cal methods. In physical methods, the flushing is a general method and the sponge ball method is a cleaning method possibly applied to the tubular type module alone. Furthermore, no ultrasonic cleaning has not been employed so far in commercial plants. Some of the chemical cleaning method widely used are listed in the Table 4.6.2.

4. Recommendation for Future Research Activities

The following research procedures are recommended to be carried out by SWCC for the removal of membrane foulants.

4.1 Basic Planning

In the experiment on removal methods of membrane foulants, the most important point is to evaluate the membrane performance before and after cleaning.

The flow sheet for the evaluation procedure is shown in Fig. 4.6.2.

4.2 Research Planning

The research activities are divided into the following two stages:

1) basic research and 2) pilot plant experiment.

Basic research includes laboratory test and bench scale test.

At the pilot plant stage, actual RO module should be used based upon the data obtained from the basic research stage.

Experimental equipment and their functions indicated in 4.4.2 of are required. The time schedule is shown in Fig.4.6.2.

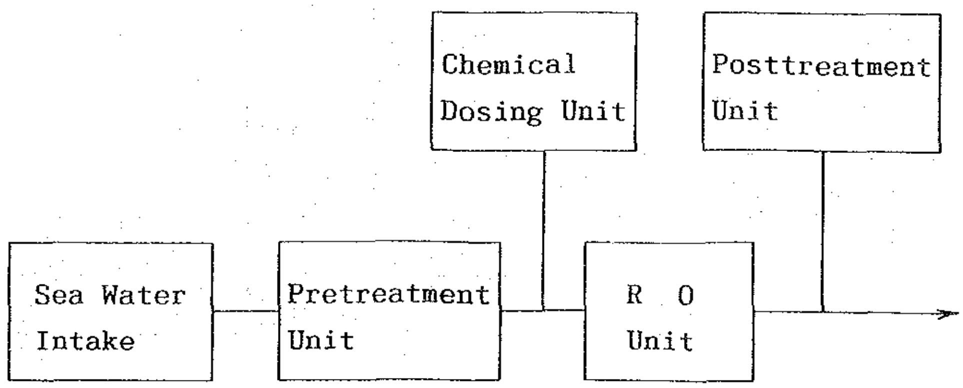

Fig. 4.6.1 Experimental Facilities

Table 4.6.2 Chemical Cleaning of Fouled Membranes

Membrane	Detergent	Conc. (%)	Temp. (°C)	P H (-)	Time (Hrs.)
PA1501 TFC-PA	Solution Y (Citric acid) Solution Z (Borax + EDTA-Na + Na_3PO_4)	2.0	25	2.5	0.75
B-10 HF-PA	Ultrasiel 10 Citric acid	0.5 2.0	35 35	12 4	25 25
GKSS G4 PF-CA/CTA	Citric acid Ultrasiel 50 Bevaloid	1.5 1.5 150(g)	35	3 9	1 1 1
CA	P3-Ultrasiel 53 (Enzyme) P3-Ultrasiel 75 (Acid)	1.0 0.3			1-1.5 0.3
PA	P3-Ultrasiel 30 (Alkaline) P3-Ultrasiel 75 (Acid)	1.0 0.5			0.5 0.3
CA	Citric acid Triton X-100 CMC	2.0 0.1 0.001		3	
CA	Sodium Toripolyphosphate Na-EDTA CMC Triton X-100	2.0 0.8 0.0015 0.1		6	
Amicon S400	Na-Dodecylsulfate n-pentanol				
	Oxalic acid	0.2		3-4	1
	TC-100 (Surfactant)	5		8-9	1

