.3.3.4²⁵ shows an example of analysis with XMA. The analysis on SEM's observation surface reveals the existence of Al as white spots. Overlapping this surface with the SEM image shows the even adherence of Al on the cake layer. The fissures of the cake layer is due to the drying of the sample for the SEM analysis.

Fig. 3.3.5²⁵ is not directly related to the RO membrane. It shows the XMA analysis of a lead phosphate layer deposited on the UF membrane surface, indicating that the particles consist of lead and phosphorus.

Fig. 3.3.6²⁶ shows a SEM image of coprecipitated particles consisting of calcium carbonate and strontium carbonate. The difference in crystalline forms is clearly recognized.

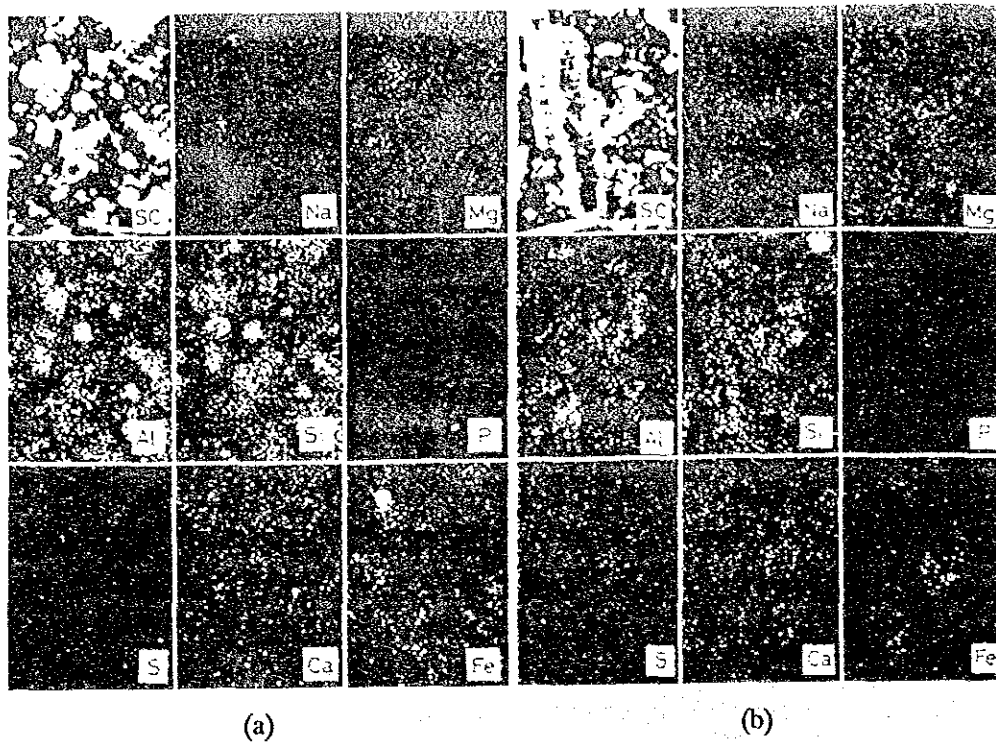


Fig.3.3.2 Sample current images and characteristic X-ray images of the particles on the membrane filter ²³
 (a) Turbidity:0.8ppm; MFT:219; (b) turibidity: 1.1ppm; MFT: 3085
 MFT:Filtering time with 0.45 μ m MF(sec/l sample)

