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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

MAIN REPORT

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JAPAN INTERNATIONAL COOPERATION AGENCY

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PREFACE

In response to a request from the Government of the Kingdom of Saudi Arabia, the Government of Japan decided to implement the technical cooperation for the project on seawater desalination technology, and entrusted the project to the Japan International Cooperation Agency (JICA).

JICA sent a team, consisting of researchers from Water Re–Use Promotion Center, to the Saline Water Conversion Corporation (SWCC) of the Kingdom of Saudi Arabia from October 1991 to February 1992 for the collaborative research activity as a part of the project.

The team conducted experimental research and literature survey together with researchers from SWCC. After the team returned to Japan, further discussions between both parties were made and the present report was prepared.

I hope that this report will contribute to the advancement of seawater desalination technology in the Kingdom of Saudi Arabia and to enhancement of friendly relations between our two countries.

I wish to express my sincere appreciation to the officials concerned of the Government of the Kingdom of Saudi Arabia for their close cooperation extended to the team.

ALC: NO

July 1992

Kenzuke Yana

Kensuke Yanagiya President Japan International Cooperation Agency

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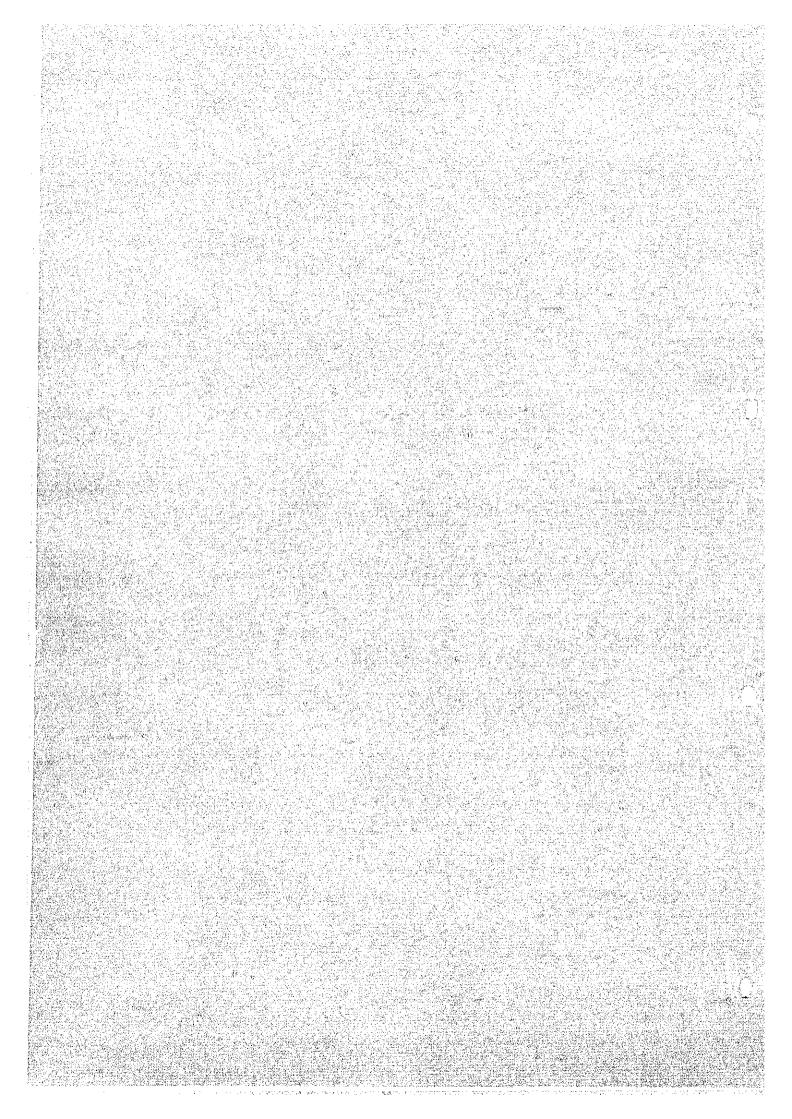
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Chapter 1 Background and Objectives



Chapter 1. Background and Outline

1.1 Background and Objectives

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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 re-extension

(4) April1991 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

The outline of each item is described below:

(1) Cooperation for establishment of research institute

When research institutes are established, the necessary procedures include design and construction of the building, and preparation of equipment and materials for research and management of the research institute.