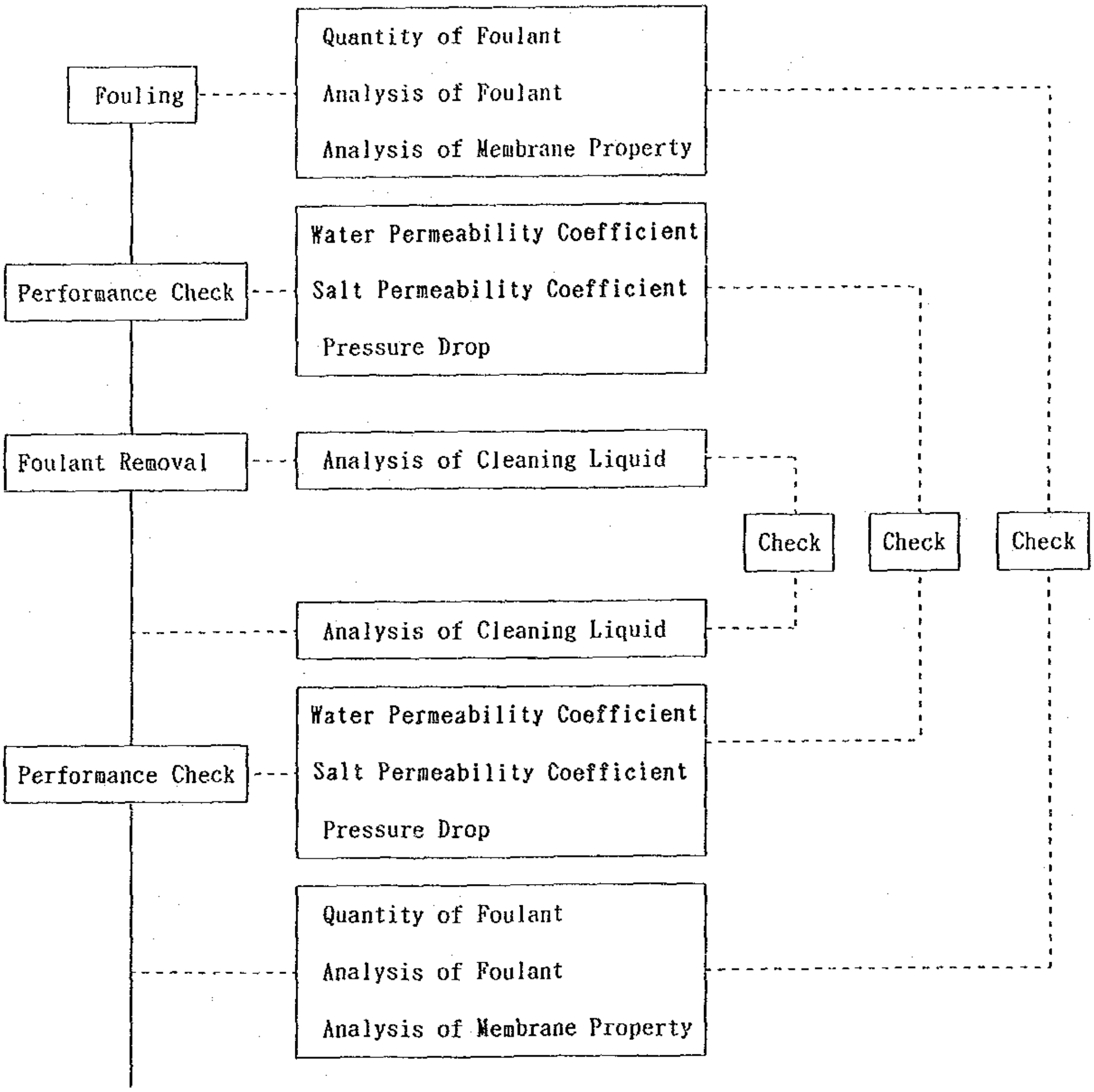

Fig. 4.6.2 Experimental Flow Sheet to Evaluate Membrane Performance

4.7 R–7 Standardization of the Main Analytical Methods

1. Introduction

The method of analysis related to the RO desalination plant was introduced.

It is the objective to introduce analytical methods for each field mentioned below and to examine the necessary documentation related to the required standardized analytical methods for the RO sea water desalination plants in SWCC.

2. Planning

2.1 Method of Retrieval

Analytical methods to be introduced to this study were based on internationally accepted standards such as ASTM, JIS etc. in the field as shown below.

(1) Standardization of analytical methods

(2) Specific testing methods

2.2 Contents

The performance of the membrane modules is effected by salinity of seawater, temperature and other conditions such as flocculants, suspended solids and micro organisms, present in the raw seawater. The most appropriate methods were discussed.

(1) Water quality at each stage of RO system

(2) Qualitative analysis on the cause of fouling of the membranes

(3) Analysis of polluted seawater

(4) Analysis to determine the quality of drinking water produced by RO

(5) Analysis of waste water from RO plant

3. Results of Literature Survey

In general, such analysis is divided into two main categories. One is for water (raw seawater, feed water, and product water) and the other is for the RO membrane which is the most basic component of the RO system. These two types of analysis are quite different in nature.

