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THE KINGDOM OF SAUDI ARABIA

RESEARCH COOPERATION FOR THE PROJECT OF THE SEA WATER DESALINATION TECHNOLOGY

BETWEEN

SALINE WATER CONVERSION CORPORATION (SWCC)

AND

JAPAN INTERNATIONAL COOPERATION AGENCY (JICA)

FINAL REPORT

SUMMARY

JULY 1992

JAPAN INTERNATIONAL COOPERATION AGENCY

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Chapter 1. Background and Outline

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1.1 Background and Objectives

The Kingdom of Saudi Arabia established a policy for large scale industrialization and infrastructure in a second Five-Year Plan. Thereafter it has been steadily promoting the country's industrial development. For this purpose, it is an important policy for the government to secure great quantities of industrial and municipal water. Since it is unavoidable that most water supplies rely on sea water due to Saudi Arabia's particular meteorological conditions, desalination plants have recently been playing an increasingly important role.

Due to these circumstances, the Governor of the Saline Water Conversion Corporation of Saudi Arabia (SWCC) requested the Japanese Government's cooperation concerning seawater desalination technology in November 1975.

According to this request, several preliminary discussions were made between Saudi Arabia and Japan. As a result, the Japan International Cooperation Agency (JICA) and SWCC signed the Records of Discussions (R/D) concerning this project in January 1982 and a desalination technical cooperation project (the Technical Cooperation Project) was commenced.

The Technical Cooperation Project is aimed at the transfer of Japanese desalination technology to the Kingdom of Saudi Arabia.

It consists of research cooperation and training cooperation. In this report, the contents concerning the above research cooperation (Research Cooperation) are summarized.

1.2 History

The main historical points of the Research Cooperation are as follows:

(1) January 1982 Signing of R/D for the Technical Cooperation Project
(dated January 12, 1982)
(2) October 1987 Signing of the document for 3-year extension of the Technical Cooperation Project (up to February 28, 1989)
(3) December1990 Reaching basic agreement related to research cooperation for reextension
(4) April 1991 Signing for re-extension which was delayed by the Gulf War
(up to February 29, 1992)

1.3 Outline of Research Cooperation

The contents of the Research Cooperation consist of the following four items:

(1) Establishment of research institute

(2) Basic experiments and studies on desalination by Multi Stage Flash process (MSF) using a test plant, etc.
(3) Basic experiments and studies on desalination by Reverse Osmosis (RO) using a test plant, etc.
(4) Studies on chemical analysis

During the above research cooperation, the collaborative research activities which have so far been performed are mainly classified as follows:

(1) Cooperation for establishment of research institute
(2) Cooperation for research equipment for collaborative research activity
(3) Training of the Saudi researchers in Japan
(4) Cooperation through implementation of collaborative research activity

Chapter 2. Contents and Method of Implementing Collaborative Research Activity

Chapter 2. Contents and Method of Implementing Collaborative Research Activity

2.1 Contents of Collaborative Research Activity

The research themes concerning MSF are as follows:

(1) M-1 Laboratory experiment on scale prevention
(2) M-2 Corrosion tendency for some kinds of materials
(3) M-3 Study on some materials by corrosion measurement apparatus
(4) M-4 Analysis of oil dispersed in raw seawater at the heat rejection section of MSF plants

Research themes concerning RO are as follows:

(5) R-1 Sterilization
(6) R-2 Pretreatment of seawater
(7) R-3 Pollution effect of membrane cleaning discharge
(8) R-4 Selection of membrane
(9) R-5 Chemical cleaning of the fouled membrane
(10) R-6 Selection of membrane for hybrid type RO
(11) R-7 Standardization of the main analytical methods

In the meeting between JICA and SWCC in July 1991, concrete methods for executing the eleven research themes were discussed.

It was proposed that the research themes should be classified into research themes for which experiments are essential (experimental research), and into ones for which experiments are not necessarily essential and literature survey is more important (literature survey).

In the above research themes, M-1, M-4, R-2, and R-6 were classified as "experimental research" themes and M-2, M-3, R-1, R-3, R-4, R-5 and R-7 were classified as "literature survey" themes.

2.2 Implementing Organization for Collaborative Research Activity

Collaborative research has been carried out according to the following activities:

(1) Top-level decisions for implementing the collaborative research activity were made at a "joint meeting" consisting of selected persons from JICA and SWCC.

(2) The Joint Technical Meeting (JTT) was guided by the above "joint meeting" committee.

(3) Two team leaders, one selected from JICA and one from SWCC, discussed and determined daily issues.

(4) In the case of experimental research, two RO groups and two MSF groups were managed by one team leader each.

2.3 *Implementation of Experimental Research and Literature Survey*

Before the commencement of research, in October 1991, 10 researchers from JICA were dispatched to SWCC to explain and discuss the basic policy, contents and implementing methods, the matters organized by SWCC and so on for collaborative research activity.

The researchers dispatched from JICA stayed at the project site from October 1991 to February 1992, and conducted experimental research and literature surveys together with researchers from SWCC.

Computer retrieval of literature was carried out by the JICA team. The SWCC team supplied the relevant materials to the JICA team. Review of these materials was jointly carried out.

Concluding the experimental research and literature surveys, the JICA team presented SWCC with the Report on Experimental Research and Literature Surveys in the form a Draft Final Report, discussed the contents of the Report with the SWCC researchers, and jointly completed the Final Report.

Chapter 3. Experimental Research

3.1 M-1 Laboratory Experiments on Scale Prevention

1. Introduction

There are two methods presently employed, the acid dosing method (A.D.Method) and the chemical dosing method (C.D.Method).

The C.D.Method is the most commonly used method for the prevention of scaling in the Middle East, due to its anti-corrosiveness and easy operation. However, recently, as the pollution of seawater has become an apparent problem, how effective this scale prevention method is, when contaminated seawater is used to raw seawater, remains uncertain. Consequently, the main objective of the research is to determine, by laboratory-scale experiments, what effect contaminated seawater has on the C.D.Method.

2. Literature Survey

The properties of contaminated seawater(using crude oil pollution as a model) and the technology necessary for the prevention of scaling were investigated.

2.1 Item of Survey

Influence of seawater contaminated with oil on the effects of scale inhibitors.

2.2 Method of Survey

Online retrieval using data bases such as JOIS-JICST and DIALOG.

2.3 Result of Survey

No literature corresponding to the item of search could be found, though literatures issued over the past ten years were searched.

3. Experiment

3.1 Plan of Experiment

The aim of this experiment is to quantitatively grasp how the effects of scale inhibitors are influenced by the presence of oil. To clarify this issue, the temperature and the concentration factor of brine must be adjusted in accordance with those of the actual plants, and scale must be generated in the case where scale inhibitor is not added.

Consequently, the following two matters have been taken into consideration.

(1) To add Na_2CO_3 solution for the breakage of supersaturated state and the formation of precipitation.

(2) To evaluate the amount of precipitation formed by the amount of decrease in M-alkalinity.

The concentration of seawater has been determined to be 1.4 times of that of the Arabian Gulf in accordance with the Al-Jubail Phase-II plants.

The experiments are divided into two separate stages - the primary experiment and the main experiment.

(1) Preliminary Experiment

The primary experiment was tried to clarify the attention items for experiments beforehand, so that the main experiments could be conducted effectively and quickly.

(2) The Main Experiment

Most of the experimental conditions were obtained by the primary experiment.

3.1.1 Breakage of Supersaturated state and Formation of Precipitation

Sea water in the Arabian Gulf does not cause precipitation even though it is concentrated to 1.4 times at 60°C and then it is heated up to 95°C keeping the concentration factor constant. That is, this water is stable in the supersaturated state.

When Na_2CO_3 is added to the brine in this state, carbonate is consumed for the formation of precipitation of $CaCO_3$ and M-alkalinity begins to decrease. When Na_2CO_3 is further added, there is a point at which M-alkalinity begins to rise. Brine is put in the saturated state under this condition. When Na_2CO_3 is added further, the formation of precipitation and the increase in M-Alkalinity continue with the solubility product of $CaCO_3$.

However, the degree of the rise of M-alkalinity greatly changes according to the presence and the retention time (reaction time) of a scale inhibitor and also the presence of oil. To clarify these relationships is the most important point of this experiment.

3.1.2 Amount of Precipitation Formed and Decrease in M-alkalinity

In the batch type of experimental equipment like that used for this experiment, the amount of $CaCO_3$ precipitation formed and the amount of decrease of HCO_3, i.e. the amount of decrease in M-alkalinity are in proportional relationship. Consequently, the amount of decrease in M-alkalinity (unit: ppm as $CaCO_3$) is used as a measure for the formation of precipitation, looking upon it as precipitation converted to $CaCO_3$.

3.2 Experimental Conditions

Though the experimental conditions have been established in accordance with the initial plan, they have partly been modified in order to adapt them to the actual operating and environmental conditions as much as possible. The variable factors are shown below.

(1) Brine Temperature

Since the outlet temperature of the brine heater during normal operation is 90.56 °C in Al-Jubail Phase-2 plants, brine temperature has been determined to be 95 °C, and 80°C and 50°C have been added.

(2) Brine Concentration rate

It has been determined to be 1.4 times that of the normal seawater of the Arabian Gulf in accordance with the operating condition in Al-Jubail Phase-II plants.

(3) Concentration of Scale Inhibitor to be Added

It has been determined by using the standard concentration of 5 ppm of polymeric polycarboxylic acid base scale inhibitors as a yardstick. However, concentration of 3 ppm and 10 ppm were also considered for comparison.

(4) Concentration of Oil to be Added

Three conditions in the range of $1-100x10^{-3}$ ml/liter have been adopted.

(5) Retention Time of Scale Inhibitor

Three conditions, i.e. 5 min., 17 min., and 60 min. have been adopted.

3.3 Experimental Methods

Experimental methods can be roughly classified to the following two items.

(1) Preparation of concentrated seawater
(2) Experiment on the deposition of precipitation

3.3.1 Preparation of Concentrated Seawater (Brine)

To imitate the recirculating brine of the actual plants which have adopted the chemicals dosing method for prevention of scaling, vacuum evaporation must be adopted under the temperature of 60°C and below to concentrate seawater to 1.4 times without causing precipitation. For this reason, a rotary evaporator on the market has been used.

3.3.2 Experiment on Deposition of Precipitation

The three-neck flask attached to the cooler has been used and condensed water has totally been returned to this flash. An oil bath and a vacuum pump have been used for raising temperature and keeping it constant.

4. Experimental Results and Discussion

4.1 Experimental Results

Residual M-alkalinity for each influence factor has been summarized, looking upon that the amount of precipitation corresponds to the value which is calculated by deducting residual M-alkalinity after the occurrence of precipitation from that at the time of the charge of brine. Figs. 3.1.1, 3.1.2 and 3.1.3 show summarized results.

4.2 Discussion

4.2.1 Influence of Retention time and Concentration of Oil on M-alkalinity

Fig. 3.1.1 shows the relationship between residual M-alkalinity and retention time at each 5, 17 and 60 min. after the moment when precipitation has been forcibly formed by adding in Na_2CO_3 to brine which was added with a scale inhibitor of 5ppm beforehand. (Initial alkalinity is 1,000 + 181.7 ppm as $CaCO_3$.)

When comparing the blank value at 5 min. after with the value when a scale inhibitor of 5ppm has been added, the residual M-alkalinity of the latter is larger and it means that this scale inhibitor has slowed down the growth of precipitation. However, when oil is added, the growth speed of precipitation increases (the reduction rate of M-alkalinity increases.). When oil of as much as 100 ppm is added, the reduction rate of M-alkalinity increases up to nearly three times of that in the case of no added oil.

On the other hand, as retention time becomes longer, the difference in M-alkalinity mentioned above becomes smaller gradually and, 60 min. after, residual M-alkalinity values under all conditions converges in around 150 ppm as $CaCO_3$. This value corresponds to the M-alkalinity value before Na_2CO_3 is added and it means that both the scale inhibitor and oil are hardly concerned in keeping a supersaturated state.

When looking data of 60 min. after, the presence of oil has no relation to the occurrence of precipitation and the action of the scale inhibitor can be said to be only the effect giving the distortion to crystals. The retention time of circulating brine is two to three minutes in actual plants of 20,000 t/d class and data of 5 min. after therefore seem to be the most important.

From these data, it can be said that the presence of oil in actual plants with retention time of two to three minutes becomes the cause of accelerating precipitation and higher oil concentration accelerates more.

4.2.2 Influence of the Concentration of Scale Inhibitor on M-alkalinity

Fig. 3.1.2 shows the correlation between the residual M-alkalinity and the concentration of a scale inhibitor added at five minutes after the scale inhibitor comes into contact with precipitation under the conditions of oil concentration 100 ppm and 95 °C.

It is clearly seen from this figure that the inhibitor of more than 3 ppm has no effect to prevent precipitation. This value perfectly coincides with the concentration of the scale inhibitor added of three to four ppm in Al–Jubail Phase–II plants. This fact has proved that scale prevention has been carried out effectively and economically in these plants. This fact has also proved the adequacy of this evaluation method.

4.2.3 Influence of Temperature on M–alkalinity

Fig. 3.1.3 shows the correlation between temperature and residual M–alkalinity at 60 minutes after the scale inhibitor comes into contact with precipitation under the conditions of the concentration of scale inhibitor 5ppm and the same of oil 1 and 100 ppm, together with blank values. The followings can be concluded from this experiment.

(1) Though the influence of oil is not so large under the conditions of retention time 60 min. and 50°C, the higher concentration of oil still lowers residual M–alkalinity and accelerates the growth of precipitation.
(2) Under the conditions of retention time 60 min. and 80 °C, the decrease in M–alkalinity is similar to that at 50°C when oil is not included. However, the higher the concentration of oil is, the larger decrease in M–alkalinity in comparison with that at 50 °C when oil is included.
(3) Under the conditions of retention time 60 min. and 95 °C, the effect of the scale inhibitor and the influence of the concentration of oil completely disappear, and the decrease in M–alkalinity is accelerated.

5. Conclusion

Experiments and investigations have been conducted on the relationships between the effects of inhibitors on precipitation and each of the concentration of oil, retention time (reaction time), temperature, and the concentration of inhibitors by excessively adding carbonate ion, being different from practice in general, to brine and forcibly forming scale to clarify the change in the performance of scale inhibitors which are now used in the actual plants, when crude oil intruded into raw seawater.

The results acquired by these experiments are as follows:

(1) The presence of oil is a factor to accelerate scaling and the degree of scaling becomes larger for higher oil concentration.
(2) Polymeric polycarboxylic acid base scale inhibitor "X" which has been used in this experiment has ability to suppress scaling when it comes into contact with brine under scale forming conditions. However, its ability diminishes as contacting time (retention time) becomes

longer and it completely disappears after 60 min.

(3) There is no difference in the effect of scale inhibitor "X" in the range of temperature tested when oil is included, even through this inhibitor of more than 3 ppm is added.

6. Recommendation for Future Research Activities

In this experiment, the amount of precipitate has been evaluated from the decrease in M–alkalinity by primarily grasping the generation of precipitate when grasping the phenomenon of scaling in MSF. However, all of 'scaling substances', i.e. precipitation, do not necessarily adhere to heat transfer tubes as scale.

Concentration gradients in the vicinity of heat transfer surfaces are necessary for the adhesion of scale and it allows the phenomenon of scaling to be connected with the conception of the fouling factor which is most important for the stable operation of MSF over a long term. Also, there is a close connection between the difficulty in removing scale by ball cleaning and the decrease in fouling factor.