JICA provided the technical advice when the building and attached facilities of the research institute were built by SWCC. JICA also provided advice concerning the responsibility of the research center, research themes, fostering of human resources, information control and so on, related to management of the research institute.

(2) Cooperation for research equipment for collaborative research activity

JICA performed the designing and manufacturing of the MSF test plant and RO test plant suitable for the Research Cooperation and sent them to SWCC.

Basically, necessary equipment and instruments for the research institute for desalination technology had been sent before the commencement of experimental work. Furthermore, experts had been dispatched to give engineering instructions for use of the equipment and instruments delivered.

(3) Training of the Saudi researchers in Japan

The Saudi researchers working in SWCC were trained in Japan in 1989. In the training, lectures and experiments of each professional field were conducted, along with a general lecture on seawater desalination technology assisting in effective implementation of the research coop-

eration.

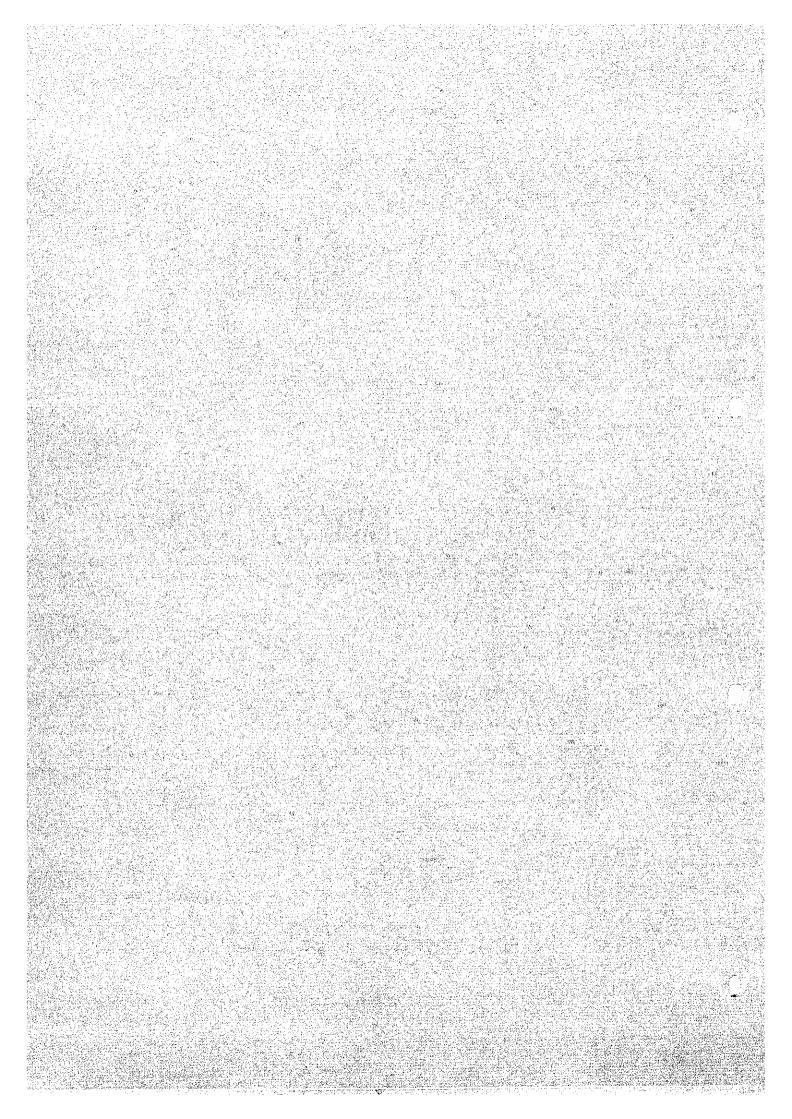
(4) Cooperation through implementation of collaborative research activity

JICA and SWCC agreed to the implementation of eleven themes in total for research, consisting of four themes related to MSF and seven themes related to RO in October 1984.