3.1 Chemical Analysis for RO System and its Items

(1) The performance of the RO system is evaluated by conducting the standard tests on NaCl solution that is made with the same salt concentration as raw seawater. The recovery rate, permeation and qualities of the product water will indicate the performance of the system. Such data are closely related to substances dissolved in raw seawater.

(2) One of the functions of the membrane is to remove the substances contributing to turbidity.

However, unlike the UF membrane, the RO membrane is intended to remove ions. To make the most of the RO membrane, therefore, it is necessary to remove turbidity substances beforehand. Thus, the necessity of pretreatment and the choice of a treatment process depend on the quality of raw seawater.

(3) As product water is recovered through the RO membrane, raw seawater becomes increasingly concentrated and refractory salt (e.g. carbonate, sulfate, silicate, etc.) may be deposited. In consequence, scale layers and/or cake layers may be formed, thereby greatly lowering the performance of the membrane. That is why it is very important to estimate and prevent the deposit of refractory salt for the smooth operation of the RO system. To serve this purpose, some preventive measures has been standardized.

The deposit and control of refractory salt depends on the qualities of seawater. The chemical analysis is necessary to design a desalting plant using the RO system, evaluate its performance and operation. As a result of the review, approximately 40 items were chosen for further analysis.

3.2 Review of Standard Methods for analyzing Raw Seawater

The analysis explained above belongs to the water quality analysis type. Our investigation has shown that the methods stated in the following documents are widely employed as the standard method for water quality analysis. These methods are used for daily analysis.

(1) ASTM (American Society for Testing Materials)
(2) Standard Methods for the Examination of Water and Waste Water
(3) JIS K0101 Test Method for Industrial Water
(4) JIS K0102 Tests for Industrial Waste Water

Among these methods, K0102 is currently under revision (the revised version will be published shortly), and hence omitted from our review.

The standard water quality analysis tends to be converged into ISO (International Standardization Organization).

3.2.1 Comparison of Standard Methods

With regard to the 40 items mentioned previously, we compared the standard methods stipulated in ASTM, the Standard Methods and JIS K010, by choosing out main points of each method and arranging them side by side. This comparison revealed that all the methods were basically similar to each other.

As far as RO related parameters such as pH,turbidity, electric conductivity (EC) and TDS are concerned, although the analyzing methods were basically the same, the specific ways for conducting the analysis differ according to each purpose. When any of the standard methods is applied to an actual sample, reliable data may not be obtained unless relevant equipment, tools, reagents, reference standard, and operational procedures are standardized or well established. For pH and turbidity, the present situation surrounding the standardization of the relevant items is shown.

Chemical analysis of water, the amount of each substance present in water (or each defined quality) is measured and estimated. Chemical analysis, however, is being replaced more and more with analysis using equipment (instrumental analysis). In the latter type of analysis, indirect measurement is done using calibrated reference standards. More specifically, the atomic absorption photometer (with or without flames) and ICP, is applied for measuring all metal substances and some anions, and the IC or electrode method is applied for measuring most anions.

In the near future, by combining ICP, IC and computers, it may become standard to measure anions, cations and other substances contained in a sample simultaneously in one operation.

As a result of comparative study of the standardized methods, we have reached the conclusion that ASTM, covering many methods for the RO system, will serve most of the purposes.

3.2.2 Considerations for the Standardization of Analyzing Methods

Any standard methods should be based on the conditions of each country concerned, and written in that country's native language. Generally, in standardizing the methods, the following items should be taken into consideration.

(1) Limitation of Methods

Although it is desirable to limit the method applied to one factor/substance to just one, such limitation is often hard to implement. Also important is to carry out joint analysis or a cross-check by more than one competent institute and review the accuracy or deviation of the data considering inductive statistics. It may confirm the reliability of data.

(2) Improvement of Methods and Suppression of Interfering Factors

Samples taken from seawater are characterized by a complex matrix. Such samples have many coexistent factors that interact with each other, so it is hard to obtain accurate data. In standardizing the methods, therefore, consideration should be given to an effective way to suppress interfering factors.

(3) Instrumental Analysis

Since instrumental analysis does not require as much skill as chemical analysis, it is employed in many of the standard methods. As mentioned previously, since reference standards are used as calibration, effects of interfering factors are minimized. Also necessary is the more precise definition of reference water for calibration.