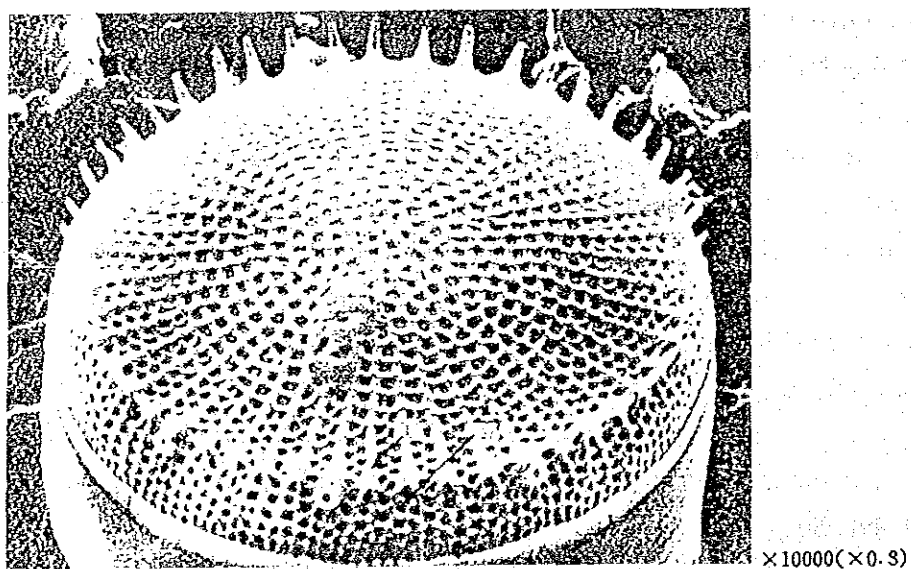
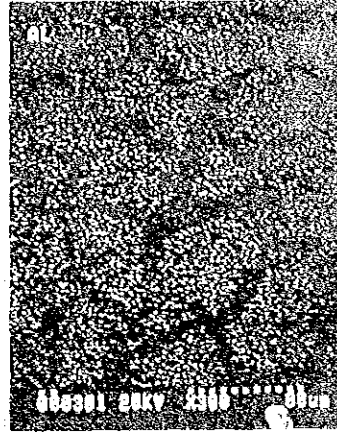


Fig.3.3.3 SEM image of diatom ²²

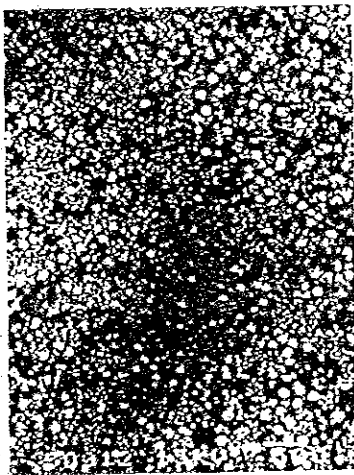


SEM

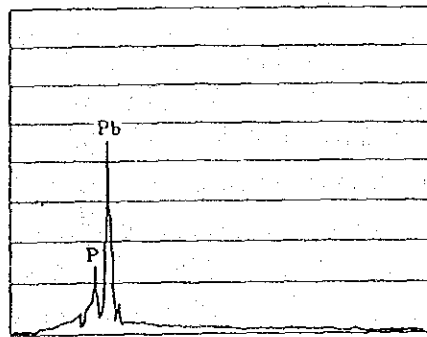


XMA
(surface analysis: Al)

Fig.3.3.4 SEM, XMA image of RO membrane fouled by the coagulant ²⁵



SEM



X-MA chart

Fig.3.3.5 XMA analysis of lead phosphate crystal deposited on the UF membrane ²⁵

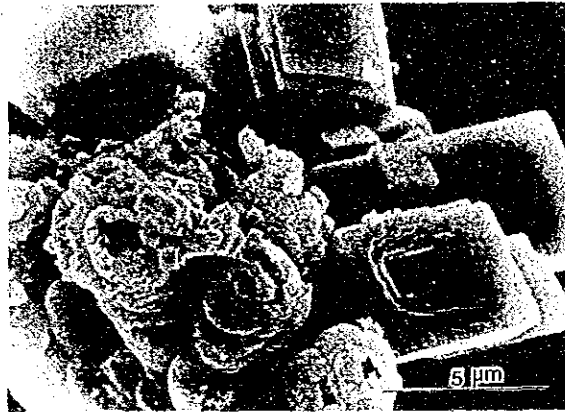


Fig.3.3.6 SEM image of coprecipitated particles of calcium carbonate and strontium carbonate ²⁶