In July 1991, the eleven themes were reviewed and as a result it was decided that seven of the themes would be by literature survey and four by experimental research in addition to literature survey.

The chapters following Chapter 3 describe the implementation results of collaborative research activity.

Chapter 2 Contents and Methods of Implementing Collaborative Research Activities



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.

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Fig. 2.1 shows the above mentioned organizational diagram and Table 2.1 shows the person responsible for SWCC and JICA for each research theme.

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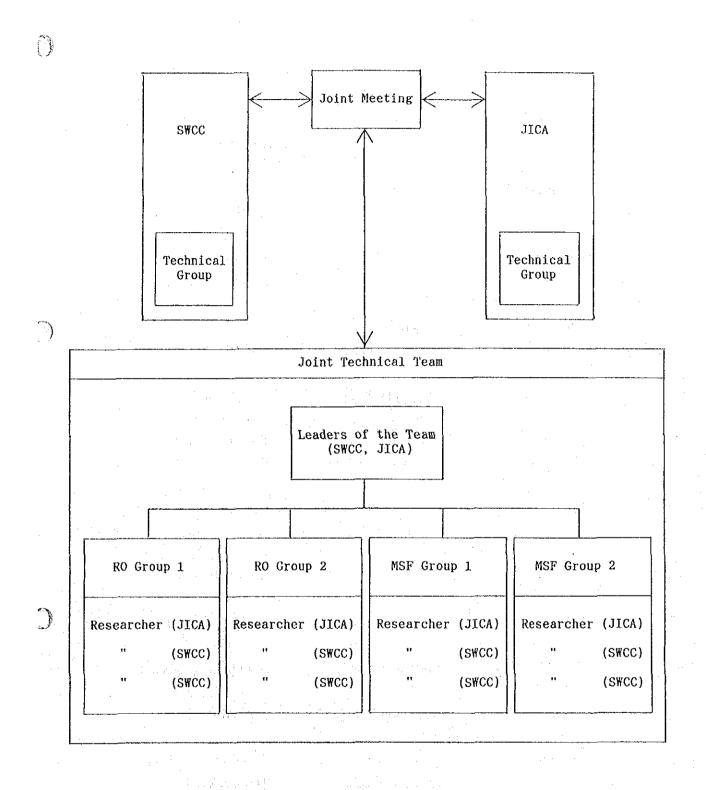


Fig. 2.1 Organization of Collaborative Research Activity

Project	Туре	JICA Team	SWCC Team
M-1	Experimental	Hamada Tadatsugu Fujita Kozo	Essam E.F. ElSayed Saad A. Al-Sulami
M2	Literature	Fujiwara Kazuo	S. Basu Nadeem A. Siddiqi
M-3	Literature	Togano Hideo	S. Basu Shahreer Ahmed
M4	Experimental	Hamao Yoshio Inoue Shiro	Saad A. Al–Sulami Zahar A. Nomani T.S.Thankachan
R-1	Literature	Sugimoto Yukinobu	Hassan Munshi
R-2	Experimental	Kitagawa Masahiro Bairinji Ryoichi	Abdulrahman Abanmy Talal Al–Jerfaley Thomas Mani Atta M. Hassan
R-3	Literature	Kubo Yoshihiko	Ibrahim Al-Tisan
R4	1)	Taniguchi Yoshio	Abdulrahman Abanmy
R-5	11	Kuratomo Rokuji	Talal Al–Jerfaley
R-6	Experimental	Hirai Mitsuyoshi Iwahori Hiroshi	Abdulrahman Abanmy Thomas Mani Atta M.Hassan
R-7	Literature	Tanaka Yoshihiro	Saad A. Al–Sulami

Table 2.1 Responsible Persons for Collaborative Research

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.