From the above–mentioned viewpoint, a long–term experiment under various conditions changing the kind and concentration of oil and the kind of scale inhibitor is considered necessary as research to be carried out in the next stage to clarify the decrease in heat transfer coefficient (increase in the fouling factor of a heat transfer tube) when oil intruded into raw seawater.

Though it can be thought to use a test plant directly for these experiments in a heat transfer state, it needs a complicated process such as the cleaning of the inside of equipment when experimental conditions are changed, since oil is introduced into the test plant. If contingency planning is necessary in SWCC, it is considered that bench–scale tests using equipment having heat transfer surfaces should be carried out and then confirmation tests using a test plant should be conducted after experimental conditions have been strictly selected through bench–scale tests.

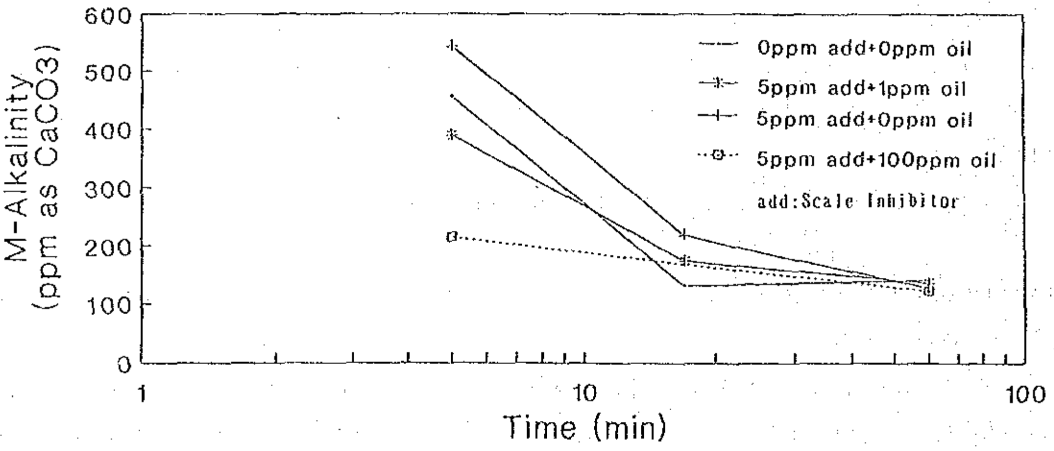


Fig. 3.1.1 Effect of Retention Time on M–Alkalinity (95 °C)

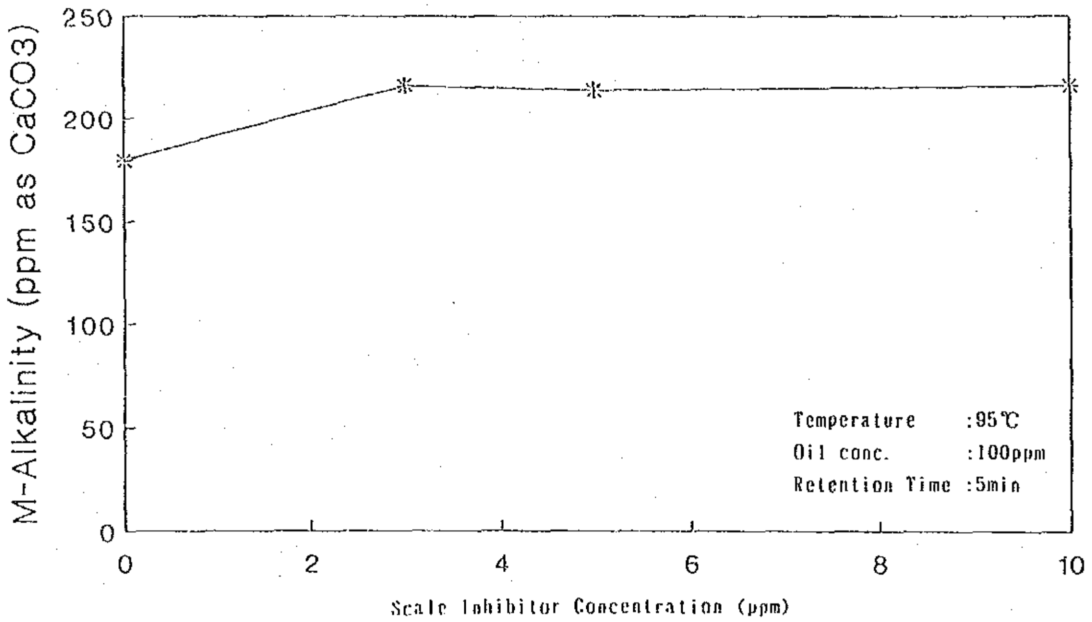


Fig. 3.1.2 Effect of Scale Inhibitor Concentration on M-Alkalinity

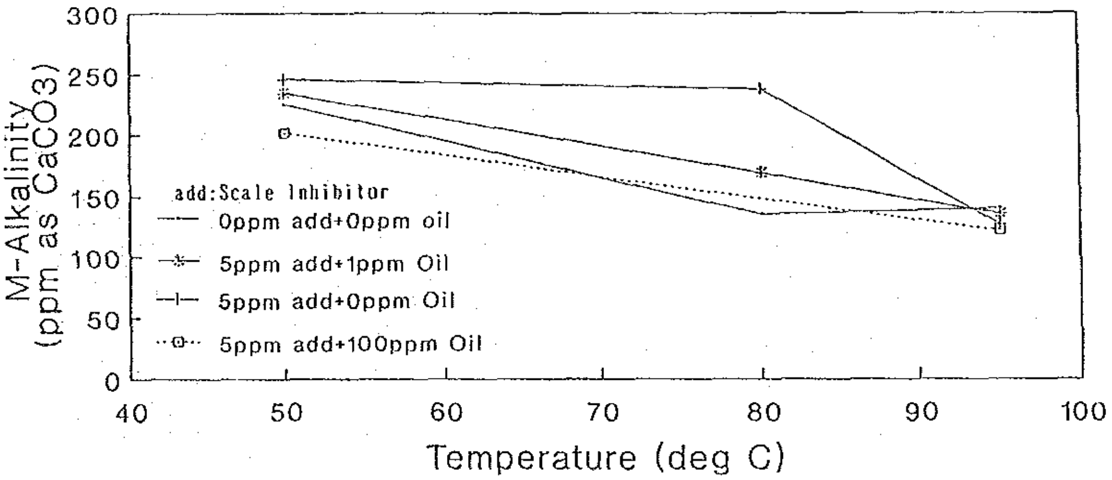


Fig. 3.1.3 Effect of Temperature on M-Alkalinity(Retention Time: 60 miin.)

3.2 M-4 Analysis of Oil Dispersed in Raw Seawater at Heat Rejection Section of MSF Plant

1. Introduction

In order to devise countermeasures to protect the internal equipment of the MSF plants, together with developing an understanding of behavior of oil in flash chamber and evaluating its effects on the quality of the product water, it is necessary to develop a method of analysis of oil in seawater and product water.

Moreover, it is important to survey the relevant data to study several phenomena (particularly evaporation of water and evaporation/condensation of oil which occur in parallel with it) which occur concurrently within the plant.

The main aim of this task is to study transferring mechanism of the oil constituents by carrying out a bench top laboratory experiment and to find a suitable method of oil analysis in sea and product water.

2. Literature Survey

(1) To survey the most suitable analytical method for oil present in product water, seawater and brine

(2) To survey the information on behavior of contaminants, particularly oil, in an MSF plant

2.1 Method of Survey

On-line data retrieval was carried out from data base such as JOIS-JICST, STN and DIALOG.

2.2 Result of Survey

Some literature was found for the evaporation process of oil-contaminated sea water. The most comprehensive report was "Countermeasures against oil contamination of sea water desalination plant by MSF" published by the Water Re-use Promotion Center, Japan.

For the analysis of oil-containing water, scanty literature was found. However, none seemed to serve our purpose, and hence we reached a conclusion that an experiment was required.

3. Experiment

Using a device consisting of a rotary evaporator and other parts, brine* (containing 10, 50 and 100 mg/l of diesel oil**) was evaporated at three stages (95 °C, 630 mmHg -> 80 °C, 350 mmHg -> 50 °C, 90 mmHg) for around ten minutes each, thus imitating the flash chamber of the actual system. Approximately 20 ml of distillate was collected after each flashing for analysis.

In addition, to simulate the deaerator and first stage vapor room of the actual system, brine (containing 10 mg/l of oil) was evaporated under the condition of 50 °C, 90 mmHg -> 95 °C, 630 mmHg.

*) pH: 8.08, electric conductivity: 7.83 x 10^4 μS/cm, Cl: 32,900 mg/l
**) C: 87.5 %, H: 11.4 %, N: not detected, S: 1.6 %

4. Results

4.1 Evaluation of Methods of Oil Analysis

In this experiment, comparison of three widely recognized methods for analyzing organic substances in water was made (TOC, IR, and GC/MS methods).

Needless to say, for the comparison of analyzing methods, the same sample should be used. However, in the case of water mixed with oil (i.e. double fluid phase), it is difficult to take out samples with exactly the same quality because of unevenness of the sample. Therefore, all of the samples obtained from each experiment were used for IR and GC/MS. In other words, the sample for each method was prepared from separate evaporation experiment. The results are shown in Table 3.2.1.

As shown in Table 3.2.1, even if some fluctuations in the evaporation experiments for three methods are taken into account, the values obtained by the IR method is generally the same as those by the GC/MS method, whereas the TOC's values greatly differ from them.

The TOC method is unsuitable for the samples containing refractory organic substances (the sample in this experiment is the case in point). This is due to the fact that, with the TOC method, samples must be taken directly from mixed fluid (water plus oil) rather than from organic solvent.

The results of the experiments show that both the IR and GC/MS methods can be applied to measure whole oil compounds in water. Between them, GC/MS method is capable enough to analyze not only total oil but also it can identify each individual oil compound. Moreover, in the GC/MS method, the extraction solvent is less toxic (methylene chloride is less toxic than carbon tetrachloride). Thus, the GC/MS is superior to the IR method.

4.2 Amount of Transferred Oil and Oil Concentration in Distillate

Table 3.2.2 shows the amount of oil transferred into distillate and oil loss. The values were measured by the GC/MS method (average).

As seen in Table 3.2.1, under the condition that brine flashes, the distillate resulting from the first evaporation process showed the greatest amount of oil regardless of temperature and pressure.

Table 3.2.1. Evaluation of Analytical Methods for Oil

mg/l oil in brine	Method	Analytical Oil mg/l in collected fractions Conc. 95°C	80°C	50°C	Brine
	TOC	3.0	0.94	4.02	NA
10	IR	0.6	2.5	1.1	0.7
	GC/MS*	19.1	6.29	2.75	0.90
	TOC	73.0	17.3	23.3	NA
50	IR	193.1	97.7	75.2	11.33
	GC/MS*	146.9	146.05	61.6	3.35
	TOC	285	78.2	69.8	NA
100	IR	445	351	273	9.63
	GC/MS*	537	453	245	7.55

NA=Not analyzed(because of high salt concentration)
* Average

Table 3.2.2 Transfer of Oil to Distillate (Mass Balance)

oil in Brine mg	Oil in Fractions 95°C 630mmHg	80°C 350mmHg mg	50°C 90mmHg	oil in Conc. Brine mg	Total % Recovery	% loss Escape Sedimentation Adherence etc.
5.01	0.54	0.11	0.03	0.31	20.0	80.0
4.71	0.41	0.12	0.11	0.39	21.9	78.1
4.86(Avg.)	0.48	0.12	0.07	0.35	21.0	79.0
26.02	4.91	3.65	1.70	1.87	46.7	53.3
25.69	3.40	2.69	1.07	1.05	32.0	68.0
25.86(Avg.)	4.16	3.17	1.39	1.46	39.4	60.6
50.64	10.4	10.6	7.55	3.45	63.2	36.8
50.06	11.4	7.26	3.77	3.14	51.2	48.8
50.35(Avg.)	10.9	8.93	5.66	3.30	57.2	42.8
	50°C	95°C				
4.98	2.52	0.85				
5.05	1.57	0.98				
5.02(Avg.)	2.05	0.92				

With a high degree of vacuum, the oil amount in the first distillate was particularly high. After the second evaporation process, the transfer of oil gradually decreased.

Undetected oil (the difference between the amount of oil contained originally in brine and the total oil contained in evaporated brine and distillate) may be due to the transfer of oil to the outside without being condensed (mainly light–gravity crude oil), the adherence of oil on the walls of the equipment, or, the change of efficiency of extracting organic solvent (methylene chloride) caused by the change of oil quality. Such loss of oil decreases as the oil originally contained in brine becomes greater.

Table 3.2.3 shows the oil concentration in the distillates and brine after evaporation.

As shown in Table 3.2.3, the oil concentration in the distillate reaches two to ten times the initial concentration in brine.

As for the composition of oil in distillates and brine after evaporation, their carbon number distribution patterns are basically the same as the distribution pattern of diesel oil (the greatest peak at C_{16}). For the first distillate, however, although C_{10} – C_{11} components exist in the case of 95°C (low degree of vacuum), there are no C_{10} – C_{11} in the case of 50°C (high degree of vacuum). For the third distillate, C_9 – C_{13} disappear completely. C_{11} – C_{13} remain in the post–evaporation brine.

Table 3.2.3 Oil Concentration in Distillate and Brine after Test

Oil in Before Test mg/l	Oil in Fractions 95°C 630mmHg mg/l	80°C 350mmHg	50°C 90mmHg	Oil in Conc. Brine After Test mg/l
10	19	6.3	2.8	0.9
50	147	146	62	3.4
100	537	453	245	7.6
	50°C	95°C		
10	96	51		

5. Conclusion

(1) Under the flash condition, the amount of oil transfer into distillate was greatest in the first distillate.
(2) For analyzing oil in water, the GC/MS and IR methods, which are standardized in the "Standard Methods" or JIS, are suitable.

6. Recommendation for Future Research Activities

As far as the transfer of oil into product water is concerned (when oil-contaminated sea water is used as feed water), the results of the experiment were consistent with the results of the values that were expected by the volatility of oil and evaporating condition. This theoretical analysis, however, was based on many assumptions. It will be necessary to further clarify those assumptions by conducting experiments using a test plant which simulates the conditions of the actual plants.

3.3 R-2 Pretreatment of Seawater

1. Introduction

Recently, oil pollution of seawater is becoming serious problem, and the pretreatment of seawater is one of the important processes of the total RO desalination process. Therefore, laboratory scale experiments were carried out to obtain fundamental data on effect of oil in seawater on the pretreatment process.

2. Literature Survey

2.1 Items of Survey

(1) The behavior of oil discharged in seawater, the oil concentration in seawater, and the particle diameter of oil in seawater

(2) Coagulating sedimentation and sand filtration of oil in water

(3) Effect of oil-contaminated water on the performance of RO membranes

2.2 Method of Survey

On-line information was retrieved from the following databases: DIALOG, JOIS-JICST, and STN. Information was studied and summarized.

2.3 Results of Survey

(1) In-line coagulation of raw water and filtration with a sand filter, is a general pretreatment process for seawater desalination equipment. No report could be found on whether this process was effective in removal of oil from contaminated seawater.

(2) As for the general treatment of oil contaminated waste water, there were reports on the process of air floatation separation with an oil separating agent like hydroxyethylcellulose, but there was no report on coagulation/sedimentation or coagulation filtration with flocculant.

(3) Oil in seawater is affected by the sun, waves and ocean currents, and the components which have a low boiling point, are evaporated into the air. The remainder are dispersed in seawater as oil drops. The oil concentration is in order of 10 to 50 mg/l, and the diameter of an oil drop is less than 5 - 20 millimicrons. The main component of remaining oil drops is a hydrocarbon, which has a boiling point of nearly 270 °C.