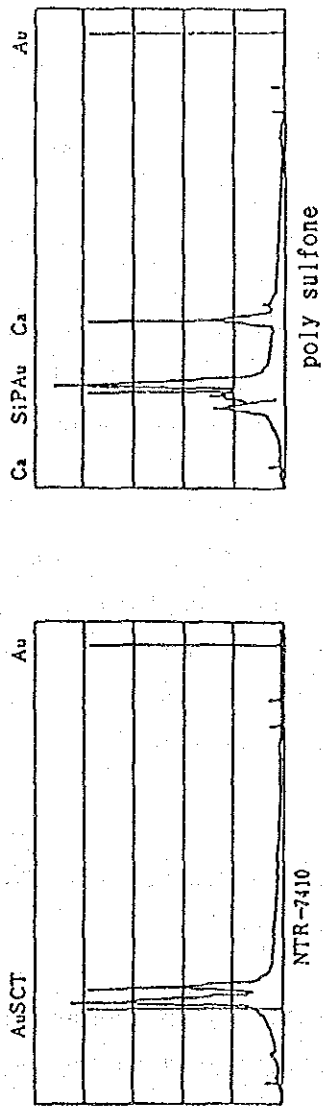
EPMA can be applied for all the examples stated above. For the case of scales containing refractory salt (such as carbonate, sulfate, silica, etc.), EPMA provides a very effective method for observing the forms of deposit and identifying the compounds.

Recently, several types of fouling-resistant membranes have been made available. EPMA is also used to evaluate membrane's performance and helps in selecting one that has excellent fouling-resistant quality.

The XMA analysis (Fig.3.3.7²⁵) shows that, in ground water containing a large amount of colloidal silica, the adsorption rate of Si and Ca depends on the type of membrane. The spectrum of Au is due to the gold vapor deposition of the sample for analyzing.

In actual RO facilities, ferric chloride is often added to the pretreatment. ²⁷

In a seawater desalting plant (capacity: 800 m³/day) where the desalting function of the membrane module decreased, it is estimated that the decrease was due to the accumulation of ferric substances on the membrane surface, which caused chemical deterioration of the membrane through catalytic action. ²⁸ Usually such ferric substances deposited on the surface of RO membrane are removed by the chemical cleaning with citric acid solvent. It is not rare that a trace amount of ferric substances remained in the feedwater after pretreatment contribute the fouling of RO membranes. EPMA can be used to explain such phenomena.



S means absorption from membrane itself

Fig.3.3.7 Difference of siliceous absorption rate ²⁵

(2) Examples of Analysis Using the Infrared Analyzer

Fig. 3.3.8²⁵ shows the measurements of the FT-IR spectrum of UF membranes made of different materials. The spectrum was measured after each membrane was put in electro-deposition paint solution.

The difference spectrum between each membrane with a adsorption layer and a new membrane was measured. It is evident that the formation of a adsorption layer depends on the type of membrane.

FT-IR provides an effective way to evaluate the fouling caused by the adsorption of organic substances. As mentioned in previous (1), the use of anionic or cationic high molecular coagulant for removing turbidity may lead to the deterioration of membranes. FT-IR may also be used to investigate such problems.

(3) Estimation and Prevention of Scale Formation Caused by Refractory Salt in Seawater

ASTM standardizes the calculation methods for estimating the formation/deposition of CaCO_3 scales, refractory sulfate scales and silica scales. Other than scale layers, e.g., formation of cake layers or adsorption layers can usually be estimated with calculations and simple experiments.

(4) Estimation and Prevention of Contamination of Seawater by Organic Substances

As industrialization develops, seawater is increasingly contaminated by organic substances. It is, therefore, necessary to monitor/detect substances that may damage the RO membranes, and take preventive measures to ensure good quality of feed water.

For this purpose, the following analyzers are used.