(1) Experimental Research

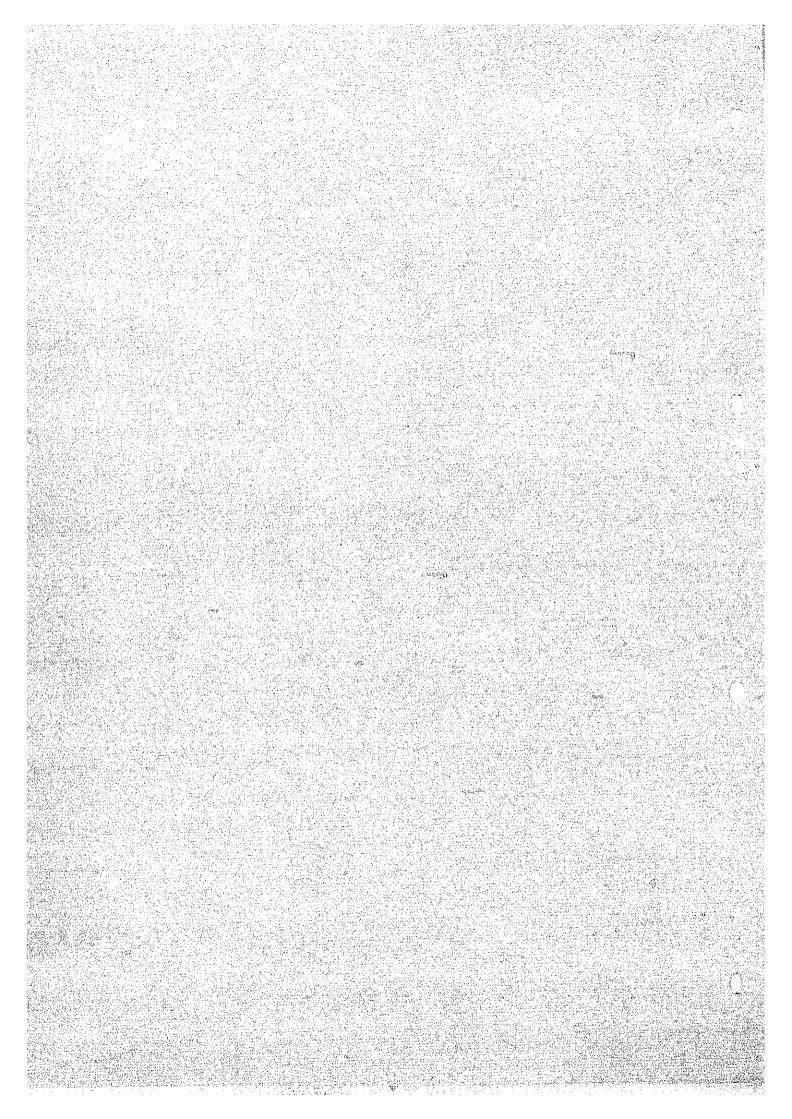
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- 1) The researchers dispatched from JICA stayed at the project site from October 1991 to February 1992, and conducted experimental research and literature surveys together with researchers from SWCC.
- 2) Computer retrieval of literature was mainly carried out by the JICA team and some important references which could not be surveyed by JICA were supplied by SWCC. Review of these materials was jointly carried out.
- 3) The researchers from JICA and SWCC jointly prepared and conducted the experiments and arranged the experimental results. Furthermore, they jointly reorganized the relevant information.
- 4) The researchers from JICA and SWCC jointly prepared the report of collaborative research activity.

(2) Literature Survey

- 1) Computer retrieval of literature was carried out by the JICA team.
- 2) The SWCC team supplied the relevant materials to the JICA team.
- 3) Review of these materials was jointly carried out.
- (3) 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 Experiment on Scale Prevention

MSF DESALINATION EXPERIMENTAL RESEARCH NO.1, M-1

LABORATORY EXPERIMENTS ON SCALE PREVENTION

"Prevention of Scaling in the Multi-Stage-Flash Evaporation Plant Using Oil Contaminated Seawater"

JULY 1992

By

Hamada Tadatsugu Fujita Kouzou JAPAN INTERNATIONAL COOPERATION AGENCY

And

Essam E.F. El-Sayed Saad A. Al-Sulami SALINE WATER CONVERSION CORPORATION

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1. Introduction

Two main factors which have the greatest influence on the reliability of the Multi-Stage-Flash-Evaporator Plant (MSF) are A) increases in temperature and concentration that cause the soluble constituent found in seawater to be deposited out, and subsequently, to obstruct the plants's heat transfer efficiency; and B) corrosion of the materials used in the construction of the MSF plant, in particular, corrosion of the heat transfer tubes.