3. Experiments

After the literature survey on the removal of oil spill in sea water by coagulation/sedimentation process, the following steps were carried out in experimentally simulating the effect of coagulation/sedimentation and sand filtration on oil separation from contaminated seawater..

Step 1.

Preparation of simulated oil contaminated seawater.

Step 2.

Coagulation/sedimentation test using Jar-tester.

Step 3.

Filtration of coagulation/sedimentation effluents by filter paper, simulating sand filter unit.

Step 4.

Analysis of oil concentration in the raw oil contaminated water and filtrate of filter paper.

3.1 Plan of Experiment

As pretreatment of seawater for RO desalination equipment, coagulation and filtration processes are considered appropriate. In these processes the oil content of seawater is first coagulated with inorganic flocculant and then filtered through sand. To examine if this process is suitable as pretreatment for oil-contaminated seawater, experiments were carried out with simulated oil-contaminated seawater prepared by mixing oil with seawater.

3.2 Experimental Procedure

(1) From the results of the literature survey, it was thought that the component of oil in the water taken in by seawater desalination equipment was almost the same as the component of Japanese fuel oil "A". Consequently, fuel oil "A" was combined (as contaminating oil) with seawater by a mixer to prepare oil/water emulsion. This emulsion was used as simulated oil-contaminated seawater for a series of coagulation and filtration tests.

(2) By mixing fuel oil "A" with seawater, thick oil/seawater emulsion was made. Leaving the emulsion to stand produced large diameter particles of oil which floated and separated on top. By adding seawater to the emulsion, stable oil-contaminated seawater with drops of less than 5 microns was prepared.

(3) Coagulation tests were carried out adding four kinds of flocculants at different concentration to oil-contaminated seawater in a jar tester of laboratory size, as the coagulating performance testing equipment.

(4) Usually a sand filter is used in the pretreatment equipment of feed to seawater RO desalination plants. To remove the flocs generated by the addition of flocculant, a batch type filter medium was required in this laboratory experiment. A preliminary test was, therefore, carried out to select a batch-type filter medium of laboratory size which provided a similar performance to that of a sand filter.

A filter medium is a porous solid and has the property of oil adhering to its surface. Filter mediums used for these experiments, however, must not have the property of removing oil from raw water by surface adhesion, and also it must be able to completely collect the floc generated by adding flocculant. To find a filter medium to satisfies these contradictory conditions, performances of various filter mediums were compared.

As a result, it was found that 0.18 g glass wool filled in a funnel almost satisfied the conditions. A series of coagulation and filtration experiments were, therefore, carried out using the filter medium.

(5) Although the flocculants generally used for the treatment of waste water are ferric chloride, aluminum sulfate, or PAC, hydroxyethylcellulose, a typical oil separating agent for the floatation separation of oily waste water, was also used.

4. Results and Discussion

(1) Use of Glass Wool as Filter Medium

A 1.5 to 20 ppm flocculant, such as ferric chloride, hydroxyethylcellulose, aluminum sulfate and PAC, was added to the simulated oil-contaminated seawater of 19 to 38 mg/l oil concentration, and the liquid was filtered through a 0.18 g filter medium of glass wool. The relation between each flocculant, quantity added (mg/l), and the oil concentration (mg/l) of the filtrate, obtained as a result of coagulation and filtration experiments, is indicated in the table below.

With the addition of more than 3 mg/l ferric chloride, the oil concentration of raw water was reduced to less than 0.25mg/l. With the use of aluminum flocculant, however, it was not possible to make an accurate analysis of the oil content because the floc generated by the flocculant went through the filter medium.

Type of flocculants, quantity of flocculants added(mg/l), and the oil concentration(mg/l), before and after the coagulation-filtration are listed in Table 3.3.1.

(2) Aluminum flocculant like aluminum sulfate and PAC is not considered appropriate because the floc generated by the flocculant is weak and fine, and has the possibility to go through a filter. Moreover, after a long period of operation when the aluminum which goes through a filter accumulates on RO membranes, it is difficult to remove the aluminum with cleaning. In contrast, however, flocculant with an iron base like ferric chloride is considered appropriate because it can be removed with acid cleaning even if it has accumulated on RO membranes after a long period of operation.

Table 3.3.1 Oil Concentration in Seawater before and after the Coagulation-Filtration Process (in mg/l)(Filter: 0.18 g of glass wool)(Oil concentration before coagulation (19 to 38 mg/l)

Dosage	1.5 mg/l	3 mg/l	5 mg/l	10 mg/l	20 mg/l
$FeCl_3$	1.1	<0.25	<0.25	<0.25	<0.25
PAC*			0.2	3.0	3.4
$Al_2(SO_4)_3$			2*	2*	2*
HEC^{3*}			5	2.8	1.3

Remarks:
*: Poly Aluminum Chloride
2*: Cannot be determined as the fine flocs in the filtrate passed through the glass wool filter
3*: Hydroxyethylcellulose

5. Conclusion

Four different coagulants -- 1) ferric chloride, 2) poly aluminum chloride, 3) aluminum sulfate and 4) hydroxyethyl cellouse --- were applied to the coagulation-filtration of oil in oil contaminated seawater. Oil employed was Fuel Oil "A" according to Japanese Industrial Standard corresponding to No. 4 in ASTM.

An emulsion in seawater containing 33 mg/l of Fuel Oil "A" was prepared by blending for a total period of 20 minutes. Ferric chloride was the most effective coagulant in the removal of oil from the oil-seawater emulsion using glass wool which has relatively low oil retention as filter medium. No detectable oil which was measured using nondestructive infrared oil meter ACM 220 was observed in the filtrate even when the ferric chloride was added to the oily emulsion at concentration as low as 3 mg/l. Remaining coagulant failed to produce the same result even at a higher coagulant concentration of 20 mg/l.

6. Recommendation for Future Research Activities

(1) In the experiments using the small size batch-type filter medium, it was confirmed that the process of coagulation by filtration with ferric chloride, was effective for the removal of oil in seawater. In the future, it will be necessary to carry out experiments to check the effect of this process on RO membranes, and to examine pretreatment using membranes and the air floatation separation method. This may be done by operating continuous coagulation and filtration equipment using a sand filter, and also by operating both the above equipment together with and without seawater RO desalination equipment on a long time and continuous basis.

(2) The design configuration of the dual media filter such as height of the media, particle size, and the linear velocity of water,is to be established in the new experiment.

(3) The membrane oil tolerance level and means of cleaning is also to be established.

(4) It is necessary to find out a quick and reliable method to analyze the oil concentration of seawater. The method must make it possible to analyze even a very low concentration of oil using preferable instruments.

3.4 R–6 Selection of Membrane for Hybrid RO Process

1. Introduction

In this study, the objective is to conduct first experiment using the flat membrane tester to test membrane performances and to establish the membrane most suited to the hybrid SWRO–MSF plant; in other words, the membrane module with the optimal salt rejection and flow rates. Another objective is to obtain basic information for different types of membranes.

2. Literature Survey

Various key words related to RO and their combinations were searched using JICST, DIALOG data bases.

2.1 Items of Survey

Membranes or membrane modules suitable for the hybrid RO process.

2.2 Method of Survey

On–line information was retrieved using the data base of STN, DIALOG, etc.

2.3 Results of Survey

Literature introducing advantages of the hybrid RO–MSF process was available but literature relevant to the items of the survey, i.e., identification of membranes suitable to hybrid system could not be found.

3. Experiment

The experiment was divided into two:

(1) Preliminary Experiment

Conducted on various samples to establish factors affecting experimental conditions for this type of test.

(2) Main Experiment

(a) Based on the results of the above preliminary experiment, experiments were conducted to confirm the reproducibility of RO membranes.
(b) Membranes with fouling were also analyzed.

3.1 Objective

The performance of several types of flat membranes which are considered to be potential candidate for hybrid SWRO-MSF desalination plants was measured to determine their salt rejection rate, amount of permeate, changes in their properties with time. Furthermore, used membranes were analyzed.

3.2 Experiment Items

(1) 3 types of flat seawater RO membranes were selected with different performances of low rejection rate and high water permeation rate.
(2) The feed water supply concentration was fixed 3, 3.5, 4 %, the changes in their RO performance over continuous operation were studied.
(3) The operational pressure was set at a steady, but relatively low pressure less than 5.5 MPa which was raised after accumulating sufficient data to 4.9, 5.9, 6.4 MPa. This was done to establish dependence of RO performance on changes in pressure.
(4) Fouling properties of fouled membranes were also analyzed.

3.3 Method of Experiment

The following materials were needed for the experiment, a flat sheet membrane testing device, RO membranes, an electric conductivity meter, a pH meter and others. All equipment were tested, calibrated and fixed or modified to suit the experiment.

RO membranes used in the experiment were: one type of cellulose acetate membrane, two types of polyamide composite membranes having a high salt rejection rate, two types of polyamide composite membranes having a slightly lower salt rejection rate, and one type of polyamide composite membrane having a low operating pressure.

The experiment was divided into tow parts: the primary test and the main test. The former was to confirm efficiency of each membrane under standard conditions and the latter to confirm efficiency under different conditions.

Based on the result of this experiment, applicability of membranes to the hybrid process was studied in reference to the efficiency of the module based on calculation from the simulation program.

4. Results and Discussion

Specifications of flat sheet membranes used for the experiment are shown in Table 3.4.1 and the test conditions in Table 3.4.2.

As a result of the experiment, the salt rejection rate of membranes was almost the same as the rate indicated by manufacturers, but in many cases the quantity of permeate exceeded their estimates. The relation between the salt rejection rate and the quantity of permeate is indicated in Fig. 3.4.1. The performance of membrane at the module level was calculated from the difference these amounts by simulation using a special simulation program.

When designing an actual module, it is necessary to restudy these conditions because the quality of product water fluctuated somewhat when the quantity of product water (a value to be used in the design of module) was changed.

Application of the hybrid process with the evaporation process was studied as a combination system, based on the result of this simulation. The effects of using each of the membrane in hybrid system were as follows, keeping in mind that further experimental work for a much longer period is required.

(1) For UTC80HR, the blending (mixing of the product water from the evaporation process) was not necessary but operating pressure of 6 MPa was needed.

(2) For UTC80HF, the blending ratio (a mixing ratio of the product water from the evaporation process) was 0.03 to 0.54 and the operating pressure reached 5.6 MPa at maximum.

(3) For SC8000, the blending ratio was 0.75 to 0.91 and the operating pressure was 7.05 MPa at maximum.

(4) For UTC70, the blending ratio was 0.72 to 0.82 and the operating pressure was 5.16 MPa at maximum. This was lower than the pressure of other types, however, the pressure exceeded the operating range of this membrane.

(5) For NTR759SW, the blending ratio was 0.28 to 0.52 and the operating pressure was 6.09 MPa at maximum.

(6) For NTR759HR, the blending ratio was 0.39 to 0.6 and the operating pressure was 5.57 MPa at maximum.

According to the above results, the two membranes UTC80HF and NTR759SW can be used in a low pressure range and have a blending ratio of 0.3 to 0.5 from which the hybrid process is practically applicable. These are polyamide composite membranes of the type having a slightly lower salt rejection rate.

5. Conclusions

The performance of five different types of seawater flat sheet membranes: "NRT759HR", "NRT759SW", "UTC80HF", UTC80HR", "SC8000" and one brackish water membrane "UTC70" was established using an Osmo 16Y-100F-TCB membrane tester that allows for the testing of 12 membrane samples at the same time. All the membranes are made of polyamide and are of the thin film composite type, except for the membrane "SC8000" which is made of cellulose acetate and has an asymmetric structure.

The membrane types and membrane makers are listed along with membrane structure and membrane performance in Table 3.4.2 which also lists the test conditions. With the exception of membrane "UTC70" which is a brackish water membrane, the remaining five are SWRO membranes. Amongst the SWRO membranes, the highest flux of 1.067 $m^3/m^2 \cdot d$ was obtained from the membranes "UTC80HF" and "NTR759HR" followed by the membranes "UTC80HR" and "NTR759SW", which have a flux of 0.8 $m^3/m^2 \cdot d$ each. The least flux of 0.56 $m^3/m^2 \cdot d$ was obtained from the "SC8000" membrane which also has the least salt rejection in the membrane series.

The highest salt rejection of 99.4 % was obtained from the membrane "UTC80HR" followed by the membrane "UTC80HF" with salt rejection of 99 %/ This test which was of limited duration, five days per membrane, was too short to draw a definite conclusion on the long term performance of the various membranes.

In order to evaluate whether these tested RO membranes are suitable for the hybrid RO membrane process, the process design simulation was calculated for these membranes, and it was found that the polyamide composite membranes with a slightly lower salt rejection rate, were suitable for the hybrid RO membrane process.

From this initial data, however, it can be concluded that the membranes "UTC80HF" and "NTR759HR" may be considered as the best in overall performance and may be used in a single purpose SWRO plant or in a combines hybrid Power–MSF–SWRO plant.

From this simulation study, we found that it is very important to consider not only permeate quality but also water flux to get the sufficient net driving pressure within a reasonable system design flux range in an evaluation of the hybrid RO system.

6. Recommendation for Future Research Activities

(1) To establish the long term performance of the two best performing membranes ("UTC80HF" and "NTR759HR") in this screening experiment, a long term testing of those two membranes is to be carried out on a pilot plant scale using large size modules. Evaluation shall also include the determination of the membrane properties in resisting fouling, and in resisting chemicals, etc., along with establishing their temperature and pH tolerance.

(2) Other high performance commercial membranes, not necessarily of Japanese origin, are also to be evaluated in this proposed JICA/SWCC study along with the above two membranes.

Table 3.4.1 Specification of Flat Sheet RO Membranes

Name	Material	Structure	Rejection* %	Flux* m^3/m^2 day	Test Condition
NTR759HR NITTO	Polyamide	Composite	99.0	0.60	3.2%NaCl $56Kg/cm^2$
NTR759SW NITTO	Polyamide	Composite	99.0	1.00	3.2%NaCl $56Kg/cm^2$
SC8000 TORAY	Cellulose acetate	Asymmetric	98.1	0.52	3.5%NaCl $56Kg/cm^2$
UTC80HF TORAY	Polyamide	Composite	99.3	0.90	3.5%NaCl $56Kg/cm^2$
UTC80HR TORAY	Polyamide	Composite	99.6	0.57	3.5%NaCl $56Kg/cm^2$
UTC70** TORAY	Polyamide	Composite	99.6	1.15	0.15%NaCl $15Kg/cm^2$

* As recorded by the manufacturer under the test conditions shown above.