1) Fluorescence analyzer

The spectrofluorometer analyzer detects more than 90 types of organic substances in water. There is a standardized method for general use.²⁹

2) Ultraviolet (UV) analyzer

For many organic substances, the absorption spectrum appears in the UV region of 220 – 260 nm. Use a mercury lamp as light source, and measure the absorption in the UV region with a non-dispersive photometer, then the existence of organic substances in seawater can be confirmed.

In Japan, the Environment Agency sets forth the regulatory maximum amount of organic substances ascribed by the "Water Pollution Prevention Acts" that each factory can daily discharge into the sea or lakes. The UV analyzer is used for measuring this amount.

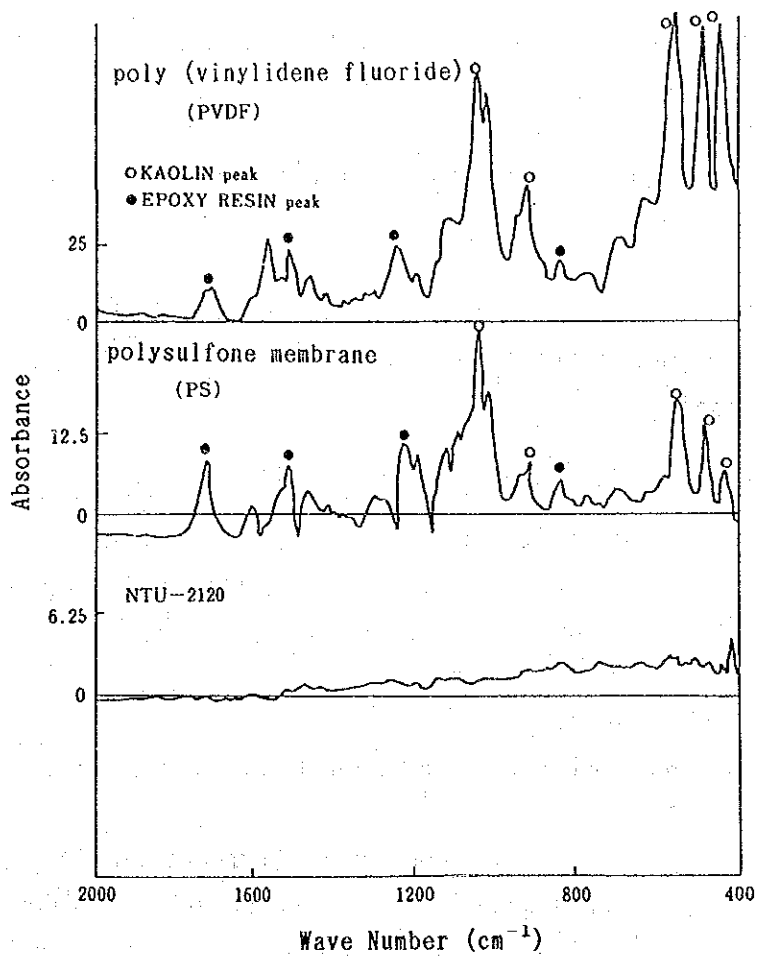


Fig.3.3.8 Measurements of the FT-IR spectrum of UF membranes ²⁵

3) GC-MS

Organic substances extracted with solvent from water are analyzed with GC-MS³⁵.

4) TOC analyzer (refer(25) in Table 3.2.4, in 3.2.1)

The TOC analyzer is widely used for detecting organic substances.

5) Petroleum

Petroleum is one of the substances that hinder the smooth operation of a RO plant. It is not rare that petroleum flow from a polluted source into the sea. For the quantitative analysis of petroleum in general.

There are standardized methods for analyzing the sources contaminated with petroleum. The apparatus to be used with these methods include the spectrofluorometer³⁰, gas chromatograph³¹, high performance liquid chromatograph³², and infrared spectrophotometer³³. For the quantitative analysis of S, Ni, and V, the fluorescent X-ray analyzer³⁴ is used.

(5) Analysis of Cleaning Process

The following factors are involved in forming foulings that need to be cleaned.