In the case of A), there are two methods presently employed, the Acid Dosing Method (A.D. Method) and the chemical dosing method (C.D. Method). Theoretically, the A.D. Method totally inhibits the formation of scale, but if this method is used, the pH of brine falls to the range of 7.0-7.5 (25°C) giving much lower pH values compared to the C.D. Method values of 8.5-9.5 (25°C), and these low pH values create a corrosive environment.

The major problems with this method are that the concentration of acid dosing must be reliably controlled, and that the effective prevention of corrosion can not be guaranteed at all and that corrosion is highly sensitive to even small change in pH since no scale adheres to heat transfer surfaces.

For this reason, this method is generally considered unsuitable, from the viewpoint of the corrosion of plant equipment and is hardly ever used in the Middle East at present.

On the other hand, with the C.D. Method, although total prevention of alkaline scale theoretically impossible, the rate of formation of scale can be slowed down and the property of scale can be changed. The higher pH values of 8.5–9.5 (25°C) of the brine in this method in comparison with the former method provide an environment which is less prone to corrosion. Also, in this method adherence of scale to heat transfer surfaces exhibits effective prevention of corrosion. For the reasons mentioned above, the chemicals dosing Method together with ball cleaning (a mechanical method for removing scale) is becoming the main stream method of scaling prevention in the Middle East particularly from the viewpoint of general corrosion prevention and expediency of operation. However, in connection with the problem of crude oil spillage outflow into the sea, the effect of the chemical dosing methods must be examined.

Substantive experiments with a test plant which has the same environmental conditions as those of actual plants are the most effective for this purpose.

However, the acquisition of fundamental data through laboratory-scale experiments is necessary in the preliminary stages to enable the anticipation of test results to be gained with the test plant and the selection of optimum experimental conditions in order to effectively and quickly conduct substantive experiments. Consequently, this research will investigate the performance of scale inhibitors which are now in use, in the case where oil has intruded.

3.1.1

2. Literature Survey

The results of various kinds of research which were conducted over the past 25 years have been summarized in Appendix I. In this section, the authors would like to explain the mechanism of scaling and the techniques of preventing deposition of scale and to refer to the necessity of further experiments from the results of the research and investigation which have been conducted until today.

2.1 Mechanism of Scaling

Since seawater is accompanied by concentration and temperature rises in multi-stage flash evaporator plants, dissolved solids having the solubility which decreases with temperature rise such as calcium carbonate and magnesium hydroxide which are called soft scale or alkaline scale and calcium sulfate which are called hard scale, make up the major constituents of scale.

The process of the deposition of such scale and its solubility are shown in Fig. $2.1.1^{1}$ and Table $2.1.1^{2}$ respectively.

2.2 Techniques for Preventing Deposition of Scale

2.2.1 Soft Scale

(1) Acid Dosing Method (pH Control Method)

The pH control method is the most effective for the prevention of soft scale and it removes bicarbonate and carbonate ions, which form soft scale, before they come into contact with heat transfer tubes.

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Thanks to the above method, the top temperature and concentration of brine can be raised. In order to effectively strip seawater of its total CO_2 content, the majority of bicarbonate and carbonate ions, which are present in the pH range of 8.0-8.3, must be converted to CO_2 first, as shown by Equation (6) in Fig. 2.2.1. In order to confidently convert these ions to CO_2 , H_2SO_4 is generally used and its amount to be added is controlled by the measurement of pH. Needless to say, pH lowers when acid (H⁺) is added by the amount less than the equivalent of M-alkalini-ty. However, when this low-pH seawater is sprayed into the top of the decarbonator, pH rises due to the presence of bicarbonate ion which has not reacted yet, together with the dispersion of CO_2 . The equilibrium relationship between them is shown in Fig. 2.2.1³. As clearly can be seen from this figure, though this method uses acid as inferred by its name, the plant is not operated under low-pH conditions. Brine is neutral and its pH is in the range of 7-7.5, and the plant is not operated under a corrosive environment.