** A brackish water membrane, the remaining five membranes are SWRO membranes.

Table 3.4.2 Membrane Test Conditions

Test	Membrane Name	Conditions (Feed)	
		Salt Concentration (NaCl.%)	Pressure (MPa)
Trial	SC8000	3.0	5.5
Primary	NTR759HR NTR759SW SC8000 UTC80HF UTC80HR UTC70	3.0, 3.5	5.5
Main	NTR759HR NTR759SW SC8000 UTC80HF UTC80HR	3.0, 3.5, 4.0	4.9, 5.5 5.9, 6.4
Main	UTC70	0.15	1.5

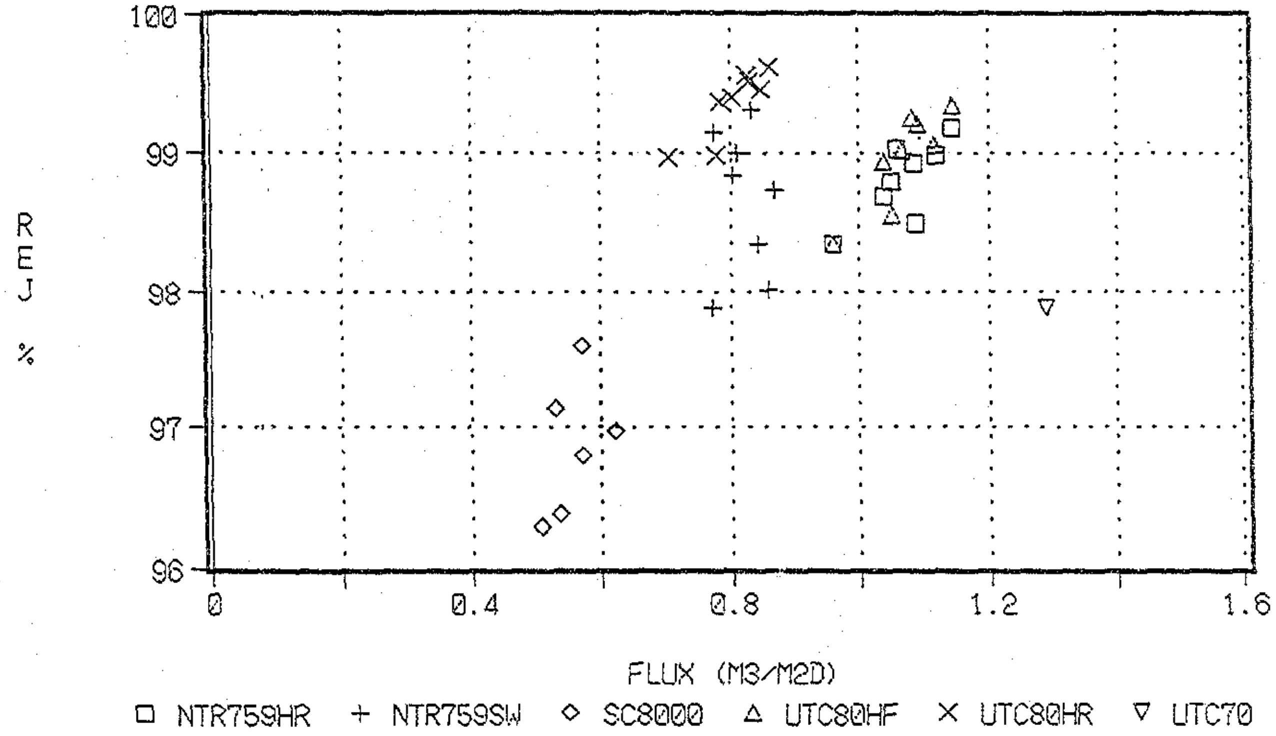


Fig. 3.4.1 Membrane Flux vs their Salt Rejection

Chapter 4. Literature Survey

4.1 M-2 Corrosion Tendency for Some Kind of Materials

1. Introduction

This is an attempt to evaluate the use of corrosion resistant materials in the MSF sea water desalination plant and try to determine the reasons and conditions focusing on materials for use in the heat transfer tubes. Also, it is necessary to investigate corrosion resistant materials now under development with possibilities of using them and based on the results of this research it is tried to find a future course and to determine a practical solution to deal with present technology for the prevention of corrosion, local corrosion such as galvanic corrosion mentioned above in particular. Consequently, this research will investigate up–to–date information already published and, with these results, examine and propose subjects for which the SWCC should conduct the necessary research and development project.

2. Planning

2.1 Method of Retrieval

The most widely recognized data bases are JOIS in Japan and DIALOG in the USA, and these were used as the main source of information.

2.2 Contents

(1) The characteristics of corrosion resistant materials used in the MSF seawater desalination plants.

(2) The corrosion behavior and technology for inhibiting corrosion of various types of corrosion resistant materials in a seawater environment.

(3) To provide information for the extraction of future research topics and for the planning of R&D by SWCC.

3. Result of Literature Survey

3.1 MSF Plant Metal Materials

3.1.1 - 3.1.3

First of all, the major metallic materials used for heat transfer tubes and structural materials in MSF plant were summarized in tables including items of the names, letter symbol of JIS grade, chemical composition, cost, physical properties, and mechanical characteristics of each material.

3.1.4 Corrosion Resistant Properties of Metallic Materials against Seawater and Brine

(1) Copper Alloys

First of all, experimental results on various samples to sea water were shown in figures. The influence of the flow rate and the dissolved oxygen concentration on the corrosion rate, the jet impingement test results, and various guideline data for flow rate selection, were introduced using figures and tables.

Next, the corrosion behavior of copper alloys in MSF, the failure rates (ratio of tubes with blind plugs) of the heat transfer tubes at the heat rejection section and the heat recovery section were studied. Furthermore, the corrosive effect of the acid additive method and the chemical additive method were compared by examining the failure rate of the heat transfer tubes at the heat recovery section. Next, monitoring results were shown on the test samples which had been placed inside the plant and monitored over 30 months at the heat recovery section and the brine heater. Also, in regards to comparing the corrosion resistant properties of 90/10 Cu–Ni and Al–Brass (Cu–Zn–Al), a lot of data was indicated on the log–log plotting, and there was a report which emphasized that there is no discernible difference between either.

In regards to corrosion from contaminated seawater, first of all, there are experimental facts that indicate that if the sulfides in the seawater do not coexist with oxygen, then it is not corrosive and can be explained electrochemically. Furthermore, the affect of contaminated seawater on the heat transfer tube, and the effectiveness of cathodic protection for the tube plate, were discussed. There was also discussion concerning the interchange process between the sulfide film and the normal oxide film. In addition, the effectiveness of the coating of artificial nonorganic film (composite of natural oxide film and corrosion resistant properties) developed by BNF (British Nonmetals Foundation), was shown.

In regards to chlorine dosing conditions, there were differing conclusions among researchers. For example, BNF has determined the specific chlorine dosing conditions for each kind of copper alloy. Also, in research on chlorine dosing for Yorkoron, a small amount of chlorine dosing (<0.5 ppm) is absolutely necessary for corrosion prevention. By stopping this, the activity microorganisms on the metal surfaces is promoted, the corrosion potential of the metal increases, and if the chlorine dosing amount is increased beyond this, the metal will have a high corrosion potential, resulting in localized corrosion.

There are several reports on the relationship between the hydrotalcite film and erosion corrosion which occurs on Al brass. The conclusion is that, on this white corrosion product, it is difficult for the iron compound film necessary for corrosion protection to adhere to this film. Therefore, it is explained that erosion corrosion occurs easily and consequently, there is research going on in different places to prevent generation of hydrotalcite. Finally, it was confirmed that there is a need to produce a small amount of iron hydroxide on the surface inside the tube. Furthermore, as there is a tendency of chlorine treatment of seawater to promote generation of white colored films, when the first iron ion is injected, it is desirable for chlorine treatment to be stopped. It is also advised that new ferric ions solution be used continually.

In failure data where stress is involved, there are explanations on ammonium stress corrosion in stored seawater, and intergranular stress corrosion cracking from high temperature steam and water. There are also reports on stress corrosion occurring in the expansion section of the Al-brass heat transfer tube and on the effectiveness of the cathodic protection. lastly, the report also touches on corrosion fatigue.

(2) Titanium and Titanium Alloys

Titanium has excellent corrosion resistance. There are problems with crevice corrosion in high temperature saline water, and hydrogen absorption. First of all, data on critical conditions for crevice corrosion to occur in titanium varies according to the method of experiment. However, according to data from Japanese researchers in particular, limiting condition based on electrochemical data on the passivation potential, limiting concentration, and limiting temperature, after corrosion occurs, have been announced. Also, the method for preventing crevice corrosion, atmospheric oxidation treatment of the surface and the method of forming the PdO/TiO_2 film (heat decomposition of $PdCl_2$ and $TiCl_3$ after coating) have been developed.

At the high temperature section of the titanium heat transfer tube in the MSF plant, it was discovered that hydrogen was easily absorbed. However in regards to this phenomenon, Japan has done the most research, and several hypotheses have been proposed concerning this mechanism. However, nothing definite has been confirmed. In experiments which have coupled titanium with several kinds of metals, when it is coupled with soft metal titanium hydrogen absorption is the highest.

Also, with the amount of hydrogen absorption at around 25 ppm, hazardous hyudride generation above this was confirmed. It has been confirmed that when copper alloys are coupled with titanium, (though it undergoes galvanic corrosion, and if that coupling is maintain at a potential range of 0.5 to 0.65 V), the copper alloy will be completely corrosion-prevented cathodically, and the titanium will not absorb hydrogen. The appropriate sacrificial anode material for this purpose is Fe-8Ni.

The crevice corrosion resistant property of Ti-0.15 Pd(Gr-7) compared to pure titanium, is excellent. However, as it contains a substantial amount of noble metals, it has the demerit of being expensive. Therefore, a cheaper material is being developed with the crevice corrosion resistant property comparable to Gr-7. In Japan, TICOREX (Ti-Ru-Ni) and Ti-0.05 Pd and Ti-0.05Pd-0.3 Co which has a lower Pd than Gr-7 has been developed. It has been confirmed that each have excellent crevice corrosion resistant properties.

(3) Aluminum Alloy

5,000 series or 3,000 series aluminum alloys are useful for their seawater resistance properties. However, these are also unreliable in their resistance to pitting corrosion. Therefore, there are only a few cases where they are used in desalination plants. As much data as possible concerning pitting was gathered and studied. Emphasis of the study was not on the occurrence of pitting itself but the rate of pitting growth, and especially preventing or inactivating pitting corrosion.

Aluminum alloys are extremely light, have a high thermal conductivity and are comparatively cheap. Therefore, there are high expectations for it is a material for heat transfer tubes in MSF plants. Research and development on aluminum alloys for heat transfer tubes in desalination plants is being done mainly in Germany and Saudi Arabia. One such development is an improvement on the Al-Mg type alloy. For example, seawater resistant properties of Al-0.6 Mg-0.7 Si-0.3 Cr are being researched in Saudi Arabia. With this series of alloy, after 8,500 hours, the depth of the pitting corrosion did not proceed further, and the inactivation of pitting was assumed. In other cases, it was presented that Al-6 to 8 Fe alloys with a small amount of Cr, Mn cooled rapidly by a special method showed a high pitting potential in seawater.

(4) Stainless Steel

Only super stainless steel can be recommended as stainless steel which has high resistance to seawater. This type of stainless steel was introduced into the market from the mid-1970's to the 1980's. It has undergone a testing period at production sites and has now entered the stage of practical application. The composition indicator used for developing this type of steel is the pitting index (PI). Many data on the relationship between the PI and the pitting characteristics of stainless steel have been obtained. The super stainless steel which is currently being actually used is classified into the austenite and ferrite series.

In the austenite series, as most of the steel types contain 6% Mo, this series is sometimes called 6Mo stainless steel. Typical of this type of steel is the Avesta Company's 254SMO (20Cr-18Ni-6.1Mo-0.7Cu-N). The superiority of resistance to pitting corrosion, crevice corrosion of the stainless steel in this series, compared to regular stainless steel, is clear from the data. Moreover, in a report concerning this type, a new method was proposed for indicating the level of crevice corrosion using the crevice ranking number based on the amount of crevice corrosion and its maximum depth.

Features of the ferrite series are its composition of high Cr, Mo, and extremely low C, N. Normally, more than 25% of Cr is contained. The superiority of the anti-pitting properties, anti-crevice corrosion properties, and the anti-stress corrosion properties of the typical steel types in this series, compared to regular stainless steel, has been confirmed.

When super stainless steel and brass based material were coupled, cathodic protection is required. In this case, an appropriate corrosion protective potential range with consideration for hydrogen embrittlement prevention of stainless steel, was obtained.

Moreover, in order to reduce material costs of MSF plants by suppressing the usage of 316 series in a low corrosive environment, substitutes of 11.5 Cr (409 steel) and 16.5 Cr (430 steel) were proposed. Electrochemical experiment verified that the above two types of steel had enough resistance to at least distilled water.

3.2 Non–Metallic Materials for MSF Plants

Non–metallic materials have not yet been used in large quantities for component materials of this type of plant, for which metallic materials are most popularly used. The reason for this is that metallic materials are essentially superior in, for example, heat conductivity as heat transfer tube materials, but it can more easily be attributed to insufficient basic data related to corrosion resistance and workability in utilizing nonmetallic materials and to a lack of reliability due to the absence of these data. When conventional nonmetallic materials have been used, improper selection of materials or improper working has caused accidents, frequently impairing the reliability of nonmetallic materials themselves.

However, in general, many nonmetallic materials provide excellent corrosion resistance to seawater and are insensitive to pH, oxygen, carbon dioxide and hydrogen sulfide, which constitute problems in the case of metallic materials, and have an advantage of lower installation costs than those of metal. Consequently, except for the case in which no other material than metal can be used, such as for heat transfer tubes, more nonmetallic materials should be used for other components, and for this purpose, data must be collected to put nonmetallic materials into practical use and experimental equipment should be completed to systemati–cally acquire these data. It is also essential to collect the details of application examples available to date in the form of data bases and establish guidelines for the selection of correct materials, the selection of correct applications, and correct working.

4. Recommendation for Future Research Activities

4.1 Suggestions on Metallic Materials

First of all, materials should be monitored over a long period of time referring to the properties of materials currently used. When a corrosion related incident occurs, thorough survey should be made from the aspect of both the environment and the material, the cause should be elucidated, and enter the information should be entered into a data base. Moreover the costs for this research needs to be adequately budgeted.

For future problems, with the realization of an all aluminum MSF plant in mind, precise investigation on aluminum alloy heat transfer tubes must be carried out (especially with empha–

sis on the inactivation of pitting). Also, it is necessary to research the environmental operating conditions which are compatible with the material, to prevent occurrence of pitting in aluminum alloys.

4.2 Suggestions on Non-Metallic Materials

There are very few examples of using cement and non-metallic materials such as FRP for MSF seawater desalination plants. In order to positively use non-metallic materials and capitalize on their properties for MSF seawater desalination plant equipment, it is necessary to accumulate data, and to provide experimental facilities required for this.

4.2 M-3 Study on Some Materials by Corrosion Measurement Apparatus

1. Introduction

This research will focus on investigating the current levels of evaluation test facilities of anti-corrosion properties required for devising a R&D plan for anti-corrosion materials associated with the SWCC sea water desalination, which was mapped out in the related research paper M-2 and on investigating and planning the installation of evaluation test facilities of corrosion resistant properties which SWCC should prepare from now.

2. Planning

2.1 Method of Retrieval

The most widely recognized data bases are JOIS in Japan and DIALOG in the USA, and these were used as the main source of information.

2.2 Contents

(1) To determine what experimental equipment, for example corrosion/electrochemical experimental apparatus and various types of analytical equipment, is needed in order to evaluate the corrosion resistant properties of the materials used in the MSF seawater desalination plant.

The research will be divided into three areas —— experimental equipment in the laboratory, experimental equipment for monitoring and experimental equipment for the tests on the actual plants.

(2) Planning of experimental equipment to evaluate corrosion resistant properties for study on corrosion resistant materials related to seawater desalination in SWCC.

3. Result of Literature Survey

Evaluation of materials used in MSF seawater desalination facilities is normally done divided into the stages of the experimental laboratory level, the corrosion monitoring level, and the actual equipment operation level.

3.1 Test Equipment on Laboratory Level

Although a field survey is best to evaluate the corrosion resistant properties, it requires a long time to reach a conclusion and it is necessary to carry out an accelerated corrosion test in the laboratory to obtain this evaluation efficiently.