- 1) Although most of crushed rocks, sand, clay and other minerals carried into the sea by rain and wind are sedimented on the bottom of the sea, some remain in the shallow part and, through interaction between water, CO₂, O₂ and H₂S, repeat the process of association/dissociation (particles colloid dissolution). In seawater, there are substances which can form refractory salt (i.e., Ca, Mg, Sr, Al, Fe, Mn, SiO₂, PO₄, SO₄, CO₂, etc.). Those substances exist in a dissolved state (as ion or hydrate ion), or as colloid or crystalline particle. Although such salt or particles are removed in the pretreatment, a small amount of them still remains in water. *In order to prevent them from forming refractory salts, the concentration of pH, and HCO₃⁻ is controlled to keep it below a saturation level.*

Nonetheless, some of such substances deposit on the membrane surface. Also, a small amount of chemicals used for the pretreatment remain in water and deposit on the membrane surface. It is evident that Fe used as coagulating electrolyte deposits on the membrane surface, but the detail is still unknown. Whether Fe should be removed from feed water or by cleaning the membrane is to be selected from the economic point of view.

- 2) Products of metabolism on the ground, petroleum infiltrated onto the ground, and part of digged-out, petroleum finally flows into the sea. Although most of such substances are assimi-

lated by sea bacteria, a small amount of lignin, humin, tar, asphalt, pitch and other substances that cannot be assimilated by bacteria remain in the sea along with products of metabolism of sea creatures.

In addition to a wide variety of types, those substances are all macromolecules and have a wide molecular weight distribution. Some of them are estimated to have strong affinity with the RO membrane, and provide a factor contributing to the formation of an adsorption layer or a gel layer.

- 3) As bacteria, yeast, mold and other microorganism multiply themselves, slime is formed together with the products of their metabolism.

For the cleaning of fouling membranes, it is required to know the nature of each fouling constituent in relation with the selection of cleaning agent.

However, as explained above, in addition to the complexity of the system, the types of fouling constituents are so wide-ranging that it is often hard to obtain satisfactory results even with the analyzing apparatus mentioned in 3.2.

Some people attempt to clarify the formation of scales and the effect of cleaning using the salt labeled with radio-isotopes. This method, however, is time consuming and not very practical. More generally, cleaning effect is evaluated by comparing fluxes permeated through the membrane before and after cleaning. The recovery rate of flux is regarded as the criteria.

Another practical way for evaluating cleaning effect is to dry the deposit, put it in a cleaning solvent (with a constant temperature and concentration) for six hours, and then measure the loss of weight³⁸.

A large amount of water is used for cleaning. Cleaning water must meet the following requirements.

Fe < 0.05 mg/l

Mn < 0.02 mg/l

SiO₂ < 40 mg/l

Number of bacteria < 1000/ml

Number of coliform bacteria = 100/ml

NTU ≈ 0 mg/l

Free chlorine < 0.1 mg/l

In the cleaning process, scales and cakes are dissolved in acid or alkali, or they must be dissolved or removed by chelating agent (e.g. EDTA), chelate/complex compounds (e.g. polyphosphoric acid, formic acid, oxalic acid, citric acid, etc.).

The compounds of natural origin are removed by dissolving or dispersing by alkali or acid,

decomposition by oxidizing agents, digestion by enzyme, formation of micelle by surfactant or emulsification.

Microorganisms are sterilized by oxidizing agents, heating, or ultraviolet irradiation.

Some types of membrane have little resistance to acid, alkali, or oxidizing agent. Some have low durability not only to oxidizing agent but also to dissolved oxygen. Sodium hypochlorite to be used for sterilization does not permeate the membrane, so that the permeation side of membrane surface cannot be sterilized. When used in the high pH area, sodium hypochlorite turns out to be effective, but, if pH is lowered, it may produce chlorine and cause the corrosion of the module or the deterioration of the membrane.