The most difficult problem of this method is to accurately control pH values so as to save a small quantity of bicarbonate ion which does not react with acid yet to prevent metallic corrosion. This metallic corrosion. This method also has various issues to be investigated on

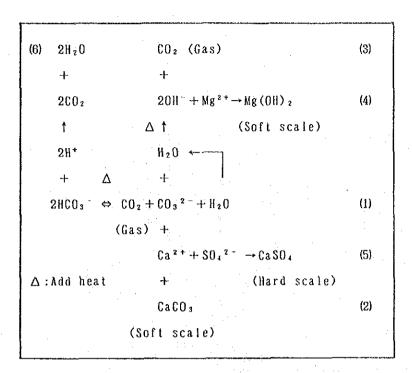
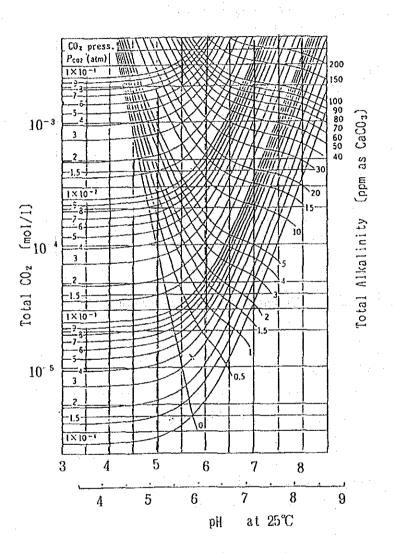


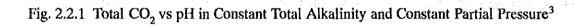
Fig. 2.1.1 Deposition Process of Scale Forming Compounds in Seawater¹

Table 2.1.1 Solut	bility of Salt	Precipitated ²
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Formula	Equilibium Equation	рК	
		60°C	100°C
CaSO ₄	pK = pCa +pSO ₄		3.08
CaSO₄· 1/2H₂O	$pK = pCa + pSO_4$	7.52	2.63
Mg(OH) ₂	рК = 2рН – рМg	15.35	14.59
CaCO ₃	pK = pCa – pALK	3.00	2.60
	CaSO ₄ CaSO ₄ 1/2H ₂ O Mg(OH) ₂	CaSO ₄ $pK = pCa + pSO_4$ CaSO ₄ · $pK = pCa + pSO_4$ 1/2H ₂ O Mg(OH) ₂ $pK = 2pH - pMg$	$60^{\circ}C$ $CaSO_{4} pK = pCa + pSO_{4} -$ $CaSO_{4} \cdot pK = pCa + pSO_{4} 7.52$ $1/2H_{2}O Mg(OH)_{2} pK = 2pH - pMg 15.35$





the design of the system such as the uniform mixture of concentrated sulfuric acid and seawater.From the above-mentioned viewpoint, this method is not being adopted in Saudi Arabia at present. Though the Yanbu Medina Plant was designed and operated using this method on an early stage, it is now being operted using this method on an early stage, it is now being operated using the chemical dosing methods because the above-mentioned corrosion problems had sometimes occured.

(2) Chemical Dosing Methods

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For the chemical dosing methods, the quantity of chemicals to be added can not be stoichiometrically calculated unlike the Acid dosing method in 2.2.1 and it expects the threshold effects of chemicals. Only chemicals of two to three ppm in relation to the quantity of feed seawater are usually enough and polyphosphate base chemicals (brand name: Hagevap L.P) were often used formerly as inhibitors to suppress the formation of soft scale $(CaCO_3, Mg(OH)_2)$. It is said that these chemicals preferentially combine calcium and magnesium into soluble complex salt and they are usually added to seawater at the inlet of the deaerator. However, only the operation up to about 90°C has been allowed, if scaling should be severely prevented.

Polymeric carboxylic acid base inhibitors have been announced ten- odd years ago to compensate defects of polyphosphate base inhibitors and their sales points are that the operation is allowed up to the brine temperature of maximum 120°C. Scale inhibitors have the crystal distortion effect besides the threshold effect, both are summarized as follows.