(1) Immersion Type Corrosion Test

The immersion type corrosion test is a method often used whereby the test piece is dipped into the test solution and according to the depth of dipping and the decrease in mass, corrosion resistant properties of the material is evaluated. Equipments and methods of the total immersion test, and the partial immersion test are established to evaluate the material depending on its actual environment.

(2) Alternate Immersion Test (Cyclic Dry and Wet Test)

This is a test method whereby the environment alternately wets and dries on the material surface.

(3) Corrosion Test under Mechanical Action

This is not a corrosion test under simple fluid circum– stances but rather a technique in which protective film on the metal surface is destroyed and removed by mechanical action such as the impingement of liquid or friction, and corrosion is accelerated, that is, an erosion corrosion test method.

Typical of this test method is the damage test by impingement of fluid droplets or a liquid jets; or the damage by impingement of slurry containing solid particles in the liquid and the cavitation erosion test. In the case of the first two test methods, it is not unusual to use loop type test equipment with pipe channel, and also there are examples where electro–chemical measuring methods are used.

Since the loop type test equipment is designed to simulate the operation of the actual equipment and also to obtain data for equipment design, generally it is large in scale, and uses large amount of liquid (large loop test equipment is usually classified as the test equipment of actual equipment level).

(4) Stress Corrosion Cracking Test

When metallic materials are placed in a specific corrosive environment with tensile stress loaded, cracking may occur in a crystal grain or along grain boundaries. In general, it takes a long time to recognize the occurrence of stress corrosion cracking under a practical environment, but as a test method, it is a common practice to generate high–level stress and produce a severe environment for acceleration testing. There is a specified combination between the metal which can generate stress corrosion cracking and the environment.

For the stress application method, there is a constant strain method and a constant load method, as well as that belonging to the intermediate. The constant strain method carries out tests in the elastic or plastic range, while the constant load method carries out tests in the elastic range.

(5) Corrosion Test under Heat Transfer

Of the corrosion cases evolving in heat exchangers, a typical component which has a heat transfer surface in chemical plants, more than 70% of corrosion occur in heat exchanger tubes. That is, heat exchanger tubes handle two fluids of completely different properties, and moreover, the change of stage takes place on the heat transfer surface due to evaporation and condensation. It is one of the severest environments from the viewpoint of corrosion.

Generally, corrosion on the heat transfer surface are affected by the surface temperature, the heat flux, evaporation and condensation, and scaling. Therefore corrosion test equipment which gives consideration to and reproduces corrosion on the heat transfer surface, has been proposed.

Also, when heat transfer surface corrosion is considered, measuring the heat transfer surface temperature, which is the most important factor, is carried out by inserting a thermocouple directly into the pipe wall. However, recently, a new method for direct measurement of the heat transfer surface temperature using the pn junction of a semiconductor, has been proposed.

3.2 Corrosion Monitoring Testing Apparatus

Monitoring is a method for evaluating the corrosion behavior of actual equipment in operation. As the corrosion rate of actual equipment can be different from that predicted by laboratory data, monitoring is very important. The corrosion rate is calculated normally based on the assumption of uniform corrosion, and is represented as thickness of corrosion per year (mm/year). For local corrosion such as pitting, the maximum depth is important.

To measure the corrosion rate, there is the physical measuring method, and the chemical measuring method. The former measures the decrease in mass, changes in thickness, amount of dissolved metal ions, amount of generated hydrogen, amount of consumed oxygen, and changes in electrical resistance on probe electrodes, to grasp the progress in corrosion. Also, in the latter case, as corrosion reaction is a electrochemical reaction, electrode potential and polarization curve are measured.

Generally, as the physical measuring method is a method for measuring the amount of corrosion, its sensitivity is low, and response to changes in corrosion speed is slow. On the other hand, with the electrochemcal measuring method, as the immediate value of the corrosion rate is measured, the measuring sensitivity is high, and it is sensitive to fluctuations in the corrosion rate. However, depending on conditions, there are cases where the measured value des not correspond to the actual corrosion rate.

It is necessary to select or combine the various measuring metods, in accordance with monitoring objectives and the item to be monitored.

(1) Physical Measuring Method

A specimen is installed to actual equipment, and the changes in electrical resistance related to corrosion with time is obtained by the electrical resistance probe method. In order to understand the progress of corrosion, the mass decrease measuring method is used. The test piece is attached inside the equipment, and the piece is periodically removed to measure the decrease in mass.

The thickness of matereials can be measured by the methods of ultrasonic wave reflectance pulse, radiographicexamination, and Eddy-current flaw examination. To grasp conditions of corrosion there are the chemical analysis methods of using an ion sensor to measure metal ions in liquid, using a probe to measure the amount of hydrogen and oxygen in liquid, and using a inductively coupled plasma emission to measure ions in liquid.

In addition, it is now possible to observe the pipe channel directly by using a fiber image scope which uses bundle fibers or by usig a small camera. It has been reported in Japan, that an extremely small camera with a diameter of 12 mm, length of 35 mm, weight of 7 g which can be used 10 m away from the controller has been successfully developed recently.

(2) Electrochemical Measuring Method

As corrosion reaction of matereials is electrical reaction, corrosion rate can be evaluated by electrical method measuring current density. Advantages of this method are that, the corrosion rate at the moment of measuring can be obtained, continuous long-term nondestructive measurement is possible and this has high sensitivity and quick response.

Therefore, since it can be installed in the automatic system and it can be used in environments that are dangerous for humans by remote measurements, it is a practical and effective measuring method. This measuring method, according to differences in concrete methods, is classified into the electrode potential measuring method and polarization curve measuring method.

3.3 Test Equipment on Actual Plant Level

The objective here is, testing the material under actual or similar operating conditions of the plant.

Though there is a method whereby materials which have undergone laboratory level and monitoring level testing, are into the actual equipment and the corrosion behavior is observed, there are some cases where materials are carefully tested using special test equipment closely resembling the actual equipment.

The most typical example of this is shown in the project for development of MSF seawater desalination plants carried out by the Industrial Technology Institute of the Ministry of

International Trade and Industry of Japan, from 1969 to 1977. This project involved development of the MSF seawater desalination process, research on use of byproducts, and development of material for heat transfer tubes which has a great effect on the functioning and costs of equipment. Here, equipment for a dedicated loop test and field test were constructed, and corrosiveness of various heat transfer tubes were evaluated.

The loop test was on a scale of 5,000 kg/hr of sea water being circulated, and test pieces made of copper alloy, aluminum alloy, titanium, low apploy steel, stainless steel, stainless steel, and coated steel, were evaluated.

For the field test, a seawater desalination facility producing 24 m^3 per day of desalinated water product was newly cpmstricted and operated to verify the total process and to evaluate the corrosiveness of heat transfer tubes. In regards to the heat transfer tubes, they were made using the material selected based on the results of the loop test, and this was installed in the equipment and testing was done under close to actual operating conditions. Local corrosion, average corrosion rate, surface roughness, amount of attached scaling, and the heat transmission coefficient were measured and evaluated.

4. Recommendation for Future Research Activities

4.1 Usefulness of SWCC Experience

SWCC has had a long record of operating desalination facilities and system which can accumulate data from the results of setailed surveys on corrosion conditions of desalination equipment. The research is useful to predict and extend plant equipment life. The required test and research facilities are as follows:

4.2 Laboratory Level Testing Apparatus

Since the laboratory level testing apparatus forms the basis of electrochemical or corrosion engineering studies, as many apparatuses as possible should be accommodated. For example, immersion type test facilities for measuring or regulating the specimen potential with a microcomputer, test facilities for corrosion under heat transfer, and facilities for cyclic dry and wet test, should be prepared.

4.3 Corrosion Monitoring Apparatus

The corrosion monitoring test apparatus consists of a chemical balance, an electronic balance for measuring the mass reduction, ultrasonic wave equipment and eddy current flaw detection for thickness measuring devices, chemical analysis equipment for measuring the number of ions, electrochemical analysis equipment for measuring electrode potential and polarization resistance.

4.4 Test Equipment on Actual Plant Level

Loop test or field test equipment, software of extreme value statistics analyzing pitting depth.

4.5 Corrosion Incidence Analysis Equipments

When corrosion failure occurs, analysis of its cause is important and following equipments should be prepared.

- * Oservation equipments such as video microscope, scanning electron microscope and corrosion measuring equipment.
- * Analysis equipments such as ICP analyzer, atomic absorption photometer, and X–ray micro analyzer.
- * Laboratry level corrosion test equipments required for corrosion reproduction experiments.

4.3 R-1 Sterilization

1. Introduction

There are some solutions for dealing with bacterial fouling, such as disinfection by the chlorine, SBS (Sodium Bisulphate) and the copper sulphate and UV method. Each of these disinfection methods has its good and bad points. As it is difficult to discriminate among them, in the Middle East region, the most suitable method is selected by comparative examination of the technological details, tinged with price considerations.

In the present survey, the outline, principle, equipment and effect of the above-mentioned processes on feed water disinfection and on the membrane itself will be reviewed including techniques and economical analysis.

2. Planning

2.1 Method of Retrieval

Literature retrieval was based on JOIS, DIALOG and available literature with both research portion from SWCC and JICA.

2.2 Contents

(1) Specification of microorganisms and their number in raw seawater.
(2) Outline of disinfection system

A. Chlorine gas method
B. UV radiation method
C. SBS method
D. Copper sulphate method

(3) Cost evaluation

Cost evaluation for the above methods will be made taking consideration into materials, labors, utilities, depreciation expenses etc.

3. Results of Literature Survey

3.1 Identification of Types and Number of Bacteria in Water

This is described in the main text in detail.

3.2 Sterilization Using Chlorine Gas

Before the RO technology for seawater desalination was developed and industrialized, it was used in the water works to provide drinking water taken from rivers and lakes. It is well known that chlorine has been the major method for for drinking water sterilization. The positive aspects of chlorine is that it is highly affective against bacteria and other organisms, and disinfects very quickly. Moreover, chlorine residue allow for water disinfection for a good period of time.

Also, the various chlorine injection equipment and the large plant facilities can be purchased on a commercial basis, and injection can be continuous. On the other hand, the demerits of chlorine are that it is toxic, troublesome to handle, and is a substance that is easily oxidized. Also, if exposed to sunlight, it disappears in a very short period. In addition, the free chlorine reacts with organic matter in the fluid undergoing treatment, and is widely known to produce the carcinogenic substance, trihalomethane, and there is also need to take precautions on the concentration and the method of use.

However, there are reports of many seawater desalination plants using the RO membrane which have reached the conclusion that sterilization by chlorine is the most cost-effective and the most effective sterilization method.

Based on these features of the chlorine sterilization method, this study discusses the following topics.

3.2.1 Principles

The physical and chemical properties of chlorine, functions as a disinfectant, the chemical equations for hydrochlorine solutions, definition of free chlorine and its sterilizing power, definition of bonded chlorine and its sterilization power, relationship between the amount of injected chlorine and residual chlorine, chlorine consumption volume and chlorine demand volume, and fundamental principles concerning chlorine sterilization, were discussed.

3.2.2 Effect of Chlorine Sterilization

The conditions for chlorine treatment and disinfecting power, the chlorine standard injection rate for various organisms, and the method for determining the chlorine injection volume, were discussed. Furthermore, discussion was made concerning chlorine resistance and chlorine method of usage for the following RO membranes.

(1) Chlorine-Resistance Properties of Cellulose Acetate

A large amount of chlorine being continuously injected with a continual high chlorine content damages the physical strength of the membrane, and the permeation characteristics of the solute, and therefore should be avoided. The conclusion is that though there is no clarified definite limit value, it is estimated that if 2 to 1 mg/liter is injected in cellulose acetate membranes feed, it has an extremely little negative affect on the membrane characteristics.

(2) Chlorine Resistance of Aromatic Polyamide

As the chlorine resistance of aromatic polyamides are extremely low, either injection of chlorine must be avoided, or if chlorine was injected at the previous pretreatment stage and residual chlorine exists, feed dechlorination before it emter the membrane must be done either by use of activated carbon filtration or by use of reducing agent. In this case, chlorine concentration in the feed to RO will be zero.

(3) Dissolved Chlorine Gas Permeation Properties of Cellulose Acetate

In the case of cellulose acetate, if the pH is low, the dissolved chlorine satisfactorily passes through the membrane. From this aspect, both the water production and the desalination system are sterilized.

3.2.3 Example of Chlorine Usage for Sea Water Desalination Plants

When chlorine is used in an actual industrial plant of large capacity, the components of the raw water include; water, suspended matter, dissolved salt, general inorganic matter, organic matter, living organisms, bacteria, and other microorganisms. Furthermore, the components differ according to where the raw water is drawn, the season, temperature, and how long the area has been industrialized.

Therefore, this cannot be only looked at from the aspect of sterilization, but also overall feed water quality, plant facilities, the piping system, and especially RO membrane fouling and corrosion. And these need to be looked at as factors which can cause major problems such as decreased performance, plant stoppages, equipment replacement, increased costs, etc. While giving consideration to these factors, the chlorine sterilization treatment of the following representative RO plant in Japan were introduced as ecamples.

(1) Chigasaki Laboratory of Water Re-Use Promotion Center
(2) Hakuhojima Sea Water Desalination Plant
(3) Tonaki Village Sea Water Desalination Plant
(4) Mitsubishi RO Sea Water Desalination Plant
(5) Sumitomo Metal Industries Kashima Steel Works
13,400 m^3/d Desalination Plant

3.2.4 Chlorine Injection Facilities

The chlorine injector (chlorine sterilizer) itself is already on the market on a commercial basis. The equipment is safe and reliable, and there are no particular problems. However, as the chlorine itself is a toxic gas with a stimulating odor, the utmost care is required. In this section, the sterilization costs was calculated. To clarify the operation procedures of chlorine injectors, information was collected from related manufacturers and are discussed.

3.2.5 Cost of Chlorine Sterilization

As the preconditions, 5 ppm concentration of chlorine is injected into 100,000 t/d of raw water in the pretreatment process, and dechlorinization and use of dechlorinization agent are not used. Also other chemicals are not included in the calculated costs for chlorine sterilization. With water product at 30,000 t/d, the unit cost per ton of chlorine is estimated at 60,000 yen/t. Required number of operating staff shall be 9 persons per day, wages shall be 4,000,000 yen a year per person.

As to the cost of equipment, the injector facility is 140 million yen, and building cost is 135 million yen, and the life of the former is 7 years with straight line depreciation, and the latter is 35 years with straight line depreciation. Utility costs are small enough to be ignored. However ventilation system operating costs are excluded.

Sterilization Costs per 1 ton product water (yen/t) are as follows:

Material costs	1.0 yen
Labor costs	3.3 yen
Depreciation costs	2.2 yen
Utility costs	0 yen
Total	6.5 yen

3.3 Sterilization Treatment by Ultraviolet Irradiation

The ultraviolet irradiation method can be listed in comparison to other ways of sterilization.

a) Greater safety and relatively easier to use.
b) Not selective of types of bacteria, and is effective on almost all kinds of bacteria.
c) Does not produce harmful materials or cause secondary water fouling as in chemical treatment, because it sterilizes bacteria without destroying microorganism bodies.
d) The required time for sterilizing is very short, less than a minute. A large space for the system is not necessary.

With the merits mentioned above, this type of treatment is considered to be an important process especially in the production of ultra pure water, requiring the highest level of purity. The highly clean systems are needed in the fields of most advanced technologies. Ultraviolet light sterilization treatment is gaining importance as an efficient way of sterilization to meet stringent demands. Not many domestic and foreign desalination plants use this form of treatment on a large scale yet.