Instead, hydrogen peroxide or hydroxy acetic acid (bacteria-resistant spectrum is wide) which can permeate the membrane is generally used. Also, sodium hydrogensulfite is used to suppress the multiplication of aerobic bacteria.

Thus, the choice of cleaning solvent is an important factor in cleaning. Some part of the method for analyzing cleaning solvent and wastewater after cleaning is standardized (21). This method, however, remains rather simple, only specifying the way to titrate the amounts of acid, alkali, organic acid, oxidizing agent, etc.³⁹

In many cases, the effect of sterilization is measured by the number of living bacteria. In ASTM, Standard Methods, and JIS, the test methods are standardized for general bacteria and heterotrophic bacteria.

If necessary, test should be conducted for yeast or mold.

(6) Proposal on Analyzing Methods

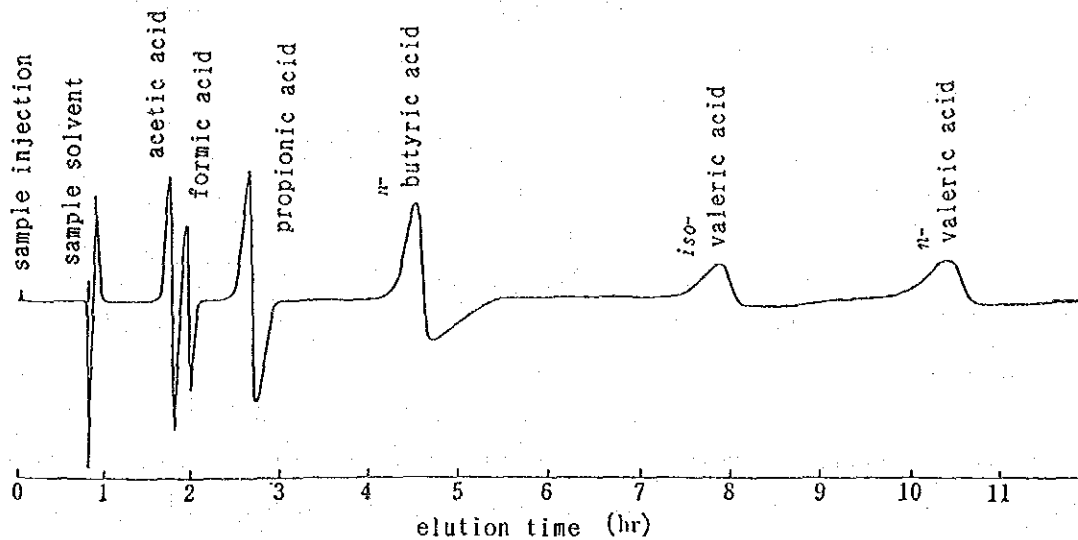
As explained in the preceding section, cleaning agents used in the cleaning process are wide-ranging and complicated. It is, therefore, hard to apply a uniform method for analysis. The following is the list of promising method for analyzing cleaning solvent as well as wastewater after cleaning.

1) HPLC

Fig.3.3.9⁴⁰ shows an example of the analysis of organic acid using HPLC. Besides organic acid, HPLC may be applied for the isolation-estimation of organic constituents used for cleaning. For measuring the molecular weight of natural macromolecular organic substances, the column of HPLC can be changed to the column of GPC (Gel Permeation Chromatography).

2) Automatic titration equipment

This equipment is used for pH titration of acid or alkali, potentiometric titration, amperometric titration, coulometric titration, etc.



Setting Conditions

separation column : length 1000mm, diameter 8mm
 detection column : length 70mm, diameter 8mm
 stationary phase : AG 1×8 (230-400mesh)
 eluate : 0.1N HCl
 development temp. : room temp.
 detection temp. : 35°C
 velocity : 0.63 ml/min

Fig.3.3.9 Chromatogram of lower fatty acids mixture ⁴⁰

3) Coulometric titration equipment

This equipment is used for estimation of various substances such as free chlorine, oxidation-reduction compounds and chelates.