(4) Forms of Substances

Silica, phosphoric, iron and other substances in the sea take complicated forms. When they exist as colloid, particle, refractory salt, macromolecules, or complex forms, normal chemical methods cannot be applied. To make chemical analysis possible, they must be dissolved into ions. It is, however, difficult to dissolve them completely.

To measure substances, their forms must be clearly defined, and, if total amounts are to be analyzed, consideration must be given to reach an effective way to dissolve the substances into ions.

(5) Exclusion of Polluting Chemicals

The use of Hg, Cd, and other chemicals which could pollute the environment, should be kept to a minimum.

(6) Legal Aspects

If standardized methods become legally enforceable, they would be widely applied. If this was the case, the purposes of the application would also be wide-ranging, so the choice of appropriate methods would become more important.

3.3 Analysis of the Fouling of the RO System

Water molecules permeated through the RO membrane are taken out as recovered water, so that the concentration of feed water becomes higher. Water molecules i.e. ions and molecules that can freely move in solvent are discharged outside together the membrane with concentrated water, but not-so-mobile hydrate molecules, macromolecules, colloids, and refractory particles remain in the vicinity of the membrane, thereby contaminating it through complicated interaction.

In general, this phenomena is called "deterioration" if the contaminating substances are so firmly adhered to the membrane that they cannot be removed, and "fouling" if they can be removed from the membrane by cleaning or other means.

To understand and prevent fouling, it is necessary to obtain information about the chemical bonds between fouling substances and the membrane molecules, the forms of the substances, and the process of the deposit formation. It is in this aspect that the analysis of fouling is different from the chemical analysis of water, which mainly concerns itself with the amount of each substance.

3.3.1 Fouling Phenomena and its Prevention

Actual phenomena of deterioration and fouling are divided into several categories according to their content. It is made clear that clarification, prevention, and cleaning, all presuppose the analysis of fouling.

3.3.2 Analysis of Fouling

To observe and analyze fouled membranes, SEM, XMA, X-ray diffraction, IR, FT-IR, and ESCA, are generally used.

3.3.3 Equipment used for the Analysis of Fouling

To analyze composition and status of fouling substances, the use of equipment for surface analysis is increasing. Such equipment is capable of observing and measuring the forms, chemical types, chemical bonds and structures of micro particles on surfaces.

(1) Optical Microscope
(2) X-Ray Diffraction
(3) Fluorescent X-Ray Analysis
(4) XMA
(5) ESCA
(6) SEM
(7) EPMA
(8) Infrared Absorption Spectrum Analysis

3.3.4 Example of the Analysis of Fouling

Some examples of analysis using IR, FT-IR, scale formed by refractory salts, organic substances, etc. have been cited.

3.3.5 Analysis of Cleaning Process

In the process of cleaning, the following seawater substances are removed from the membrane surface.

(1) Substances contributing to turbidity and refractory salt deposited in concentrated water.

(2) Substances which cannot be assimilated by bacteria, that is, tar and pitch originated from petroleum, humic substances, lignin, products of metabolism of marine creatures, macromol–ecules organisms, etc.
(3) Slime produced by bacteria, etc.

No cleaning agent is almighty. Therefore, appropriate cleaning method for each type of foulant is indispensable.

At the same time, it is also necessary to analyze cleaning agents and cleaning waste water. Some methods are standardized in this aspect.

4. Recommendation for Future Research Activities

To analyze cleaning agents, cleaning waste water, and to clarify the interaction between fouling substances and the membrane, the following equipment are effective.

(1) HPCL (High–Pressure Liquid Chromatograph)
(2) Automatic titration equipment
(3) Coulometric titration equipment
(4) Polarograph
(5) Ion chromatograph
(6) Zeta potential
(7) Oxidation–reduction potentiometer

Electrochemical methods should be applied from the viewpoint of aqueous chemistry that is essential to the RO system.

Chapter 5. Summary

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Introduction

Since the signing of R/D in January 1982, considerable cooperation was carried out by providing both hardware and software in order to improve the developing ability of seawater desalination technology at SWCC. In particular, many fruitful results were obtained by collaborative work such as experimental research and literature survey between the specialists of JICA and SWCC since October 1991. The results are summarized as follows:

5.1 MSF Process

M-1 Laboratory Experiment on Scale Prevention

The literature survey shows that the effect of oil on the functions of a scale inhibitor has not been studied yet. Consequently, a laboratory experiment was performed to determine the effect. It was found that the presence of oils in seawater reduces the capacity of the scale inhibitor. Elaborate discussion is necessary before making a decision about further experiments with an MSF test plant because a large amount of used oil-contaminated seawater must be treated before discharge.