However, when there is a demand for this, there will be a need to develop appropriate ultraviolet light sterilizing technology which can accommodate RO method desalination technology. As one of the limitations of chlorine is that though chlorination controls the formation of slime. The residual chlorine assists bacteria to decompose the cellulose acetate membrane, and therefore there are reports in such case use of the ultraviolet irradiation as one of the effective ways for sterilization.

Furthermore, there is a patent which emphasizes the merits of introducing raw water into the RO membrane without chlorination. A part of the permeate is used repeatedly to clean the membrane, and the other part of the permeate is treated by the ultraviolet light irradiation.

There are few engineers who are interested in the technological aspects of using ultraviolet rays as a mean of sterilization in RO membrane desalination. On the other hand, though ultraviolet light sterilization has excellent features as mentioned above, in practical applications it has certain limitations.

a) The permeability of ultraviolet light varies with the water quality. The sterilization effect may decline depending on the water to be treated.
b) Suspended particles screen the ultraviolet light, and reduce the effect of the ultraviolet light on microorganisms.
c) The illuminance of the low pressure mercury lamp used as the ultraviolet light source depends on the ambient temperature.
d) Duration of the sterilization effect is shorter than that of chemical treatment.

Therefore, to make the ultraviolet sterilization system practical, some measures to counteract these demerits should be taken .

This survey discusses the following items.

3.3.1 Principles

The mechanism of ultraviolet light sterilization, and the wavelength distribution of the low pressure mercury lamp are presented in the text.

3.3.2 Sterilization Effect of Ultraviolet Irradiation

The values of the required ultraviolet ray dosage for killing various organisms, selectivity for the type of bacteria, procedures for determining the UV dosage required for sterilization, the impact of water quality on ultraviolet permeability, and the duration of the sterilization effect, were discussed.

3.3.3 Characteristics of Low Pressure Mercury Lamp

Characteristics of the sterilizing light energy temperature, correction of ultraviolet illuminance for different water temperatures, basic data required for designing the sterilization system, the life of the low pressure mercury lamp, and fundamental features of the low pressure mercury lamp required for sterilization were also discussed.

3.3.4 Types and Structures of UV Sterilization System

The types of ultraviolet sterilizing equipment can be broadly divided into the outer irradiation type, and the internal irradiation type. For the outer irradiation type, the ultraviolet light is irradiated from the outside of the treated water, while for the internal irradiation type, the lamp is soaked in the treated water in which the ultraviolet light is irradiated. Each of the types have their own merits and are used according to the objective. The merits and demerits of the two types were compared.

3.3.5 Cost of Ultraviolet Light Sterilization

In considering the application of ultraviolet irradiation in sterilizing equipment for a RO seawater desalination plant, the related manufacturers were surveyed to determined the possibilities, facility costs, and operating costs.

The preconditions for the facility design were 100,000 t/d of water to be treated, water product of 30,000 t/d, sterilization at water intake and after sand filtration for escherichia coli and vibrioid class bacteria, excluding phytoplankton whose energy consumption is large. Not only to sterilize, but also to improve the effect and the maintenance of the RO membrane, the UV irradiation is located in front of the RO membrane, and the plant is operated 24 hours a day.

The initial investment for the required equipment is 314,500,000 yen (8,500,000 yen / set x 37 sets). Of this, the lamps cost are 47,360,000 yen (40,000 yen per lamp x 32 lamps x 37 sets). The life of the lamps in the initial investment amount are 1 year. As they are consumables, the lamps are accounted as maintenance costs. The lamp installation equipment and the auxiliary equipment including the various instruments were accounted for as depreciation costs.

The channel to flow the raw water, the power supply, and the buildings were excluded from the calculations. Depreciation is straight line for 7 years. In regards to the maintenance costs, as the life of a lamp is 1 year, as mentioned above, only the cost of the lamps are estimated as a maintenance expense. All of the lamps will be exchanged every year. Annual maintenance costs are 47,360,000 yen, with cost of maintenance per ton of water product is 4.33 yen/t.

Power costs are calculated based on the rating (1.92KW) given in the catalog of the proposed equipment. 71 KW (1.92 KW/unit x 37 units) is adequate as the power supply, and depreciation is minimal.

Labor costs are almost negligible. However, as the lamps require maintenance and inspection, and manpower is needed to exchange the lamps, one hour per day as the labor cost for inspection was included in the estimation. Labor costs are on the basis of 4,000,000 yen per year.

The sterilization cost per ton of water product is as follows:

Depreciations costs	3.49 yen/t
Facility maintenance costs	4.33 yen/t
Electric power costs:	0.97 yen/t
Labor costs:	0.07 yen/t
Total	8.86 yen/t

3.4 Sterilization with Copper Sulfate

It has been known for a long time that the metal itself has the property of suppressing the growth of bacteria, and copper sulfate has been used as a disinfectant for drinking water for a long time. It is widely recognized as being especially effective for the extermination of algae. The merits of copper sulfate as a disinfectant is that as a solid, it is safer and easier to handle than gas, and raw water is easy to treat with copper sulfate. Also, its potency as a chemical lasts for a comparatively longer time when used as a disinfectant. Copper sulfate is also said to control the decomposition of organic matter in sludge deposits, and checks the decay of the sludge.

On the other hand, the demerits of copper sulfate are that it takes a long time to take affect, and it is reported to have the potential for inducing the multiplication of algae which are not affected by the copper.

Few cases have been documented for the use of copper sulfate as a disinfectant or as an agent to exterminate algae in RO method seawater desalination plants. There is no clear data on the actual sterilizing or algae extermination effect of copper sulfate, nor there is any data on its protracted use for membranes. According to reports on a model experiment, copper sulfate used with cellulose acetate membranes, controls the multiplication of microorganisms, and does not cause definite damage to the membrane.

This survey discussed the following items:

3.4.1 Principles

The physical and chemical properties of copper sulfate, and its functions as a disinfectant were discussed.

3.4.2 Examples

Examples of seawater desalination plants which use copper sulfate as a disinfectant are as follows.

Biological treatment with copper sulfate is widely applied to remove algae. However there are a few seawater desalination plants which actually use copper sulfate for biological treatment, even at the test stage.

There are two plants which use copper sulfate as disinfectant, both are located on the Red Sea coast of Saudi Arabia and utilize TFC polyamide membranes.

(1) Umm Luji 4,400 t/d RO Plant, Saudi Arabia
(2) Jeddah 12,000 t/d RO Plant, Saudi Arabia

3.4.3 Cost of Sterilization with Copper Sulfate

Though copper sulfate is toxic, it is solid and soluble in water, and there is no particular information to suggest that equipment for injection of copper sulfate requires a high technology and high cost. Primarily, biological treatment with copper sulfate is most suitable for algae extermination of dead water in lakes, marshes, and reservoirs. The equipment required for injecting copper sulfate can be installed on a boat. The cost required for injecting copper sulfate is quite low compared to the overall water production cost, or the costs required for chlorine injection equipment. Accordingly, the report estimates that only the cost of the copper sulfate itself is required for biological treatment.

As preconditions, generally, industrial standard copper sulfate in a moisture-proof paper bag is used, and the amount used is 2.5 mg/l. The water product volume is 30,000 t/d, and the amount of water treated is 100,000 t/d.

The amount of copper sulfate used daily is 0.25 t/d. With unit cost of copper sulfate ($CuSO_4 \cdot 5H_2O$) at 200,000 yen a ton, with water product cost per ton at 1.7 yen/t.

3.5 Sterilization with SBS (Sodium Bisulfite)

As SBS has a strong reducing property, it is used as a reducer, for the synthesis of dye-stuff and chemicals, for coloring and bleaching, as a disinfectant, a dechlorinating agent, an antiseptic, and so forth.

However, in our research of sterilization for seawater desalination plants using RO membranes, only one plant using SBS as a disinfectant was found. Even reference books on water treatment, rarely explain or refer to SBS.

However, SBS is used as a dechlorinating agent in seawater desalination plants which use RO membranes made of aromatic polyamide or polyether.

3.5.1 Principles

The physical and chemical properties of SBS were given, however there were no examples given of the standard injection rate of the biological treatment agent.

3.5.2 Example

Example of SBS usage at a seawater desalination Plant

Ras Abu Jarjur RO Plant

It is noteworthy that a seawater desalination plant of this scale from the aspect of its water production capacity, should be using SBS as a disinfectant. No other RO seawater desalination plant was found in the reports which uses SBS as a disinfectant.

3.5.3 Costs for Sterilizing with SBS

There were few examples found in the reports studied, of SBS being used as a disinfectant. And no information could be obtained in regards to the standard injection rate of SBS required to sterilize specific bacteria and algae. Some references to the SBS concentration applied to the shock treatment of plants, but there was no clear report found on the amount of SBS required per ton of water product.

This is a wrong assumption since the 2 to 3 ppm will be consumed by the oxygen in water.

Based on the assumption that the amount of SBS required is almost the same as that of copper sulfate (2 – 3 ppm), and the unit cost of SBS is almost the same as the unit cost of copper sulfate, which is 200,000 yen/t the sterilization costs for SBS are therefore virtually the same as copper sulfate.

4. Recommendation for Future Research Activities

4.1 Summary of Sterilizing Methods

Summary of sterilizing methods of RO desalination Plants in various countries is as follows.

Based on the reports studied, and the information collected from the manufacturers of

RO plant equipment, the raw water sterilization methods introduced in the RO seawater desalination plants of several countries are summarized.

At all the Japanese plants, chlorine was used for sterilization. When the membrane is cellulose acetate, dechlorination after disinfection with chlorine is not required. However when the membrane is a material other than cellulose acetate, dechlorination with SBS is accomplished. The same concepts apply in plants in the United States.

In the Middle East also, similar technological concepts are employed. However some plants use copper sulfate or SBS for sterilization, and this is probably due to the property of the raw water and membranes. (Chlorine cannot be used when sulfide such as H_2S exists in the raw water.)

4.2 Technical Issues of Current Sterilization Methods

4.2.1 Problems with Chlorine Sterilization.

The greatest problem with chlorine sterilization is that trihalomethane is generated when seawater is chlorinated. It is reported that when the seawater of the Arabian Gulf is sterilized with chlorine, trihalomethane with a high bromine content like bromoform, di-bromochloromethane and dichlorobromonethane are generated, especially when the seawater is contaminated with oil. As the chlorine concentration is raised, the trihalomethane concentration is also increased.

Furthermore, a report which refers to the trihalomethane rejection ratios of RO membranes, states that the cellulose acetate membrane rejection ratio is the lowest. Aromatic polyamide membrane is next, and the composite membrane has the highest rejection. However, even with the composite membrane, the rejection ratio is low and is 38 % rejection ratio chloroform. Currently, sterilization with chlorine is applied to most cellulose acetate RO seawater desalination plants. The use of cellulose acetate membranes will probably become more controversial in the future, as its rejection ratio of trihalomethane is very low.

4.2.2 Problems with Chlorination/Dechlorination.

For sterilization of raw water with chlorine in sea water desalination plants using RO membranes of polyether or polyamide, it is essential to carry out dechlorination with SBS (sodium bisulfite) after chlorination.

Not all bacteria are killed with chlorine, and there is aftergrowth of existing bacteria after dechlorination, and eventually there is biological fouling. According to the report, the aftergrowth of bacteria is dependent on the temperature and pH level. In particular, if the temperature is as high as 25 - 35 °C, aftergrowth of bacteria will occur rapidly, and consequently biological fouling is speeded up.

4.3 Suggestions on New Sterilization Methods

Suggestions on new sterilization methods, especially sterilization with chloramine, are as follows.

There is a report which proposes chloramine as an excellent disinfectant to replace chlorine. The merits of chloramine are given as follows:

a) Chloramine does not break down humic acid.
b) Treatment with chloramine does not cause bacterial aftergrowth.
c) Though chloramine has an affinity for aromide membranes, there is no negative effect.
d) Chloramine has a satisfactory disinfectant property.

Also, other patents propose the use of one of the specific chlorine compounds of organic bonding such as chloramine T, dichloramine T, chloramine B, halazone, chlorodimethylhydantain, N- chlroacetanilide, N-dichloroacetanildide, N-chloronitroacetanilide, and N-chloroacetluide, as a disinfectant to reduce the fouling of membranes and to sterilize microorganisms. Multiplication of microorganisms will then be controlled, biological fouling can be decreased, and thus long and continuous operations are possible.

No complete sterilization process is available at present. Research and development are to be continued to establish the process that controls the biological troubles without harmful side effects.

4.4 R–3 Pollution Effect of Membrane Cleaning Discharge

1. Introduction

First of all, investigative research was conducted using literature survey for examining treatment processes. The volume and quality of waste water will differ due to the generation source, the process, the membrane materials and the washing process. With each of these several factors, data was collected and assessed in order to evaluate the volume and quality of the waste water.

Finally, with the results corresponding in general to the evaluation of the waste water, investigations into methods for its treatment was conducted.

2. Planning

2.1 Method of Retrieval

(1) By means of JOIS, DIALOG data base, screening the past 15 year data related to membrane cleaning and its waste water discharge.

(2) Evaluation of the important references on MSF and RO covering the above period.

2.2 Contents

(1) Information collection from membrane makers

(2) Requests to SWCC for the related materials

1) Brine quality and quantity from the existing RO module.

2) Saudi Arabian laws and rules related to environmental protection, the actual state of disposal of industrial wastes, the local conditions and the conventional way of life.

3. Results of Literature Survey

3.1 Survey Materials

Literature related to quality, quantity, and treatment of waste water from the seawater desalination plant by means of the RO process was retrieved and descriptions related to this survey theme were accumulated and summarized.

For the retrieval, files containing expert water treatment technologies from DIALOG which has the maximum amount of data base in the world as well as files from JICST of Japan were used. In the retrieval, original papers of 61 documents were obtained from about 750 abstracts and then more important documents were selected out of those 61 as the literature related to this survey theme.

Although the literature retrieval was conducted using a wide range of data bases as mentioned above, not much information concerning the membrane storage solution could be found. Therefore, more information of this solution was gathered from plant suppliers and membrane manufacturers. Since the survey result indicated that the chemical solution commonly used for membrane storage was formalin, literature describing the treatment of formalin was separately retrieved from JICST.

In this retrieval, 10 out of 28 documents were selected and summarized. As can be seen from the small number of selected documents compared with the total number of retrieved documents, not much literature related to this survey theme could be found despite the large volume of literature retrieval as mentioned above.

Also, even though some documents related to this survey theme could be obtained, their descriptions were limited to the use of chemicals only and few documents contained a description of waste water treatment. However, some of the documents showed concern for the influence of cleaning waste water with chemicals on the environment.

There were some reports on the research of cleaning processes without using chemicals or with lesser amounts of chemicals, and it is said that these intended to make waste water harmless from membrane cleaning. As for the treatment of brine, there were some reports describing the need for certain countermeasures and introducing methods for its treatment.

In the case where many facilities are planned to be installed on limited land space or in the case where the water source is brackish and concentrated brackish water is returned underground like in Florida of the United States, the treatment of brine has already become an important problem. It can be seen that its solution is now being searched for.

As mentioned above, the importance of problems on the treatment of waste water from desalination plants using the RO process has been recognized, but detailed descriptions of waste water treatment processes could not be found. Though there were some documents about actual desalination plants, none of them made reference to the waste water treatment process. Accordingly, no actual desalination plants which were provided with waste water treatment facilities could be found in these documents, except the brackish water desalination plants in inland areas.

However, there are a few plants in Japan which have given consideration to the waste water treatment, and these will be introduced later. Also, the newer the documents were, the more documents related to this survey theme could be detected. This means that there is a high possibility of obtaining more literature or useful data related to the waste water treatment process by continuing this survey.