4) Polarograph

This equipment is used for reviewing the behavior of electrochemical oxidation and reduction of organic substances and the estimation of organic compounds.

5) Ion chromatograph

This equipment is used for the separation/estimation of anion, cation, organic acid, and ionic organics.

6) Zeta potential ⁴¹

By measuring electric charge, adherence/adsorption of colloidal or micro particles on the membrane surface may be analyzed.

7) Oxidation–reduction potential (ORP) meter ⁴²

This equipment is used for the control, analysis and concentration measurement of the process that uses oxidizing / reducing agent (e.g. sterilization).

Recent development of analyzing equipments have been remarkable. Interest is mounting in the methods utilizing nucleus bonding energy of inner-shell electrons, especially in the status analysis and surface analysis.

For analysis, water has been used as solvent, but, since water is only a medium and not essential, recent trend is to adopt the dry method (without using water) instead of the wet method. The RO, however, is a technique for treating water, so it is natural as well as practical to carry out analysis in water solution. To analyze the fouling phenomena, it is necessary to get to know the behavior of collids and particles on the membrane interface in water. In other words, recent development of electrochemical methods should be employed from aqueous chemistry point of view.

3.4 Measurement and Analytical Techniques for the Operation Management of Wastewater Treatment Plants

A wastewater treatment plant constitutes a system which incorporates various biochemical processes designed to adequately treat the wastewater from a designated source, with special consideration given to its discharge characteristics.

As discharge characteristics wastewater differ from source to source, even when they represent industrial premises of businesses in the same industry, it is generally the case that wastewater treatment system configurations also differ depending on the source. This means that operation management methods vary from plant to plant and therefore it is essential that each wastewater treatment plant be operated and managed in accordance with its own designated 'operation manual'. In this respect, it is also important that this be done with a thorough understanding of the technical principles involved in each process as well as the basic facts about the entire treatment system. Experience shows that the most suitable operating conditions of a wastewater treatment plant are found through the everyday practice of operation management.

The major components of the effluent from an RO plant are used plant-cleaning water, preservation liquid for membrane modules and concentrated wastewater released from membrane separation processes, of which the cleaning water and preservation liquid are the compo-

nents to be treated.

Since these are both organic wastewater for which biological treatment processes are generally used, the activated sludge process is taken as a typical example of such processes, and the basic measurement and analytical techniques involved in the operation management of a plant incorporating this process will be discussed hereafter.

3.4.1 The Activated Sludge Process

(1) Principles and Characteristics

When wastewater containing organic matter is aerated and stirred under suitable conditions, various aerobic microorganisms propagate and turn into so-called activated sludge by coagulating with the suspended matter and colloidal substances in the wastewater. This sludge is a biological sludge consisting of gelatin-like flocs containing numerous aerobic microorganisms with an excellent capability of adsorbing and oxidizing organic matter as well as having good settling characteristics.

The activated sludge process is a method used to remove organic matter by mixing this biological sludge with wastewater and aerating as well as stirring this mixture so as to take advantage of the metabolisms of the microorganisms. When left still the mixed liquor easily separates into supernatant liquid and activated sludge, thereby allowing the former to be released as treated wastewater and the latter sent back to the aeration tank for reuse in treating raw wastewater.

The purifying mechanism of the activated sludge process involves the following three steps:

- a. The adsorption of organic matter
- b. The oxidation and assimilation of the adsorbed organic matter
- c. The formation of flocs with good settling characteristics

The activated sludge process is a method of wastewater treatment based on biological oxidation action, incorporating a mixed matrix-sludge culture and is represented by the superimposition of metabolic functions and biological characteristics of various microorganisms, each similar to the fermentation action of an enzyme in the fermentation industry.

The activated sludge is a mixed-matrix sludge culture such as (i) bacteria, (ii) eumycetes, (iii) protozoa and (iv) metazoa, which purify wastewater together while interacting with each other through a food chain.

Fig. 3.4.1⁴³ is a graphical representation of a typical example of change over time of population sizes of various microorganisms.