A. Threshold Effect

Scale inhibitors, which have the threshold effect, have properties to prevent or retard the deposition of salt, which forms scale, by using an inhibitor amount less than stoichiometrical concentration. In other words, they have properties not to deposit scale, that is, to keep a super-saturated state for a certain period, though scale naturally deposits under this concentration from the viewpoint of solubility. The point to be attended to here is that the period, during which this supersaturated state is kept, is limited and they only retard the deposition of scale.

B. Crystal Distortion Effect

Polymeric carboxylic acid base scale inhibitors have properties to reduce the number of nuclei available for scale formation, in addition to those to retard the deposition of scale mentioned above. For this reason, scale becomes noncrystal and hard to adhere to heat transfer surfaces. Since this phenomenon is caused by the presence of organic substances, it can be anticipated that this phenomenon is naturally changed by the intrusion of oil. This point seems to be the item to be attended to in this experiment. In any case, the chemicals dosing method does not decrease the amount of scale unlike the acid dosing method and it suppresses the adhesion of scale to heat transfer surfaces. Consequently, the chemicals dosing method is naturally inferior to the acid dosing method in its performance, but it has the greatest merit that the operation of plants can easily be controlled.

2.2.2 Hard Scale

Since calcium sulfate has solubility which decreases with temperature rise and its scale is very difficult to be removed by acid cleaning same as soft scale $(CaCO_3, Mg(OH)_2)$, the maximum working temperature and the concentration rate of brine of MSF must be adjusted so as not to deposit this scale.

There are three types of calcium sulfate (CaSO₄anhydrite, CaSO₄·1/2H₂O, CaSO₄·2H₂O). Among them, CaSO₄ anhydrite is prone to go into supersaturation and CaSO₄·2H₂O deposits under the condition of concentration rates of three or more. Consequently, the maximum working temperature and the concentration rate of brine of MSF are practically determined in such a way that CaSO₄·1/2 H₂O is not deposited.

Fig. 2.2.2⁴ shows the relationship between temperature and concentration rate against the deposition of three types of calcium sulfate mentioned above.

This figure shows the thermal cycle of brine in a recirculation type MSF plant with specifications of final stage flash room temperature 30°C, concentration rate 2 and maximum working temperature 120°C. In a MSF plant of 20,000 t/d class, CaSO₄ anhydrite does not deposit because the retention time of brine in such a plant is two or three minutes and it keeps supersaturated condition even though the operating conditions of the plant momentarily exceed the depositing conditions of CaSO₄ anhydrite.

2.3 Policy to Execute This Experiment

As clearly seen from Appendix I, there is no literature which has studied the relationship between scaling and seawater characteristics, water quality and water contamination as a main theme, the majority of the available literature contain theoretical construction of various data which have been obtained from MSF plants using ordinary scale preventing methods and the arrangement of measured data. In these literatures, investigation, experiment and research are not carried out at all for the case where seawater contaminated with oil is used as feed water, which this research aimed at.

It has been decided to examine the following for the case where the chemicals dosing



1

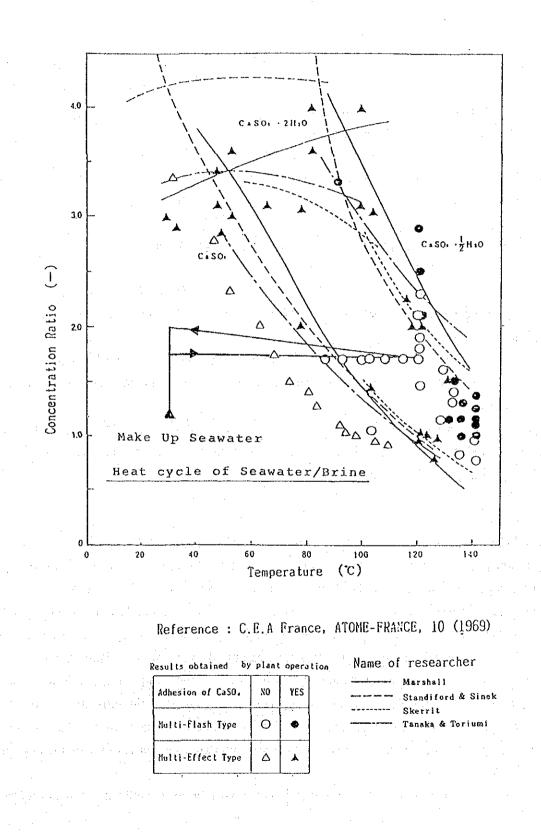


Fig. 2.2.2 Deposition Limits of Three Kinds of Calcium Sulfate Compounds in Seawater⁴