M-2 Corrosion Tendency for Some Kinds of Materials

A literature survey was carried out on the corrosive characteristics of metallic materials (copper alloys, titanium and titanium alloys, aluminum alloys and stainless steels) and non-metallic materials which were used for MSF plants. Research and development themes to be studied in the future have been proposed, based on the survey results.

M-3 Study on Some Materials by Corrosion Measurement Apparatus

Concerning the corrosion-measuring apparatuses for metallic materials of MSF plants, the latest information on test equipment in laboratories, monitoring equipment and test systems for practical plants have been provided by a literature survey. In addition to that, proposals have been made for the systems and methodology of estimation tests on metallic materials.

M-4 Analysis of Oil Dispersed in Raw Seawater at the Heat Rejection Section of MSF Plants

The results of the literature survey showed that there is only a little information on the behavior and chemical analysis of oil when oil-contaminated seawater is used for feed of an

MSF process.

Assuming an accident of crude oil spill, a laboratory experiment on evaporation of oil-contaminated sea water was performed in order to predict the contamination of the product water and to find an analytical method for oil. It was found that the amount of water transferred to the product water was highest at the deaerator, and decreased from higher temperature stages to lower ones in turn. GC/MS and IR are suited to the analysis of oil.

However, more accurate, detailed experiments will be necessary, because the above experiment had not perfectly simulated the actual performance of plants in operation.

5.2 Reverse Osmosis Process

R-1 Sterilization

The literature survey shows that the most popular method of sterilization is the chlorine process, but that this process is not always the best because of recent organic contamination of feed seawater. Some new processes other than chlorine sterilization are being searched for to settle environmental problems. It is necessary that the most suitable process for local conditions be established for each plant.

R-2 Pretreatment of Seawater

It is found that a pretreatment process for oil-contaminated seawater has not been established yet. The laboratory experiment revealed the possibility of removing dispersed oils considerably from seawater by precipitation with a coagulant. It is advisable to experiment on oil removal further, based on the results of the experiment.

R-3 Pollution Effect of Membrane Cleaning Discharge

Summarization was made for the quantity and quality of various kinds of waste water which might be discharged from a reverse osmosis plant with a capacity of 200,000 m^3/d fresh water. The laws and regulations on waste water discharges in Japan have been reviewed to plan a treatment system for the waste water. The waste water does not raise environmental problems for the time being because there are a few large scale plants. However, there will probably be more public debate when a considerable number of plants with large capacities are in operation in the future.

R–4 Selection of Membrane

A systematic literature survey was carried out to review the characteristics of reverse osmosis membranes. They are summarized in tables. As regard to potential membranes to be used for seawater desalination in the Arabian Gulf with high salinity and temperature, much attention will be paid to the three types of membrane. The research themes in future will be: Evaluation of Membranes or Modules Resistant to Higher Pressure, Higher Temperature and Higher Oxidation, Establishment of the Optimum Operation Conditions Fitted to Higher Temperature and Salinity, etc.

R–5 Chemical Cleaning of the Fouled Module

Technology on membrane fouling and cleaning has been investigated by a literature survey. It was found that few systematic studies have been made in the field of reverse osmosis membranes for sea water desalination. The membranes are usually cleaned according to the instruction manual provided by the membrane manufacturers. How to estimate a membrane cleaning process was summarized and presented.

R–6 Selection of Membrane for Hybrid RO Process

Only a little information on membranes suitable for a hybrid process is available, although the process of seawater desalination has a considerable number of advantages. Therefore, fundamental experiments were performed with flat membrane test equipment on membranes that were expected to perform well. The results obtained showed that some membranes were found suitable for the hybrid process because of high flux rates. Further detailed experiments will be needed for practical purposes.

R–7 Standardization of the Main Analytical Method

The items of analysis necessary for the reverse osmosis process are classified into two groups; one is concerned with water and another is related to membranes. The standard methods of analyzing water developed in the U.S.A. and in Japan, were given and compared with each other. Some comments to be taken notice of, were presented in standardizing the analytical procedures.

In addition, the methods required for analysis of membrane fouling were also reviewed with some examples of membrane fouling.

JICA