3.2 Survey of Membrane Manufacturers and Plant Suppliers

As a result of literature survey, information on the waste water from RO systems could be obtained, but this was limited to fragmentary information and insufficient to make a plan for the waste water treatment. Therefore, three typical Japanese RO membrane manufacturers having large-scale plant construction experience, and two Japanese plants were selected and information was gathered from them. Information related to the actual plant flow, quality and quantity of waste water, membrane cleaning solution in actual use, type and quantity of membrane storage solution, waste water treatment process, etc., was also obtained and reorganized.

The plant flow system, quality of raw seawater, quality of product water, manufacturers and type of RO membranes, plant supplier's point of view, etc. somewhat differs according to the plant's location. The quality and quantity of waste water from the plant also differs accordingly.

However, when considering the case of producing fresh drinking water from ordinary raw seawater, the approximate quality and quantity of waste water could be estimated. Also, in actual large-scale plants, a waste water treatment was not specially provided because the waste water was diluted with a large quantity of concentrated brine. In exceptional cases, there are plants provided with waste water treatment facilities in Japan and these will be introduced later.

In the case where waste water is not diluted or mixed with concentrated brine, the following shows that type of waste water having quality problems when discharged without any treatment and the details of such quality problems.

Multilayer filter cleaning waste water:
SS: about 130 mg/l(Coloration of waste water is another problem.)

Chemical solution cleaning waste water:
COD: 10,000 mg/l or more in the case where 2 % citric acid is used.
(In addition, when surface-active agent is used as clean ing chemical solution for organic contaminants, control of foaming is sometimes needed.)

Storage solution waste water:
COD: About 4,000 mg/l in case 0.5% formalin is used.
(When formalin is used, an odor tends to be generated even if the concentration is diluted. Also, when SBS is used, decomposition is needed.)

3.3 Laws and Regulation in Japan and Saudi Arabia

In the conference between the first Japanese field survey team and SWCC held in October and November 1991, both parties were asked to produce the waste water quality standards in their respective countries. The environmental laws and regulation stipulating water quality in Japan were surveyed and are discussed below. The Saudi Arabian regulations were in Appendix 1 of the main text.

For environmental laws, publications containing English translations of the Japanese

Environmental Pollution Prevention Act, the Water Pollution Prevention Act, and the Acts for Sea Pollution Prevention and Prevention of Disaster at Sea, were attached, and the constitution was briefly discussed.

Also, the effluent standard of the Tokyo Metropolis was introduced as an example of a standard established in addition to prefectural standards, together with the uniform effluent standard issued by the Order of the Prime Minister's Office.

Also introduced were some regulations covering not only concentration of effluent but also total amount of COD in effluent, and that regulation of nitrogen and phosphor was now under study.

3.4 Waste Water Treatment in RO Seawater Desalination Plants in Japan

In the conference between the first field survey team and SWCC held in October and November 1991, information of the present status of waste water treatment in Japan was requested. Therefore, the waste water treatment in RO seawater desalination plants in Japan is introduced in this section, and general matters concerning waste water treatment technologies are described in Paragraph 5.

The scale of RO seawater desalination plants existing in Japan is small compared with the scale of plants constructed in Saudi Arabia. Also, installation of RO seawater desalination plant in Japan, who is favored by relatively high rainfall, is limited to special cases. Both of the two plants mentioned below have been provided with waste water treatment systems.

These systems have been installed not because the waste water treatment was required under the standards established pursuant to Japanese laws but because consideration was given to each plant for the environment surrounding it.

In other words, Plant (1) mentioned below, which is an installation to supply service water for a nuclear power plant, needed to reduce the unfavorable influence on the environment as much as possible in order to gain the respect of surrounding inhabitants on the utilization of unclear energy. Plant (2) is an installation to supply drinking water in the resort facilities. It was necessary for the plant to minimize an unfavorable influence on the environment in order to secure the sightseeing population.

The following information describes outlines for these two plants:

(1) RO seawater desalination plant for the supply of service water in a nuclear power plant.
Capacity of product water: 1,300 m^3/d x 2 units
Process for waste water treatment:

1) Chemical solution cleaning waste water: After aeration and pH adjustment, waste water is diluted by mixing with other waste water and then discharged.
2) Membrane storage solution waste water: After aeration and pH adjustment, waste water is diluted by mixing with other waste water and discharged. (In this plant, sodium bisulfite is used as membrane storage solution and can be made harmless by aeration.)
3) Concentrated brine: After injection of sodium bisulfite, mixing with other waste water, aeration, and pH adjustment, brine is discharged. Sodium bisulfite is injected to decompose residual chlorine contained in concentrated brine coming through the membrane. Also, aeration is provided to mix with other waste water and to prevent SS sedimentation.)

(2) RO seawater desalination plant for drinking water in resort facilities.
Capacity of water product: 1,000 m^3/d
Process for waste water treatment:

Multilayer filter cleaning waste water: After removing most of SS by sedimentation, waste water is mixed with other waste water and discharged. Removed SS is mechanically dewatered and disposed by the entrusted contractor for disposal of industrial wastes.

As is done in the above (2) plants, disposal of wastes produced along with industrial activities and having difficulty in the in-plant disposal are often entrusted to the intermediate contractors engaged in disposal of industrial wastes. By bringing up these intermediate contractors who are engaged in the disposal of industrial wastes as a business, the waste water can be treated without installing waste water treatment facilities as a part of the plant. The above briefly introduces the system as well as the role played by intermediate contractors for disposal of industrial wastes.

3.5 Waste Water Treatment in RO Seawater Desalination Plant

In this section, waste water treatment facilities were discussed by considering the RO seawater desalination plant with a capacity of 200,000 m^3/d product water as an example, together with the introduction of general matters concerning waste water treatment.

For general matters concerning waste water treatment, contaminants and the unit operation for corresponding waste water treatment, together with its system configuration, were introduced.

In the discussion of waste water treatment for the RO seawater desalination plant, a plant of 2,000,000 m^3/d scale was used as an example because an increase in the quantity of product water at each plant was anticipated in future. Quality and quantity of waste water from the plant was estimated from the survey results mentioned in Section 3.2. If the various waste waters are discharged independently from the plant, chemical solution cleaning waste water, membrane storage solution waste water, and multilayer filter cleaning waste water, containing contaminants in high concentration are in need of some treatments.

However, if the waste waters are discharged with a large quantity concentrated brine, the values of COD, SS, and pH will become less than the standard values in Japan. To achieve this, it will be necessary to install adequate capacity waste water storage facilities and also facilities for mixing and dilution. The latter, however, can be coped with by simple facilities.

As mentioned before, by mixing waste water with large quantities of concentrated brine, chemical solution cleaning waste water and membrane storage solution waste water can be discharged from the plants. However, since the laws and regulations stipulate the minimum treatment level to avoid an unfavorable influence on the environment, it is needless to say that a higher grade of treatment is desired.

Moreover, when considering installation of large-scale plants near seas like the Red Sea or the Arabian Gulf, further study of higher-grade waste water treatment will be needed as a future subject. From this viewpoint, treatment systems for multilayer filter cleaning waste water, chemical solution cleaning of waste water, and membrane storage solution waste water, all of which cannot be independently discharged without dilution, have been introduced in this paper.

4. Recommendation for Future Research Activities

The following suggestions relating to the present state of membrane cleaning waste water treatment are as follows:

(1) Not many seawater desalination treatment facilities have been installed. This is because the waste water is diluted by a large quantity of concentrated brine and no waste water treatment is required under the laws in Japan and elsewhere.

(2) In contrast, however, since a large quantities of waste water will be produced in large-scale plants and even if the concentration of contaminants meets stipulations of such laws, the total amount of discharged contaminants will be greatly increased and it will be necessity to give more consideration to its influence on the environment in the future.

(3) Therefore, the future subject of waste water treatment technologies is to find a system which can satisfy regional characteristics. Furthermore, development of a cleaning process which does not discharge any harmful chemical solutions and the development of a storage solution where waste water can be easily treated, will be other future subjects. Finally, when considering the future environmental impact of large congregation of industries, the establishment of a contract system for disposal of wastes to be discharged along with industrial activities should be one direction of development.

4.5 R–4 Selection of Membrane

1. Introduction

The aim of this research is to show what kind of RO membranes are the most suitable ones under the conditions in Saudi Arabia and to make comparative investigations of the characteristics of the RO membranes, that are currently in use with due regard to;

(1) High concentration of dissolved solids in raw feed seawater
(2) High temperature of raw feed sea water

2. Planning

2.1. Method of Retrieval

Literature survey was performed using the following retrieval methods: DIALOG, JOIS and collection of the catalog published by membrane makers.

2.2. Contents

(1) Present condition of sea water desalination technology using RO membrane

The latest information was collected concerning the principle and production plants based on sea water desalination.

(2) Investigation on RO Membrane

Collected information for RO membrane are classified according to the materials used, maker and its type of module. Importance factors considered are: permeate velocity, operation pressure, greater heat-resistance, low cost, high quality, chemical composition, chemical structure, life and RO membranes resistance to chlorine.

3. Results of Literature Survey

3.1 Survey Materials

In implementing this investigation and with the above objectives in mind, the following reference materials were used:

(1) Technical information obtained by searching through the entries in DIALOG, the world's largest database, over the last ten years (1981 - 1991) and JICST, Japan's largest database.
(2) Pamphlets and brochures issued by manufacturers
(3) Other published literature/references

3.2 Classification of RO Membranes

3.2.1 Classification of RO Membranes based on Cross-sectional Forms

According to their cross-sectional forms, RO membranes can be classified into three groups – homogeneous, asymmetric and composite.

3.2.2 Classification of Composite Membranes

Based on cross-sectional form, composite membranes can be classified into five types: polymer coating, monomer polymerization, polymer surface crosslinking, blocked surface and interfacing polymerization membranes.

3.2.3 Classification of RO Membranes based on Separation Performance

* High rejection membranes:

Those with salt rejections of more than 99%, typically used for single stage desalination of seawater.

* Medium rejections membranes:

Those with rejection around 90%, typically used for desalination of brackish water or industrial water.

* Low rejection membranes:

Those with rejections of 30–70%, typically used for separation of organic compounds with medium molecular weights and inorganic ions.

3.2.4 Classification of RO Membranes based on Operating Pressure

High pressure type
Intermediate pressure type
Low pressure type
Ultralow pressure type

3.2.5 Classification of RO Membranes according to Module Structures

Plate–and–frame type module
Spiral–wound type module
Hollow fiber type module
Tubular type module

3.2.6 Classification of RO Membranes based on Membrane Material (Chemical Structure)

(1) Cellulose Acetate Membranes(Asymmetric Membranes)
Membranes Characteristics:

1) Rejections ranging from 95 to 98 %.
2) Easily hydrolyzed.
3) A narrow range of suitable operating pH, 5 – 7.
4) Low bacteria resistance (bacteria attacking).
5) Easily dissolved in various organic solvents.
6) High chlorine resistance (in terms of free chlorine concentration range of 0 – 2.0 ppm).
7) Limited heat resistance.

(2) Cellulose Triacetate Membranes(Asymmetric Membranes)
Membrane Characteristics:

1) High rejection rates, capable of single stage desalination of seawater.
2) Easily hydrolyzed.
3) A narrow range of suitable operating pH, 3 – 8.
4) Low bacteria resistance (bacterial attacking).
5) High chlorine resistance (in terms of free chlorine concentration range of 0 – 2.0 ppm).
6) Limited heat resistance.

(3) Linear Fully-Aromatic Polyamide Membranes(Asymmetric Membranes)
Membrane Characteristics:

1) High rejection rates, capable of single stage desalination of seawater.
2) A wide range of suitable operating pH, 3 – 11.
3) Very low chlorine resistance (in terms of free chlorine concentration range of 0 ppm).

(4) Crosslinked Fully-aromatic Polyamide Membranes(Composite Membranes)
Membrane Characteristics:

1) A variety of RO functions incorporated with good balance, also with the best future prospects.
2) High degrees of cross-linking and hydrophilicity.

3) Low operating pressures.
4) High rejections.
5) High flux.
6) A wide range of suitable operating pH, 3 – 11.
7) High oxidation resistance (durability).
8) Very low chlorine resistance (in terms of free chlorine resistance range of 0 – 0.1 ppm).
9) High hydrogen peroxide resistance
10) High bacteria resistance
11) High SiO_2 rejection
12) High TOC rejection

(5) Aryl–Alkyl Polyamide/Polyurea Membranes
Membrane Characteristics:

1) High rejection rates –> A similar level to those of crosslinked fully–aromatic polyamide membranes.
2) High flux.
3) Very low oxidation resistance (durability).
4) High TOC rejection rates
5) High SiO_2 rejection rates
6) Very low chlorine resistance (0 ppm)

(6) Piperazine Polyamide Membranes (Composite Membranes)
Membranes Characteristics:

1) High flux
2) High chlorine resistance
3) High hydrogen peroxide resistance
4) Low rejection rates – loose RO membranes, food industry applications

(7) Sulfonated Polysulfon Membranes (Composite Membranes)
Membrane Characteristics:

1) High heat resistance
2) Low rejection rates – loose RO membranes
3) High chlorine resistance – food industry applications

(8) Cross-linked Polyether Membranes (Composite Membranes)
Membrane Characteristics:

1) Super high rejection rates (NaCl rejection 99.9 %), capable of full single stage seawater desalination.
2) Very low oxidation resistance - very low resistance against dissolved oxygen and to chlorine.

3.3 High Heat-Resistance RO Membranes

The commercial membranes with high heat resistance are shown in Table 4.5.1.

Table 4.5.1 Example of Heat Resisting Membrane

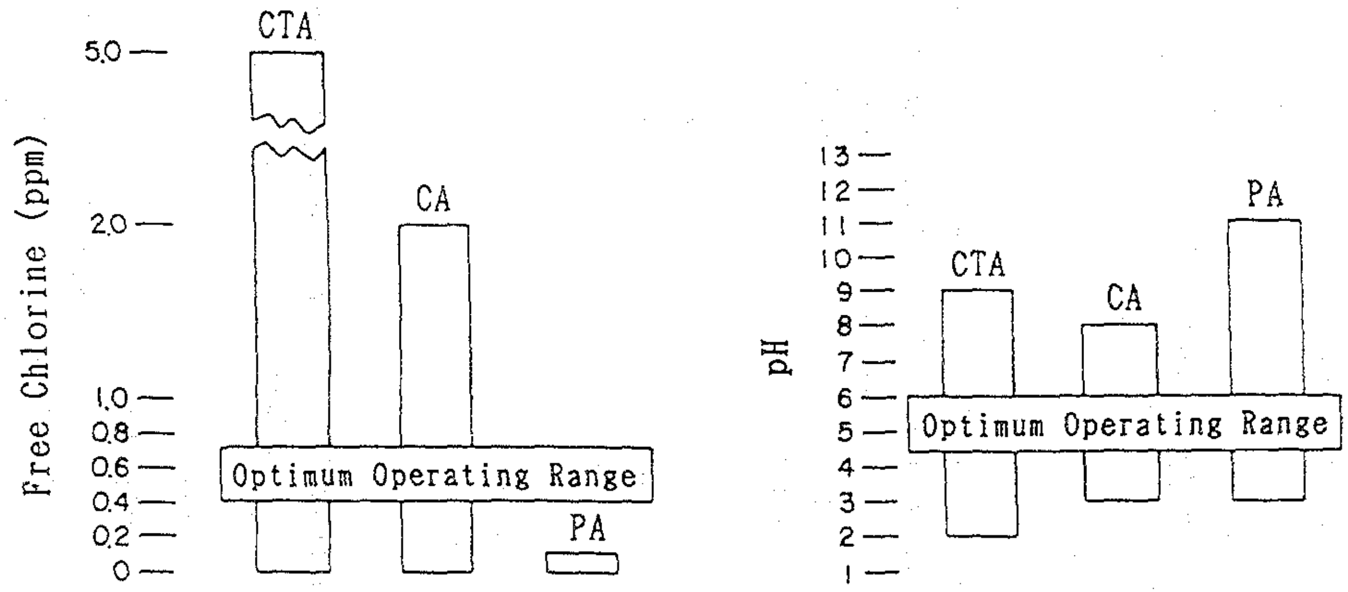
Manufacturer	Membrane	Heat Resistance(°C)
TEIJIN	PBIL	60
North Star Research	NS-100	>35
North Star Research	NS-200	>35
FilmTec.	FT-30	50
UOP	PA-300	45
TOYOBO	Hollosep	40
Toray Industries	SU-800	45
Du Pon	B-10	40

3.4 Chlorine Resistance Characteristics and Operating pH Ranges of RO Membranes

Chlorine resistance characteristics and operating pH ranges of various RO membranes are shown in Fig.4.5.1.