method is adopted as a scale preventing method with Batch type experimental equipment to clarify whether or not present methods can accomplish the objective of scale prevention in the case where oil has intruded into feed seawater and what kinds of other methods are available if present methods cannot sufficiently accomplish this objective.

- * Relationship between inhibitory effect on scale deposition and scale inhibitor concentration
- * Relationship between inhibitory effect on scale deposition and retention time of a scale inhibitor
- * Relationship between inhibitory effect on scale deposition and oil concentration

One of the factors that reduces the heat transfer coefficient in an MSF plant is the adherence of corrosion products to heat transfer surfaces besides the calcium carbonate and magnesium hydroxide.

However, as a result of the retrieval of literatures mentioned above, any literature which treated the behavior of corrosion products generated by corrosion in brine contaminated with oil could not be found.

Consequently, it has been decided to measure the polarization characteristics of carbon steel and stainless steel, which are materials composing an evaporation chamber, in brine con-taminated with oil in parallel. Appendix II shows measured results.

3. Experiment

3.1 Plan of Experiment

The aim of this research is to quantitatively grasp how the effects of scale inhibitors are impeded by the presence of oil. To clarify this issue, the temperature and the concentration rate of brine must be adjusted in accordance with those of actual plants, and scale must be generated in the case where scale inhibitors are not added. Though this work does not become an issue in the case where heat transfers and brine flows, experimental techniques to accomplish it are necessary in the case where experiments are carried out under static condition like this research, since seawater and brine are liable to maintain supersaturated state stoichiometrically. Furthermore, effective data must be acquired from charged brine of 500 ml while taking account of the accuracy of analysis, as the condition of restriction from the experimental equipment mentioned later.

For the above-mentioned reasons, the following two matters have been taken into consideration.

A) To add Na₂CO₃ solution for the breakage of supersaturated state and the formation of precip-

itation (hereinafter referred to as precipitation).

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

The concentration of seawater was determined to be 1.4 times the normal sea water in the Arabian Gulf in accordance with the actual results of Al Jubail Phase–II plants.

3.1.1 Breakage of Supersaturated State and Formation of Precipitation

For a concentrated brine that is 1.4 times sea water of the Arabian Gulf at 60°C, no formation of precipitate is expected. The concentrated brine is therefor heated up to 95°C keeping the concentration constant. That is, this brine is stable in the supersaturated state. When Na₂CO₃ is added to brine in this state, it is totally consumed for the formation of precipitation of CaCO₃ and M-alkalinity begins to decrease. When Na₂CO₃ is further added, there is a point where Malkalinity begins to rise. Brine is put in the saturated state under this condition. When Na₂CO₃ is added further, the formation of precipitation and the increase in M-alkalinity continue with the solubility product of CaCO₃.

However, the degree of the rise of M-alkalinity greatly differs 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 research. Fig. 3.1.1 shows the relationship between M-alkalinity and the amount of $IN Na_2CO_3$ added under the condition of 95°C and concentration rate 1.4.

3.1.2 Amount of Precipitation Formed and Decrease in M-alkalinity

As shown in Chapter 2, 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, in this research, the amount of decrease in M-alkalinity (unit: ppm as $CaCO_3$) is used as a measuring scale of the formation of precipitation, looking upon it as precipitation converted to $CaCO_3$. Though it can also be considered to directly measure the amount of precipitation formed in weight, measured values by this method have been used for reference only, since it is very difficult to separate and clean only precipitation by a simple method under the temperature condition under which precipitation has been formed and there are various factors to incur errors.

Though IN solution is used for adding Na_2CO_3 , the M-alkalinity after having added Na_2CO_3 can be calculated by Equation 3.1.1. (The measurement of M-alkalinity by acidimetry is impossible due to precipitation formation.)