3.5 Cross-Comparison of Various RO Membranes

A performance diagram (a diagram plotted to give a correlation between rejection and flux for each membrane) for various RO membranes under the operating conditions of 0.5w% NaCl, 42 kg/cm^2 and 25°C is shown in Fig. 4.5.2(Some membranes are not available at present.).



CTA: Cellulose Triacetate
CA : Cellulose Acetate
PA : Polyamide

Fig. 4.5.1 Chlorine Restance Characteristics and pH

Source: R.E.Kesting & S.Sourirajan, Reverse Osmosis and Synthetic Membranes, Theory–Technology–Engineering, National Research Council Canada, Ottawa, p89 (1977)

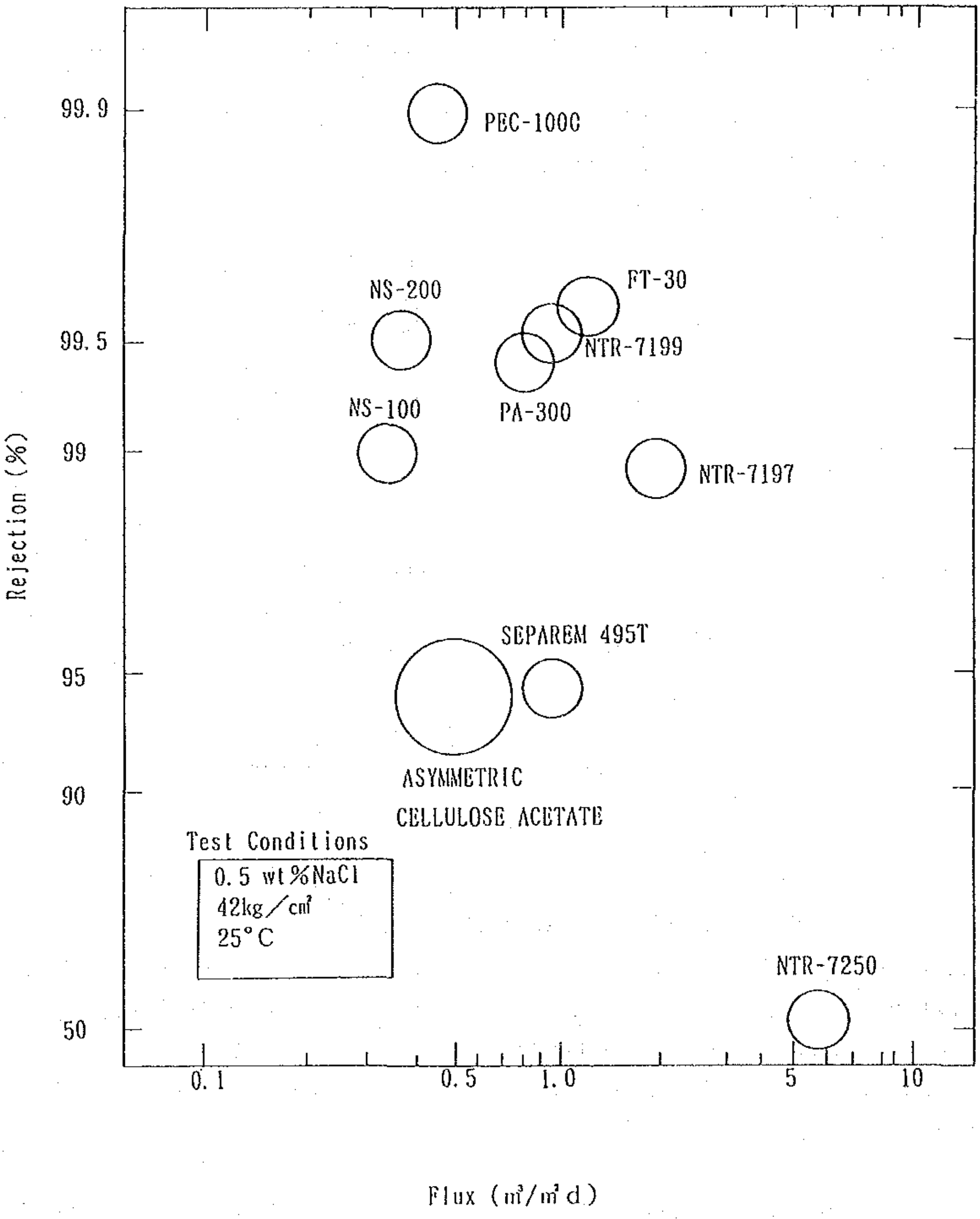


Fig. 4.5.2 RO Performance of Various RO Membranes
Source: E.Driori, Desalination, 63, p57 (1987)

3.6 RO Membranes for the Desalination of Seawater

Representative RO membranes for the desalination of seawater is shown in Table 4.5.2.

Table 4.5.2 RO Membranes for the Desalination of Seawater

Manufacturer	Membrane No.	Module Type
Du Pont	B-10	Hollow Fiber
UOP	PA-300 (RC-100)	Spiral
Filmtec	FT-30 (BW-30)	Spiral
Toray Industries	SU-800	Spiral
Toyobo	Hollosep (HR5355)	Hollow Fiber
Nitto Denko	NTR-70SWC	Spiral

3.6.1 RO Membranes for the Single Stage Method

The single stage method refers to the RO method used for the desalination of seawater which desalinates seawater with a salt concentration of 35,000 mg/l after passing through a single process once to obtain a product less than 500 mg/l.

RO membranes capable of single stage seawater desalination are small in number and are shown below:

(1) CTA hollow fiber membranes: Hollosep (HR-8350), a rejection rate of more than 99.5 %
(2) Linear aromatic polyamide membrane: B-10
(3) Crosslinked fully-aromatic polyamide membranes:
BW-30, SU-810, SU-820, NTR-70SWC-S4
(4) Crosslinked polyether membranes: PEC-1000, a rejection rate of 99.8 %
(5) Allyl-alkyl polyamide/polyurea membranes: PA-300, NTR-7199

3.6.2 RO Membranes for the Double Stage Method

The two stage method refers to the RO method used for the desalination of seawater which desalinates seawater with a salt concentration of 35,000 mg/l after going through two processes. Each process uses a membrane with a rejection rate of 90 to 95% to obtain a final product less than 500 mg/l. The raw water is fed to the first membrane process at a pressure of 50 to 70 kgf/cm^2 to obtain a first stage product with a salt concentration less than 3000 to 4500 mg/l. This is then fed to the second membrane process at a pressure of 50 to 70 kgf/cm^2 to obtain the final product.

3.7 Conclusion

In brackish water desalination where RO membranes are most extensively used, the spiral-wound type has emerged as the definite favorite choice and the hollow-fiber type is only utilized in some special applications. It is therefore necessary to pay close attention to the development of the situation.

The seawater desalination RO membranes currently on the market are:

(1) Spiral-wound type, cross-linked fully-aromatic polyamide membranes
(2) Hollow-fiber type, TCA membranes
(3) Hollow-fiber type, fully-aromatic polyamide membranes.

It is expected that the performance of the above membranes will continue to improve in the future. Before commencing with further research on membranes however, it is recommended that the focus of research subjects should be narrowed bearing in mind the following:

For stable operation of a desalination plant, the largest disadvantage of the RO-based desalination process is degradation in performance resulting from the fouling of membranes (fouling caused by SS and bacteria). This problem is further complicated due to the fact that the nature of fouling varies in time depending on the quality of the feed water even within the same plant. Research and study of these problems, as well as the process to artificially change the properties of seawater are thus required.

4. Recommendation for Future Research Activities

To maintain the economic and technical advantage of the RO membrane equipment seawater desalination, it is necessary to continue research in the following fields:

(1) Evaluation of Membrane Material which Resists Higher Pressure Operation

Development of a membrane material which resists higher pressure operation is required in order to completely desalinate high salinity seawater in the Middle East with ;single stage desalination. The recovery rate is raised with high pressure operation and that makes the operation more economical.

(2) Evaluation of a Membrane Module which Resists High Temperature Operation

There already exists membranes which resist seawater of 40 °C in the desalination process, but there is no membrane which can resist both high pressure and high temperature operation. Heat resistant parts for the membrane module are especially demanded. If an RO membrane which can resist high pressure and high temperature over long period of operation is developed, desalination will become more economical.

(3) Evaluation of Membrane with High Oxidation Resistance

RO membranes become fouled with the growth of microorganisms in seawater, and the permeate flow rate of the membranes diminishes. As a measure, disinfectant containing a strong oxidation agent is added, however the membranes of high desalination capacity normally have low oxidation resistance. If an RO membrane with high oxidation resistance and high desalination capacity can be developed, the system of RO membranes and the control of the system operation will be simplified, thus eventually the cost will be reduced.

(4) Establishment of Optimum Operation Conditions for the Desalination of High Temperature and High Salinity Seawater

It is necessary to optimize the overall system (pretreatment filtration, disinfection and operation pressure for the desalination of seawater) in order to suit membranes newly installed in the module.

(5) Durability of Membrane Module

As a conclusion, the following is taken into consideration for development and selection of membranes:

To select a membrane, it is important to consider not only cost performance but also capacity to supply safe drinking water. In other words, it is necessary to select a membrane which has the capacity to remove even a trace quantity of harmful substances.

In order to further the development and selection of new membranes suggested above, it is necessary to establish a system for the exchange of latest information on membrane technologies and to work in cooperation.

4.6 R–5 Chemical Cleaning of the Fouled Module

1. Introduction

Oil pollution trends of Arabian Gulf due to Norwuz oil spill during 80's and recently during the Gulf war necessitated experimental research for establishing methods of eliminating oil from RO plants feed and to study the effects of oil on the nature of membranes.

2. Planning

2.1 Method of Retrieval

(1) Investigation of the data and actual results offered from RO module suppliers
(2) Review of literatures and patents
(3) Suggestions based on the results of the above mentioned literature surveys

2.2 Contents

Since fouling mode is dependent on materials and modular configuration of membranes, the investigation was conducted to study the following:

(1) The influence of fouling on membrane material and module configuration.
(2) Depending upon the fouling causes, selection of cleaning chemicals and appropriate methods of cleaning suitable to the membrane in use.
(3) The evaluation method of the degree of fouling and effectiveness of cleaning.
(4) The method of the analysis.

3. Results of Literature Survey

3.1 Survey Materials

(1) Collection of information submitted by Japanese manufacturers
(2) Investigation and study of literature and patents by using an online information retrieval system

3.1.1 Information Procured from Japanese Manufacturers

Almost all information concerning cleaning methods are related to fouling by inorganic substances, however, few describe surface active agents such as the cleaning method against fouling due to oil. Furthermore, the effect of oil fouling on RO performance is not described quantitatively.

3.1.2 Results of Literature Search with Online Information Retrieval System

(a) JOIS

Key word: Semi-permeable membrane, Oil Number of retrieval operations: 32
Number of acquired original reports: 4

(b) STN

Key word: Membrane, Oil, Cleaning, Sea water Number of retrieval operations: 20
Number of acquired original reports: 5

(c) DIALOG

Key word: Membrane, Oil, Sea water, Cleaning Number of retrieval operations: 50
Number of acquired original reports: 0

3.1.3 Results of Investigation on Oil Fouling

Though information procured from membrane manufacturers and acquired by using an on-line retrieval system was thoroughly screened, it was hard to substantiate effects of oil on RO membrane and its removal from the feed.

This accentuated the need to perform future experiments to investigate effects of oil on membranes types, performance of membranes and feed water.

This investigation reports causes of membrane fouling, methods of removing membrane foulants and evaluation methods of membrane foulants.

3.2 Elucidation of Cause of Membrane Performance Degradation

The causes of RO membrane performance are due either to membrane deterioration or to membrane fouling. Membrane deterioration while membrane fouling as classified as fouling or scaling.

To work out a countermeasure against membrane performance degradation, the causes must be elucidated. The causes of membrane performance degradation and the phenomena of membrane fouling are sorted and arranged as in the Table 4.6.1.

3.3 RO Membrane Fouling and Performance Maintenance Method

Mechanism of RO membrane fouling is explained as follows.

(1) Accumulation of colloidal substances existing in feed sea water on the membrane surface.
(2) Precipitation of a small amount of organic or inorganic substances dissolved in the vicinity of the membrane surface.
(3) Propagation of bacteria or adhesion to the membrane in the system.

Table 4.6.1 Causes of Membrane Performance Degradation

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

(4) Physical or chemical action of components in feed sea water on the membrane surface.
(5) On the membrane surface, flocculation and accumulation of organic or inorganic components as insoluble molecules.

To prevent such membrane fouling, the optimal pretreatment of feed sea water and the periodic cleaning suitable for the types of membrane and the RO modules according to foulants, are essential techniques for the maintenance of membrane system performance.

3.4 Elucidation of Cause of Membrane Fouling

3.4.1 Presumption by Physico-Chemical Analysis

If degradation in membrane performance is presumed to result from membrane fouling, the analysis of foulants is important work to deduce the formation process of foulants and to determine methods of removing them.

As a means of analyzing foulants on membrane surfaces, the following procedures are suggested.

a) Visual observation and odor analysis (sensory analysis) of attached substances.
b) Determination of amount of attached substances.
c) SEM observation of membrane surface.
d) XMA analysis of membrane surface —— (Analysis of elements attached to membrane surface).
e) X-ray diffraction and emission spectral analysis of attached substances —— (Analysis of inorganic substances).
f) IR analysis of attached substances —— (Analysis of organic substances).
g) FT-IR analysis of membrane surface —— (Analysis of organic substances).
h) Incubation and identification of microorganisms —— (Analysis of microorganisms).

The analysis of feed seawater is also needed which involves the following procedures. The analysis of feed sea water involves the following procedures.

a) Measurement of SDI (FI).
b) Incubation and identification of microorganisms.
c) Oil analysis.
d) Analysis of soluble inorganic components.
e) Analysis of soluble organic components.
f) pH
g) Analysis of surface active agents.

3.4.2 Experiments for Elucidating Causes of Membrane Fouling

Though the cause of membrane fouling can be deduced by means of the analyses in the above section, it is sometimes necessary to set a hypothesis and verify it by conducting tests to elucidate the real causes. The following flow system shown in Fig. 4.6.1 can basically be considered for the experimental facilities.

3.5 Removal of Membrane Foulants

Methods of removing membrane foulants are classified into physical methods and chemi-